BRITISH CHEMICAL ABSTRACTS

Foreword.

The "A" section of the abstracts, dealing with pure chemistry, will be issued to Fellows of the Chemical Society and other subscribers at the end of each month, whilst the "B" section, covering applied chemistry, will appear each week, and will be circulated along with the *Journal of the Society of Chemical Industry* to members of that Society and to special subscribers.

The price of the "A" and the "B" sections is £3 13s. 6d. each per annum, post free (including joint Index), but Fellows of the Chemical Society may obtain the "B" abstracts for £1 10s. 0d., whilst Members of the Society of Chemical Industry may obtain the "A" abstracts for £2 0s. 0d. [The yearly membership subscriptions are £3 0s. 0d. in the case of the Chemical Society and £2 10s. 0d. in the case of the Society of Chemical Industry.] Copies of "A" or "B" abstracts printed on one side of the paper, and suitable for filing purposes, may be obtained at reasonable charges.

The general basis of classification adopted in the two sections is printed below. For the guidance of readers of "A" abstracts, it should be pointed out that abstracts of analytical papers may be found not only at the end of each section as tabulated below, but sometimes also, when the analytical method described has a very specialised object, in the body of the section, according to the material with which the analytical method deals. In such cases there will be a reference in the "analytical" portion to other abstracts of analytical interest appearing in the same section.

A—PURE CHEMISTRY.

General, Physical, and Inorganic Chemistry.

Sub-atomics.

(*a*) Atomic spectra. Infra-red, visible, ultra-violet, *X*-ray emission and absorption spectra, Zeeman and Stark effects, Compton effect.
(*b*) Electrical properties: Ionisation potentials of atoms, photo-electric and thermionic effects.
(*c*) Properties of electrons and gaseous ions. Magnetic properties.
(*d*) Isotopes—atomic weights.
(*e*) Radioactive processes.
(*f*) Other sub-atomic processes.
(*g*) Theories of atomic structure and sub-atomic mechanism.
(*h*) Atomic dimensions (except in solid state).

Molecular Structure.

(*a*) Molecular spectra: Emission and absorption spectra of organic and inorganic substances. Fluorescence, luminescence, and phosphorescence. Raman effect.
(*b*) Ionisation potentials. Photo-electric effect with compounds.
(*c*) Conductivity. Dielectric constants. Dipole moment.
(*d*) Molecular volumes.
(*e*) Optical properties: Molecular refraction, dispersion, rotatory dispersion, optical activity, magnetic rotation.
(*f*) Theories of molecular structure. Valency, secondary valency, including co-ordination, electronic and magnetic theories, constitutional formulæ of inorganic substances.
(*g*) Molecular sizes and forces. Surface tension.

Crystal Structure.

(*a*) *X*-Ray examination.
(*b*) Crystal models.
(*c*) Magnetic and electrical properties of crystals: Piezo-electricity; magnetostriction.
(*d*) Optical properties. Rotatory dispersion.
(*e*) Compressibility. Tensile strength.
(*f*) Mesomorphic state.

Physical Properties of Pure Substances (not included above).

(*a*) Molecular weights.
(*b*) Electrical constants: Conductance, thermoelectric power, light sensitivity, etc. Magnetic susceptibility.
(*c*) Optical constants.
(*d*) Thermal constants: Specific heats, heat of change of state, boiling points, freezing points, transition points.
(*e*) Chemical constants.
(*f*) Pressures and volumes: Density, vapour pressure, coefficient of expansion, equations of state, theory of corresponding states.
(*g*) Compressibility.
(*h*) Viscosity; fluidity; plasticity.
(*i*) Diffusion.

Solutions and Mixtures.

(*a*) Gaseous mixtures, liquid mixtures (excluding dilute solutions), solid solutions (including alloys), property–composition curves.
(*b*) Miscibility of liquids and of solids. Solubility of gases and solids in liquids.
(*c*) Distribution phenomena: Partition, absorption, adsorption, surface films, surface energy, membrane effects.
(*d*) Dilute solutions: (i) Non-electrolytic solutions; (ii) Solutions of electrolytes. Colligative properties; non-colligative properties.
(*e*) Disperse systems. Preparation and properties of suspensions, emulsions, smokes, foams, sols, gels, jellies. Coagulation, peptisation, ageing, cataphoresis, imbibition, etc.

B

Kinetic Theory. Thermodynamics.

(*a*) Equilibrium in homogeneous systems; equilibrium, dissociation, ionisation constants, activity coefficients, etc.
(*b*) Equilibrium in heterogeneous systems; uni- and multi-component systems, phase rule.
(*c*) Thermochemistry.

Electrochemistry.

(*a*) Electrical conductance.
(*b*) Transport phenomena.
(*c*) Electrode and diffusion potentials; *E.M.F.*, concentration cells, etc.
(*d*) Polarisation, overvoltage, passivity, etc.
(*e*) Application of electrochemical methods.

Reactions.

(*a*) Velocity studies in (i) Homogeneous systems; (ii) Heterogeneous systems.
(*b*) Catalysed reactions: (i) and (ii) as above.
(*c*) Electrode reactions.
(*d*) Photochemical reactions.
(*e*) Irradiated reactions.

New Methods of Preparing Substances arranged according to periodic table), etc.
Improved Methods of Preparing Substances, etc.
Analysis.
Apparatus.
Lecture Experiments.
Historical.

Geochemistry.

Organic Chemistry.

Aliphatic.

Hydrocarbons.
Halogen, nitro-, and nitroso-derivatives.
Alcohols.
Ethers.
Alkyl salts.
Sulphur compounds, including sulphonic acids.
Acids.
Thio- and sulpho-acids.
Aldehydes.
Aldoximes.
Ketones and diketones.
Ketoximes.
Sugars, glucosides, and carbohydrates.
Amines.
Amino-alcohols.
Amino-acids.
Cyano-acids, thiocyano-acids.
Amino-aldehydes and -ketones.
Amides (including cyanic, cyanuric, and thiocyanic acids).
Nitriles, carbylamines, metallic cyanides.
Amidoximes, imino-ethers.
Diazo-compounds.
Phosphorus compounds.
Arsenic, antimony, boron, silicon, etc. compounds.
Aliphatic organo-metallic compounds.

Homocyclic.

Hydrocarbons C_nH_{2n} to C_nH_{2n-6}.
Halogen, nitroso-, and nitro-derivatives.
Sulphonic acids.
Hydrocarbons C_nH_{2n-8} to C_nH_{2n-} Derivatives under each.
Amines. Includes anilides, carbamides, thiocarbamides, and sulphonic acids.
Azoxy-compounds.
Azo- ,,
Hydrazo- ,,
Diazo- ,,
Diazoamino- ,,
Phenols. Aminophenols, thiophenols, sulphides, sulphonic acids.
Alcohols.
Phenol-alcohols.
Acids. Sulphonic acids and hydrazines under each member.
Aldehydes. Derivatives under each.
Ketones. ,, ,, ,,
Diketones and oxyketones.
Quinones.
Camphor group.
Terpenes.
Ethereal oils.
Resins and balsams.
Bitter principles and indifferent substances.
Colouring matters (unclassified natural and artificial).
Tannins.

Heterocyclic, etc.

Furan group.
Thiophen group (Se).
Bases: N_1, N_2, N_3, etc.
Alkaloids.
Phosphorus compounds.
As, Sb, Bi, B, Si compounds.
Organo-metallic compounds.
Proteins.

Analysis.

Biochemistry.

Respiration.
Blood: Gases; constituents; reactions (hæmolysis, anti-body formation, etc.).
Organs and their Proximate Constituents: Analytical data of constituents of organs: pure substances isolated from organs.
Secretions: Milk; lymph, etc.
Excretions: Urine; fæces; other excretions.
Diseases: Natural and experimental (in alphabetical order).
Metabolism: General; special; intermediary; fate of substances in the animal body.
Physiological Action: Variation of physiological conditions; action of drugs; toxicology.
Enzymes: General; specific.
Micro-organisms: yeasts, moulds, protozoa, bacteria.
Hormones.
Vitamins.
Vegetable Physiology: General; reproduction and fertilisation; respiration; growth; proximate principles; diseases; poisons.
Analysis.

B.—APPLIED CHEMISTRY.

I. General; Plant; Machinery.
II. Fuel; Gas; Tar; Mineral Oils.
III. Organic Intermediates.
IV. Dyestuffs.
V. Fibres; Textiles; Cellulose; Paper.
VI. Bleaching; Dyeing; Printing; Finishing.
VII. Acids; Alkalis; Salts; Non-Metallic Elements.
VIII. Glass; Ceramics.
IX. Building Materials.
X. Metals; Metallurgy, including Electrometallurgy.
XI. Electrotechnics.
XII. Fats; Oils; Waxes.
XIII. Paints; Pigments; Varnishes; Resins.
XIV. Indiarubber.
XV. Leather and Glue.
XVI. Agriculture.
XVII. Sugars; Starches; Gums.
XVIII. Fermentation Industries.
XIX. Foods.
XX. Medicinal Substances; Essential Oils.
XXI. Photographic Materials and Processes.
XXII. Explosives.
XXIII. Sanitation; Water Purification.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JANUARY, 1931.

General, Physical, and Inorganic Chemistry.

Absolute intensity of the aurora line in the night sky, and the number of atomic transitions required to maintain it. (LORD) RAYLEIGH (Proc. Roy. Soc., 1930, **A**, **129**, 458—467).—The brightness of the green auroral line of the night sky, λ 5577, is found to be $3 \cdot 2 \times 10^{-5}$ candles per sq. m. The energy of emission is 6·4 ergs per sec. per sq. m., requiring for its maintenance $1 \cdot 81 \times 10^{12}$ atomic transitions per sec. per sq. m. L. L. BIRCUMSHAW.

Transverse Zeeman effect of the green auroral line; experimental proof of the existence of quadrupole radiation. R. FRERICHS and J. S. CAMPBELL (Physical Rev., 1930, [ii], **36**, 1460—1467; cf. Rubinowicz, A., 1930, 513, 653).—Since the existence of quadrupole radiation can be demonstrated from measurements of the transverse but not of the longitudinal Zeeman effect, the former for the green auroral line excited in a helium–oxygen mixture was photographed. Results are in complete agreement with the theoretical predictions.

N. M. BLIGH.

Spectra of several long-period variable stars. P. W. MERRILL and C. G. BURWELL (Astrophys. J., 1930, **71**, 285—335).—Hydrogen, Fe I, Fe II, Mg I, Si I, Mn I, Sr II (?), and In I (?) have been identified in the spectra of long-period variable stars of type Me and Se. L. S. THEOBALD.

Flashing afterglow in a discharge tube. H. J. J. BRADDICK (Nature, 1930, **126**, 725).—After passing a discharge from an induction coil a strong afterglow persisting several seconds has been observed in a tube of pyrex glass with nickel electrodes. The afterglow is probably due to the dissipation of charges on the walls of the tube. L. S. THEOBALD.

Multiple interference spectroscope. E. GEHRCKE and E. LAU (Physikal. Z., 1930, **31**, 973—974).—A multiple interference spectroscope of high resolving power is described in detail. The spectroscope has revealed the fine structure of the mercury line at 5461 Å., and helium λ 5876 Å. is shown to consist of two lines separated by 0·33 Å. The resolving power of the instrument is approximately 2×10^6 and the instrument can be used for measuring the Doppler effect in spectral lines. W. R. ANGUS.

Correlation of atomic *J* values and molecular quantum numbers, with applications to halogen, alkaline-earth hydride, and alkali molecules. R. S. MULLIKEN (Physical Rev., 1930, [ii], **36**, 1440—1450; cf. Wigner and Witmer, A., 1929, 117).—Theoretical. Rules are deduced for determining certain quantum relations for the molecular states resulting from the union of two atoms with specified *J* values, for cases of strong *L*,*S* coupling. Examples are considered, and the difficulties of extending the method to cases of weak coupling are discussed. Electron configurations and dissociation products are examined for the halogen molecules, and the analogies and differences of spectra for the halogens, alkali and alkaline-earth metals are interpreted in terms of electron configurations. N. M. BLIGH.

Oscillating arc in spectrochemical analysis. E. Z. STOWELL and W. S. HUXFORD (Physical Rev., 1930, [ii], **36**, 1348—1351; cf. A., 1929, 1359).—It is shown that the alkaline-earth metals but not the alkali metals will allow radio-frequency oscillations to be generated across an arc in hydrogen. Spectra were photographed of the two groups of elements when burned in the hydrogen arc, and the intensification and reduction of the lines of various elements are described. The effect of minute additions of magnesium in large amounts of rubidium and sodium is described, and from the oscillations produced a method for determining the content of magnesium is indicated (cf. Crew, A., 1929, 366; Duffendack, A., 1930, 2). N. M. BLIGH.

General electric type *S*-1 lamp as a spectroscopic source. D. DOOLEY (Physical Rev., 1930, [ii], **36**, 1476—1479).—The lamp is a 300-watt alternating-current tungsten–mercury arc in argon. Spectrograms were obtained of radiation from the lamp and also when hydrogen, helium, neon, or carbon dioxide was substituted for argon, with and without a small amount of mercury. In nitrogen alone the second positive bands were greatly modified; hydrogen with mercury showed the mercury hydride bands, and carbon dioxide showed the third positive bands.

N. M. BLIGH.

Conditions for initiation of electrodeless discharges in gases. N. T. GORDON and S. DUSHMAN (Physical Rev., 1929, [ii], **33**, 632).—The minimum current through a copper coil which is sufficient to start a glow in a bulb placed inside the coil when this is supplied with high-frequency current from a vacuum tube oscillator has been determined at various gas pressures (0·1—40 mm.) and frequencies for neon, helium, and oxygen. For each frequency there exists a critical pressure at which the current required to initiate the glow is a minimum. A parallelism with positive column discharges exists.

L. S. THEOBALD.

Formation of MH molecules; effects of H atom on M atom. R. S. MULLIKEN (Physical Rev., 1929, [ii], 33, 285—286).—Observed electronic states of diatomic hydride molecules (CH, NH, OH, MgH, etc.) can be derived from unexcited H and familiar low-energy states of M atoms. The observed states and $\Delta\nu$ intervals in ^2P or ^3P states of such MH molecules indicate that the effects of the H on the M atom are confined to the following effects: (i) the couplings between l_τ vectors of M atom outer electrons to give a resultant l are broken down by the field of the H nucleus, (ii) the uncoupled vectors l_τ are separately space-quantised with reference to the electric axis, (iii) the electron of the H atom takes its place with the M electrons, and (iv) the original couplings of s_τ vectors are often broken down.

L. S. THEOBALD.

Influence of slit width on the intensity distribution in spectral lines. P. H. VAN CITTERT (Z. Physik, 1930, 65, 547—563).—The expression for the intensity at any point in the focal plane of the telescope for an infinitely narrow collimator slit is integrated across the width of the slit to determine the intensity distribution in an actual spectral line. Three cases are distinguished, viz., when radiation falls on the collimator slit from (i) an incoherent unfocussed source, (ii) a coherent unfocussed source, and (iii) a coherent focussed source. In (i) a maximum brightness of the centre of the spectral line occurs when the product of the slit width, in wave-lengths, and the angular aperture of the collimator equals unity; the slit width should, in practice, be less than this. In (ii), the spectral line becomes double when the above product equal two, and the incident beam just fills the collimator lens. The spectroscope is most efficient when the slit width and the angular width of the incident beam have approximately three quarters these limiting values. In (iii) an indefinite condenser focus complicates the calculation, but the results of (ii) apply approximately.

A. B. D. CASSIE.

Theory of complex spectra. E. U. CONDON (Physical Rev., 1930, [ii], 36, 1121—1133).—Mainly mathematical. The work of Slater is extended (cf. A., 1930, 126) and it is shown that the assignment of definite electron configurations to spectral terms is an approximation, having meaning only when the multiplet systems of the several configurations are widely separated. The effect of including spin terms is outlined. Non-diagonal matrix elements for the N-electron problem are reduced to corresponding elements for the two-electron problem, and the results are applied to the theory of two-electron jumps.

N. M. BLIGH.

Principle of identity and the exclusion of quantum states. G. N. LEWIS (Physical Rev., 1930, [ii], 36, 1144—1153).—Theoretical. Considerations are presented to show that all exclusion rules of quantum states, of which rules Pauli's was the prototype, are direct mathematical consequences of quantum mechanics when full consideration is given to the identity of certain elementary particles. The assumption that a system of two bodies, both having the same mechanical and electrical properties, would show the same behaviour gave rise to the Gibbs-Einstein paradox of the change of entropy on mixing two gases continuously approaching complete identity, and must be abandoned in favour of a distinction of identical and quasi-identical particles. The new mathematical condition of complete identity, operating with the wave equation and its boundary conditions, gives rise to the empirically obtained exclusion laws. The method is applied to the rotational states of monatomic and diatomic gases. The influence of spin is discussed.

N. M. BLIGH.

Passage of an electric discharge through gases. J. B. SETH and B. MOKAND (Nature, 1930, 126, 808).—The effect previously observed with air (A., 1928, 107) has been extended to hydrogen, oxygen, nitrogen, carbon dioxide, and chlorine with nearly similar results. For a fixed *P.D.* the amount of shift of the interference fringes varies with pressure to a maximum which is different for different gases and voltages. The effect is greatest in carbon dioxide and least in hydrogen. The shift and pressure change can be observed at the ordinary pressure with no visible glow when long electrodes reaching the end of the light beam are used. That the effect is due to the pushing away of gas from the discharge can be demonstrated by means of lycopodium powder.

L. S. THEOBALD.

Energy levels of atoms in an electric field. J. S. FOSTER (Nature, 1930, 126, 845).—The conclusions of Ishida (A., 1930, 1327) are discussed.

L. S. THEOBALD.

Intensities and summation rules for quadrupole multiplets. A. RUBINOWICZ (Z. Physik, 1930, 65, 662—676).—Theoretical. Radiation transitions can occur only between dipoles possessing "proper" functions of opposite symmetry, whereas quadrupoles must have "proper" functions of like symmetry. Thus, lines due to transitions between dipoles and between quadrupoles must be distinct. Relative transition probabilities for quadrupole multiplets are determined, and from them a summation rule is shown to exist. Examples are the O II multiplets, $^2D-^2P$, and $^6D-^6S$, and the Fe II multiplets, $^4F-^4G$, found in stellar spectra. A. B. D. CASSIE.

Evidence for quadripole radiation. E. SEGRÈ (Nature, 1930, 126, 882).—The transverse Zeeman effect of the 4642·17—4641·58 potassium doublet, which is a $S \longrightarrow D$ combination, has been observed. The Zeeman pattern agrees with the predictions of Rubinowicz for quadripole and not dipole radiation.

L. S. THEOBALD.

Spectra in condensed discharges. J. W. BEAMS (Physical Rev., 1929, [ii], 33, 1086).—The light emitted by an electric spark between metallic electrodes in air together with that emerging from condensed discharges at low pressures has been investigated by the rotating-mirror method. Photographs of single discharges have been obtained. The velocities of propagation of the luminosity of metallic vapours in the spark have been measured. The air lines appeared first, followed successively by the spark and the arc lines of the metal. The spark probably appears first as a narrow thread and then expands rapidly during its initial stage.

L. S. THEOBALD.

Existence of a "resonance time" or a time-lag in light emission. H. T. Wolff (Z. Physik, 1930, **65**, 730—733).—It is shown that where it is necessary to assume the presence of a fading-out period ("Abklingzeit"), a time-lag ("Verweilzeit") need not also be required. An experiment which definitely shows the existence of a fading-out time is given.

A. J. Mee.

Refraction of X-rays for the determination of the specific charge of the electron. H. E. Stauss (Physical Rev., 1930, [ii], **36**, 1101—1108).—With the view of correcting discrepancies in existing values of e/m, a method depending on the refraction of X-rays by a prism is described. For crystalline quartz of density 2·6480 g./cm.^{3} the value of $1-\mu$ was determined for the $K\alpha_1$ and radiation of molybdenum as $1{\cdot}804\pm0{\cdot}001\times10^{-6}$ and $1{\cdot}436\pm0{\cdot}001\times10^{-6}$, respectively. Using the absolute X-ray wave-lengths of Bearden (cf. A., 1929, 984) and of Cork (cf. A., 1930, 1079), the calculated values of e/m were found to lie between those given by spectroscopic and deflexion methods. N. M. Bligh.

X-Ray scattering coefficient as a function of wave-length and atomic number. E. N. Coade (Physical Rev., 1930, [ii], **36**, 1109—1115).—With an improved form of the apparatus of Mertz (cf. A., 1927, 83) the mass scattering coefficients for gold, tin, silver, iron, and carbon were compared with those of aluminium for the wave-length range 0·48—1·09 Å., by collecting the scattered radiation in an ionisation chamber surrounding the scatterer on one side. The primary beam consisted of characteristic fluorescence radiation excited in radiators of tin, silver, molybdenum, and selenium by a water-cooled tungsten tube. Results obtained are tabulated, and are transformed into absolute scattering coefficients, which are plotted against wave-lengths.

N. M. Bligh.

Atomic scattering powers of nickel, copper, and iron for various wave-lengths. R. W. G. Wyckoff (Physical Rev., 1930, [ii], **36**, 1116—1120; cf. A., 1930, 655; Armstrong, A., 1929, 1354).—Using the methods previously described, the atomic scattering powers were measured for the atoms in nickel, copper, and iron reflecting the $K\alpha$ lines of molybdenum, copper, nickel, and iron, and show that the scattering power of an atom passes through a minimum at its K absorption limit to a maximum at or near its resonance wave-length. The atomic F curves of the nickel atom in the metal and its oxide are practically identical. N. M. Bligh.

X-Ray anomalous dispersion in the region of the L series of platinum. E. Dershem (Physical Rev., 1929, [ii], **33**, 120; cf. A., 1929, 747).—The indices of refraction of platinum in the neighbourhood of its L absorption limits have been measured by the total reflexion method. One depression in the curve obtained by plotting $1-\mu=\delta$ against λ shows lowered values of δ at a wave-length corresponding with the mean of the wave-lengths of the L_{I} and L_{II} limits and another at the L_{III} limit. Different surfaces of the same material may have indices of refraction which are markedly different. L. S. Theobald.

Position and structure of the modified line of the spectrum of scattered X-rays. F. L. Nutting (Physical Rev., 1930, [ii], **36**, 1267—1272).—Measurements were made of the shift in wave-length of scattered X-rays by a photographic method for molybdenum X-radiations scattered by a paraffin block, and by a single-crystal ionisation method for scattering by graphite. Photomicrographic analysis for the shift of the centre of gravity of the lines and of the peaks gave h/mc 0·02305 and 0·02374 Å., respectively. Some error may be due to the $K\gamma$ line. The average value from the ionisation curves was $0{\cdot}0240\pm0{\cdot}00024$ A., in good agreement with the theoretical value, 0·02422 Å. The value and the fine structure of the modified line reported by Davis and Purks (cf. A., 1929, 986) are not supported. N. M. Bligh.

Relative intensities of X-ray lines in the tantalum L spectrum. V. Hicks (Physical Rev., 1930, [ii], **36**, 1273—1284).—Special precautions are described for an investigation of the relative intensities of 17 lines in the L spectrum of tantalum, using the ionising spectrometer. The results for lines of small wave-length separation agree well with those of Allison and Armstrong (cf. A., 1925, ii, 1015) on tungsten, and their qualitative estimates for lines of longer wave-length. The assumption that the ionisation currents produced are proportional to the relative intensities is supported by Compton (cf. A., 1930, 138). If the ν^4 correction, indicated by quantum mechanics, is made to the intensities at high voltage the summation rules are approximately valid except for lines having the initial state L_1.

N. M. Bligh.

Relation between continuous and line spectra of X-rays from thin targets. D. L. Webster and W. W. Hansen (Physical Rev., 1929, [ii], **33**, 635—636).—K-Electron ionisation by cathode-ray impact has a continuous-spectrum counterpart in the emission of a quantum of any frequency above the K limit. For thick targets of silver, the ratio of the probability of the former to the latter process appears to be constant, whilst for thin targets the same constancy probably holds, but is subject to wider limits of error. The calculated probability of the continuous-spectrum process is approximately proportional to the $K\alpha$-line intensities between 25 and 85 kilovolts, furnishing additional evidence that the ratio is constant for thin targets. L. S. Theobald.

Intensities of general X-radiation proceeding from an atom in different directions. W. Duane and J. C. Hudson (Physical Rev., 1929, [ii], **33**, 635). —The radiation projected forward at an angle of 45° from the direction of motion of a homogeneous stream of electrons impinging on the atoms of mercury vapour is approximately twice as intense as that projected backward at an angle of 135° from the same direction. L. S. Theobald.

Fine structure of scattered X-rays. D. Mitchell and B. Davis (Physical Rev., 1929, [ii], **33**, 292).—Four lines attributed to Mo-$K\alpha$ have been found in the scattering of Mo-$K\alpha$ rays from aluminium. Two of these are shifted lines corresponding with approximately 2·3 and 5·6 X from Mo-$K\alpha_1$. Two of

the aluminium absorption limits are given as 57±6 and 136±6 equivalent volts. L. S. THEOBALD.

X-Ray spectroscopic measurements of the L absorption of elements between 74, tungsten, and 92, uranium. A. SANDSTROM (Z. Physik, 1930, **65**, 632—655).—The three L levels for the elements from tungsten to bismuth and from thorium to uranium were determined with a Siegbahn tube spectrometer. Absorption edges are most clearly defined when the intensity difference between wave-lengths at equal but opposite distances from the edge is greatest. This, with the Jonsson's absorption law (Diss., Uppsala, 1928), determines the thickness of the most efficient absorbing layer for each element. These layers were prepared in three ways: (i) by pouring an emulsion of the element and cellulose lacquer on to a glass plate, (ii) by distillation and subsequent deposition on an aluminium foil 6 μ thick, and (iii) by sputtering. The edges were examined photometrically, and some absorption lines were detected. The results are discussed, and compared with those of other workers. Their deviation from Moseley's linear law, due to the presence of outer electron shells, is noted. A. B. D. CASSIE.

Structure of K-radiation in the ultra-soft X-ray region. M. SODERMAN (Z. Physik, 1930, **65**, 656—661).—Recent measurements on X-ray lines in the region 49—115 Å., where optical measurements have been made, are described. The photographic plate was examined with a microphotometer, using a slit width corresponding with 0·08—0·2 Å. The $K\alpha$ X-ray lines obtained with carbon, boron, and beryllium are broad compared with the optical lines obtained from a condensed spark. This broadening is not due to satellites, but may be due to the use of solids in obtaining the X-ray photographs, as compared with the gaseous atoms or ions which are effective in producing the quenched spark. A. B. D. CASSIE.

X-Ray spectra of gases. K Series of krypton and of xenon. A. DAUVILLIER (Compt. rend., 1930, **191**, 937—939).—The gaseous anticathode method was used, the pressure being regulated by an oil-mercury manometer adjusted so that the volume of the anticathode was of the order of 10 c.c., *i.e.*, about 15 cm. of mercury for krypton at 45 kilovolts and xenon at 60 kilovolts. The values $\alpha_1\alpha_2$ 978 and 417, and β 875 and 360 found for 36 Kr and 54 X, respectively, are in accord with theoretical predictions. Owing to the feeble dispersion, the $\beta\gamma$ and $\alpha_1\alpha_2$ doublets cannot easily be distinguished, and the continuous spectrum is too feeble to enable the limits of energy distribution to be defined. J. GRANT.

New bands in the secondary spectrum of hydrogen. G. S. MONK and A. E. ELO (Physical Rev., 1929, [ii], **33**, 114).—Using the electronic and vibrational levels associated with the Balmer lines, the wave-numbers of the remaining lines of the band groups have been computed and compared with lines already measured. Only Q branches are present. Bands attributable to the H_3 molecule have been found in some new measurements and are discussed. L. S. THEOBALD.

Displacement of hydrogen terms in intense electric fields. C. LANCZOS (Z. Physik, 1930, **65**, 431—455).—Theoretical. The method of direct asymptotic investigation of the wave functions for the Stark effect in intense fields is applied in improved form to a determination of proper values. A closed formula is deduced for these proper values in place of the older successive approximations, which become divergent with increasing field intensity. A. B. D. CASSIE.

Molecular states of hydrogen with two excited electrons. W. WEIZEL (Z. Physik, 1930, **65**, 456—463).—The two hydrogen molecular terms X and 3^1K cannot, on account of the angular momenta which show coupling, be associated with a molecule containing a $1s\sigma$ electron. These terms may coincide with $(2p)\sigma^2\,{}^1\Sigma$ and $2p\sigma3p\sigma\,{}^1\Sigma$, respectively. A. B. D. CASSIE.

Continuous spectrum of hydrogen. J. KAPLAN (Physical Rev., 1929, [ii], **33**, 638—639).—A discussion. L. S. THEOBALD.

Relativity separation of spectral lines of hydrogen-like atoms in parallel and crossed electric and magnetic fields. D. P. R. CHAUDHURI (Z. Physik, 1930, **65**, 824—829; cf. Sen, A., 1929, 1115).—The calculation of Sen is extended, taking into account the small relativity effect for very weak fields. The separation of the H_α lines in weak parallel fields is calculated. Owing to the complexity of the calculation, only the Lyman lines can be considered for crossed fields. For these lines the intensity of the split lines is easily obtained. For H_α lines in parallel fields of strength 10^4 volts and 10^4 gauss, the relativistic separation of some lines is of the order of 0·008 Å., whilst for the first Lyman line in crossed fields the relativity effect results only in a displacement of the line, which is approximately fifty times as great as this. A. J. MEE.

Numerical calculation of the $2S$ terms of ortho- and par-helium. E. A. HYLLERAAS and B. UNDHEIM (Z. Physik, 1930, **65**, 759—772).—An accurate calculation of the ground term of ortho-helium and the $2S$ terms of par-helium is carried out. The calculated figure shows almost complete agreement with the experimental value (cf. A., 1930, 1487). The effective quantum number is 1·689. For par-helium, the difference between the observed and the calculated values amounts to 0·7% of the energy associated with the "light electron," or 0·05% of the total energy. Expressed otherwise, the effective quantum number is calculated to be 1·858, as against 1·851 for the experimental value. A. J. MEE.

Life-period of excited helium atoms and a direct method of determining the diffusion coefficient of excited atoms. E. EBBINGHAUS (Ann. Physik, 1930, [v], **7**, 267—292; cf. Meissner and Graffunder, A., 1928, 212).—Experiments are described from which, by determining the absorption of light by helium atoms in the 2^3S_1 state at known intervals of time after their excitation, the rate of decay of the excited atoms and their rate of diffusion can be calculated. The diffusion coefficient at the ordinary temperature and 1 mm. pressure is 400 cm.^{2} per sec., which gives $4{\cdot}5\times10^{-8}$ cm. as the effective

diameter of the excited atom, assuming that of the normal atom to be $2 \cdot 5 \times 10^{-8}$ cm. The degradation of the excited atoms occurs only by collisions of the second kind, and in the conditions of these experiments only collisions with the walls of the tube are effective. F. L. USHER.

Band spectrum of He_2 in stellar spectra. O. STRUVE and A. CHRISTY (Astrophys. J., 1930, **71**, 277—282).—An examination of the spectrum of 88 γ Pegasi shows that whilst several coincidences are present, the band spectrum of the helium molecule is not sufficiently strong to appear in this star.
L. S. THEOBALD.

Series relationships in Be I. R. F. PATON and R. E. NUSBAUM (Physical Rev., 1929, [ii], **33**, 1093; cf. A., 1929, 226).—With higher resolution and a low-pressure arc the beryllium line at 4553·07 Å. has been resolved from the barium line at 4554 ± 1 Å. in the furnace spectrum of beryllium. L. S. THEOBALD.

Arc spectrum of carbon C I. F. PASCHEN and G. KRUGER (Ann. Physik, 1930, [v], **7**, 1—8).—C I spectral lines and series have been measured. The fundamental $(2p)^2\,{}^3P_{2,1,0}$ term is the limit of three series of strong lines: from the terms $2pns^3P_{2,1,0}$ there result a series of PP' groups of which the first three only are fully resolved; the terms $2pna^3P_{3,2,1}$ yield narrow groups of strong lines of which the first three are resolved, the remainder being characterised by diffuse lines; the terms $2pnd^3P_{2,1,0}$ yield with the fundamental term partly resolved groups, each value of n corresponding always with three adjacent groups of lines in the sequence 1, 2, 3, from the longer wave-lengths. Most members of series 2 have been observed, and the value of $(2p)^2\,{}^3P_2$ is $90{,}836 \pm 10$ (11,212 volts). The fundamental term $(2p)^2\,{}^1D_2$ is the limit of at least four series, viz., $2pnd^1F_3$, $2pnd^1P_1$, $2pnd^1D_1$, and $2pns^1P_1$; a term nX, in which $n=5$, is probably the continuation of the first of these, and gives very strong lines which for a given value of n lie close together in the sequence 1, 5, 2, 3, 4 from the longer wave-length region. The third of these four series yields the strongest lines, and gives for $(2p)^2\,{}^1D_2$ the value $80{,}686 \pm 3$ (99,588 volts). The fundamental term $(2p)^2\,{}^1S_0$ is the limit of a series having the terms $2pns^1P_1$, from which the value of $(2p)^2\,{}^1S_0 = 69{,}231 \pm 3$ (85,449 volts). Of the series derived from the term $2pnd^1P_1$, only the first line, n—3, has been observed. Fowler and Selwyn's values (A., 1928, 450) of —139 and —626 for the triplet and single terms are corrected.
H. F. GILLBE.

Metastable states of atomic nitrogen. K. T. COMPTON and J. C. BOYCE (Physical Rev., 1929, [ii], **33**, 115).—The analysis of near-visible lines made by Kiess has been extended to give almost the entire spectral structure predicted by the Hund theory. The "ground" state $2p^4S$ has a term value of about 117,345; the next lowest states, which are metastable, are $2p^2D_{2,3}$ and $2p^2P_{1,2}$ about 98,143 and 88,537, respectively. The energies of the active nitrogen states are 2·37 and 3·56 volts, which are the energies of the entities in active nitrogen found necessary by Kaplan and Cario to account for the production of the afterglow by excitation of the ^3S metastable molecules, and for excitation of other spectra in active nitrogen. L. S. THEOBALD.

Active nitrogen. J. KAPLAN (Physical Rev., 1929, [ii], **33**, 638).—The fact that the bands arising on the B_{11} level are the most intense in the nitrogen afterglow can be accounted for by the recombination between two normal atoms to form a metastable molecule possessing 9·1 volts and then the subsequent excitation of this molecule by an atom in the ^2D state. L. S. THEOBALD.

Decay of the spectrum of the afterglow of nitrogen mixed with argon. A. G. WORTHING and H. E. WAY (Physical Rev., 1929, [ii], **33**, 1086).—Three spectrograms of the afterglow in succeeding stages have been obtained with periodic discharges in a mixture of 99% of argon and 1% of nitrogen at about 2 cm. pressure. The early stage shows a maximum in the orange sequence for the $8 \longrightarrow 4$ vibrational transition and in the red sequence for the $8 \longrightarrow 5$ and the $4 \longrightarrow 1$ transitions; the third stage shows maxima for the $11 \longrightarrow 7$, $9 \longrightarrow 5$, and $9 \longrightarrow 6$ transitions, whilst the second stage shows an intermediate shift. With time the afterglow spectrum appears to approach that in pure nitrogen.
L. S. THEOBALD.

O and N spectra in the extreme ultra-violet. D. C. SHELDON (Physical Rev., 1929, [ii], **33**, 267).—Using the method of grazing incidence with a concave speculum metal grating, spectra for O and N have been observed down to 225 Å. L. S. THEOBALD.

Red coronal line in oxygen. J. J. HOPFIELD (Nature, 1930, **126**, 846).—The nebular lines 6300 and 6364 Å., as well as the strong line 6374·29 Å., have been identified in the spectrum of oxygen. The last line appears to be identical with the red coronal line 6374·2. This is supported by the fact that the line occurs in an isolated position in the oxygen spectrum only when lines of O I are present. Strong evidence of the presence of oxygen in the sun's corona is thus afforded. L. S. THEOBALD.

Band spectrum of fluorine. H. G. GALE and G. S. MONK (Physical Rev., 1929, [ii], **33**, 114—115).—The bands consist of P, Q, and R branches with alternate weak and strong lines in each branch; the Q branch is about twice as strong as the other two. The bands at $v=16{,}378 \cdot 8$, $17{,}439 \cdot 5$, $15{,}337 \cdot 6$, $17{,}075 \cdot 0$, and $18{,}550 \cdot 0$ have been analysed either partly or completely. There are strong perturbations in all bands in both frequency and intensity. The bands are probably of the ${}^1S \longrightarrow {}^1P$ type. The ratio of intensity of weak to strong lines is about 1 : 3, indicating that the fluorine atom possesses a nuclear spin of one half. L. S. THEOBALD.

Excitation functions in the neon spectrum. W. HANLE (Z. Physik, 1930, **65**, 512—516).—The excitation functions of some red and yellow neon lines were measured. The large variation of intensity distribution with pressure is discussed.
A. B. D. CASSIE.

Discharges in neon. P. JOHNSON (Phil. Mag., 1930, [vii], **10**, 921—931).—The relationship between *E.M.F.* and current in high-frequency discharges through neon has been determined by Townsend and

Nethercot's method (A., 1929, 482). As in the case of nitrogen, the mean force in the luminous column of a high-frequency discharge in neon is independent of the current in the tube for 1—10 milliamp. and of the wave-length of the oscillator from 30 to 120 m. The force in the uniform column of a direct-current discharge has substantially the same value as the above. The mean force X in the high-frequency discharge increases linearly with the pressure p above values of the latter of 10 mm., but at a little below this value the ratio X/p increases with fall of pressure. Addition of 1% of helium increases by 6 or 7% the electric force required to maintain the current. Neon can be satisfactorily tested for impurities by observing the spectrum of a high-frequency discharge in a wide tube containing the gas at high pressure.

M. S. Burr.

Extreme ultra-violet spectra of neon and argon excited by electrodeless ring discharge. K. T. Compton, J. C. Boyce, and J. L. Nickerson (Physical Rev., 1929, [ii], **33**, 1085; cf. A., 1929, 1359).—The electrodeless discharge brings out higher stages of excitation than do the controlled electron impacts. The ionisation potential found for Ne III is 511,700 ν and the higher limits occur at 545,350 and 566,517, approximately. Metastable singlet states are about 22,300 and 52,250 above the low triplet state. Two triplet series of three members each and one singlet series of two are found together with the low quintuplet state and the low states associated with the higher limits. All predicted $a-b$ lines are found. The ionisation limit of A III is 329,476 ν. The $a-b$ lines of Ne IV and A IV are strong, whilst those of Ne V or A V are too weak to be identified.

L. S. Theobald.

New terms in the spectrum of Al I. R. F. Paton and W. D. Lansing (Physical Rev., 1929, [ii], **33**, 1099; cf. A., 1929, 1206).—The vacuum furnace spectrum of aluminium gives lines of the sharp and diffuse series in both absorption and emission; in addition, the well-known lines 3057·15 and 3050·07 appeared in emission at the same temperature as the first lines of the diffuse series. These lines, together with a weaker one at 3060·20, are assigned to the transition $3^2P-3p^1\,{}^2D$, where the latter term arises from the configuration $3s3p^2$. A pair observed by Sawyer and Paschen at 1910·91 and 1906·57 are assigned to the transition $3^2p-3p^1\,{}^2S$. The term values, based on the ${}^1S_0$ state of the Al II core, are $3p'\,{}^2D_3=15{,}468$, $3p'\,{}^2D_2=15{,}504$, and $3v'\,{}^2S_1=-4166$.

L. S. Theobald

New resonance series of sulphur vapour. J. Genard (Bull. Acad. roy. Belg., 1930, [v], **16**, 923—930).—The fluorescence spectrum of sulphur vapour, emitted at 600° and 2 mm. pressure, when excited by a copper arc, has been studied. The series excited by the lines 3248, 3274, and 3287 Å. consist of 21, 17, and 17 lines, respectively, of ranges 3032—5086, 3060—4567, and 3069—4602 Å. The lines of the second series appear to be triplets.

C. W. Gibby.

Relative intensities of lines in a generalised multiplet of Ti II. H. Engwight (Physical Rev., 1929, [ii], **34**, 541).—Measurements have been made on the multiplets $a^4P'-a^4D'[(3d)^2]3d-4p$ of Ti II and $a^2P'-a^2D'$ together with their inter-system combination lines, many of which are strong. The quadruplet, doublet, and their inter-system lines form a generalised multiplet. When an excitation correction corresponding with 3500° Abs. is applied the total intensities of quadruplet to doublet have the theoretical ratio 2 : 1.

L. S. Theobald.

Spectra of trebly-ionised vanadium, V IV, and quadruply-ionised chromium, Cr V. H. E. White (Physical Rev., 1929, [ii], **33**, 286).—The neutral atoms of vanadium and chromium contain five valency electrons, $3d^34s^2$, and six valency electrons, $3d^54s$, respectively. The removal of three electrons $3d4s^2$ from vanadium and four electrons $3d^34s$ from chromium gives two isoelectronic systems V IV and Cr V, the lowest energy levels of which are represented by the two remaining electrons $3d^2$. The spectra from these two systems should resemble those of neutral calcium, Sc II, and Ti III, and extrapolations have led to the identification of 30 energy levels in both V IV and Cr V. The strongest lines arise from combinations between ${}^3P$, ${}^3D'$, ${}^3F$, ${}^1P$, ${}^1D'$, ${}^1F(3d4p)$ and $3D$, ${}^1D(3d4s)$, and ${}^1S$, ${}^3P'$, ${}^1D$, ${}^3F'$, ${}^1G(3d)^2$. The voltages necessary to remove one $3d$ electron from the normal state ${}^3F_2(3d)^2$ of V IV and Cr V to the normal state ${}^2D_2(3d)$ of the atoms again ionised are approximately 48·2 and 72·4 volts, respectively.

L. S. Theobald.

Probe and radiation measurements in the normal copper arc. W. B. Nottingham (Physical Rev., 1929, [ii], **33**, 280).—With an increase in arc current from 2·5 to 6·0 amp., the electron temperature fell from 19,000° Abs. to 15,500° Abs. The average velocity is probably controlled by the electron transition in the copper atom from the metastable D level to the 2^2P level, involving energies of 2·14 and 2·4 volts.

L. S. Theobald.

Multiplets in the spectrum of doubly-ionised copper, Cu III. R. C. Gibbs and A. M. Vieweg (Physical Rev., 1929, [ii], **33**, 1092).—The lowest terms in the spectrum of Cu III arise from the configuration $3d^9$, and successively higher terms from the configurations $3d^84s$ and $3d^84p$. Quadruplets and doublets, as well as intercombinations, arising from the transition $3d^84p$ to $3d^9({}^2D_{2,3})$ have been classified in the region of 800 Å.

L. S. Theobald.

Zeeman effect in the ZnH and CdH bands. W. W. Watson (Physical Rev., 1930, [ii], **36**, 1134—1143).—The Zeeman effect in the ${}^2\Pi$— bands of ZnH at λ 4326 and CdH at λ 4509 with large ρ type doubling was investigated in detail for field strengths up to 30,400 gauss. Intensity relations among the twelve branches of each band are discussed. The ρ type doubling in the ${}^2\Sigma$ states is measured by the separation of the satellite and main lines having the same K values and is proportional to $K+\frac{1}{2}$ rather than to K. The positions and widths of the blocks of components for all the lines are computed from the quantum formulæ of Hill (cf. A., 1930, 265). Results are in good agreement with experimental data on a number of details unique to these bands, and are fully tabulated for a field of 16,400 gauss.

N. M. Bligh.

Fine structure of zinc lines in the visible and ultra-violet regions. W. Mohammed and P. N. Sharma (Phil. Mag., 1930, [vii], **10**, 916—921).—Eighteen zinc spectral lines have been carefully examined and the following found to possess one satellite: λ 4722·26, 3345·13, 3303·03, 3075·99, 3035·93, and 2770·94. The line λ 4298·54 has two satellites, one strong and the other very faint and diffuse. M. S. Burr.

Spectrum of γ Geminorum. S. Albrecht (Astrophys. J., 1930, **72**, 65—97).—H_γ is the strongest line, followed by Mg^+ 4481; 276 lines are due in nearly equal proportions to ionised and neutral atoms, the former including Fe^+, Ti^+, Cr^+, Sc^+, Ce^+, Zr^+, Sm^+, Rb^+, V^+, Mo^+, Mn^+, Mg^+, and Pr^+ and the latter Fe, Ti, Cr, Mn, Ca, V, and Ni. Other elements have also been identified. There appear to be no appreciable relative displacements between lines due to neutral and those due to ionised atoms. L. S. Theobald.

Second spark spectrum of krypton. D. P. Acharya (Indian J. Physics, 1930, **5**, 385—405).—The spark spectrum of krypton has been explored in the region 2500—1900 Å. Previously-measured lines of the Kr^{++} spectrum are classified and together with the newly-measured lines are given in tabular form. The ionisation potential of Kr^{++} is calculated to be 31·4 volts. J. W. Smith.

Structure of the spectra of doubly- and trebly-ionised zirconium. C. C. Kiess and R. J. Lang (Bur. Stand. J. Res., 1930, **5**, 305—324).—The spectral lines of Zr III and Zr IV have been photographed and analysed, and the terms found accord fully with the quantum theory; the spectra resemble closely the corresponding Ti III and Ti IV spectra. The Zr IV spectrum is a doublet spectrum resulting from the migration of a single 4_3 electron. The value of the fundamental $4^2D_{3,2}$ term, derived from a series of S terms, is 274,067 cm.$^{-1}$, corresponding with an ionisation potential of 33·83 volts. The Zr III spectrum is derived from the interaction of two 4_3 electrons, and exhibits singlet and triplet systems; sequences of ^1D and ^3D terms, resulting from one electron in an n. orbit and one in a 4_3 orbit, yield for the fundamental term $^3F_2$ 194,441 cm.$^{-1}$, corresponding with an ionisation potential of 24·00 volts. The transition $4f \longrightarrow 4d$ is represented by multiplets which, like those derived from inter-system combinations, exhibit anomalous intensities. H. F. Gillbe.

Polarisation of cadmium resonance radiation 1^1S_0—2^3P., 3261 A. A. Ellett (Physical Rev., 1929, [ii], **33**, 124).—This line is completely polarised in the absence of a magnetic field and also in a field parallel to the electric vector of the exciting, plane polarised light. The mean life of the 2^3P state of cadmium is $2·30\times10^{-6}$ sec. L. S. Theobald.

Magnetic extinction of iodine fluorescence and its relation to predissociation phenomena. L. A. Turner (Z. Physik, 1930, **65**, 464—479).—The extinction of iodine fluorescence by a magnetic field and its dependence on the exciting wave-length were investigated. Both monochromatic light and light from a carbon arc passed through a spectrometer were used. Passing from long to shorter wave-lengths, extinction begins suddenly and then gradually diminishes; it appears almost as predissociation in the vibrational degree of freedom. This phenomenon is fully discussed on Bonhoeffer's theory of predissociation, and appears to fit in with this scheme. The conception of predissociation in the vibrational degrees of freedom also explains Norrish's results (A., 1929, 893) on the fluorescence and photochemical decomposition of nitrogen peroxide. A. B. D. Cassie.

Excitation of iodine fluorescence with monochromatic light. L. A. Turner (Z. Physik, 1930, **65**, 480—488).—The determination of the quantum numbers (vibrational and rotational) defining the excited state due to absorption of a given monochromatic radiation is fully discussed. The examples of the two yellow mercury lines at 5771·2 and 5792·3 Å., the neon line at 5852·5 Å., and the cadmium line at 5085·9 Å. are worked out. A. B. D. Cassie.

Interference measurements in the first spectra of krypton and xenon. C. J. Humphreys (Bur. Stand. J. Res., 1930, **5**, 1041—1055; cf. A., 1929, 1118).—New determinations of the stronger arc lines of the krypton and xenon spectra in the region 4000—9000 Å. have been made with the Fabry–Perot interferometer. Accurate relative values of all the $1s$, $2p$, and $3p$ terms of the krypton spectrum have been established, the average deviation of the calculated term combinations from the observed wave-numbers being 1 in 20×10^6. In the xenon spectrum all the $1s$, $2p$ (except $2p_{10}$), and $3p$ terms, and four of the $4p$ terms have been redetermined. Nearly 75% of the combinations permitted by the selection principle have been observed. Since the infra-red combinations which are photographically inaccessible can now be predicted accurately, it is suggested that their wave-lengths should be employed as standards in the infra-red region. Fine structure has not been observed with any of the krypton lines, and the intensities of any satellites which may exist are too small to influence the wave-lengths; five of the xenon lines show satellites. The "pressure effect" of McLennan and Quinlan (Trans. Roy. Soc. Canada, 1929, **24**, III, 1), which causes a change of wave-length of the xenon lines as the emission tube ages, appears to be due to experimental error; under conditions required to excite the spark spectrum a change of wave-length of the arc lines of both elements has been observed, and is ascribed to the Stark effect. H. F. Gillbe.

Characteristics of the electric furnace spectra of europium, gadolinium, terbium, dysprosium, and holmium, 3900—4700 Å. A. S. King (Physical Rev., 1929, [ii], **33**, 540).—The separation of lines arising from neutral and ionised atoms, respectively, and the temperature classification of both groups have been accomplished. Groups of strong low-temperature lines were noted, especially for europium, dysprosium, and holmium, and the furnace emitted strongly many lines which are faint in the arc and were unidentified hitherto. Hyperfine structure was distinguished for many lines, usually ionised, in the spectra of europium, terbium, and holmium; in the

graduated spacing of components these often resemble the lines of ionised praseodymium.

L. S. Theobald.

Spectral terms of platinum, and classification. P. J. Ovrebo (Physical Rev., 1929, [ii], **33**, 1098; cf. A., 1929, 1352).—Forty-nine new terms have been found for platinum; of these 17 are low, 12 intermediate, and 19 upper levels. Combinations with previously-known levels give 250 lines, of which 150 are newly described. Combinations between low and high levels have been found. The term 29,600·8 combines with high, intermediate, and low terms; 31,900·5 combines with low as well as other intermediate terms, whilst 44,760·9 acts as both intermediate and high levels. New levels have been classified.

L. S. Theobald.

Origin of the bands in the spectrum of mercury vapour. S. Mrozowski (Physical Rev., 1930, [ii], **36**, 1168—1171).—A reply to the arguments of Rollefson (cf. A., 1930, 970). New observations are reported of shaded absorption bands at 2267 and 2247 Å. N. M. Bligh.

Electro-optical modification of light waves. L. H. Stauffer (Physical Rev., 1930, [ii], **36**, 1352—1361).—Broadening of the satellites of the mercury green line λ 5461 was observed when the light passed between the plates of a Kerr cell containing nitrobenzene, on which was impressed a varying *E.M.F.* The broadening was in agreement with the classical and quantum theories of dispersion, and increased rapidly with the oscillator voltage. N. M. Bligh.

Optical constants of solid mercury. R. S. Baldwin (Physical Rev., 1929, [ii], **33**, 1072).—The refractive index for the solid state is at least 10% greater than that for the liquid for the wave-lengths used (5790—5769, 5460, and 4358 Å.). The absorption coefficient is practically unchanged.

L. S. Theobald.

Continuous spectrum of mercury. W. N. Thornton and W. H. Crew (Physical Rev., 1929, [ii], **33**, 1072; cf. A., 1929, 1).—Photographs with a small quartz spectrograph of the continuous spectrum of mercury support the view that it is due to the recombination of electrons with molecules or with atoms held in molecular linking. A low current and voltage, high-frequency, condensed discharge in the vapour between two liquid mercury surfaces gave two strong bands with maximum intensities at approximately 4500 and 3300 Å. and four weak lines 5461, 4358, 4047, and 2536 Å. L. S. Theobald.

Mercury spectrum by high-voltage electrodeless discharge. O. Stuhlman, jun., and M. W. Trawick (Physical Rev., 1929, [ii], **33**, 287—288).—Spectra of the electrodeless discharge through a capillary and of the ring discharge in a 12-cm. spherical bulb have been compared with that from a quartz mercury vapour lamp. The spectra of the discharge through the capillary and of the ring are identical, with spark and arc lines about equal in number. No continuous spectra were observed. The frequencies of $1s-mp_1$ up to $m=17$ have been classified. L. S. Theobald.

Polarisation phenomena in the gradual excitation of the fluorescence of mercury. E. F. Richter (Ann. Physik, 1930, [v], **7**, 293—328; cf. A., 1929, 741).—The colour effects obtained in the gradual excitation of fluorescence in mercury vapour by polarised light from a quartz mercury arc have been examined spectroscopically in relation to the direction of an applied magnetic field. The results are discussed theoretically. Measurements of the degree of polarisation confirm theoretical expectations qualitatively. Under conditions where the line 4047 Å. should be completely polarised the maximum polarisation observed was 80%, the discrepancy being attributed to fine structure. Ultra-violet lines showed similar behaviour. The life-period of the excited atoms, determined by two independent methods, varied from about 10^{-9} to 10^{-7} sec., that of λ 5461 Å. being four times as great as that of the other triplet lines. In all the experiments nitrogen was present in the mercury vapour. F. L. Usher.

Spectrum of doubly-ionised thallium. P. Pattabhiramayya and A. S. Rao (Indian J. Physics, 1930, **5**, 407—416).—The spark spectrum of thallium in air and in hydrogen at different pressures and under varying conditions of excitation has been re-examined. The results have been combined with those of previous investigators in a systematic classification of the Tl^{++} spectrum. In accordance with the theory of Hund, the spectrum consists of two parts, an ordinary doublet spectrum and a quadruplet–doublet spectrum the deepest term of which is a metastable ${}^{2}D$ term which is inverted and very low. The two types of ion on which these two spectra are built are (d^{10}) and ($d^{9}s$), which are spectroscopically terms of the type ${}^{1}S$ and ${}^{3}D$ and ${}^{1}D$. J. W. Smith.

Spark spectra of bismuth, Bi II and Bi III. Evidence of hyperfine structure. J. C. McLennan, A. B. McLay, and M. F. Crawford (Proc. Roy. Soc., 1930, **A**, **129**, 579—588).—Progress has been made in the identification of the multiplet term structure of Bi II and Bi III from a study of the frequencies of the wave-lengths in (*a*) the spectrum of a condensed discharge in heated bismuth vapour (λ 7050—2000 Å.), (*b*) that of a condensed spark between metallic terminals in hydrogen (λ 2000—1340 Å.), and (*c*) that of a hot spark between metallic terminals in a vacuum (for wave-lengths below 1340 Å.). Evidence of hyperfine structure was apparent in the spectra, the effect in a few cases being of large magnitude. L. L. Bircumshaw.

Occurrence of addition and subtraction potentials of 1·4 volts in the mercury atom. R. G. Loyarte (Physikal. Z., 1930, **31**, 929—939; cf. this vol., 18).—The origin of certain optical lines of the mercury spectrum can be explained by adding to or subtracting from the value of the potential energy of a line of known origin 1·4 volts or low multiples of this value. The physical significance of the procedure is discussed. The good agreement between observed and calculated values is shown by a number of tables.

W. R. Angus.

Dependence of photo-electric properties of cæsium on its adsorption on salt layers. J. H. de Boer and M. C. Teves (Z. Physik, 1930, **65**, 489—505).—Experiments on the adsorption of sublimed alkali metals by thin sublimed salt layers are

described. The surface ions of the thin salt layer induce dipoles in the metal molecules or atoms, and so form a firmly-adsorbed layer. This process recurs, and metal layers of one, two, or more atoms thick are obtained. The polarisation greatly affects light absorption; thus iodine on calcium fluoride is brown, whilst cæsium is blue. Increasing thicknesses of cæsium displace the absorption towards the violet. Cæsium layers adsorbed on calcium or barium fluoride show a photo-electric sensitivity (to white light) which increases to a maximum with increasing thickness, then falls to a constant value. The maximum of the wave-length–photo-electric sensitivity curves, and the long wave-length limit are displaced towards the violet with increasing thickness of the metal layer. Pure cæsium shows a photo-electric sensitivity of 0·17 μ amp. per lumen for white light, whilst cæsium adsorbed on barium or calcium fluoride may show 1·6 μ amp. per lumen. In similar experiments with cæsium oxide replacing barium fluoride the limiting wave-length is displaced towards the red to 1·15 μ. A. B. D. CASSIE.

Influence of gases on photo-ionisation of cæsium by line absorption. F. L. MOHLER and C. BOECKNER (Bur. Stand. J. Res., 1930, 5, 399—410).—The influence of nitrogen, hydrogen, helium, and argon on the photo-ionisation of cæsium vapour by line absorption has been studied by space-charge measurements. Nitrogen reduces the ionisation at all wave-lengths greater than 3200 Å., and at constant cæsium vapour pressure $E_0/\Delta E$, where E_0 is the probability of ionisation in absence of a foreign gas and ΔE is the change of the probability produced by the gas at pressure p, appears to be a linear function of $1/p$; the same obtains for helium, except at pressures above about 2 mm. The ionisations of the states from $4P$ to $8P$ are reduced by nitrogen to about the same extent, whereas helium increases the ionisation of the $4P$ state and decreases that of other lines. The influence of nitrogen increases with fall of the cæsium pressure on account of the change of the life of the excited state. The theoretical significance of the results is discussed with especial reference to the types of transition which occur. H. F. GILLBE.

Effect of systematic surface treatment on the photo-electric emission from metals. R. F. HANSTOCK (Phil. Mag., 1930, [vii], **10**, 937—944).—An investigation has been made of the photo-electric emission from metal surfaces in a vacuum at intervals during the process of polishing, beginning with the surface in an annealed state. The polishing was carried out by rubbing with a metal harder than the one under consideration. The curves obtained by plotting degree of polish against photo-electric current indicate that the current is increased when the metal surface is rubbed, and that the increase is approximately a linear function of the number of rubs until just before a constant maximum value is reached. The ratio of the current after polishing to the current from the annealed surface shows no regular dependence on the pressure of gas in the tube. The effect is obtained with radiation of a restricted wave-length as well as for the full spectrum. The increased activity due to rubbing does not disappear, even after several days, but by heating to above 150° the metal can be reduced to its less active state. The results are reproducible by successive heating and polishing, and seem to be best explained as due to the modified layer of thickness 50—500 μ known to be produced at the surface of a metal by rubbing, and restored to its original state by heat. M. S. BURR.

Origin of the photo-electrons in the copper–cuprous oxide photo-cell. W. SCHOTTKY (Physikal. Z., 1930, **31**, 913—925).—The photo-decay of the cell, copper plate–cuprous oxide layer–auxiliary electrode, with increasing distance between electrodes follows an exponential law. The decay distance is a few mm., and can be calculated from resistance measurements. The photo-effect is due to a unidirectional layer at the surface of the copper plate, the photo-electrons being liberated at the copper–cuprous oxide boundary after the light has penetrated the oxide layer. J. E. MILLS.

New kind of photo-cell. B. LANGE (Physikal. Z., 1930, **31**, 964—969; cf. A., 1930, 391).—The behaviour of the new photo-cells is compared with that of the crystal detector. Such comparison is made possible by the fact that in each there are two materials in the crystal detector, the crystal and the needle, whilst in the new photo-cell there is a metal plate and a unidirectional layer of a unipolar half-conductor through which liberated photo-electrons are made to pass. New copper–cuprous oxide photo-cells are described and discussed. The spectral sensitivity of these cells is selective and the spectral range for which a cell is sensitive depends on the thickness of the unidirectional layer of cuprous oxide. The industrial application of such photo-cells is considered. In conjunction with a microphotometer these cells can be used for measuring the absorption of substances within the limits of the spectral range of their sensitivity. A differential photo-cell has been devised on the same principles. W. R. ANGUS.

Variation with temperature of the unidirectional layer photo-electric effect in a copper–copper oxide cell. H. TEICHMANN (Z. Physik, 1930, **65**, 709—713).—The copper–copper oxide cell is fully described. Measurements of the photo-electric emission at different temperatures show that the cell has a negative temperature coefficient. A. B. D. CASSIE.

Preparation of photo-electric cells with thin films of lithium as the photo-active material. H. E. IVES (Physical Rev., 1929, [ii], **33**, 1081—1082).—A method for preparing thin films of lithium on a plate of tungsten, avoiding the usual difficulties of handling lithium in a vacuum, is described. The film at one stage in its formation is sensitive to red light at 6708 Å. L. S. THEOBALD.

Photo-*E.M.F.* in single crystals of selenium. R. M. HOLMES and N. L. WALBRIDGE (Physical Rev., 1929, [ii], **33**, 281).—With thin lamellar single crystals of selenium the photo-*E.M.F.* is greater than that found for acicular crystals (A., 1929, 1371). When the radiation from a tungsten lamp passes through one of two platinum films sputtered on each of the two parallel faces of the crystal, electrons flow

from selenium to platinum at the illuminated contact. The photo-current increases with an increase in illumination, reaching the value 5·5 microamp. for 4 lumens per cm.^{2} L. S. THEOBALD.

Photo-electric effect of liquid tin and two of its allotropic modifications. A. GOETZ (Physical Rev., 1929, [ii], **33**, 265).—The photo-electric emission of tin has been measured from the ordinary temperature up to 550°. The red limit of emission is different for the liquid and the crystalline phases. The photo-electric threshold changes at the transition tetragonal⟶hexagonal tin. The photo-electric thresholds are liquid tin (232—550°), 2925±10 Å.; hexagonal tin (203—232°), 2820±10 Å.; and tetragonal tin (70—150°), 2740±10 Å. The change tetragonal⟶hexagonal tin is slow and occurs between 203° and 100°. L. S. THEOBALD.

Infra-red sensitivity of cæsium oxide photo-electric cells. J. W. BALLARD (J. Opt. Soc. Amer., 1930, **20**, 618—623).—The maximum sensitivity of cæsium oxide photo-electric cells lies between 7500 and 8000 Å., and the minimum at 5500 Å. The sensitivity extends into the infra-red almost to 12,000 Å. C. W. GIBBY.

Departure from Einstein's photo-electric equation with certain alkali metal films. W. B. NOTTINGHAM (Physical Rev., 1929, [ii], **33**, 1081).—The long wave-length limit is probably greater than 8400 Å. for sodium and 9600 Å. for potassium, and departures from Einstein's photo-electric equation have been found for thin films of both metals near their long wave-length limits. L. S. THEOBALD.

Ionisation of helium, neon, and argon by electron impact. P. T. SMITH (Physical Rev., 1930, [ii], **36**, 1293—1302).—In view of the divergencies of existing data on the efficiency of ionisation by electron impact in gases, the total number of positive charges produced per electron path at constant pressure was determined as a function of the energy of the impacting electrons up to 4500 volts in helium, neon, and argon, the respective maximum efficiencies being found as 1·256 at 110, 3·008 at 170, and 13·01 at 88 volts. An empirical relation is given for the efficiency of ionisation of helium for energies greater than 60 volts. Results are not in agreement with those of other investigators (cf. Compton and Van Voorhis, A., 1926, 769; Hippel, A., 1929, 228; Bleakney, cf. following abstract). N. M. BLIGH.

Ionisation potentials and probabilities for the formation of multiply-charged ions in helium, neon, and argon. W. BLEAKNEY (Physical Rev., 1930, [ii], **36**, 1303—1309).—Using the mass-spectrograph method previously described (cf. A., 1929, 970; 1930, 969) the multiply-charged ions in helium, neon, and argon were investigated. The He^+ ion was strong, but only faint evidence was found for the formation of He^{++}. Neon gave Ne^+, Ne^{2+}, and Ne^{3+} as the result of single-electron impacts at minimum electron energies of 21·5, 63, and 125 volts, respectively. Curves are given for the efficiency of ionisation as a function of the electron velocity and show maxima for Ne^+ and Ne^{2+} at 2·75 and 0·16 for 150 and 250 volts, respectively. In argon, the ions A^+, A^{2+}, A^{3+}, A^{4+} and A^{5+}, were observed, with ionisation potentials for the first four of 15·7, 44, 88, and 258 volts, respectively, for single impact, and efficiency maxima of 11·4, 1·1, and 0·04 at 50, 115, and 250 volts for A^+, A^{2+}, and A^{3+}, respectively (cf. preceding abstract). There were indications of critical potentials above the ionisation potentials for Ne^{3+} and A^{4+}. N. M. BLIGH.

Ionisation of cæsium vapour by light of frequency greater than the series limit. E. O. LAWRENCE and N. EDLEFSEN (Physical Rev., 1929, [ii], **33**, 265; cf. A., 1929, 1121).—The ionisation of cæsium vapour by light of wave-length from the series limit to 2200 Å. has been studied. The ionisation efficiency of the light falls rapidly from the limit to shorter wave-lengths except for wave-lengths near 2536 Å., where it is of the same order of magnitude as that of the series limit. The anomalous ionisation by light of wave-length 2536 Å. is probably due to a trace of mercury vapour. L. S. THEOBALD.

Optical excitation function of helium. W. C. MICHELS (Physical Rev., 1930, [ii], **36**, 1362—1374; cf. Hanle, A., 1929, 1116; Elenbaas, A., 1930, 387).—The excitation function of helium for electrons with energies between the excitation potentials and 100 volts was investigated, using a special discharge tube, and a method designed to eliminate collisions of the second kind, ionisations, and recombinations, to give a linear dependence of intensity on current or pressure, and to allow a determination of the electron velocity distribution curve. Intensity–voltage curves are given for the singlet and triplet system of helium, correcting existing data, and allowing the true optical excitation function values to be obtained; these are plotted against electron energies, and show that each line has maximum excitation probability at or near the excitation potential, the probability falling above this value, but more rapidly for the triplet than for the singlet system. N. M. BLIGH.

Electro-osmose theory of the electrolytic rectifier. A. DOBIAS (Z. Physik, 1930, **65**, 859; cf. A., 1930, 999).—Polemical against Müller, who claims priority (A., 1929, 770; 1930, 165). A. J. MEE.

Thermionic emission of oxide-coated cathodes containing a Ni–Ba alloy core. N. C. BEESE (Physical Rev., 1930, [ii], **36**, 1309—1313; cf. Reimann, A., 1930, 657; Lowry, *ibid.*, 973).—Comparisons were made of the electron emission of an alloy containing 0·15% Ba, and of pure nickel, and of the alloy after removal of the barium content. Curves of electron emission plotted against time show the marked influence of the added barium on increased emission. N. M. BLIGH.

Diffusion of ions of salts into aluminium. CICHOCKI (Compt. rend., 1930, **191**, 841—842; cf. A., 1929, 482).—A tube of aluminium, 2 mm. internal and 4 mm. external diameter, filled with nickel chloride was drawn out until its external diameter was 0·83 mm., and placed in the centre of a copper tube 20 mm. in diameter, the whole being enclosed in a vacuous glass tube. A *P.D.* of 80 volts was maintained between the copper and aluminium tubes, and the latter heated electrically to 600°. No negative

thermionic current passed, but the positive emission increased with time for 60 min., and then rapidly decreased. This is attributed to absorption of the salt by the metal followed by emission of ions into the vacuous space around the tube.

C. A. SILBERRAD.

Shot effect of the emission from oxide cathodes. H. N. KOZANOWSKI and N. H. WILLIAMS (Physical Rev., 1930, [ii], **36**, 1314—1329; cf. A., 1929, 736).—An apparatus for the investigation of the fluctuations associated with the emission from barium–strontium oxide cathodes, especially in the space-charge region, is described. The presence was verified of positive ions, which, moving in an electron space charge, cause abnormally high shot fluctuations in an aperiodic circuit at high amplifier frequencies. The characteristic fluctuations associated with the emission from oxide cathodes have been reproduced in a special vacuum tube in which positive ions from an independent Kunsman potassium ion emitter interact with the electron space charge about a metal emitter, indicating a similar process in the emission from barium–strontium oxide cathodes. Some results are given of the shot effect of films evaporating from a tungsten wire.

N. M. BLIGH.

Abnormal shot effect of ions of tungstous and tungstic oxide. J. S. DONAL, jun. (Physical Rev., 1930, [ii], **36**, 1172—1189).—The formation of positive ions when oxygen attacks a hot tungsten filament is discussed. The ions consist of a mixture of tungstous and tungstic oxides. The abnormal shot effect when these positive ions are accelerated through the dense electron space-charge region surrounding the filament and drawn to a collecting electrode in series with a tuned shot circuit was investigated, using the apparatus of Williams and Vincent (cf. A., 1927, 85). Assuming that the shot voltage arises from fluctuations in the inter-electrode capacitance of the tube, caused by variations of thickness of the electron sheath with penetration by the ions, an expression for the resulting mean square-shot voltage is deduced, in good agreement with experiment. When positive ions were trapped in the minimum of potential surrounding a hot cathode, an abnormal shot voltage resulted, varying inversely with the square of the resonance frequency of the tuned-shot circuit; an expression is obtained for the mean square-shot voltage, from which are deduced values of the average plate current increase, the number of electrons released by each positive ion, average time of trapping of the ions, and electron space-charge density in the minimum of potential, in good agreement with available data.

N. M. BLIGH.

Secondary radiation of solid elements in relation to the nature of the element and the hardness of the primary *X*-rays. E. VETTE (Ann. Physik, 1930, [v], **5**, 929—990; cf. Espe, A., 1929, 1122).—The emission of secondary electrons and characteristic radiation by elements from aluminium to bismuth was investigated, using strongly filtered impulse radiation from a tungsten anticathode. The results showed the increase in the velocity of the secondary electrons with increase in the hardness of the exciting radiation, and the decrease in velocity with increase in the atomic number of the element irradiated. For the characteristic radiation it was found that only that portion of the spectrum of the primary radiation that is shorter in wave-length than the characteristic radiation was effective, so that, with constant voltage, as the atomic number of the irradiated element increased the emission increased first to a maximum, and then decreased as the K absorption edge of the element passed through the spectrum of the exciting radiation, and finally increased again with increasing proximity to the L absorption edge.

H. A. JAHN.

Distinction between contact-potential effects and true reflexion coefficients for low-velocity electrons. H. E. FARNSWORTH and V. H. GOERKE (Physical Rev., 1930, [ii], **36**, 1190—1194; cf. A., 1929, 1212).—A method is described for determining the apparent electron reflexion coefficient in two ways, with distinction between a contact potential and a true reflexion coefficient for very low-velocity electrons. Results indicate that for a carefully degassed copper target the true electron reflexion coefficient approaches zero with the primary voltage, and that the apparent increase in reflexion coefficient below about 1 volt is due to a change in the contact potential between the target and the surrounding electrodes, the increase for the copper specimen tested being about 1·2 volts.

N. M. BLIGH.

Velocity distribution of secondary electrons from molybdenum. T. SOLLER (Physical Rev., 1930, [ii], **36**, 1212—1220).—Using the magnetic deflexion method with improved vacuum conditions, the velocity distribution curves of secondary electrons from a molybdenum target were investigated for primary electron velocities of 7·5—100 volts, and were similar to those for other metals, showing a broad low-velocity maximum of secondary electrons, and a sharp "reflected" peak, with measured velocity 2 volts less than the corresponding accelerating voltage, in agreement with contact potential considerations. Degassing at 850° produced only slight changes in the curves, whilst for 1250° a marked decrease in the low-velocity maximum and an increase in the height of the "reflected" peaks were found, both changes being ascribed to the degassing. The curves height of reflected peak–primary electron velocity show several maxima, the voltages corresponding with the critical potentials of molybdenum.

N. M. BLIGH.

Scattering of light by electrons. G. GLOCKLER (Physical Rev., 1929, [ii], **33**, 116).—The scattering of light by fast electrons can be predicted from the principle of microscopic reversibility. The equation showing the change of wave-length for head-on collision between a quantum and a free fast electron is given. The interaction of visible light with fast electrons should modify the quantum. The mercury line 5461 Å. should show a change of 685 Å. when interacting with a 1000-volt electron in a head-on collision.

L. S. THEOBALD.

Scattering of electrons by atomic fields. E. C. BULLARD and H. S. W. MASSEY (Proc. Camb. Phil. Soc., 1930, **26**, 556—563).—Mathematical. The

variation of the intensity of elastic scattering with velocity and angle of scattering is obtained by applying the Thomas-Fermi electron distribution to Born's approximate scattering formula (cf. Mott, A., 1930, 974). For heavy atoms the scattered intensity is shown to be a function of the electron mass, scattering angle, and atomic number of the scattering medium. This function is tabulated, and the range of validity of such values is discussed. Born's formula is inaccurate for electrons of less than 400 volts velocity, except for atoms of low atomic number. For high-velocity electrons an approximate expression is obtained for the angular distribution, allowance being made for screening by the extra-nuclear electrons.

N. M. Bligh.

Scattering of electrons by crystals and adsorbed gas films. H. J. Verweel and J. M. Bijvoet (Chem. Weekblad, 1930, 27, 626—629).—A survey. H. F. Gillbe.

Optical determination of the sphere of action of atoms for electrons. L. S. Ornstein and A. M. van Dommelen (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 683—689; cf. Ornstein and Elenbaas, A., 1930, 392).—By using a mixture of helium and mercury, it is possible to extend the measurements of the effective diameters of atoms to electronic energies below the excitation potential. At 48·35° and 0·012 mm. pressure (mercury) the values of the active diameters of the helium and mercury atoms for 30-volt electrons are 8·2 and 63 cm.^{2}/cm.^{3}, respectively, in fair agreement with the values of Ramsauer and of Brode. O. J. Walker.

Attachment of free electrons to neutral molecules in air and oxygen. A. M. Cravath (Physical Rev., 1929, [ii], **33**, 266—267).—The fraction, h, of the collisions between electrons and neutral electrons which result in the formation of a negative ion has been measured over a wide range of field strength and pressure in air and in oxygen. In oxygen, h has a minimum at 0·9 volt average electronic energy, whilst at constant energy, pressure has little effect. In air, h rapidly increases as the electronic energy falls below 0·9 volt, and varies rapidly with pressure. Proof of the permanence of the negative ions in weak fields, and evidence of the detachment of electrons from negative ions in high fields, were also obtained.

L. S. Theobald.

"Anomalous dispersion" of electron waves by nickel. C. J. Davisson and L. H. Germer (Physical Rev., 1929, [ii], **33**, 292—293).—The dispersion curve for nickel has a discontinuity near 1·3 A. which suggests optical anomalous dispersions.

L. S. Theobald.

Polarisation of electrons. G. P. Thomson (Nature, 1930, **126**, 842).—The difference in the intensity of a beam of electrons twice reflected from gold surfaces observed by Rupp (A., 1930, 392) could not be confirmed. L. S. Theobald.

Behaviour of methane molecules and argon atoms in collisions with very slow electrons. H. L. Brose and J. E. Keyston (Nature, 1930, **126**, 806—807).—Using Townsend's diffusion method, the absolute value of the effective cross-section, Q, of methane molecules is found to be low, like that of argon. The curves obtained by plotting Q against voltage$^{1/2}$ closely resemble each other in both cases, and for methane the minimum value of Q is 4·3 cm.^{2}/cm.^{3} at a velocity $0{\cdot}52V^{1/2}$, but the similarity does not mean that the molecule of methane behaves in collisions with slow electrons like the atom of argon. The use of Townsend's method for investigating the collisions of gases is defended. L. S. Theobald.

Search for radiation accompanying the scattering of comparatively slow electrons at the surface of incandescent solids. E. Rudberg (Proc. Roy. Soc., 1930, **A**, **129**, 652—656).—Experiment shows that there is no appreciable radiation emitted in the visible region and the ultra-violet above 2300 Å., under the conditions for which the characteristic energy losses suffered by electrons scattered from incandescent solids have been found to occur.

L. L. Bircumshaw.

Energy losses of electrons in nitrogen. E. Rudberg (Proc. Roy. Soc., 1930, **A**, **129**, 628—651).—Measurements have been made, with a greater accuracy than those of previous investigators, of the energy given up by electrons at inelastic impacts in nitrogen under such conditions that no appreciable amount of multiple collisions occurs. Only collisions for which the resulting deflexion of the colliding electron from the original line of flight is very small can be studied with the apparatus used. The method of velocity analysis adopted is similar to that of Harnwell (A., 1929, 619). Seven maxima have been measured in the distribution curves in the region corresponding with individual energies 0—30 volts less than the primary voltage. The smallest energy loss observed is attributed to collisions with the electrodes. The strongest maximum observed indicates a loss of 12·78 volts, and, together with a further prominent maximum, is interpreted as being due to excitation of the first singlet levels of the nitrogen molecule. Two further maxima are probably related to similar unknown levels. From the fact that a sensitive test for a characteristic energy loss connected with the ionisation of the nitrogen K level gave negative results, it is concluded that the probability for the colliding electron to produce the emission of a K electron is small compared with that of displacing an outer electron, for the range of primary velocities studied (up to 600 volts).

L. L. Bircumshaw.

Elastic scattering of electrons in molecular hydrogen. H. S. W. Massey (Proc. Roy. Soc., 1930, **A**, **129**, 616—627).—Mathematical. Using Born's collision formula, the scattering cross-sections presented by hydrogen molecules to electron beams are calculated. Diffraction effects are found to occur, and the intensities of these are determined. The effects would be very difficult to detect experimentally, owing to the smallness of the peaks relative to the "atomic background. L. L. Bircumshaw.

Low-voltage electron impacts in hydrogen. F. G. Slack (Physical Rev., 1929, [ii], **33**, 1085).—The effect of electron impacts with hydrogen streaming at 0·05—0·50 mm. pressure in a three-electrode tube with a unipotential, oxide-coated, hot filament has been investigated. The breaks in the curves of

Richardson and Tanaka (A., 1925, ii, 13) below 10·2 volts are missing, confirming the view that they were due to mercury vapour. No Balmer lines could be detected. L. S. THEOBALD.

Experiments on electron diffraction. F. KIRCHNER (Physikal. Z., 1930, **31**, 1025—1028).—Electron diffraction patterns give a sharper atom factor curve than X-ray patterns, because the nucleus governs the scattering of electrons, and the electron cloud the scattering of X-rays. In electron diffraction patterns, then, the second order spectra due to the (111) planes of sodium fluoride are not entirely extinguished, since the nuclear charges of Na^+ and F^- are unequal. Debye–Scherrer diagrams due to electrons diffracted by comparatively large crystals sometimes show interference points at the ends of a diameter of one or more of the rings. This can be ascribed to a mosaic-like structure of the crystal. Sublimation, under vacuum, of mercuric chloride from a heated platinum strip to a celluloid surface gives a cubic instead of a rhombic crystal. Diffraction by gaseous nitrogen, oxygen, or carbon dioxide gave patterns in accord with Debye's X-ray patterns. A. B. D. CASSIE.

Electron diffraction and molecular structure. R. WIERL (Physikal. Z., 1930, **31**, 1028).—Electron diffraction by gases can be used to determine the distance between atomic nuclei in an molecule. The distance S—S in carbon disulphide is 3·20 Å., O—O in carbon dioxide is 2·26 Å., N—N in nitrous oxide is 2·38 Å. The distance S—O in sulphur dioxide is doubtful, because of the triangular structure of the oxide, but it may be 1·37 Å. A. B. D. CASSIE.

Heats of condensation of electrons on metals in ionised gases. C. C. VAN VOORHIS and K. T. COMPTON (Physical Rev., 1930, [ii], **36**, 1435—1439; cf. A., 1927, 926, 1001).—Heats of condensation of electrons on electrodes of molybdenum, platinum, and tungsten coated with potassium were measured in ionised argon, neon, helium, nitrogen, and hydrogen by measuring the heat developed in Langmuir collectors of these metals when a known number of electrons of known energy was received by the collector. Results varied from 5·21 volts for platinum in nitrogen to 0·93 volt for potassium-coated tungsten in helium, and depended on the metal and the ionised gas, the effect of the latter being indicated as due to its ions rather than its neutral atoms. N. M. BLIGH.

Direct determination of the volume of the electron. V. POSEJPAL (Compt. rend., 1930, **191**, 1000—1002).—The volume is deduced from the formula $\sigma_s/\rho=-r^2/m_H$, where σ_s/ρ is the specific coefficient of true scattering of very hard γ-rays in hydrogen, r the radius of the electron, $(-1{\cdot}662\times 10^{-24})$ the mass of the hydrogen atom. Using the values of σ_s/ρ for γ-rays from radium-$B+C$ filtered through 2·6 cm. of lead, for water (0·0383) and glycerol (0·0406) the values $1{\cdot}42\times10^{-13}$ and $1{\cdot}47\times10^{-13}$ cm., respectively, are obtained for r, which agree with its electromagnetic value, $1{\cdot}9\times10^{-13}$ cm. The same formula is deduced from the author's corpuscular theory of an ether consisting of neutrons of diameter approximately equal to that of an electron, a neutron being defined as resulting from the emission by a normal hydrogen atom of energy equal to m_Hc^2. C. A. SILBERRAD.

Affinity of the hydrogen atom for the electron. P. STARODUBROVSKI (Z. Physik, 1930, **65**, 806—813).—Mathematical. The affinity of the hydrogen atom for the electron is calculated to the fourth approximation, and the result is claimed to be better than that of Hylleraas (A., 1930, 518, 1231). The value obtained is 16·40 kg.-cal. per mol. A. J. MEE.

Evidence of gas degeneration and applicability of Pauli's exclusion to metallic conduction electrons. J. DU MOND (Physical Rev., 1929, [ii], **33**, 123).—The distribution of velocities of the scattering electrons can be inferred from the breadth and structure of the Compton shifted line. The structure of this line has been studied experimentally and the results support the assumption that conduction electrons are subject to the Pauli exclusion principle and have the velocity distribution predicted by Sommerfeld. L. S. THEOBALD.

Geiger–Müller tube as a quantitative ion counter. J. A. VAN DEN AKKER (Rev. Sci. Instr., 1930, **1**, 672—683).—The conditions for the use of the new type Geiger–Müller tube as a quantitative detector of individual ions were investigated (cf. Geiger and Müller, A., 1929, 114). The rate of counting at various voltages was measured, using very weak sources of radium-D and mesothorium. The count–voltage curves are analysed and discussed. The tube is found to be quantitative when the rate of counting is moderate, the accuracy increasing when the rate of counting is very low. Spurious discharges seem inseparable from this form of tube. N. M. BLIGH.

Absorption of slow hydrogen positive rays in hydrogen. R. E. HOLZER (Physical Rev., 1930, [ii], **36**, 1204—1211).—The absorption coefficients of H^+, H_2^+, and H_3 in hydrogen were measured for the range 60—850 volts, using an ionisation tube and a Dempster mass spectrograph for analysing the rays. The values obtained were, for H^+, nearly constant at 8 cm.²/cm.³; for H_2^+, 40 decreasing to 20 cm.²/cm.³ from 60 to 850 volts, and for H_3^+, 17 decreasing to 12 cm.²/cm.³ from 60 to 500 volts; no minimum of absorption was found. Qualitative experiments indicate that the absorption of H_2^+ is due to neutralisation, and that scattering is the main factor in the absorption of H^+ and H_3^+ ions. N. M. BLIGH.

Collisions by canal rays. C. GERTHSEN (Physikal. Z., 1930, **31**, 948—953).—By allowing canal rays to pass from the observation chamber into a gas-filled chamber considerable ionisation results, the number of ion pairs produced being proportional to the initial energy of the ionising particles. The reflective power of metals for high-velocity canal rays is approximately proportional to the square of their at. wt. Methods of measuring the scattering of canal rays by thin films and the velocity of secondary electrons from these films are discussed. Consideration is given to the distribution of secondary electrons from metal films; the discharge of doubly-charged helium atoms by means of He^+ canal rays; the velocity and energy decrements of canal rays by

passage through celluloid films of various thicknesses, and the ionising power and range of canal rays in air as a function of their velocity. W. R. ANGUS.

Velocities of H^+ ions formed in hydrogen by dissociation following electron impact. W. W. LOZIER (Physical Rev., 1930, [ii], **36**, 1285—1292; cf. Bleakney, A., 1930, 969).—An apparatus is described for the study of the velocity distribution of ions formed by single electron impact, the velocity distribution being determined from the positive ion current collected expressed as a function of the retarding voltage. If, as shown by theory, the H_2 molecule, on ionisation by electron impact, dissociates into H^++H, the H^+ ions should occur at minimum electron velocities of about 27—40 volts, and possess 5—11 volts velocity, and if into H^++H^+ with removal of two electrons, the corresponding values should be 46—56 volts and 7·5—12·5 volts velocity. In agreement with theory, the velocities of the ions resulting from dissociation, and the ionisation potentials were found to satisfy linear relationships. The results are considered to confirm the essential correctness of the quantum mechanical theory of the hydrogen molecule. N. M. BLIGH.

Diffraction phenomena in molecular rays. O. STERN (Physikal. Z., 1930, **31**, 953—955).—A *résumé* of work in this field with special reference to reflexion of molecular rays from polished surfaces and crystal cleavage faces and diffraction from the "Kreuzgitter" of crystal cleavage faces. W. R. ANGUS.

Experiments with high-velocity positive ions. J. D. COCKCROFT and E. T. S. WALTON (Proc. Roy. Soc., 1930, A, **129**, 477—489).—The advantages of experiments with positive ions accelerated by high potentials over α-particle experiments in dealing with problems of the atomic nucleus are discussed. The main difficulty lies in the production and application of the very high potentials required to accelerate the particles if velocities approaching that of the α-particle are to be obtained. It is decided that 300 kilovolts is the minimum acceleration voltage at which useful work can be carried out in this field. Full details are given of the experimental arrangements. The canal-ray tube is used as a source of protons, which are accelerated by means of a steady potential produced by rectifying the current from a low-frequency transformer. From preliminary experiments carried out at voltages up to 280 kilovolts with a mixed stream of protons and molecules, targets of lead, and a beryllium salt, definite indications were obtained that the impact of protons on matter produces a radiation of a non-homogeneous type. The intensity of the radiation was of the order of 0 0001 of that produced by an equal electron source, and increased very rapidly between 250 and 280 kilovolts. L. L. BIRCUMSHAW.

Electrodeless ring discharge and the production of atomic rays of hydrogen. J. KUNZ amd J. T. TYKOCINER (Physical Rev., 1929, [ii], **33**, 117).—Atomic rays are produced by inducing high-frequency discharges in an electrodeless quartz bulb supplied with hydrogen. L. S. THEOBALD.

Ionisation of nitrogen and air by positive-ion bombardment. R. M. SUTTON and J. C. MOUZON (Physical Rev., 1929, [ii], **34**, 547—548; cf. A., 1929, 483).—Nitrogen and air both show ionisation for accelerating potentials greater than 100 volts at pressures between 0·1 and 0·7 mm. The abnormally high pressures indicate the presence of long mean free paths for the positive ions. The calculated ionisation at 750 volts expressed as the number of ions formed per initial positive ion per cm. path at 1 mm. pressure is: argon 0·288, neon 0·112, nitrogen 0·124, air 0·098, and hydrogen none detectable. L. S. THEOBALD.

Hydrogen molecular ion as a wave-mechanical perturbation of the helium ion. P. M. MORSE and E. C. C. STUECKELBERG (Physical Rev., 1929, [ii], **33**, 290).—The molecular electronic levels have been obtained from the perturbation caused by splitting the nucleus of a simple atom. The hydrogen molecular ion has been obtained from the helium ion. The electronic energy as a function of nuclear separation gives a curve in agreement with that calculated by Barrau for the ground state. The curves for the excited states show the "promotion of the electron" predicted by Hund and Millikan. L. S. THEOBALD.

Reflexion of atoms from crystals. A. ELLETT and H. A. ZAHL (Physical Rev., 1929, [ii], **33**, 124; cf. A., 1929, 1125).—Cadmium and arsenic are diffusely reflected from crystals of fluorite and orthoclase. Cadmium incident upon potassium chloride gives a specular beam, whilst arsenic upon sodium chloride gives a weak specular beam with considerable diffuse scattering. Thick layers of arsenic deposited at the temperature of liquid air are black; these change abruptly to deep red, then to bright yellow, and finally to the usual grey modification on warming to the ordinary temperature. L. S. THEOBALD.

Repeated reflexion of atoms from crystals. A. ELLETT and H. A. ZAHL (Physical Rev., 1929, [ii], **33**, 635; cf. A., 1929, 1125).—The beam of cadmium atoms specularly reflected from a crystal of halite and impinging upon a second crystal is specularly reflected only when the angle of incidence on the second crystal is equal to or nearly equal to the angle of reflexion from the first. A change of 10° in the angle of incidence causes marked loss of intensity in the reflected beam which disappears when the angles differ by 25—30°. The specular reflexion probably depends in a critical manner on the velocity of the incident atoms. L. S. THEOBALD.

Velocity of cadmium atoms specularly reflected from rock-salt crystals. A. ELLETT and H. F. OLSON (Physical Rev., 1929, [ii], **33**, 118—119).—The beam of cadmium atoms specularly reflected from a crystal of rock salt consists of atoms all having nearly the same velocity, which varies with the angle of incidence but not with temperature of the crystal. An equation which represents the results and can be interpreted in terms of de Broglie's wave equations is given. L. S. THEOBALD.

Polarisability of the helium atom and the lithium ion. H. R. HASSÉ (Proc. Camb. Phil. Soc.,

1930, **26**, 542—555).—Mathematical. The method of Eisenschitz and London (cf. A., 1930, 525) for calculating the approximate force between two atomic systems at large distances apart from the disturbance produced by a small external electric field is used to confirm the work of these authors for hydrogen, and is extended to the polarisability of helium and the lithium ion. N. M. BLIGH.

Mobility of aged ions in air. O. LUHR and N. E. BRADBURY (Physical Rev., 1930, [ii], **36**, 1394—1397; cf. A., 1930, 974, 1231).—The mobility of air ions produced by X-rays was measured by the Rutherford alternating-current method using a slightly modified form of the apparatus previously described. No change in mobility with age was detected for ions aged to one second. The average mobilities of positive and negative ions in dry air was $1{\cdot}64 \pm 0{\cdot}05$ and $2{\cdot}25 \pm 0{\cdot}05$, falling in moist air to 1·4 and 1·8 cm./sec. per volt/cm., respectively. No satisfactory explanation was found for the continual decrease in the coefficient of recombination with age while the mobility remains unchanged. N. M. BLIGH.

Molecular rays of hydrogen chloride in an electric field. M. J. COPLEY and W. H. RODEBUSH (Physical Rev., 1929, [ii], **33**, 1083—1084).—Deflexion of a large fraction of molecules is indicated by passing a beam of hydrogen chloride molecules initially at $-80°$ through an electrostatic field between a wire and a cylinder with a *P.D.* of 10,000 volts and condensation on a target cooled in liquid air and bearing a layer of condensed ammonia.

L. S. THEOBALD.

Positive-ray analysis of hydrogen sulphide. J. H. BARTLETT, jun. (Physical Rev., 1929, [ii], **33**, 117; cf. A., 1929, 379).—The ions $(S)^+$, $(HS)^+$, $(H_2S)^+$ are all formed by the initial process of the electrons colliding with the gas molecules. Hydrogen ions, $(S_2)^+$ ions, or negative ions could not be observed in studying hydrogen sulphide by Dempster's method of positive-ray analysis. L. S. THEOBALD.

Basis of the chemical at. wts. A. VON GROSSE (Z. physikal. Chem., 1930, **B**, **10**, 395—396).—Owing to the complications arising from the fact that oxygen is composed of isotopes, it is proposed that helium (=4·0000) should be employed as the basis of the at. wt. system. The importance of the helium nucleus in atomic structure, and the fact that the difference between the at. wt. of atoms containing an integral number of α-particles and the next integer represents the energy of formation of the atom from α-particles and electrons, are adduced in favour of the proposal. H. F. GILLBE.

New graphical arrangement of the periodic table. A. E. CASWELL (Physical Rev., 1929, [ii], **34**, 543).—The elements are represented by a spiral plotted on polar co-ordinate paper.

L. S. THEOBALD.

Determination of the abundance ratios of isotopes from band spectra. A. ELLIOTT (Nature, 1930, **126**, 845—846; cf. A., 1930, 1232).—The determination of the correction to be made in order to obtain the relative abundance from the intensity ratio of isotopic bands of boron is described. For Chilean boron the mean isotope ratio is $3{\cdot}63 \pm 0{\cdot}02$, giving an at. wt. 10·794 corrected for O^{17} and O^{18}.

L. S. THEOBALD.

Evidence from band spectra of the existence of a carbon isotope of mass 13. A. S. KING and R. T. BIRGE (Astrophys. J., 1930, **72**, 19—40).—The evidence bearing on the existence and appearance of C^{13} is reviewed and discussed. Faint band structures appearing in different regions of the spectrum can be accounted for by a carbon atom of mass 13 and the relative abundance of C^{13} and C^{12} appears to be of the order 1 : 400. Furnace and low excitation sources, especially N-type stars, are effective emitters of the C^{13} spectrum; in the arc, the only evidence of C^{13} is a group of lines in the cyanogen band at 3883 Å.

L. S. THEOBALD.

Constitution of tungsten. F. W. ASTON (Nature, 1930, **126**, 913).—The mass spectrum has been obtained using the carbonyl $W(CO)_6$. Tungsten has four isotopes of which the two strongest give lines of practically equal intensity. The mass numbers and relative abundances (provisional) are 182 and 22·6, 183 and 17·2, 184 and 30·1, and 186 and 30·0, respectively. The at. wt. deduced is 183·96.

L. S. THEOBALD.

Half-life period of uranium II. Ratio of weights of the isotopes uranium I and uranium II in the mixed element uranium. E. WALLING (Z. physikal. Chem., 1930, **B**, **10**, 467—475).—The half-life period of uranium II has been calculated from measurements of the activity of uranium-X and the uranium II formed from it, taken in conjunction with the known period of the former, to be $3{\cdot}4 \times 10^5$ years, with a maximum uncertainty of $\pm 15\%$. From this value it is deduced that ordinary uranium contains 13,200 atoms of uranium I for each atom of uranium II. R. CUTHILL.

Behaviour of radioactive coatings on heating. W. SEITH and A. H. W. ATEN (Z. physikal. Chem., 1930, **B**, **10**, 296—298).—By heating to 600—700° a material on the surface of which a radioactive substance has been uniformly deposited the latter breaks up into discrete agglomerates; the effect is less marked with a glass surface than with platinum. By application of this phenomenon it has been shown that an exchange of lead ions can take place between a film of thorium-*B* chloride and a lead oxide surface on which it is deposited. H. F. GILLBE.

Unsuccessful attempt to influence the normal decay of a weak source of polonium. N. FEATHER (Proc. Camb. Phil. Soc., 1930, **26**, 538—541; cf. A., 1930, 659).—An apparatus is described by which the effect of γ-rays from mesothorium on the rate of decay of a weak source of polonium was investigated. From counts of particles taken over long periods during normal decay and during irradiation no anomaly was detected. N. M. BLIGH.

Experiments on influencing radioactive disintegration. (FRL.) S. MARACINEANU (Physikal. Z., 1930, **31**, 1032—1036, 1038—1039).—A reply to criticisms by Behounek (A., 1930, 516; also following abstract) of work by the author (A., 1926, 879; 1927, 710, 807; 1928, 455). It is suggested that the different experimental arrangements used by the two

authors account for many of the discrepancies in their results. W. R. ANGUS.

[Experiments on influencing radioactive disintegration.] F. BEHOUNEK (Physikal. Z., 1930, **31**, 1036—1038).—A reply to Maracineau (cf. preceding abstract). W. R. ANGUS.

[Experiments towards] decomposition of the lead atom. III. A. SMITS and (FRL.) H. S. VENING MEINESZ (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 737—748).—In confirmation of the work of Maracineanu (A., 1928, 455), it is found that lead sheets exposed to sunlight become radioactive and emit α-particles. Further work has been done on the irradiation of lead by X-rays (cf. Smits and Frederikse, *ibid.*, 933), and the production of active lead by this means confirmed both by electrometer measurements and by counting of scintillations. The activation increases at first with the period of irradiation, but on further exposure to the X-rays the lead loses its activity. This indicates that the activation is not produced by radioactive dust. Similar results of Pokrowski (A., 1930, 1086) are discussed. O. J. WALKER.

Directional distribution of H-particles expelled from aluminium by polonium α-rays. H. POSE (Physikal. Z., 1930, **31**, 943—945; cf. Bothe, A., 1930, 1339).—Disintegration experiments on aluminium have shown that three energetically different groups of H-particles are expelled (*ibid.*, 7) and that the number and energy of the H-particles depend on the primary energy (*ibid.*, 1232). The directional distribution of H-particles was measured for a primary range of 3·72 cm. with different angles (between 0° and 135°) between the primary and secondary rays. As the angle is increased the range of H-particles in each group diminishes, but the yields of the different groups do not change appreciably. Assuming that the α-particles are captured by collision with atomic nuclei, the change in the velocity of H-particles with the angle between the primary and secondary rays can be calculated from the energy and impulse states. The end-points of the velocity vectors lie on a circle, the centre of which is at a distance, d, from the origin of the α-rays. The value of d is obtained from the formula $d=m_a v_a/(M+m_H)$, where m_a and v_a are, respectively, the mass and velocity of the α-particle, M is the mass of the nuclear residue, and m_H the mass of the H-particle. The values of d for the three groups are 0·23, 0·18, and $0{\cdot}22\times10^9$ cm./sec., in good agreement with values obtained theoretically. The results are in good agreement with conceptions which have been made on the basis of the new quantum theory. W. R. ANGUS.

Theoretical treatment of atomic disintegration processes. G. BECK (Physikal. Z., 1930, **31**, 945—946).—In collisions between α-particles and atomic nuclei five types of quantum processes are encountered: (*a*) elastic collisions, (*b*) inelastic collisions during the emission of the radiation, (*c*) inelastic collisions during the excitation of the nucleus, (*d*) disintegration processes, (*e*) disintegration with subsequent emission of radiation. The characteristics and probabilities of these processes are discussed. Assuming that each nuclear particle behaves as if it were under the influence of a central field, three quantum numbers can be assigned to each H- or α-particle. These determine the total rotational momentum and the rotational momentum round a certain axis in the particular state. W. R. ANGUS.

Range of the α-particles from thorium. G. H. HENDERSON and J. L. NICKERSON (Physical Rev., 1930, [ii], **36**, 1344—1347).—With the view of correcting divergent existing data, the range of α-particles from thorium was determined photographically, using a modified Wilson expansion chamber (cf. Laurence, A., 1928, 684) as 2·59±0·05 cm., in fair agreement with, and extending the applicability of, the Geiger–Nuttall relation. N. M. BLIGH.

New magnetic spectrograph for α-rays. S. ROSENBLUM (Compt. rend., 1930, **191**, 1004—1006).—The apparatus described is capable of giving a field of 18 kilogauss, and utilising merely the resources of an ordinary laboratory, *e.g.*, a current of 1·9 amp. and 110 volts. With it the fine structure of the thorium-*C* α- and α′-rays (cf. A., 1930, 837) was confirmed. C. A. SILBERRAD.

Scattering of γ-rays. J. C. JACOBSEN (Naturwiss., 1930, **18**, 951—952).—The scattering of radium γ-rays on passing through solutions of various substances was followed by means of a gold-leaf electrometer. A graph of the ionisation current against the number of electrons per c.c. gives a smooth curve, showing that the weakening of the radiation is determined by the number of electrons encountered. F. O. HOWITT.

Wave-length measurements of γ-rays from radium and its products. L. T. STEADMAN (Physical Rev., 1929, [ii], **33**, 1069).—A method which gives the background of the spectrum directly is described; the relative intensities of the lines can then be obtained in a simple manner. The twelve lines of the shortest wave-length are 8·72, 7·45, 6·78, 5·55, 4·97, 4·12, 3·38, 2·86, 2·38, 1·59, 0·95, and 0·42 X. L. S. THEOBALD.

Directional distribution of recoil radiation produced by scattered γ-rays. D. SKOBELZYN (Z. Physik, 1930, **65**, 773—798).—The directional distribution of the recoil electrons produced in the Compton effect is investigated by the cloud chamber method. The results of a great number of experiments are given. The mean statistical distribution is in good agreement with the conclusions of the quantum theory. It is shown that ordinary theories lead to the same result for the distribution formulæ as far as the larger recoil angles (*i.e.*, smaller scattering angles) are concerned. Within this range (60—90°) there is also satisfactory agreement between experimental results and the theoretical curve. The forward displacement of the emission direction for a diminution of wave-length, predicted by all the theories, is clearly shown. There is some disagreement with the Dirac–Gordon solution, the results of the experimental investigation agreeing better with the older Compton method. Many conclusions from the experiments support the recent theory of Klein and Nishina (A., 1929, 373). The distribution shows a heaping at an angle of 10°, predicted by this theory

but not by others, and there are other quantitative coincidences. The dependence on frequency is also correctly predicted by this theory alone. The statistical results require the existence of certain favoured directions in the distribution, *i.e.*, secondary, sharp maxima and minima impressed on the distribution curve, which were not expected. A. J. MEE.

Influence of nitrogen peroxide on the glowing of phosphorus. F. SCHACHERL (Coll. Czech. Chem. Comm., 1930, 2, 665—679).—The oxygen pressure p_x at which white phosphorus begins to glow in a mixture of nitrogen peroxide and oxygen has been determined as a function of the nitrogen peroxide concentration at 15·1°, 20·0°, and 25·1°, the phosphorus vapour pressure being maintained at the saturation point. The results are in accordance with Tausz and Gorlacher's equation (A., 1930, 876) $p_x=k/(a+x)$, where $x=[NO_2]/[O_2]$ and k and a are constants; this equation has been deduced theoretically. The values of p in absence of nitrogen peroxide are in good agreement with those of earlier observers, although the variations with temperature are not, as proposed by Kowalski (A., 1929, 1242), directly related to the vapour pressure of phosphorus. The influence of nitrogen peroxide increases with rise of temperature, and is greater in oxygen mixtures than in air. The poisoning action of nitrogen peroxide, as given by the slope of the p_x–x curve at $x=0$, is of the same magnitude as that of allyl iodide or *cyclo*hexane, and is due to its reaction with oxygen atoms produced by thermal dissociation, and consequent disturbance of the chain reactions responsible for the glowing. Determination of the quantity of gas or vapour admixed with air or oxygen by measurement of the lowering of p produced is unsatisfactory, as the sensitivity of the method falls rapidly with increasing concentration and the measurements of p are rather untrustworthy. H. F. GILLBE.

Quantum defects for non-penetrating orbits. L. PAULING (Physical Rev., 1929, [ii], **33**, 270).—The contribution of polarisation of the atomic core to the quantum defect for "non-penetrating" orbits of alkali-like atoms and ions has been calculated. These values are smaller than the observed quantum defects. Values calculated by taking into account both penetration and polarisation of the atom core agree well with those observed. L. S. THEOBALD.

New theory of the rectifying action of the aluminium cell. W. B. PIETENPOL and A. P. FRIESEN (Physical Rev., 1929, [ii], **33**, 277—278).—The oxide layer–gas film theory is modified. The behaviour of the cell is attributed to a double layer of aluminium oxide and aluminium hydroxide, the latter acting as a semipermeable membrane to certain ions. The accumulation of negative ions in the double layer when aluminium is the anode accounts for the high resistance and for the contra-*E.M.F.* observed. The layer also accounts for the capacity of the cell. L. S. THEOBALD.

Helium ratios of the basic rocks of the Gwalior series. V. S. DUBEY (Nature, 1930, **126**, 807; cf. A., 1929, 622).—The thorium, uranium, and helium contents of four rocks from the Morar group of the Gwalior series are recorded. Geologically, these rocks are of the same age. Helium is retained better by fine- than by coarse-grained basaltic rocks. The ages now given for Tertiary, late Carboniferous, and late Pre-Cambrian rocks as exemplified by Cleveland Dyke, Whin Sill, and Gwalior basalt are 26, 182, and 468×10^6 years, respectively. L. S. THEOBALD.

Optical treatment of Fourier analysis. B. GERMANSKI (Ann. Physik, 1930, [v], **7**, 453—469).—The application of Fourier analysis to the determination of wave form and of lattice structure is discussed. The mathematical theory and practical details of a new and widely applicable technique are given. H. F. GILLBE.

Interaction of inert gases. M. DELBRÜCK (Proc. Roy. Soc., 1930, **A**, **129**, 686—698).—Mathematical. The inertness of the inert gases is studied from a quantum-mechanical point of view, and it is shown that the attractive field of the higher rare gas atoms is probably due to the first-order perturbation rather than to polarisation. The electrostatic as well as the exchange energy of two rare gases can be written as a sum, of which the terms correspond with the interaction of pairs of completed shells. The electrostatic energy is always negative for great distances, whilst the exchange energy tends to negative values for increasing azimuthal quantum numbers. L. L. BIRCUMSHAW.

Perturbation problems in quantum mechanics. J. E. LENNARD-JONES (Proc. Roy. Soc., 1930, **A**, **129**, 598—615).—A modified form of the Schrödinger perturbation theory is given, and applied to calculating the van der Waals field of two hydrogen atoms at large distances. A more general perturbation theory is also developed, which is not limited to small perturbations. The advantages of this method are illustrated by a consideration of the perturbation of rotating polar molecules under the influence of an external electric field. L. L. BIRCUMSHAW.

Dependence of emissivity on temperature for black-body radiation. A. PRESS (Z. Physik, 1930, **65**, 734—738).—Theoretical. The Stefan–Boltzmann fourth-power law is extended to more complex cases, in which it does not hold strictly. A. J. MEE.

Recombination of atoms. E. L. KINSEY and J. KAPLAN (Physical Rev., 1929, [ii], **33**, 545).—The collision of two atoms can result in the formation of a homopolar molecule only when the minimum energy in an excited state of the molecule is equal to or less than the heat of dissociation of the normal molecule. L. S. THEOBALD.

Transition effect of cosmic radiation shown by varying the absorbing medium. E. STEINKE (Physikal. Z., 1930, **31**, 1019—1022).—A new differential method of detecting cosmic radiation is described. Measurements of the absorption coefficient for this radiation traversing lead, iron, aluminium, water, and paraffin show that iron and the heavier elements appear to absorb anomalously; the absorption coefficient diminishes with increasing thickness, probably because of a secondary radiation excited by the cosmic radiation in the heavier atoms. An unsuccessful attempt was made to detect scattered electrons by means of a magnetic field. A. B. D. CASSIE.

Distribution of electrons in the atom. L. Goldstein (Compt. rend., 1930, **191**, 766—768).—A mathematical extension of the Fock–Dirac relation between orbital moment and atomic potential (A., 1930, 271), in which Poisson's equation is used to calculate the latter quantity. An expression is thence obtained, the terms of which represent, under limiting conditions, the Fermi–Thomas equation for the interaction of electrons between themselves and with the nucleus, and the effect on distribution of electronic exchange. It is suggested that by appropriate generalisation the Fock–Dirac equation could be applied to the statistical theory of homopolar linkings in molecular fields. J. Grant.

Electronic orbits within atoms. V. Karapetoff (J. Franklin Inst., 1930, **210**, 609—624).—Information regarding the probable number and characteristics of electronic orbits in atoms has been summarised in the form of a graphical chart for all known chemical elements. An empirical rule is described which governs the appearance of different kinds of orbits when the elements are arranged in order of atomic number. W. Good.

Potential and potential energy of space lattices. C. N. Wall (Physical Rev., 1930, [ii], **36**, 1243—1250).—Mathematical. The electrostatic potential of a general space lattice is developed, and an expression for the lattice energy is obtained which can be connected with the structure factors of the lattice. The theory is applied to sodium chloride and sodium and lithium fluorides. The lattice energy is calculated for different grating spaces, and is shown to be a minimum in the neighbourhood of the accepted grating space of the crystal. N. M. Bligh.

Atomic electric charges in the electromagnetic quantum theory. C. L. Sagui (Physical Rev., 1929, [ii], **33**, 123).—Theoretical. The magnetic fields which a proton and an electron would possess under certain conditions are described.

L. S. Theobald.

Quantised rotation of atoms. E. Loedel-Palumbo (Physikal. Z., 1930, **31**, 926—929; cf. A., 1926, 1073; 1927, 602; 1928, 100; 1929, 366).—A criticism of the work of Loyarte. The "addition potential" postulated by Loyarte has no physical significance. A table is given for the mercury spectrum showing that values other than 1·4 volts for this "addition potential" can be used to give the same results as Loyarte obtained. This can be done for any spectrum which contains a large number of lines. W. R. Angus.

Photographic method of determining atomic structure factors. D. K. Froman (Physical Rev., 1930, [ii], **36**, 1330—1338).—The intensities of X-rays reflected from powdered crystals of magnesium oxide and potassium chloride were measured photographically, higher orders of reflexion being measurable than by the ionisation method. Relative intensities and corresponding structure factors are tabulated for each substance. The radial electron distribution for each of the atoms was determined and results indicate that both compounds form polar crystals.

N. M. Bligh.

Extrapolation of atomic structure factor curves. D. K. Froman (Physical Rev., 1930, [ii], **36**, 1339—1343).—Mathematical. An approximate extrapolation formula for atomic structure factors of high order is deduced from the form of the electron distributions indicated by the wave equation, and gives results in satisfactory agreement with the factors found by Hartree (cf. Proc. Camb. Phil. Soc., 1928, **24**, 189) from the electron distribution for Na^+. An analogous treatment is shown to apply to the curves obtained from the scattering of X-rays by gases (cf. Compton, A., 1930, 834). N. M. Bligh.

Electron theory of metals. R. H. Fowler (J. Inst. Elect. Eng., 1930, **68**, 1469—1475).—A lecture.

Physical methods in the chemical laboratory. XV. Investigation of internal structure of crystallised inorganic compounds. W. Jander (Z. angew. Chem., 1930, **43**, 1057—1060).—The application of infra-red spectroscopy and of X-ray analysis to the study of atomic arrangement in crystals is briefly surveyed. A detailed description is given of the employment of comparative physical data, such as mol. vol., m. p., conductivity, and of diffusion and reactivity in the solid state, to the investigation of the internal forces operative within crystalline substances. H. F. Gillbe.

Spectrography using a non-inclined plate. A. Couder (Compt. rend., 1930, **191**, 772—774).—Since spectra inclined to the axis of the objective are obtained with non-achromatic spectrographs, an almost achromatic quartz spectrograph involving the use of a catadioptic lens is described. The objective is a simple crown-glass convergent lens, whilst the plane mirror of the ordinary Duboscq autocollimated spectrograph is substituted by a flint-glass divergent-meniscus lens, the convex posterior face of which is metallised. Calculations are given to determine the curvature of the lenses from a consideration of the aberrations of the system. An advantage is the suppression of extraneous light from the slit.

J. Grant.

Excitation of band spectra. J. Kaplan and E. L. Kinsey (Physical Rev., 1929, [ii], **33**, 114).—The β bands of nitric oxide are weakly excited in electric discharges and strongly excited in active nitrogen; the first excitation is due to electron impact, the second to collisions of the second kind. This difference can be explained by means of the Franck–Condon curves for the two levels involved in the transition. The most probable transition for electron impact is one in which the vibrational motion in the upper level is determined by the instantaneous values of the separation of the atoms and their relative momentum. L. S. Theobald.

Double refracting structure of "Corex" glass. (Lord) Rayleigh (Nature, 1930, **126**, 845).—The ultra-violet-transmitting "Corex" glass shows a doubly refracting structure. L. S. Theobald.

Validity of the Hill and Van Vleck intensity formula for the NO γ bands. R. Schmid, T. von Neugebauer, D. von Farkas, and C. Barabas (Z. Physik, 1930, **65**, 541—546).—The distribution of

intensity in the branches of the NO γ bands is given correctly by the Hill and Van Vleck intensity formula for a $^2\Sigma_{(b)} \longrightarrow {}^2\Pi_{(x)}$ transition. A. B. D. CASSIE.

Band spectrum of antimony oxide. B. C. MUKHERJI (Nature, 1930, **126**, 725).—The spectrum of the flame surrounding the antimony arc in air has at least three systems with origins at approximately 29,619, 26,480, and 24,203 cm.$^{-1}$ The bands show a doublet structure consistent with an emitter of the neutral antimony oxide molecule.
L. S. THEOBALD.

New band system probably due to singly-ionised hydrogen chloride. B. A. BRICE and F. A. JENKINS (Physical Rev., 1929, [ii], **33**, 1090—1091; cf. A., 1929, 864).—The bands form a doublet system with $\Delta\nu=663$ cm.$^{-1}$ The heads are given by $\nu=28{,}446$ (and 27,783)$+1561p-36{\cdot}3p^2-2569n$, where (p,n) are $(-1,0)$, $(0,0)$, $(1,0)$, $(2,0)$, $(3,0)$, $(4,0)$, $(5,0)$, $(0,1)$, and $(3,1)$. A $^2S \longrightarrow {}^2P$ system is indicated.
L. S. THEOBALD.

Ultra-violet absorption of aqueous solutions of hydrochloric acid. R. TREHIN (Compt. rend., 1930, **191**, 774—776).—Aqueous solutions (0·5—13M) of hydrogen chloride, purified by drying over phosphorus pentoxide and solidification in liquid air, were examined at λ 2816—1990 Å. in thicknesses of 10 and 20 mm. For a given concentration and thickness absorption increases continuously with decrease in λ. The absorption increase is a constant function of increase in concentration above 2320 Å., but below this value a maximum absorption is obtained for a particular concentration. Beer's law, therefore, is not satisfied, and absorption is due to the Cl^- ion in dilute solution only. J. GRANT.

Analysis of hydrogen chloride bands in the ultra-violet. M. KULP (Physikal. Z., 1930, **31**, 959—960).—The bands of hydrogen chloride have been examined between 3000 and 4000 Å. and it is found that each band consists of six branches, P, Q, R, and P', Q', R'. The separation between the lines of the R and Q branches is the same as between the lines of the Q' and P' branches; also the lines of the P and Q branches and of the P' and R' branches are separated by an equal amount. Such a doublet system is attributed to HCl^+. The transition $^2\Sigma \longrightarrow {}^2\Pi$ is considered the only possible. For the $^2\Sigma$ term the component of the total rotational momentum of electronic orbits (Λ) is zero. By taking into account the spin about the axis of rotation all rotational levels of the $^2\Sigma$ state are split into two except the lowest level, which remains simple. In the case of the $^2\Pi$ term Λ is unity. The alternating effect between Λ and the spin is strong and for parallel and anti-parallel disposition of spin corresponding with the doublet character two terms, $^2\Pi_{+\frac{1}{2}}$ and $^2\Pi_{-\frac{1}{2}}$, are obtained. Each rotational level in the $^2\Pi$ state is divided into two levels. The transitions from $^2\Sigma \longrightarrow {}^2\Pi_{+\frac{1}{2}}$ and from $^2\Sigma \longrightarrow {}^2\Pi_{-\frac{1}{2}}$ are discussed and the bands allocated according to selection rules.
W. R. ANGUS.

Spectrum of hydrogen bromide. W. WEIZEL, H. W. WOLFF, and H. E. BINKELE (Z. physikal. Chem., 1930, **B**, **10**, 459—466).—The emission spectrum of hydrogen bromide excited by discharge in a Geissler tube consists of a continuous spectrum of varying intensity which starts in the green, dies away below about 2500 Å., and exhibits several flat maxima in the near ultra-violet. This is interpreted as the dissociation spectrum of either HBr or HBr^+.
R. CUTHILL.

Action of the electric field on the radiations of the ions of the rare earths in chemical compounds. R. BRUNETTI and Z. OLLANO (Nuovo Cim., 1929, **6**, 345—355; Chem. Zentr., 1930, i, 2056—2057; cf. A., 1929, 1126).—The absorption spectra of the ions of the rare earths vary in compounds and a distinction is drawn between the changes which appear in the same crystal structure and those which are observed in compounds definitely of different structure. To the first type belong the changes which are brought about by lowering of temperature. The spectral displacement of the Pr^{III} radiation thus produced can be traced to changes in intensity of the intramolecular electrical field and in the different praseodymium halides is dependent on the difference in intramolecular distances. The displacements in crystals of different structure are, for the main part, to be assigned to the varying conditions for the probability of quantum transitions. Attempts were made to produce an artificial displacement of the lines of a didymium glass, but the results were of the same order of magnitude as that of the experimental error and were not greater than the displacements which are produced by strong cooling of a crystal. The order of magnitude of the intramolecular field is calculated to be 10^7 to 10^8 volts per cm. Such a field, however, has the character of a weak field. L. S. THEOBALD.

Absorption and explosion spectra of cyanogen. K. TAWADA (J. Soc. Chem. Ind. Japan, 1930, **33**, 417B).—The absorption and emission spectra of cyanogen have been measured with the view of determining the radiation from the cyanogen–oxygen flame; the results for the absorption spectrum confirm those of Baumeister. It is suggested that the spectrum resembles that of the explosion of carbon monoxide–oxygen mixtures. H. F. GILLBE.

Ultra-violet absorption of tartaric acid solutions. Influence of concentration. G. BRUHAT and J. TERRIEN (J. Phys. Radium, 1930, [vii], **1**, 351—364).—A more detailed account of work already noted (A., 1930, 1090).

Effect of adding a colloid on the absorption spectrum of the solution of a colouring matter. A. BOUTARIC and M. DOLADILHE (Compt. rend., 1930, **191**, 1008—1011).—A method of determining whether a colouring matter is colloidal or not is based on the effect on the absorption spectrum of adding a small quantity of a hydrosol to a solution thereof. If the colouring matter is in molecular solution the addition has no effect, but if it is in colloidal solution addition of a sol of a lyophile colloid causes uniform decrease in the opacity of the coloured solution, marked if the two are of different sign, very slight if of the same sign. If the added colloid is lyophile, opacity is similarly reduced to an extent dependent on the p_H of the added sol. These results are exemplified by the effects of adding sols of ferric hydroxide and arsenious sulphide to diamine-blue 4R. C. A. SILBERRAD.

New band in the absorption spectrum of methane. D. M. DENNISON and S. B. INGRAM (Physical Rev., 1930, [ii], **36**, 1451—1459; cf. Cooley, A., 1926, 659).—With the object of finding overtones of the fundamental vibrations at 3·3 and 7·7 μ, the absorption spectrum of methane was photographed in the infra-red region 6500—9500 Å., using a tungsten filament as a source of continuous radiation. A band, identified as the third overtone ($n=0\longrightarrow 4$) of the fundamental at 3·3 μ, was observed at 8900 Å., and showed complex irregular fine structure. Wave-lengths and determined intensities of 100 lines are tabulated. The theory of the overtones of a methane type molecule is examined, and a quantum analysis of the observed complexity is deduced.
N. M. BLIGH.

Infra-red measurements on rock-salt as a verification of dispersion theory. M. CZERNY (Z. Physik, 1930, **65**, 600—631).—Former experiments on the dispersion coefficients of rock-salt were confined to regions where absorption is small. An attempt has been made to complete these data by measurements of the reflecting and absorbing power of thin parallel plates. Apparatus used in both the grating spectrometer and residual ray methods, including apparatus for obtaining plane parallel plates as thin as 8 μ, is described. General formulæ for the reflecting and transmitting powers of thin, absorbing, plane parallel plates are given. Observations of the reflecting power at normal incidence and of the intensity of transmitted radiation then determine the refractive index and absorption coefficient for the plate. Near the known reflexion maximum at 52 μ, a second smaller maximum at 39 μ was found. Sylvine showed a similar maximum at 46 μ, near the known maximum at 62 μ. The simple dispersion formula, using one characteristic infra-red frequency, does not fit experimental observations between 40 and 60 μ. Closest agreement is obtained by the use of two damped infra-red characteristic frequencies. The refractive index–wave-length curve shows no systematic deviations, but the extinction coefficient–wave-length curve shows systematic deviations on the short-wave side of the characteristic frequencies. A convenient logarithmic method of applying the dispersion formula is given.
A. B. D. CASSIE.

Infra-red absorption spectrum of chlorophyll and xanthophyll. R. STAIR and W. W. COBLENTZ (Physical Rev., 1929, [ii], **33**, 1092).—In xanthophyll absorption bands have been located at 1·3, 3·05, 3·45, 4·3. 6·0, 6·9, 7·3, 8·05, 8·45, 8·80, 9·05, 9·60, 9·75, 9·9, 10·4, 10·9, 11·3, 11·6, 11·9, 12·1, 12·5, 12·9, 13·2, 13·4, 13·8, and 14·2 μ, whilst films of chlorophyll on plates of fluorite and rock-salt showed bands at 1·3, 3·05, 3·5. 3·8, 4·7, 6·0, 6·2, 6·5, 6·9, 7·3, 7·8, 8·2, 8·6, 9·1, 9·6, 10·1, 10·4, 10·8, 11·1, 11·9, 12·6, 12·9, 13·4, and 13·7 μ. None of these bands is as deep as are those found in molecules of simpler structure.
L. S. THEOBALD.

Infra-red absorption spectrum of carbon tetrachloride as related to the Raman spectrum of scattered radiation. W. W. COBLENTZ and R. STAIR (Physical Rev., 1929, [ii], **33**, 1092).—The latest observed values for the infra-red absorption spectrum are in good agreement with the values calculated by Langer (A., 1929, 379). The band at 12—14 μ is very complex, and other bands occur at 14—15 μ.
L. S. THEOBALD.

Raman effect apparatus, using standard tubular lamps. L. J. BUTTOLPH (Rev. Sci. Instr., 1930, **1**, 650—653).—An apparatus previously described (cf. Reynolds and Benford, A., 1930, 1151) is modified for use with standard tubular lamps. The reflector is of chromium-plated brass to withstand higher temperatures, and the tube can be surrounded by glass filter-jackets or jackets containing liquid filters circulated for cooling. Spectrograms of the transmission of the mercury and neon arc through special filters are reproduced.
N. M. BLIGH.

Improved technique for the Raman effect. R. W. WOOD (Physical Rev., 1930, [ii], **36**, 1421—1430).—The unsuitability of light from a mercury arc for the analysis of Raman spectra is illustrated in the case of benzene. The object of a filter is to limit the exciting light to a single wave-length, and to suppress the continuous spectrum in the Raman spectral region. Raman spectra of benzene excited by various mercury arc lines and by the hot-cathode helium arc were investigated and photographed through various filters.
N. M. BLIGH.

Temperature variations of the Raman effect in quartz. F. G. BRICKWEDDE and M. F. PETERS (Physical Rev., 1929, [ii], **33**, 116).—The Raman effect in crystalline quartz over the range 2400—5000 Å. and between −180° and 550° has been photographed. The variations of the Stokes lines and the anti-Stokes lines with temperature agree qualitatively with the assumption that the intensities of Raman lines vary as the populations of the initial states giving rise to them, which, in turn, vary with temperature in accordance with Boltzmann's law. The intensity of the Raman scattering increases markedly in passing from longer to shorter wave-lengths of incident light.
L. S. THEOBALD.

Raman effect for liquid hydrogen chloride. E. O. SALANT (Physical Rev., 1929, [ii], **33**, 1096).—The liquid at −100° shows the Raman effect when illuminated by a mercury arc. An absorption band at 3·6 μ is indicated.
L. S. THEOBALD.

Combination scattering in liquids. R. M. LANGER and W. F. MEGGERS (Physical Rev., 1929, [ii], **33**, 115; cf. A., 1929, 379).—The scattered light of modified wave-length predicted from quantum considerations differs from the incident light by a frequency equal to an absorption frequency of the scattering substance. This frequency produces a shift of wave-length which increases with the wave-length of the scattering line. Using the high dispersion of a 21-foot concave grating, modified lines have been observed to vary in character; those in benzene corresponding with a shift of 992 cm.$^{-1}$ are comparable in sharpness with the exciting mercury lines.
L. S. THEOBALD.

Raman spectra of benzene and diphenyl. R. W. WOOD (Physical Rev., 1930, [ii], **36**, 1431—1434).—Using suitable filters with mercury arc and helium arc excitation, a number of new Raman lines

for benzene has been recorded. The complete spectrum given in frequency differences is, $\Delta\nu=606$, 849, 992, 1178, 1584, 1603, 2460, 2542, 2597, 2617, 2784, 2928, 2947, 3046, 3060, 3164. Anti-Stokes lines corresponding with $\Delta\nu$ values 606, 849, and 992 were verified. The Raman spectra of diphenyl with mercury arc excitation and a quinine sulphate filter consisted of 5 faint diffuse and 7 strong lines. The $\Delta\nu$ values are: 416, 606, 731, 766, 810 and 990, 1023, 1280, 1544, 1584, 1603, 3055, 3170. Six of these coincide with benzene lines. N. M. BLIGH.

Raman effect in water. E. L. KINSEY (Physical Rev., 1929, [ii], **34**, 541).—The light of a glass mercury arc scattered by distilled water at the ordinary temperature yields three bands at 4150, 4680, and 5157 Å.; the first is a doublet excited by the 3650 mercury line, whilst the second is a triplet excited by the mercury pair 4046 and 4077. These two bands can be accounted for by the infra-red wave-lengths 2·92 μ and 3·13 μ. L. S. THEOBALD.

Incoherent scattering in Rochelle salt. R. M. LANGER (Physical Rev., 1929, [ii], **33**, 1100).—The spectrum scattered by crystalline Rochelle salt differs from that of calcite and quartz in that the modified lines are all very diffuse. Further, there are two broad continuous bands which coincide with those obtained in water and in aqueous solutions. These are due to water of crystallisation and correspond with two found in infra-red absorption. Combinations among the scattered lines appear to account for most of the frequency shifts (about 10) which range from 500 to 3000 cm.$^{-1}$ L. S. THEOBALD.

[Intensity and polarisation of coherent and incoherent light scattered by diatomic molecules.] C. MANNEBACK (Z. Physik, 1930, **65**, 574; cf. A., 1930, 840).—An error in two formulæ is corrected. A. B. D. CASSIE.

Classical theory of the Raman effect. E. H. KENNARD (Physical Rev., 1929, [ii], **33**, 289—290).—A simple example of the Raman effect is described in classical theory. L. S. THEOBALD.

Raman effect. VIII. Calculation of simple molecule models. M. RADAKOVIC (Monatsh., 1930, **56**, 447—460).—Mathematical. Raman spectra will give information concerning the direction of forces within the molecule, and from this the actual structure of the molecule can be calculated. Previously only a few systems have been examined in this way, and then only under the assumption of certain symmetry relationships with regard to the arrangement of the mass points. It is necessary to solve the problem more generally. Here the problem of three mass points is dealt with, it being pointed out that the extension of the theory to more complex molecules presents no great difficulty. A. J. MEE.

Raman effect. IX. Raman spectra of organic substances. A. DADIEU and K. W. F. KOHLRAUSCH (Monatsh., 1930, **56**, 461—476; cf. A., 1929, 976, 1127; 1930, 14, 522, 664, 1091).—The Raman spectra of the following substances have been investigated: propionitrile, phenylacetonitrile, methylene bromide, methylene iodide, and dimethylamine. The results of the whole investigation involving some 100 organic compounds are discussed. The mode of oscillation of four types of molecule is considered, the types being CH_3X, CH_2X_2, CHX_3, and CX_4. The calculation in some cases leads to quantitative results on the space structure of the molecule (the angles between the valency directions), in good agreement with structures arrived at by other physicochemical methods. In other cases the agreement is not so good, although the Raman spectra themselves are in qualitative agreement with theory. A. J. MEE.

Dependence of Raman radiation on frequency [of incident radiation]. L. S. ORNSTEIN and J. REKVELD (Z. Physik, 1930, **65**, 719—722).—Sirkar (A., 1930, 1344) has investigated the dependence of the intensity of Raman radiation on the frequency of the incident radiation, using carbon tetrachloride, and finds that Rayleigh's fourth-power law does not hold. This is at variance with previous results of the authors (*ibid.*, 840). It is denied that the deviations are due to the fact that Ornstein and Rekveld have neglected the effect of absorption (as suggested by Sirkar), it being pointed out that the error would be within the experimental error. A. J. MEE.

Scattering of light in protein solutions. I. Gelatin solutions and gels. K. KRISHNAMURTI (Proc. Roy. Soc., 1930, **A**, **129**, 490—508).—Experiments have been made on the effects of temperature on the intensity and depolarisation of the light scattered by gelatin sols and gels. These sols are considered to be polydisperse systems, part of the gelatin being molecularly dispersed and the remainder multimolecular micelles. Supersaturation is produced if the sol is cooled below 25°, with the production of fresh and larger particles. An ultracentrifugal and ultramicroscopic examination of the sols at p_H 4·8 indicates considerable aggregation of gelatin molecules. The variation of the intensity of the scattered light with the concentration of gelatin sols and gels has been investigated. The Tyndall number increases with concentration up to 4% of gelatin at 40°, and remains constant above this concentration. An explanation is suggested for the fact that, on cooling to 12°, the dilute gels are more turbid than the more concentrated. When gelatin sols of various concentrations are cooled to 10°, the depolarisation of the scattered light first decreases and then increases, this effect being most pronounced in dilute sols. The phenomenon is of importance in indicating changes in the size and shape of the micelles. The parallelism between the Tyndall intensity and the sedimentation constant in sols at different values indicates that the turbidity near the isoelectric point is produced by the aggregation of gelatin molecules. The molecular state of gelatin in its sols is discussed, with special reference to the use of the term "molecules" for protein particles. L. L. BIRCUMSHAW.

Nature and size of the luminescent centre. J. EWLES (Proc. Roy. Soc., 1930, **A**, **129**, 509—519).—Assuming that a luminescent centre, responsible for a given band in emission, consists of a definite number n of solvent molecules associated with one atom or molecule of the activator, and that if there is more than one band, each band arises from a different centre

(cf. Lenard, "Handbuch der Physik," **23**), the following expression is deduced for the relation between brightness of luminescence and concentration c of the activator: $F=Ace^{-nc}$ (A is a constant). This is tested by experiments with luminescent solid solutions formed by the intimate mixture and subsequent heating of antimony, bismuth, and lead oxides, respectively, in calcium oxide. On plotting $\log F/c$ against c for the antimony and lead solutions, each of which shows only one band, the linear relation to be expected from the theory is found to be fairly well followed. In the case of the bismuth solutions, for which two bands are shown in the direct-vision spectroscope, the calculated values of F are found to be in good agreement with the observed values. Similar experiments, carried out with luminescent solutions of uranine in water, rhodamine-6G in water, and fluorescein in ethyl alcohol, lead to the conclusion that the luminescence of liquid solutions of this type can be quantitatively accounted for by the existence of absorbing and re-emitting centres consisting of one molecule of the solute associated with a definite number of solvent molecules. L. L. Bircumshaw.

Phosphorescence phenomena in fused silica discharge tubes. R. Zouckermann (Compt. rend., 1930, **191**, 776—777).—Brilliant phosphorescence phenomena are observed after a 300-volt discharge in tubes containing nitrogen at the ordinary temperature, or metal vapours (at 0·6 mm. Hg pressure) heated at several hundred degrees. The fluorescence is probably due to ionic and electronic bombardments, and may be divided into (*a*) ultra-violet phosphorescence produced after the discharge (bluish-green) and stable only for a few minutes, but reproducible after a subsequent discharge; (*b*) a more intense bluish-green thermophosphorescence obtained several months after a discharge at above 200°, and decreasing in duration with successive or more prolonged heatings, or with rise in temperature. At high temperatures the usual violet-brown colorations are also obtained. J. Grant.

Ultra-violet fluorescence of iodine bromide and iodine. F. W. Loomis and A. J. Allen (Physical Rev., 1929, [ii], **33**, 639).—A fluorescence spectrum in the ultra-violet has been detected for iodine bromide at low pressures. A series of close groups of lines is excited by 1849 Å. and the strongest line in each can be represented by the formula $\nu=54{,}048-276{\cdot}2p+1{\cdot}28p^2$, where p is an integer. The odd terms can be identified as strong, single lines as far as $p=43$. Near 2500 Å. the line structure changes to diffuse, headless bands extending to 3700 Å. The fluorescence series of I_2 excited by 1849 and 1942 Å. show rotational structure. No fluorescence could be obtained with bromine, or with iodine and bromine monochlorides. L. S. Theobald.

Effect of impurities on the phosphorescence of calcium sulphide. D. N. Goyle and N. Singh (J. Chim. phys., 1930, **27**, 443—451).—For each impurity examined there was an optimum concentration corresponding with a maximum of the luminescence intensity of the sulphide, a higher concentration decreasing the luminescence. Fluorescent substances produced a far greater effect than metallic salts. The intensity diminishes as the mixture ages and darkens in colour, with the formation of concentric rings round the sample. The decrease in intensity is shown to be due to the hydrolysis of the sulphide and the consequent increase in the concentration of the impurity. Full results for different concentrations are tabulated.
N. M. Bligh.

Polarised fluorescence of solutions of rhodamine-*B* and uranine. E. Merritt and D. R. Morey (Physical Rev., 1930, [ii], **36**, 1386—1393; cf. Vavilov, A., 1926, 335; Pringsheim, *ibid.*, 885).—With a view of obtaining information on the symmetry of a molecule as exhibited in absorption and emission of radiation and on the duration of these processes, measurements were made of the extent of polarisation in the fluorescence of solutions in glycerol of uranine and rhodamine-B. Results indicate polarisation to the same extent throughout any one fluorescence band. For uranine, under certain conditions of concentration, two bands exist, the polarisation being constant for each band. Theoretical explanations of the processes involved are discussed (cf. A., 1926, 1193). N. M. Bligh.

Tribothermoluminescence. R. E. Nyswander and B. E. Cohn (Physical Rev., 1930, [ii], **36**, 1257—1260).—The intensity of the light emitted by glass, rendered thermoluminescent by grinding, was measured by a polarisation photometer for glass particles of various sizes. Results show that the quantity of emitted light depends on the nature of the substance and the size of the particles, and diminishes slowly with the time after grinding. Glass tubing crushed to various size grains emitted a maximum of light for particles of average linear dimensions 0·015—0·025 cm. N. M. Bligh.

Effect of water on triboelectric luminescence with mercury in glass. T. S. Logan and R. K. Taylor (Science, 1930, **72**, 89—90).—Unsaturated water vapour does not destroy the faint flashing observed with mercury moving over a surface of a pyrex glass vessel containing gas at a low pressure.
L. S. Theobald.

Spectral distribution of the inner photoelectric effect in plastically deformed rock-salt crystals. M. N. Podaschevski (Z. Physik, 1930, **65**, 799—805; cf. A., 1929, 969).—The effect of plastic deformation on the spectral distribution of the primary photo-current for rock-salt crystals coloured by X-rays was investigated. Both natural and tempered crystals were used, the method being analogous to that previously described. The thickness of the crystals was 1—1·5 mm., and the wavelength range was 410—690 mμ. With ordinary natural crystals the deformation causes a general diminution of the sensitivity and a displacement of the maximum towards the longer waves. Increase in charge causes a further decrease in sensitivity, and a displacement of the maximum of the curve. The displacement can be as much as 30 mμ. In some cases there was a regression in the size and position of the maximum with the time. When tempered crystals were used analogous results were obtained,

but there was greater sensitivity towards deformation. A. J. MEE.

Demonstration of electric lines of force, and a new method of measuring the electric moment of tourmaline. (MISS) M. E. MAURICE (Proc. Camb. Phil. Soc., 1930, **26**, 491—495).—An electrostatic charge on a substance is demonstrated by the formation of ice filaments, which follow the lines of electric force, when the substance is removed from liquid air. The same effect was shown by particles of ammonium chloride smoke and magnesium oxide smoke. The experiments were conducted with the pyroelectric crystals tourmaline and boracite. The deformation of liquid surfaces by an electric field was used to indicate the order of magnitude of the charge developed on tourmaline on cooling through about 140°. A new method of measuring the electric moment of tourmaline by observing the rotation of a charged crystal suspended near a dipole is described. N. M. BLIGH.

Application of the ultra-short wave method to the measurement of small capacities and dielectric constants. D. V. GOGATE and D. S. KOTHARI (Indian J. Physics, 1930, **5**, 417—428).—Using the same methods as in previous work (*ibid.*, **4**, 349) the harmonics always present along with ultra-short waves have been located and measured. The conditions necessary for maximum oscillations have been studied. The general theory of the coupling of two non-resonant circuits to the same valve is developed and applied to the measurement of the inter-electrode grid-plate capacity of a valve. This leads to results in fairly good agreement with those given by the resonance method. The ultra-short wave method is also applied to the determination of the dielectric constants of kerosene oil and of petrol. J. W. SMITH.

Properties of dielectrics in electric fields. G. L. ADDENBROOKE (Nature, 1930, **126**, 808—809).—Concerning nomenclature. L. S. THEOBALD.

Modern theory of dielectrics. L. G. CARPENTER (World Power, 1930, **14**, 391—396).—A review.

Oscillation method for the determination of dielectric constants of conducting liquids. W. GRAFFUNDER and R. WEBER (Z. Physik, 1930, **65**, 723—725).—A new method of finding dielectric constants of liquids which can be applied to conducting liquids is described. The conduction is compensated for by the use of parallel valves. The method has been used to determine the dielectric constants of electrolytes and other aqueous solutions. A. J. MEE.

Dielectric constant of helium. J. V. ATANASOFF (Physical Rev., 1930, [ii], **36**, 1232—1242; cf. Hylleraas, A., 1928, 698; 1929, 616).—Mathematical. The Ritz method of investigating unperturbed helium in its normal state is extended to perturbation problems. The value of the dielectric constant, which depends on the effect of a perturbing electric field on the normal levels, is calculated as a minimum of 1·0000665, which is 5% below the accepted value. N. M. BLIGH.

Electric moments of CH_3 and Br radicals in certain organic molecules. C. R. DAILY (Physical Rev., 1929, [ii], **34**, 548).—The electric moments obtained for various combinations of substituent methyl and bromine are: toluene $0\cdot50\times10^{-18}$, bromobenzene $1\cdot70\times10^{-18}$, *p*-bromotoluene $2\cdot15\times10^{-18}$, *n*-propyl bromide $2\cdot00\times10^{-18}$, *iso*propyl bromide $2\cdot20\times10^{-18}$, and ethyl bromide $2\cdot12\times10^{-18}$ e.s.u. L. S. THEOBALD.

Dipole moment of naphthalene and its monohalogen derivatives. A. PARTS (Z. physikal. Chem., 1930, **B**, **10**, 264—272).—The dielectric constants at 20° of benzene solutions of naphthalene and of certain of its derivatives have been measured, and the dipole moments of the solutes have been calculated. For all the halogen derivatives studied the density and dielectric constant of the solutions bear a linear relationship to the fractional molar concentration. The dipole moment of naphthalene is zero, in accordance with its symmetrical structure. Substitution of a halogen in the 1-position in the naphthalene nucleus results in a molecule having the same moment as the corresponding benzene derivative. The moments of the 2-monohalogen substitution products are slightly greater than those of the corresponding 1-derivatives; the properties of the β-carbon atoms of naphthalene lie between those of aliphatic and purely aromatic carbon atoms. The chloro- and bromo-, and the fluoro- and iodo-derivatives have approximately the same moments. The following constants have been determined: 1-fluoronaphthalene, $d_4^{19\cdot6}$ 1·1345, $n_{H\beta}^{19\cdot6}$ 1·61474, $n_D^{19\cdot6}$ 1·59388, $n_{H\alpha}^{19\cdot6}$ 1·58611; 1-iodonaphthalene, $d_4^{19\cdot5}$ 1·7409, $n_{H\beta}^{19\cdot5}$ 1·72995, $n_D^{19\cdot5}$ 1·70256, $n_{H\alpha}^{19\cdot5}$ 1·60244. H. F. GILLBE.

Dielectric polarisation of liquid mixtures. L. M. DAS and S. C. ROY (Indian J. Physics, 1930, **5**, 441—462).—The dielectric constants of solutions of chlorobenzene and bromobenzene in carbon tetrachloride have been measured by the heterodyne method due to Zahn (A., 1924, ii, 809) and their densities determined by use of a modified form of specific gravity bottle. From the results the molecular polarisations have been calculated. The zero concentration intercepts on the curves relating the partial polarisation and the concentration of the polar liquids give values which satisfy the Debye formula $P=A+B/T$. The dipole moments of the chlorobenzene and bromobenzene are calculated as 1·59 and $1\cdot52\times10^{-18}$, respectively. The molecular association increases with both concentration and rise of temperature. J. W. SMITH.

Dipole moments of organic sulphur compounds and related substances. III. Significance of measurements of dipole moment in the stereochemistry of carbon. E. BERGMANN, L. ENGEL, and S. SANDOR (Z. physikal. Chem., 1930, **B**, **10**, 397—413; cf. A., 1930, 1501).—The dipole moments of benzene derivatives containing sulphur and the halogens have been measured and used to calculate the characteristic angle, ϕ, of various substituents (cf. *ibid.*, 979). The value of 71° for ϕ has been derived for the PhS group, leading to the value of 142° for the angle between the two valencies of the sulphur atom. With such compounds as the aromatic ethers

and thio-ethers the dipole moment depends on the polarisability of the central atom as well as on its valency angle. The values of ϕ for the thiocyano- and cyano-groups are 127° and 154°, respectively, but the carbimido-group seems to be straight. The dipole moments of diphenyl sulphoxide, dibenzyl sulphoxide, and nitrobenzene give no evidence of the presence of semi-polar double linkings in these compounds, and it is suggested that a more probable explanation of the occurrence of optical isomerism among the sulphoxides is that the oxygen atom does not lie in the same plane as the sulphur atom and the two hydrocarbon radicals. R. CUTHILL.

Structure of some organic molecules. O. HASSEL and E. NÆSHAGEN (Tids. Kjemi Berg., 1930, **10**, 126—127).—Measurements of the dipole moments of the methyl esters of the *meso*-, racemic, and active forms of dichlorosuccinic acid at 18° give values of $2{\cdot}47\times10^{-18}$, $2{\cdot}93\times10^{-18}$, and $2{\cdot}96\times10^{-18}$, respectively. Corresponding measurements for β- (*trans*-) and α-hexachloro*cyclo*hexane (*cis*-) give 0 and $2{\cdot}20\times10^{-18}$, respectively. The bearing of these results on the question of the structure of the molecules is discussed (cf. A., 1930, 1347). M. S. BURR.

Variation of the rotatory power of camphorsulphonates in the presence of neutral salts. E. DARMOIS and J. P. PÉREZ (Compt. rend., 1930, **191**, 780—782).—Addition of inactive neutral salts (*e.g.*, thorium nitrate or chlorides of barium, sodium, or lanthanum) to aqueous solutions of camphorsulphonic acid and of its sodium and barium salts at 20° decreases $[\alpha]_{5461}$ to an extent which increases with increase in concentration of the added salt and with increase in valency of the cations. The curves $[\alpha]-f\sqrt{(\mu=\frac{1}{2}\Sigma mz^2)}$, where m is the molality of the ion and z its valency, are similar for the various salts used, the influence of valency being represented (to a first approximation) by $\sqrt{\mu}$. The failure to produce an increase in $[\alpha]$ (cf. Darmois, A., 1928, 1320) is attributed to absence of dehydration of the ions. J. GRANT.

Effect of X-rays on the rotatory power of some substances. A. A. BLESS (Physical Rev., 1929, [ii], **33**, 121—122).—No effect of X-rays on the rotation of the plane of polarisation of light passing through quartz crystals could be detected, neither could the positive results claimed by Allison (A., 1929, 1220) be substantiated for water, sugar solutions, or xylene. L. S. THEOBALD.

Magneto-optical dispersion of organic liquids. I. Magneto-optical dispersion of *n*-butyl alcohol, *iso*butyl alcohol, and propionic acid. E. STEPHENS and E. J. EVANS (Phil. Mag., 1930, [vii], **10**, 759—785).—The magneto-optical rotations and refractive indices were determined for various wave-lengths, both visible and ultra-violet. Equations are given representing the magneto-rotatory and natural dispersions of the different compounds. The controlling absorption band in the case of the two alcohols has a wave-length of approximately 0·1150 μ, and in the case of the acid 0·1051 μ. The following values of e/m have been determined in e.m.u.: *n*-butyl alcohol, $1{\cdot}07\times10^7$; *iso*butyl alcohol, $1{\cdot}11\times10^7$; propionic acid, $1{\cdot}00\times10^7$. M. S. BURR.

Thermal variation of the magnetic birefringence of *p*-azoxyanisole. (MLLE.) J. ZADOC-KAHN (Compt. rend., 1930, **191**, 1002—1004; cf. A., 1930, 524).—Determinations of the magnetic birefringence of *p*-azoxyanisole have been repeated and extended by improved methods in a field of 33,900 gauss at temperatures up to 180°. The maximum rotation of the analyser β occurs at the point of transformation (133°), and (that of nitrobenzene at 22·5° being β=1°) at 134·5° is β 77·65°, falling hyperbolically to β 4·25° at 172·6°. Previous views are confirmed. C. A. SILBERRAD.

Density and refractivity of crystallised ammonium halides. P. WULFF and H. K. CAMERON (Z. physikal. Chem., 1930, **B**, **10**, 347—367).—The following values of d^{25} and n^{25}_{D} have been determined: ammonium fluoride, 1·0092±0·0004, 1·3147 (ordinary) 1·3160 (extraordinary) ±0·005; ammonium chloride, 1·5274±0·0003, 1·63851±0·00003; ammonium bromide, 2·4295±0·0009, 1·71239±0·00003; ammonium iodide, 2·5142±0·0005, 1·70070±0·0001. The differences between the observed molecular refractivities of the crystalline salts and the values calculated from the sum of those of the anion and cation follow essentially the same law as applies to the alkali halides. There is no evidence from the optical measurements that the ammonium protons in the chloride, bromide, and iodide are displaced towards the halogen ion, but in the case of the fluoride there is some evidence of such displacement. As with cæsium salts, the ammonium halides show clearly the increase of the total refraction effect resulting from transition of the lattice type to a higher co-ordination number. H. F. GILLBE.

Molecular and atomic volumes. XXIV. Technique of volumetric measurements of densities at low temperatures. E. WÜNNENBERG, W. FISCHER, and A. SAPPER. **XXV. Space occupied by crystalline organic substances at low temperatures.** W. BILTZ, W. FISCHER, and E. WÜNNENBERG. **XXVI. Molecular volumes of silver and potassium salts of monobasic fatty acids.** W. FISCHER and A. LEMKE. **XXVII. Space occupied by some cellulose preparations and capacity of cellulose acetate for absorbing gases.** E. WÜNNENBERG, W. FISCHER, and W. BILTZ. **XXVIII. Molecular volumes of substituted benzoic acids.** L. KLEMM and W. KLEMM (Z. physikal. Chem., 1930, **151**, 1—12, 13—55, 56—64, 65—70, 71—79; cf. A., 1930, 399).—XXIV. Procedure in measuring the volume of solids at temperatures down to −195° is described, and the corrections necessitated by the compressibility of the gas used for filling and its absorption by the solid are discussed.

XXV. The densities of crystallised normal aliphatic monocarboxylic acids, alcohols, and a number of other aliphatic and aromatic substances have been determined at low temperatures with the object of securing a more accurate extrapolation to zero volume. The results confirm the "principle of additivity," the curves connecting mol. vol. with number of carbon atoms in a given homologous series being rectilinear, whilst those relating to series of different derivatives

(hydrocarbons, alcohols, mono- and di-carboxylic acids) are parallel. The following mean values are deduced for the zero volume of atoms and radicals: oxygen (hydroxyl), 4·1; methylene, 13·7; C_4H_2 (from ethylene and benzene series), 33·3; carboxyl ($\cdot CO_2\cdot$), 17·5. The alternating effect observed in a homologous series is a property characteristic of the crystals, and has not been established for amorphous substances. Examples are given to show that the zero volumes of both aliphatic and aromatic compounds can be expressed approximately as the sum of the volumes of the constituent elements, using the volume of diamond in aliphatic, and that of graphite in aromatic, compounds.

XXVI. The densities of nine silver and three potassium salts of normal fatty acids have been determined at the ordinary temperature and at $-78°$. The results are discussed from the point of view of at. vols. The following values of d_4^{25} are given: silver salts: acetate, 3·279; propionate, 2·687; *n*-butyrate, 2·428; *n*-valerate, 2·167; *n*-nonoate, 1·733; *n*-decoate, 1·686; laurate, 1·585; palmitate, 1·432; stearate, 1·391; potassium salts: acetate, 1·568; palmitate, 1·104; stearate, 1·095.

XXVII. Densities of cellulose, cellobiose, and cellulose acetate at temperatures down to $-195°$ ($-79°$ for the acetate) have been determined. Coefficients of expansion were determined for cellulose and cellulose acetate. Zero volumes of the three substances are calculated. Acetylation gives rise to a considerable expansion of the cellulose molecule. Both air and hydrogen are absorbed in appreciable quantity at the ordinary temperature by the acetate, but not by cellulose. Figures relating to the absorption are given.

XXVIII. Densities of methyl-, hydroxy-, amino-, nitro-, chloro-, and bromo-benzoic acids have been determined. The results are discussed theoretically. The following values (previously unrecorded) of d_4^{25} are given: *o*-, 1·256, *m*-, 1·232, *p*-methyl-, 1·275; *p*-nitro-, 1·597; *m*-, 1·518, *p*-chloro-, 1·534; *o*-, 1·924, *m*-, 1·823, *p*-bromo-, 1·892; *o*-amino-, 1·353.

F. L. Usher.

Structure and b. p. III. Unipolar organic open-chain compounds. B. B. Nekrassov (J. Russ. Phys. Chem. Soc., 1930, 62, 1499—1508).—The b. p. of an organic compound is given by the formula $T - KM^{3/2}/\Sigma$, where T is the b. p. Abs., K is a constant characteristic of each class of compounds and varying from 11·6 to 13·6, M is the mol. wt., and Σ is derived from the refractive index. Of 1508 compounds, belonging to 22 different classes, the b. p. is given by the above formula with an error of 5° by 80%, of 6—10° by 11·7%, and of more than 10° by 8·3%.

R. Truszkowski.

Arrangement of electrons in the commoner organic compounds. M. Dunkel (Z. physikal. Chem., 1930, B, 10, 434—458).—An attempt is made to apply the principles governing the arrangement of electrons in diatomic molecules to more complex organic molecules. Electronic configurations for the principal organic radicals and linkings are suggested, and the theory is also extended to a consideration of the effect of one organic linking on another, as in semipolar linkings, and conjugated and cumulated double linkings.

R. Cuthill.

Relation between the paramagnetic property of the molecule and its chemical constitution. D. M. Bose (Z. Physik, 1930, 65, 677—699).—The constitution of a large number of compounds is discussed. A variation is found in the magnetic behaviour of a series of halogen compounds of suitable elements of the different transition groups. In the series nickel, palladous, and platinous chloride, the first is paramagnetic and the others are diamagnetic. Nickel chloride is assumed to have heteropolar linking, either of the 4*s* electrons of nickel being transferred to a chlorine atom; in palladous and platinous chlorides both the chlorine atoms are coupled by homopolar linking with both odd electrons in the 4*d* or 5*d* shell of palladium and platinum. Nickel cyanide heptahydrate is paramagnetic, whilst the dehydrated salt is diamagnetic; during dehydration there is a change from hetero- to homo-polar linking. Compounds with complex linking, consisting mainly of four or six groups of atoms so bound to a paramagnetic atom that it has a positive or negative electrovalency, are divided into three groups by their magnetic behaviour. (1) In the hydrated salts of elements of the first transition group the magnetic moments of the cations are very nearly equal to those of the dehydrated salts. To this group belong the hexammino-complexes of manganese, iron, cobalt, and nickel. It is assumed that ammonium and water form dipole molecules which are bound to the central atom by electrostatic forces. (2) In a number of tetrammino-complexes of nickel and copper and analogous hydrazine complexes of manganese, iron, cobalt, and nickel there is a small diminution of the moments of the cations compared with corresponding simple salts. (3) Complex compounds of paramagnetic elements, which are diamagnetic or show a great reduction in the magnetic moment of the central atom, belong to the class of stable co-ordinated compounds. To this class belong double salts and cyanogen compounds of paramagnetic elements. The formation of co-ordinated compounds is as follows. Each co-ordinated group, NH_3, CO, CN^-, Cl^-, contains a pair of coupled electrons, so that both 2*s* electrons of N in NH_3, both 3*s* electrons in CO and CN^-, and the 2*p* electrons in Cl^- effect the co-ordinated linking. If the co-ordinated group is bound to the *d* shell of the central atom then one of the electron pairs of the co-ordinated group reacts in the *d* shell and the other in the *p* shell of the central atom. The magnetic moments of these compounds depend on the number of empty positions in the *d* shell.

J. Farquharson.

Molecular and atomic volumes. XXIX. Three volume laws for solids. W. Biltz. **XXX. Low-temperature volumes of crystallised nitrogen oxides.** W. Biltz, W. Fischer, and E. Wunnenberg (Z. anorg. Chem., 1930, 193, 321—350, 351—366).—XXIX. The volume relationships of compounds are classified into three groups. (1) The principle of additive volumes is exemplified by many intermetallic compounds, double salts, silicates and aluminates, ammoniates and hydrates, organic compounds, and chlorides. (2) Variations from the additive law caused by constitutive factors are demonstrated by polymorphous substances such as arsenic,

by the influence of oxygen in organic compounds and in metallic oxides, by that of ammonia in complex ammines, and particularly by the apparent reduction of the at. vol. of the alkali and alkaline-earth metals in certain compounds. (3) The principle of equivalent volumes is exemplified by the formation of higher from lower oxides without appreciable change of mol. vol., by the equivalence of the mol. vol. of many oxides with the mol. vol. of the oxygen atoms contained therein, and by the absence of a change of mol. vol. of certain ammines when the valency of the central atom increases and an additional negative atom enters the molecule. The significance of polymerisation for space chemistry, and of at. vol. for atomic structure, is discussed.

XXX. The mol. vols. of nitrous oxide, nitric oxide, nitrogen trioxide, and nitrogen peroxide, measured pyknometrically under hydrogen at −195°, are 27·4, 19·3, 42·7, 46·5, respectively, and that of nitrogen peroxide at −79° is 48·45; nitrogen pentoxide, for which an oxygen-filled pyknometer must be used, has a mol. vol. of 49·6 at −195°. The zero volumes have been determined in each case by combining these results with other determinations made at 20·42° Abs. The zero volumes of nitrogen and nitrous oxide are almost identical, whilst the differences between the mol. vol. of nitrous oxide and nitric oxide (2 mols.) and between those of nitric oxide (2 mols.) and nitrogen pentoxide are equal to the volume of 1 g.-atom of oxygen; the mol. vol. of nitrogen trioxide is the mean of those of nitric oxide (2 mols.) and nitrogen peroxide. H. F. Gillbe.

Parachor and chemical constitution. XV. Constitution of sulphonium and ammonium mercuri-iodides. H. J. Cavell and S. Sugden (J.C.S., 1930, 2572—2579).—*Dibenzyl*-n-*propylsulphonium mercuritri-iodide*, prepared according to the method of Hilditch and Smiles, has m. p. 78°, d_4 2·446−0·00174t, [P] 952·0; *dibenzyl*-n-*butylsulphonium mercuritri-iodide* has m. p. 81°, d_4 2·335−0·00147t, [P] 1000; *phenyltrimethylammonium mercuritri-iodide*, prepared by warming together in acetone solution equimolecular quantities of methyl iodide, dimethylaniline, and mercuric iodide, has m. p. 137—138°, d_4^t 2·923−0·00145T, [P] 719·1. The parachors of dibenzylethylsulphonium mercuritri-iodide, phenyldimethylethylammonium mercuritri-iodide, phenylmethyldiethylammonium mercuritri-iodide, and phenyltriethylammonium dimercuripentaiodide are 915·2, 754·0, 789·5, and 1060, respectively. The conductivities of these compounds in acetone solution indicate that they are binary electrolytes, and the results accord well with Onsager's equation, especially in the case of the sulphonium compounds. The anion appears to be HgI_3', but it is not possible to decide which of the two structures suggested, viz., $I^6{=}Hg(-I^7)_2$ and $I^6{=}Hg(-I^6)_2$, represents the structure of the anion; the parachor of the dimercuripentaiodide is in agreement with the structure $I^6—[Hg(^-I^6)_2]_2$. H. F. Gillbe.

Reality of "Neumann's triangle." N. Fuchs (Z. Physik, 1930, 65, 714—718).—"Neumann's triangle," used in calculations on capillarity, has real physical significance, which is shown by experiments described, and is not merely a mathematical fiction. A. B. D. Cassie.

Critical angle of reflexion and index of refraction of X-rays. H. E. Stauss (J. Opt. Soc. Amer., 1930, 20, 616—617).—The total reflexion of X-rays is characteristic of the body of the reflector, and is not appreciably influenced by the surface conditions of good reflectors, even for X-rays of short wave-length. C. W. Gibby.

New method of producing and controlling the emission of X-rays. F. G. Cotterell, C. H. Kunsman, and R. A. Nelson (Rev. Sci. Instr., 1930, 1, 654—661).—An apparatus is described for the investigation of the emission of K^+ ions from an emitting surface after electrolysis from a hot anode through a layer of glass. For electrolysis through glass the migrating ion is the one which is emitted thermionically. This suggested the possibility of controlling the emission by altering the alkali metal concentration on the surface. Curves are given and discussed for the voltage saturation with various types of anode, and for the variation of positive thermionic current with electrolysis potential. The positive ion emission was found to obey Richardson's equation; the advantages of this source of ions are surveyed. N. M. Bligh.

[Determination of intensity of X-rays by the ionisation method.] W. Roche (Ann. Physik, 1930, [v], 7, 375—380).—A criticism of the conclusions reached by Schechtmann (A., 1930, 843). F. L. Usher.

Representation of crystal structure by Fourier series. W. L. Bragg and J. West (Phil. Mag., 1930, [vii], 10, 823—841).—The extent to which the representation of a crystal structure on a given plane by a Fourier series (cf. A., 1929, 748) may be regarded as a faithful image of the actual structure is discussed. The diffraction of an ideal crystal of sodium chloride composed of Hartree atom models has been calculated as if observations were being made experimentally for a limited range of crystal planes. These results are expressed in the form of a double Fourier series and the projection is compared with the original model. It is shown that a truer image of the structure is obtained by making the final coefficients of the Fourier series converge by means of a temperature coefficient. M. S. Burr.

X-Ray histology. I. Determination of the texture of individual ramie fibres by an X-ray micro-method. K. Eckling and O. Kratky (Z. physikal. Chem., 1930, B, 10, 368—370).—The structure of single ramie fibres has been investigated by photographing them under illumination by a pencil of X-rays perpendicular to the axis and of smaller diameter than the thread. As different portions of the cross-section of the fibre give the same diagram, which is identical also with the usual cellulose fibre diagrams, the structure must be either completely homogeneous or extremely complex (radial or concentric). H. F. Gillbe.

Interferometric measurements with molecules. P. Debye, L. Bewilogua, and F. Ehrhardt (Ber. Sachs. Ges. Wiss., math.-physikal. Kl., 1929, 81, 29—

37; Chem. Zentr., 1930, i, 3400—3401).—Measurements of X-ray scattering for carbon tetrachloride, chloroform, and dichloromethane are described.

A. A. ELDRIDGE.

Crystal structure of solid mercury. K. LARK-HOROVITZ (Physical Rev., 1929, [ii], **33**, 121).—The crystal structure of thin deposits of solid mercury formed in a vacuum has been determined at different temperatures. At the temperature of liquid air sharp lines were obtained with the copper and iron K radiations, confirming McKechan's result; at the temperature of a carbon dioxide–alcohol mixture the structure was identical, showing that no different form of mercury exists at $-80°$. The lines are sharper at the higher temperature and their relative intensity is sometimes changed.

L. S. THEOBALD.

Crystal structure of inert gases. I. Xenon. G. NATTA and A. NASINI (Atti R. Accad. Lincei, 1930, [vi], **11**, 1009—1011).—A more detailed account of work already noted (A., 1930, 528).

Orientation of rolled aluminium. J. THEWLIS (Phil. Mag., 1930, [vii], **10**, 953—961).—The orientation of a flat-rolled aluminium sheet has been determined by an X-ray method. No definite direction in the crystal can be identified with the rolling direction or the normal direction. Four sets of crystals occur, the plane of the rolling and normal directions and the plane of the cross and the normal directions behaving like mirror planes. This result confirms that of Goler and Sachs (A., 1927, 504). A square-rolled rod of aluminium, if rolled from a rod possessing random orientation, has the same orientation as a cold-drawn aluminium wire. The result of square-rolling a piece previously flat-rolled has also been investigated.

M. S. BURR.

Space-group and crystal structure of potassium sulphate. F. P. GOEDER (Physical Rev., 1929, [ii], **33**, 120—121; cf. A., 1929, 16).—An analysis of a series of Laue photographs places potassium sulphate in space-group $2Di$-13 (V_h^{13}). The potassium sulphate molecule is clearly defined, and consists of a tetrahedral arrangement of the oxygen atoms with sulphur at the centre and the potassium atoms on a straight line and equidistant from the sulphur. The potassium ions have the general positions of the space-group, but the sulphur atoms fit no special cases of the general arrangement.

L. S. THEOBALD.

Potassium dichromate crystals. P. L. STEDEHOUDER and P. TERPSTRA (Physica, 1930, **10**, 113—124; Chem. Zentr., 1930, i, 3400).—In addition to the triclinic forms there is a monoclinic form having $a:b:c=1{\cdot}0123:1:1{\cdot}7675$, β 88° 4·5′; n_D^α 1·725, n_D^β 1·762, n_D^γ 1·891.

A. A. ELDRIDGE.

Structure of some complex cyanides. C. GOTTFRIED and J. G. NAGELSCHMIDT (Z. Krist., 1930, **73**, 357—364; Chem. Zentr., 1930, i, 3528).—The unit cells of potassium ferri- (space-group C_{2h}), chromi-, mangani-, and iridi-cyanides contain 4 mols.; that of cæsium ferricyanide contains 2 mols.

A. A. ELDRIDGE.

Structure of the *cyclo*hexane molecule. O. HASSEL and H. KRINGSTAD (Tids. Kjemi Berg., 1930, **10**, 128—130).—To determine which of the two possible structures for *cyclo*hexane, assuming a ring free from strain, is the true one, X-ray measurements have been made and the results are in agreement with a ditrigonal scalenohedral symmetry.

M. S. BURR.

Structure of some fundamental organic substances. J. HENGSTENBERG and H. MARK (Z. Krist., 1929, **70**, 283—296; Chem. Zentr., 1930, i, 3668—3669).—Diphenyl has $a:b:c=1{\cdot}445:1:1{\cdot}670$; β 94·8°, with 2 mols. in the unit cell. Phenanthrene has $a:b:c=1{\cdot}4093:1:1{\cdot}61$; β 98° 15′, with 4 mols. in the unit cell. The substances are isomorphous; space-group C_{2h}^5. Fluorene has $a:b:c=1:1{\cdot}47:1$; β 101° 53′; space-group the unit cell containing 2 (double) mols. Dibenzyl and stilbene (also C_{2h}^5) have 2 mols. in the unit cell.

A. A. ELDRIDGE.

Crystalline form of some alkylarsinic acids and alkali alkylarsinates. G. GILTA (Bull. Acad. roy. Belg., 1930, [v], **16**, 942—956).—The values of β (where given) and of $a:b:c$ for the following monoclinic crystals are: methylarsinic acid 99° 3′, 1·2579 : 1 : 1·5202; potassium ($+5H_2O$), 93° 12′, 1·3131 : 1 : 1·0554; lithium ($+5H_2O$), 95° 33′, 3·0522 : 1 : 1·2325; and ammonium methylarsinate ($+5H_2O$), 93° 23·5′, 1·2707 : 1 : 1·0550; n-propylarsinic acid, 105°, 1·1633 : 1 : 1·966; and for the following orthorhombic crystals: sodium methylarsinate ($+5H_2O$), 0·5673 : 1 : 1·2239; ethylarsinic acid, 1·2452 : 1 : 1·1416; sodium ethylarsinate ($+3H_2O$), 1·0458 : 1 : 0·9038; sodium n-propylarsinate ($+3H_2O$), 0·8317 : 1 : 1·2872. Rubidium methylarsinate ($+5H_2O$), sodium ethylarsinate ($+2H_2O$), sodium n-propylarsinate (hydrated), and n-butylarsinic acid are also monoclinic; cæsium methylarsinate (hydrated) and rubidium ethylarsinate (hydrated) are orthorhombic.

C. W. GIBBY.

***X*-Ray study of the structure of the gelatin micelle.** K. HERRMANN, O. GERNGROSS, and W. ABITZ (Z. physikal. Chem., 1930, **B**, **10**, 371—394).—Two sharp interference rings have been found in the Debye diagram of air-dried gelatin, using copper $K\alpha$ radiation, together with the four broad rings. The four innermost rings indicate crystalline interference, whereas the two outer diffuse rings are of the liquid interference type, but are not due to water. The changes of the diffraction spectra after stretching and during swelling of the gelatin in water are described, and from the manner in which the rings contract or expand a theory of the gelatin structure is developed which, with certain modifications, is in accordance with that derived by Meyer and Mark for other substances consisting of complex molecules. The structure suggested is that of a fringed micelle in explanation of the mechanical properties of gelatin sols and gels.

H. F. GILLBE.

Constitution of cellulose nitrates and acetates and their passage to colloidal film. J. J. TRILLAT (J. Phys. Radium, 1930, [vii], **1**, 340—350).—The nitrates and acetates of cotton were examined as fibres or as particles dissolved in acetone, by means of X-rays, using copper K radiation. The nitrates can be grouped, according to their nitrogen content, into classes consisting of a crystalline and amorphous phase, the latter increasing as the nitrogen content

decreases; below 6% N the interference rings of cellulose appear. The cellulose nitrate films differed slightly in structure from the nitrated cottons; certain molecular spacings were somewhat larger and the distribution of the molecules was more irregular; in the passage from nitrated cotton to film the crystalline phase persists, in agreement with the results of Hess (cf. A., 1930, 750). Intermolecular space measurements for the films agree with those for the thickness of thin layers (cf. Sheppard, *ibid.*, 287). Similar results were obtained for cellulose acetates as powders or films; the fine structure of the film is, however, the same as that of the acetylated cotton, which has passed to the colloidal state. N. M. Bligh.

Periodates as characteristic crystal forms. L. Rosenthaler (Mikrochem., Emich Festschr., 1930, 254—259).—Certain alkaloids, and notably arecoline, berberine, cinchonine, eucodal, heroine, dionine, pilocarpine, and scopolamine, may be identified by the characteristic crystalline precipitates obtained by treatment with potassium iodate. With the exception of lithium, inorganic cations yield amorphous precipitates. H. F. Gillbe.

Dependence of the susceptibility of diamagnetic metals on the field. W. J. de Haas and P. M. van Alphen (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 680—682).—At the ordinary temperature the diamagnetic susceptibility of a pure bismuth rod remains constant with varying magnetic field. At 20·3° and 13·5° Abs. the susceptibility is dependent on the field, and the curves are analogous to those obtained by Schubnikow and de Haas (A., 1930, 675) for the variation of resistance of bismuth monocrystals with the magnetic field. O. J. Walker.

Magnetic properties of iron crystals. D. Foster (Physical Rev., 1929, [ii], **33**, 1071; cf. A., 1930, 673).—Large crystals 1 mm. in diameter up to 15 cm. in length have been grown by annealing hard-drawn wires of electrolytic iron in a vacuum by a new method. The wire axis always lies at a considerable angle to the nearest (111) direction. The hysteresis loop has very steep sides with sharp corners and high remanence. The initial permeability of 175 increases to a maximum at a field intensity of approximately 0·8 gauss. L. S. Theobald.

Influence of an alternating circular field on the discontinuities in magnetisation of iron [Barkhausen effect]. S. Procopiu (J. Phys. Radium, 1930, [vii], **1**, 306—313).—Iron or steel wire is placed in the axis of an induction coil connected with a galvanometer; an alternating current can be passed along the wire, which is also subjected to a magnetic field (H) produced by the rotation of a bar magnet. By varying the distance of this from the wire, H can be varied between 1 and 20 gauss. Denoting by α' and α the Barkhausen effect (as measured by the galvanometer) in presence and absence respectively of the alternating current, it is shown that when such current is constant the ratio α'/α is large for small values of ΔH, but decreases as ΔH increases, becoming approximately unity when it equals the coercivity of the wire. Curves show this relation and also that between the Barkhausen effect and the alternating current for various values of ΔH. A new effect occurs when the alternating current is passed along the wire in absence of the rotating magnet. So long as the circular field produced by the alternating current is less than the coercivity of the wire, the galvanometer indicates no current, but on reaching that value it shows a sudden jump. These results support the author's view that the Barkhausen effect varies with the magnitude of the variation in magnetisation. Tentative explanations are offered. C. A. Silberrad.

Atomic order in ferromagnetism. L. W. McKeehan and O. E. Buckley (Physical Rev., 1929, [ii], **33**, 636).—The fields surrounding a paramagnetic atom in a ferromagnetic substance cannot possess spherical symmetry. The magnetic field has one distinguishable axis, at least, determined by the resultant magnetic moment of the atom. The mechanical field must also have distinguishable lines or planes which must be definitely oriented with respect to the magnetic axis in order to account for magnetostriction. The degree to which such distinguishable parts of different atoms in a substance have a common orientation may be called its degree of magnetic or of mechanical order. In alloys the two sorts of atomic order may be inconsistent. The effects of mechanical, chemical, and thermal processes can be predicted and specifications for a ferromagnetic material with desired combinations of properties can be given. L. S. Theobald.

Ferromagnetic materials in weak alternating fields. R. Goldschmidt [with Lakmaker] (Physikal. Z., 1930, **31**, 1058—1060).—The magnetic properties of various irons and steels and nickel–iron alloys have been determined with a view of investigating the relationship of the permeability and hysteresis constants at small field amplitudes to the magnetisation. Soft iron, steel, and transformer iron exhibit considerable and different deviations from the theoretical equation, there being a marked increase of permeability at the beginning of the magnetisation curve; further, steel does not again acquire its initial permeability at zero magnetisation after the hysteresis cycle has been completed. The nickel–iron alloys all show the same type of deviation from the theoretical curve: the initial magnetisation curve is in accordance with theory, but on continuation of the cycle deviations become apparent. Similar effects are exhibited by the hysteresis–magnetisation curves. H. F. Gillbe.

Atomic moments in ferromagnetic alloys. R. Forrer (J. Phys. Radium, 1930, [vii], **1**, 325—339).—The individual moments of the atoms of ferromagnetic substances are investigated when forming alloys by the substitution of a small number of atoms of another metal without modification of the main lattice. The variation, ΔM, of the moment by the atomic substitution is the slope of the curve of the atomic moments as a function of the atomic composition. Alloys are investigated, and curves given for nickel with copper and cobalt, and iron with nickel and cobalt. ΔM is found to be, in general, an integral multiple of the Weiss magneton. Certain assumptions are considered for the distribution of

the mean moment of the alloy among the atoms present. Some new moments for atoms in alloys are indicated, the value 14 being established for iron. It is concluded that the number of magnetons is not characteristic of each atom, but depends on the crystal lattice and the nature of neighbouring atoms. Theoretical interpretations of the results obtained and the relation of the Bohr to the Weiss magneton are considered. N. M. BLIGH.

Orientation of crystals in magnetic fields. D. E. OLSHEVSKY (Physical Rev., 1929, [ii], **33**, 278).—The statistical orientation of small crystals exposed to strong magnetic fields has been investigated. The orientation of a single crystal suspended in a viscous liquid, and the problem of a growing particle and the probability function of orientation for a crystalline deposit at the bottom of a container, are treated theoretically. Distribution curves of orientation have been obtained experimentally for a basic sulphate of iron and ammonium using field intensities of 13,500 gauss. L. S. THEOBALD.

[Magnetic] susceptibility of potassium chromium alum at low temperatures. W. J. DE HAAS and C. J. GORTER (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 676—679).—The susceptibility of potassium chromium alum has been measured from 14·33° to 290·0° Abs., and found to be independent of the field. The Curie–Weiss law is obeyed, and using $\theta=0{\cdot}16°$ and $C=36{\cdot}58\times10^{-4}$ the value $p=19{\cdot}02$ Weiss magnetons is obtained. This disagrees with the explanation of Laporte and Sommerfeld (A., 1927, 86) of the magneton number in the iron group. O. J. WALKER.

Hall effect and the magnetic properties of some ferromagnetic materials. E. M. PUGH (Physical Rev., 1930, [ii], **36**, 1503—1511).—Using the method previously described (cf. A., 1929, 126), the Hall effect and magnetic properties were accurately measured simultaneously in K.S. magnet steel and in hardened high-carbon steel in order to determine the part of the effect due to the magnetic field H and that due to the magnetisation intensity I. The Hall effect, both for the curves of the material and for the hysteresis loops, was found to be a single-valued straight-line function of I, but not of H nor of the magnetic induction B. The possibility of a formula separating the effect into two components is discussed (cf. Smith and Sears, A., 1930, 281). N. M. BLIGH.

Change in resistance of pure electrolytic iron in longitudinal magnetic fields. O. STURSTADT (Z. Physik, 1930, **65**, 575—588).—Electrolytic iron in a magnetic field exhibits a larger change in resistance than a technical iron with a high carbon content. The size of the relative change in resistance depends on previous thermal and mechanical treatment of the specimen, and on the crystal structure. It appears probable that the Frank–Sommerfeld formula is applicable to ferromagnetics. J. FARQUHARSON.

Properties of sputtered metal resistors. L. C. VAN ATTA (Rev. Sci. Instr., 1930, **1**, 687—690).—The rate of change of resistance with time was investigated for gold on pyrex and platinum on soft glass rods embedded in paraffin. The latter were the more suitable for measuring small currents with an electrometer by the resistance shunt method, and showed absence of polarisation and a negligible temperature coefficient, and obeyed Ohm's law. The nature of the ageing curves depends on the metal used, the thickness of film, conditions of sputtering, and the medium surrounding the film. N. M. BLIGH.

Resistance of bismuth in alternating magnetic fields. W. W. MACALPINE (Physical Rev., 1929, [ii], **33**, 284).—The change in resistance of a bismuth wire was found to be in phase with the field and equal to that calculated from *D.C.* measurements of resistance against field strength. L. S. THEOBALD.

Piezo-electric investigations, using the principle of Giebe and Scheibe's method. A. HETTICH (Z. Physik, 1930, **65**, 506—511).—By observing the change in the piezo-electric behaviour of crystals with change of temperature it is possible to investigate transitions between allotropic modifications and to differentiate between possible crystal lattices. A simple form of Giebe and Scheibe's circuit suitable for this purpose is described. Pentaerythritol does not lose its piezo-electric properties even when heated nearly to its melting and decomposition point. Potassium iodate is piezo-electric and therefore cannot be monoclinic prismatic in structure. An allotropic change occurs in the region 140—150°. Hexamethylenetetramine shows very pronounced changes in the piezo-electric effect with temperature, but the effect remains even at the lowest temperature attainable with carbon dioxide snow and ether. Carbon tetrachloride is not piezo-electric at −80°. An allotropic change occurs in camphor at low temperatures. J. W. SMITH.

Paramagnetic rotatory power of crystals of xenotime at very low temperatures, and paramagnetic saturation. J. BECQUEREL and W. J. DE HAAS (Compt. rend., 1930, **191**, 782—784).—The curves representing the paramagnetic rotations of xenotime (λ 5615·7 and 5780·1) as a function of magnetic field (H)/absolute temperature (T) obey a law which with rise in temperature ($T=1{\cdot}38$—$14{\cdot}34°$ Abs.) approaches the simple hyperbola-tangent law already established for tysonite and parisite (A., 1929, 633, 1134), the active magnetic moment being (approximately) 7 Bohr magnetons. Contrary to results obtained previously (*loc. cit.*), and with glasses of the rare earths, the fraction of saturation is not represented by a function of the single variable H/T. Saturation is almost total (99·2%) at the temperature of liquid helium and $H=27{,}000$ gauss (cf. following abstract). J. GRANT.

Paramagnetic rotation in uniaxial crystals of the rare earths. H. A. KRAMERS (Compt. rend., 1930, **191**, 784—786).—A mathematical extension of the law deduced by Becquerel and de Haas for the rotation (ρ) of tysonite (A., 1929, 633, 1134) to the case of xenotime at low temperatures (cf. preceding abstract). If K is a constant (1·00 cm.$^{-1}$), μ_B the Bohr magneton, $\rho_\infty(T\lambda)$ the saturation-rotation, k Boltzmann's constant, and n a whole number, then $\rho=\rho_\infty(T\lambda)[n\mu_BH/\sqrt{(n\mu_BH)^2+K^2}]\tanh\sqrt{(n\mu_BH)^2+K^2}/kT$. This law is deduced on the assumption that the lower

level of the 4_3 layer is converted by intramolecular forces into two non-magnetic levels forming a doublet of magnitude $2K$. The value $n-7$ indicates that the ions of gadolinium are responsible for the rotation.

J. GRANT.

Experimental verification of the law of paramagnetic rotation in xenotime. J. BECQUEREL, W. J. DE HAAS, and H. A. KRAMERS (Compt. rend., 1930, **191**, 839—841).—The validity of the relation given by Kramers (preceding abstract) between the paramagnetic rotation of xenotime when the optic axis is parallel to the incident light and to the magnetic field, and the magnetic field at very low temperatures, has been shown to hold, within the limits of experiment, at temperatures of 4·22° and 1·38° Abs., for values of H/T between 530·8 and 6314, and 478·4 and 19,335, respectively. The values of n (7·0) and K ($1{\cdot}96\times10^{-16}$) were deduced from observations at these temperatures and at 14·34° Abs.

C. A. SILBERRAD.

Optical constants of manganese distilled in vacuum. J. B. NATHANSON (J. Opt. Soc. Amer., 1930, **20**, 593—596).—Manganese distilled in a vacuum is very brittle and difficult to polish; this may be accomplished by using aluminium oxide and then magnesium oxide. The reflecting power of the surface, which contained pits and irregularities, varies from 61·6% to 63·5% for polarised light of wavelengths 4600—6800 Å. The values found for the reflecting power are greater at the blue end of the spectrum and less at the red end than those obtained by previous workers. C. W. GIBBY.

Metallic reflexion. J. ZAHRADNICEK (Z. Physik, 1930, **65**, 814—823).—The formulæ of Macku and Drude in connexion with metallic reflexion are reviewed. The results of the determination of the optical constants of silver by Minor, those of lead sulphide, and results for a number of metals by Drude are given and compared with the values calculated from the formulæ of Macku, Drude, and the author. A. J. MEE.

Determination of optical constants of metals in the ultra-violet by the interference method. J. MALSCH (Ann. Physik, 1930, [v], **7**, 360—374).—A method of determining the refractive index and coefficient of absorption of metals, based on the formation of a thin wedge of air between a quartz plate and a plane reflecting metal surface, is described, and values of these constants for copper are given for wave-lengths down to 2536 Å. The method possesses the advantage that no polariser or compensator is used, and it is therefore applicable in the fluorspar ultra-violet range. F. L. USHER.

Grain-growth of marble. M. KURODA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, **14**, 226—227).—On annealing samples of marble, which had been subjected to compressive stresses, at 450—800°, a slight growth of the original grains was observed, but the chief effect was growth of twins and slipping in the plane of cleavage. F. L. USHER.

Mol. wt. determination in camphor solution. R. J. W. LE FÈVRE (Nature, 1930, **126**, 760).—Historical. L. S. THEOBALD.

Conduction of electricity in liquid dielectrics. D. H. BLACK and R. H. NISBET (Phil. Mag., 1930, [vii], **10**, 842—862; cf. B., 1928, 737).—The phenomena associated with the conduction of electricity through oils of the paraffin class have been investigated. The results are shown to be in agreement with the gas theory, since $R=R_0+nI$, where R is the resistance when the steady current I is flowing, R_0 the true resistance, and n a coefficient depending on temperature. This applies for a wide range of field strengths. Measurements have been made at short intervals after the initial application and after the reversal of the voltage. The results can be expressed by various simple relationships, but cannot be explained simply. No direct evidence has been obtained as to the nature of the carriers taking part in conduction through liquid dielectrics, but it is probable that they are produced chiefly by internal causes.

M. S. BURR.

Specific resistance of beryllium. E. J. LEWIS (Physical Rev., 1929, [ii], **33**, 284).—The specific resistance of beryllium from the temperature of liquid air to 700° reached a steady state only after prolonged heat treatment. The value obtained is approximately 6·8 microhms per cm. at 20°. L. S. THEOBALD.

Electrical conductivity in silicon. A. SCHULZE (Physikal Z., 1930, **31**, 1062—1064).—The specific resistance of specimens of silicon from various sources has been determined at temperatures up to 1300°; in general the resistance falls with rise of temperature from 0° to 200°, rises to a maximum at 550—650°, and thereafter falls steadily, but the curve is continuous throughout. Investigations with a single crystal, which had a small positive temperature coefficient, indicate that the negative coefficient usually observed arises at the interface between the crystals; the resistance-temperature curve of a single crystal is linear and unbroken from 0° to 400°, a further indication that no transition takes place. Measurements of the thermal expansion of silicon at temperatures up to 1000° confirm this view.

H. F. GILLBE.

International Bureau of Physico-chemical Standards. IV. Physical constants of 20 organic compounds. J. TIMMERMANS and (MME.) HENNAUT-ROLAND (J. Chim. phys., 1930, **27**, 401—442; cf. A., 1928, 942).—The following data for the b. p., m. p., and d^0 have been determined: *m*-xylene, 139·30°, 47·4°, 0·88113; *n*-propylbenzene, 159·45°, 99·2°, 0·87864; tetrachloroethylene, 121·20°, 22·35°, 1·65582; *n*-propyl chloride, 46·60°, −122·8°, 0·91686; *n*-butyl chloride, 78·50°, −123·1°, 0·90838; *o*-chlorotoluene, 159·15°, −36·5°, 1·10180; methyl alcohol, 64·65°, −97·0°, 0·81005; ethylal, 88·0°, −66·5°, 0·85021; *n*-propyl ether, 90·1°, −122·0°, 0·76611; *n*-butyl ether, 142·4°, −98°, 0·78536; acetic anhydride, 140·0°, −73·1°, 1·10526; formic acid, 100·7°, 8·40°, d^{15} 1·22647; acetic acid, 118·2°, 16·55°, d^{20} 1·04926; propionic acid, 141·35°, −20·8°, 1·01503; methyl formate, 31·50°, −99·0°, 1·00317; ethyl acetate, 77·15°, −83·6°, 0·92453; ethyl propionate, 99·10°, −73·9°, 0·91251; ethyl carbonate, 126·8°, −43·0°, 0·99707; ethyl oxalate, 185·4°, −40·6°, 1·10169; acetonitrile, 81·60°, −44·9°, 0·80345. Data

are also given for the variation of b. p. with pressure, the density at various temperatures, coefficients of expansion, refractive indices and dispersive powers, mol. refractions, viscosities, capillarity constants, and surface tensions. The results obtained by earlier investigators are also given. N. M. BLIGH.

Influence of a magnetic field on the thermal conductivity of a paramagnetic gas. H. SENFTLEBEN (Physikal. Z., 1930, **31**, 961—963).—The thermal conductivity of air in a field of about 1000 gauss is 1% lower than without field; of the individual constituents of air, oxygen gives the effect, nitrogen does not. Nitric oxide gives the effect, whereas water vapour, hydrogen, helium, and argon do not, with neon doubtful. A quantitative investigation is made of oxygen and nitric oxide. The effect varies at first with the square of the field strength, then linearly, and finally tends to a saturation value; it also varies with pressure. The measured and computed values agree very well. The effect is explained by showing that $\sqrt{T}/p$ is a function of the mean period of collision (t_s) of the molecules, so giving an explanation of the effect of pressure and temperature on the effect. J. FARQUHARSON.

Relationships between m. p., normal b. p., and critical temperatures. R. TAFT and J. STARECK (J. Physical Chem., 1930, **34**, 2307—2317).—The data of the International Critical Tables for the ratios m. p./T_c, m. p./b. p., and b. p./T_c have been examined. The first two ratios are not even approximately constant, but certain relationships appear to exist for restricted groups of compounds. The third ratio is nearer to a constant value than are the other two. The relation that T_c is equal to the sum of the m. p. (Abs.) and b. p. (Abs.) holds for a number of common substances. L. S. THEOBALD.

Calorimetric determination of the thermal properties of saturated water and steam from 0° to 270°. N. S. OSBORNE, H. F. STIMSON, and E. F. FIOCK (Bur. Stand. J. Res., 1930, **5**, 411—480).—Details are given of the methods employed and of the results obtained in the determination of the thermal properties of water and steam from 0° to 270°. Tabulated data are given of the latent heat and of the heat contents and entropies of the liquid and vapour. H. F. GILLBE.

Review of calorimetric measurements on the thermal properties of saturated water and steam. E. F. FIOCK (Bur. Stand. J. Res., 1930, **5**, 481—505).—A critical review of earlier work and comparison with the recent determinations of the Bureau of Standards. H. F. GILLBE.

Principle of the inaccessibility of the absolute zero. H. MACHE (Phil. Mag., 1930, [vii], **10**, 931—937).—A reply to Kolosovski (A., 1930, 847). The principle of the inaccessibility of the absolute zero, as conceived by Clausius, was based on the assumption that the second law of thermodynamics is valid at the absolute zero of temperature and that the specific heat remains finite or disappears at a slower rate than T. Since, however, on the basis of the experimental work of Nernst, and of Debye's theory of specific heats, it may be assumed that the specific heat disappears more rapidly than T, it must be postulated with Nernst that, in the neighbourhood of the absolute zero, every process takes place without change in entropy, and, consequently, the second law is invalid at absolute zero. The principle of the inaccessibility of the absolute zero has thus been raised to an independent postulate with a wider physical meaning than hitherto. M. S. BURR.

Entropy of hydrogen. D. MACGILLAVRY (Physical Rev., 1930, [ii], **36**, 1398—1404; cf. A., 1930, 697).—Mathematical. The entropy difference, in the solid phase at absolute zero, between ordinary hydrogen and hydrogen in perfect equilibrium is calculated to be $0{\cdot}75R\log 3+R\log 4$, in agreement with Giauque and Johnston (cf. A., 1929, 138). The thermodynamical and statistical aspects are examined. N. M. BLIGH.

Kinetic theory of liquids. R. O. HERZOG (Z. physikal. Chem., 1930, **B**, **10**, 337—346).—Theoretical. Jäger's equation for the viscosity of an ideal liquid is shown by reference to liquid hydrogen, mercury, and ethyl ether, and to associated organic liquids, to be generally applicable provided that the velocity employed refers to the average mobile particle in the liquid phase, whether the association be of a chemical, physical, or purely statistical nature. Riecke's diffusion equation is probably valid under the same conditions, and by combination of this equation with that of Jäger an expression relating the viscosity with the mean distance between the particles has been derived; by further combination of this expression with that previously derived on hydrodynamic grounds for the viscosity (A., 1929, 1112) a simple equation has been obtained for the distance between the particles. The relationship between Lindemann's assumption, that at the m. p. the amplitude of vibration of the atoms is approximately equal to the mean distance between the atoms, Jäger's equation is demonstrated. H. F. GILLBE.

New law for real gases and vapours. E. J. M. HONIGMANN (Physikal. Z., 1930, **31**, 1064—1065).—A new thermodynamic relationship, applicable to real gases and saturated vapours, has been developed by integration of the expression $d(PV)=dU.\,A/(n-1)$ on the assumption that n is constant, which is true for all substances so far examined. A new law of thermodynamics is stated thus: no change in a system can take place spontaneously which results in a diminution of the quantity H, where dH is a complete differential defined by $dH-dQ/A$, A being the capacity of the system for doing work. For a perfect gas H is identified with entropy. The new law is shown to be compatible with the second law of thermodynamics. H. F. GILLBE.

Van der Waals' equation. E. NEUSSER (Physikal. Z., 1930, **31**, 1041—1051).—The van der Waals constants a and b are expressed as functions of temperature and pressure, and since both vary more rapidly with temperature than with pressure, they should be calculated from isothermal volume determinations made at only slightly different pressures. The gas constant has been recalculated from previous measurements with hydrogen to 0·082051 atm./degree, and the m. p. of ice to 273·20°±0·02° Abs. Existing data for hydrogen and carbon dioxide are critically

examined; the constants have been recalculated for a wide range of temperatures and pressures and the results are presented graphically. Although the liquid and gas phases appear, in the van der Waals sense, to be in general continuous, the co-volume and cohesion changing continuously in the interval in which both phases coexist, the van der Waals constants undergo considerable change during the change of state, and there exists a specific temperature effect which vanishes only at relatively high temperatures and pressures. With hydrogen the constants exhibit anomalous variations with pressure in the interval 50—100° Abs. The critical volume and pressure of hydrogen may be calculated from existing data if the critical temperature be assumed, and for carbon dioxide the vapour pressure from 0° to 30° and the critical constants may be calculated approximately. The co-volume and cohesion of carbon dioxide change continuously during the change of phase, but at any given temperature diminish rapidly with increase of pressure in the neighbourhood of the boiling pressure.

H. F. GILLBE.

Viscosity, heat conductivity, and diffusion in gas mixtures. XI. Viscosity of hydrogen, nitrogen, carbon monoxide, ethylene, and oxygen and their binary mixtures. XII. Gas viscosity at high temperatures. M. TRAUTZ (Ann. Physik, 1930, [v], 7, 409—426, 427—452; cf. A., 1930, 1105).—XI. [With A. MELSTER.] The viscosity coefficients of hydrogen, nitrogen, carbon monoxide, ethylene, and oxygen have been measured by the capillary-flow method previously described from the ordinary temperature up to 276·9°, and the results are in good agreement with the previous determinations. The Sutherland constants are (hydrogen=84·4): nitrogen 103·9, carbon monoxide 101·2, ethylene 241·7, and oxygen 126·7. Determinations have been made also with mixtures of these gases, and the cross-sectional ratios q have been calculated; q is independent of the temperature and of the concentration of the mixture. The viscosity isotherms of carbon monoxide–nitrogen, carbon monoxide–oxygen, and nitrogen–oxygen mixtures are approximately linear, and the cross-sectional ratios are almost unity. The gas triangle and its application in certain cases to the assignment of a correct value to q are described. If the values of q for two mixtures are represented by two sides of a triangle, that for the third mixture is derived from the length of the remaining side. The principle shows the experimental values of q to be mutually concordant, and demonstrates the similarity between nitrogen and carbon monoxide. The mean term $2\eta_{12} \cdot q_{12}^2/q_1 \cdot q_2$ is independent of the concentration, as shown by calculation of the constant F, which may be determined to within 1% from the maxima in the viscosity–molar fraction isotherms (A., 1929, 1227); the values of F lie between 1·0 and 1·5, and assume the higher values for mixtures having a large difference between the mol. wts. of the constituent gases. The characteristic temperature Θ, which has been calculated for a number of gases, falls with increase of the mol. wt. M, whereas $M\Theta$, which varies from 17 to 26, increases in general with M, although for the inert gases the variation is periodic. The ϕ functions $(=q_1M_1\Theta_1/q_2M_2\Theta_2)$ of the gas mixtures have been calculated. For those mixtures for which the cross-sectional ratio is high or unity ϕ is approximately equal to q, but for intermediate values of q ϕ increases to about 1·5 q.

XII. [With R. ZINK.] Comparative measurements of the viscosity of air between 20° and 830° accord well with a value of 111 for the Sutherland constant. Differential measurements of the viscosities of nitrogen, argon, and carbon dioxide between 20° and 700° made with a simple capillary tube differ only slightly from measurements made with a tube expanded at one end; by this second method results have been obtained for argon, nitrogen, carbon dioxide, oxygen, hydrogen, helium, neon, methane, and sulphur dioxide between 20° and 830°. The Sutherland formula is applicable to nitrogen, argon, and oxygen within the range studied, the constants C being 104·7, 142, and 125, respectively. For hydrogen, helium, and neon the Sutherland formula is totally invalid, but the modified Onnes equation $\eta=kT^n/(1+C/T)$, where n=0·67, 0·67, 0·6, and C=0, 2·5, and 20, respectively, gives values for η which accord well with those determined experimentally. For carbon dioxide and sulphur dioxide the Sutherland constant becomes constant only at temperatures above 300°, the values being 213 and 306; for methane C=162. The variation of the Sutherland constant with temperature has been investigated: for hydrogen, helium, and neon C increases slowly and n diminishes with rise of temperature. For hydrogen n tends to the value 1·5 at very low temperatures; for the other gases examined n converges to the value 0·5, and with falling temperature C passes through a maximum which lies a little above the critical temperature.

H. F. GILLBE.

Kordes' law. K. M. STACHORSKI (J. Russ. Phys. Chem. Soc., 1930, **62**, 1493—1497).—Kordes' law (A., 1926, 798) may be applied in the approximate evaluation of the degree of association of one or both components of a mixture. R. TRUSZKOWSKI.

Viscosity of mixtures of ethyl acetate with piperidine. N. A. PUSHIN and T. PINTER (Z. physikal. Chem., 1930, **151**, 135—137; cf. A., 1929, 994).—From the results of measurements of the density and viscosity of mixtures of ethyl acetate and piperidine it is concluded that the associated molecules of the latter substance are partly resolved by ethyl acetate into simpler complexes.

F. L. USHER.

Molecular kinetics of glasses in the softening interval. G. TAMMANN (Z. anorg. Chem., 1930, **193**, 406—408).—The abrupt changes of specific heat and of the coefficient of expansion of glasses in the softening interval are shown not to be due to polymerisation processes. It is suggested that molecular rotation commences within the glass at the lower temperature limit of the softening interval and is complete at the upper limit. H. F. GILLBE.

Alloys of iron. IX. Constitution of iron-silicon alloys. J. L. HAUGHTON and M. L. BECKER (J. Iron Steel Inst., 1930, **121**, 315—335).—Very pure alloys containing up to 73% Si have been studied by means of thermal analysis, dilatometric measurements, magnetic tests, annealing tests, and

photomicrographic observations. The liquidus and solidus curves of the α solid solution region lie close together, and fall at 35% Si to 1198°, the eutectic with the ε phase (compound FeSi). The maximum of the liquidus in the ε area is at 1410°, and falls at 51% Si to the eutectic with the ζ phase at 1213°; the ζ phase is probably Fe_2Si_5, which forms a eutectic with silicon at 59% Si and 1208°. Iron is but slightly soluble in silicon, but the solubility of silicon in iron is 18·5% at the eutectic point and falls to 15% at about 800°. Murakami's interpretation of the arrest in the cooling curve at about 1030° as being due to the formation of Fe_3Si_2 has been confirmed, and there appears to be another arrest at about 950°, the cause of which is obscure. Silicon lowers the β–α magnetic transition point rapidly until it meets the η phase boundary at 490° and 14·5% Si, after which the curve is horizontal up to 25% Si. A second magnetic transition exists at 82°, due to a transformation in the η phase. H. F. GILLBE.

Nature of the β-transition of copper–tin alloys. H. IMAI and I. OBINATA (Mem. Ryojun Coll. Eng., 1930, **3**, 117—135).—Resistance–temperature curves of copper–tin alloys show a sharp fall and subsequent steady rise of resistance at 525°; for alloys containing less tin than the eutectic mixture the curve shows a further break at 590° which is a function of temperature only and not of the time of heating, and is probably due to a change in the β mixed crystal phase. Alloys consisting of the δ+ε phase show a very pronounced fall of resistance at about 590°, and a subsequent rise. Differential heating and cooling curves show that the β transformation takes place in two stages, at 525° and 590°. Alloys quenched from 700° show marked absorption of heat at 525°, and evolution of heat at 200° and 350°; these effects, which increase with the content of the alloy, are attributed to eutectoidal breakdown of the supercooled β mixed crystals. The whole transition of the phase appears to take place in three stages, viz. $\beta \longrightarrow \beta' \longrightarrow \beta'' \longrightarrow \alpha + \delta$ and this view is supported also by the resistance–temperature curves of the chilled alloys. The β transition resembles the A2 transformation of steels and the β transformation of copper–zinc alloys in being concerned with a change of atomic energy rather than a simple phase transformation. H. F. GILLBE.

Compound SnSb. W. M. JONES and E. G. BOWEN (Nature, 1930, **126**, 846—847).—The compound SnSb has a crystal structure of the sodium chloride type; d 6·94 g./c.c., and a_0 6·092 Å. Reflexions from the 111 planes are absent, but the observed and calculated values of the plane spacings are in good agreement, as are those of intensities of the lines. The structure of the compound SnSb persists over the range 46—60% Sn with some change of lattice constant showing solubility of both constituents in it. Dissolution of up to 4% Sb changes the lattice constant to 6·106 Å. and before annealing dissolution of 10% Sn causes an expansion to 6·124 Å.; after annealing there is no measurable change. L. S. THEOBALD.

Crystal structure of the β phase of aluminium-bronze. I. OBINATA (Nature, 1930, **126**, 809).—A powder photograph of the binary alloy containing 12·5% Al taken at about 650° shows it to belong to a body-centred cubic super-lattice, of parameter 5·887 Å. Weak spectral lines belonging to the β phase are obtained from the same alloy quenched from 850°, whilst intense lines correspond with a hexagonal lattice of the β′ phase. The lattice constants are: β′ phase, a 11·13 Å., c 6·342 Å., and c/a 0·5698, and β phase, a 5·835 Å. L. S. THEOBALD.

Solubility of naphthalene in some aliphatic alcohols. A. A. SUNIER (J. Physical Chem., 1930, **34**, 2582—2597).—The solubility of naphthalene in methyl, ethyl, *n*- and *iso*-propyl, *n*-, *iso*-, *sec*.-, and *tert*.-butyl alcohols has been determined between 20° and 70° by the synthetic method. For the normal alcohols the solubility increases from methyl to butyl alcohol; at the lower temperatures *iso*propyl alcohol dissolves about 30% less naphthalene than does the corresponding normal alcohol. *iso*-Butyl alcohol is a poorer solvent than the normal compound at all temperatures in the range investigated, whilst the secondary compound is the best solvent of all the isomerides at the higher temperatures and the tertiary is the poorest at the lower temperatures. With methyl and ethyl alcohols the presence of about 2% of water reduces the solubility by about 20%. The errors introduced into the determination of solubility by the synthetic method by the presence of undissolved crystals and by too rapid heating are considered. The causes of deviation from Raoult's law are briefly discussed. L. S. THEOBALD.

[Solubility of] caseinogen. J. SLADEK (Casopis Ceskoslov. Lek., 1930, **10**, 1—7, 29—38, 61—66; Chem. Zentr., 1930, i, 3314).—The solubility of caseinogen in solutions containing constant amounts of sodium chloride and hydroxide increases with its concentration to a maximum and then diminishes. For equal amounts of caseinogen and equal concentrations of sodium chloride it increases with increasing p_H; when the concentration of sodium hydroxide is constant it increases with increasing concentration of sodium chloride but eventually falls. A. A. ELDRIDGE.

Nitric acid. VI. Total vapour pressures and densities of solutions of nitrogen peroxide in anhydrous and very concentrated nitric acid. A. KLEMENC and J. RUPP (Z. anorg. Chem., 1930, **194**, 51—72; cf. A., 1930, 543).—The densities and total vapour pressures of solutions of nitrogen peroxide in anhydrous nitric acid and in 16*N*- and 19*N*-nitric acid have been determined over a wide range of concentration at 0°, 12·5°, and 25°. As the concentration of the solution in the anhydrous acid is increased, the density rises continuously up to a maximum and then starts to fall again, which is regarded as pointing to compound formation in the mixture. The amount of peroxide dissolved increases with its partial pressure more rapidly than Henry's law would indicate; at 25° and under a total pressure of 0·8 atm., 1 volume of the anhydrous acid dissolves about 590 volumes of peroxide. The depression of the solubility caused by addition of water is probably connected with the existence of the equilibrium

$HNO_3,H_2O+NO_2 \rightleftharpoons HNO_3,NO_2+H_2O$ in the solution. R. CUTHILL.

Intensive drying. (MISS) E. J. GREER (J. Amer. Chem. Soc., 1930, 52, 4191—4201).—If in the purification of benzene special care is taken to remove all sulphur compounds, no colour is developed and no additive compounds are formed with phosphorus pentoxide. The vapour pressure of benzene was unchanged after being dried for 3 years with phosphorus pentoxide in a fused pyrex glass apparatus. A few days' contact with activated silica gel gives rise to changes in the vapour pressures of benzene, carbon tetrachloride, and carbon disulphide which are in the same direction as and of similar magnitude to those observed in other investigations on intensive drying. The observed effects are attributed to the additive effect of the partial pressure of minute traces of water in the normal liquid rather than to any catalytic effects. *E.g.*, $2{\cdot}29\times10^{-4}$ g. of water in 1 g. of benzene exerts a partial pressure of 7 mm. at 20°, and thus Raoult's law is not followed. Partial pressures of solutions of water in benzene at 20·89° have been determined. Henry's law is followed rigidly. J. G. A. GRIFFITHS.

Sorption of gases by minerals. II. Laumontite. J. SAMESHIMA (Bull. Chem. Soc. Japan, 1930, 5, 303—310; cf. A., 1929, 757).—Ammonia is absorbed by dehydrated laumontite in amounts which depend on the conditions of dehydration, but not on the temperature between 0° and 25°. Carbon dioxide is not absorbed. C. W. GIBBY.

Relation between gas content and adsorption of electrolytes by activated charcoal. V. Poisoning of platinum in platinised charcoal. S. VASSILIEV and A. FRUMKIN (Z. physikal. Chem., 1930, 151, 87—96; cf. A., 1929, 640; 1930, 683, 684).—Mercuric chloride is very strongly adsorbed by platinised charcoal, and is not displaced when the latter is afterwards saturated with hydrogen. The addition of 1 mol. of mercuric chloride per atom of platinum suffices to abolish the capacity of the charcoal to assume a higher oxygen potential, *i.e.*, it adsorbs the same quantity of acid as unplatinised charcoal. In an acid medium, desorption of acid by hydrogen is not affected by the presence of mercuric chloride. If, however, the mercuric chloride is adsorbed from an alkaline solution, or is previously "fixed" by means of hydrogen, the platinum is poisoned and desorption of acid is incomplete. Reduction of adsorbed oxygen by means of hydrogen (development of a hydrogen potential) is also inhibited under similar conditions. Mercuric chloride influences only slightly the development of a hydrogen potential by oxygen-free charcoal. F. L. USHER.

Adsorption time and its measurement by streaming methods. I. P. CLAUSING (Ann. Physik, 1930, [v], 7, 489—520).—The phenomenon of adsorption of a gas at a solid interface is discussed in the light of the kinetic theory, and a critical survey is given of earlier work on the subject. It is shown that the mean adsorption time τ of a molecule colliding with the surface is equal to the mean interval during which the molecules adsorbed in an element of time dt are retained after collision with the surface, and is related to the probability of re-evaporation, and that the mean adsorption time of the adsorbed molecules in the stationary state is 2τ. If at time $t=0$ a vessel containing gas at a given pressure is put into communication with a second, empty, vessel, by means of a tube, the delay experienced before the first molecules of gas enter the second vessel will be governed by the length of time that each molecule is retained by the walls of the tube after each collision, *i.e.*, by the adsorption time. The theory of the determination of adsorption times by streaming methods based on this principle is developed by regarding the phenomenon purely as one of diffusion, and also by regarding the adsorption times as very great compared with the time of flow of the gas. H. F. GILLBE.

Stabilising effect of adsorption layers of surface-active substances on disperse systems. II. Stability of bubbles and drops at surfaces of separation. P. REHBINDER and E. WENSTROM (Kolloid-Z., 1930, 53, 145—158).—The factors determining the stability of disperse systems and the methods of measuring it are discussed. The stabilising effect of surface-active substances of sufficient surface rigidity on aqueous suspensions and emulsions is at a maximum when the adsorption layer is completely saturated. Suspensions of barium sulphate, ferric oxide, mercuric oxide, aluminium sulphate, and silica in benzene, toluene, and heptane are stabilised by adsorption layers of polar molecules and excess of the stabilising agent brings about coagulation. In such cases stability is at a maximum at a medium concentration of stabiliser. When a foam is stabilised by a "liquid" adsorption layer such as *iso*amyl alcohol in water, an optimal concentration of the liquid corresponds with maximum stability, but when the stabiliser forms a semi-solid adsorption layer the stability increases with concentration up to saturation of the layer. The stability of foams and emulsions has been measured by determining the time, τ, taken for bubbles or liquid droplets to disappear. In the case of emulsions τ depends on which of the pair of liquids is in the disperse phase. Curves relating the time or stability to concentration of the stabilising agent have led to the recognition of two groups of adsorption layers—liquid and solid. For pure liquids τ is 0, with liquid stabilisers the curve passes through a maximum before saturation is reached and then falls, whilst with solid adsorption layers τ increases with concentration to a limiting value at saturation. Iodine, eosin, crystal-violet, and night-blue form a transition between the two groups. Similar experiments have been extended to more massive systems, such as a broken mercury surface in solutions of stabilising agents.
E. S. HEDGES.

Unimolecular films on water and on mercury. I. Surface films on water. E. FAHIR (J. Chim. phys., 1930, 27, 471—492).—Three classes of substances which spread on water to form films are recognised: (1) those which spontaneously form stable films (oleic and myristic acids, cetyl alcohol), (2) those giving a film which disappears more or

less rapidly through its high solubility (lauric acid) or volatility (camphor), and (3) substances which give a film only when previously dissolved in a suitable volatile liquid, such as benzene or chloroform. Palmitic and stearic acids belong to the third class, but give spontaneous stable films at higher temperatures. The stability of these films on water has been studied by Marcelin's method and curves connecting the area of the film with the pressure have been constructed. The results confirm that oleic, myristic, palmitic, and stearic acids and cetyl alcohol form unimolecular films with one end of the molecule towards the water. The following values for the lengths of the molecules have been determined and are in good agreement with the values calculated from X-ray spectrographic data: oleic acid, 23·2; myristic acid, 16·3; cetyl alcohol, 23·5; palmitic acid, 17·8; stearic acid, 19·8 Å.

E. S. HEDGES.

Change of the osmotic water attraction of a system of phases. I. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 694—701).—A mathematical consideration of the thermodynamics of general osmotic systems with special reference to the influence of changes of pressure and volume on the osmotic water attraction of the systems.

O. J. WALKER.

Osmotic pressure and mol. wt. of cellulose acetate. E. H. BÜCHNER and P. J. P. SAMWEL (Proc. Akad. Wetensch. Amsterdam, 1930, **33**, 749—754).—A preliminary account of osmotic pressure measurements of cellulose acetate (cellite) in acetone, acetophenone, and benzyl alcohol by the method of van Campen (unpublished) which depends on measuring the velocity with which the solvent diffuses through the semipermeable membrane against an applied pressure and extrapolating for zero velocity. A partly denitrated collodion membrane was found satisfactory. In some cases the osmotic pressure is proportional to the concentration and the temperature, but in other cases deviations are obtained. The mol. wt. in the various solvents is approximately the same, viz., 32·6 to $35{\cdot}8\times10^3$. Different samples of cellite which have different viscosities give the same value for the mol. wt., so that there is no connexion between the latter and the viscosity.

O. J. WALKER.

Cryoscopic study of paraldehyde in solutions of sodium and barium chlorides. F. BOURION and E. ROUYER (Compt. rend., 1930, **191**, 1062—1064).—Paraldehyde [taken as $(C_2H_4O)_3$] in 0·5M solutions of sodium chloride at 0° (mean K_c 23·3) exists as an almost stable molecule, but in 1·225M solutions is depolymerised to an extent which increases as the concentration decreases, and corresponds with equilibrium between simple and triple molecules only. In 0·25M- and 0·6125M-barium chloride solutions (mean K_c 22·40 and 28·60, respectively) there is no indication of depolymerisation (cf. Bourion and Tuttle, A., 1929, 648, 1236).

J. GRANT.

[Cryoscopy and rotatory powers of] solutions of tartrates in molten calcium chloride hexahydrate. E. DARMOIS and J. CESSAC (Compt. rend., 1930, **191**, 1053—1055).—The mean cryoscopic constant obtained from solutions of calcium, methyl, and ethyl tartrates dissolved in molten calcium chloride hexahydrate (m. p. 29·8°) is 40·4, corresponding with the normal mol. wts. of these salts. The solutions of methyl and ethyl tartrates are lævorotatory, and determinations of [α] at 20—80° for the yellow, green, and (mercury) indigo rays indicate an equilibrium between two or more isomeric tartrates, depending on the concentration and temperature. Solutions of calcium tartrate are only feebly lævorotatory, and [α] is only slightly affected by variations in concentration and temperature (cf. A., 1929, 259).

J. GRANT.

Osmotic relations of strong electrolytes in solution and hydration of their ions. K. FAJANS and G. KARAGUNIS (Z. angew. Chem., 1930, **43**, 1046—1048).—A lecture. E. S. HEDGES.

Generality of the colloid state. P. P. VON WEIMARN (Kolloid-Z., 1930, **53**, 246—247).—A claim for priority. E. S. HEDGES.

Colloid science, electrotechnics, and heterogeneous catalysis. WO. OSTWALD (Kolloidchem. Beih., 1930, **32**, 1—113).—The fundamental principles of the physics and chemistry of colloids are discussed in terms of the degree of subdivision of matter. It is emphasised that most physico-chemical properties vary with the degree of subdivision and that this variation is greatest in the region of colloidal dimensions, where maxima or minima are often to be observed. Many examples of the change of properties with the degree of dispersion are illustrated by curves. The importance of dimensional characteristics in properties which lie beyond the usual scope of colloid science is indicated, and insulators, electrolytic valves, detectors, photo-cells, and heterogeneous catalysis are discussed from this point of view.

E. S. HEDGES.

Evolution of colloidal molecules. General exposition. P. BARY (Rev. gen. Colloid., 1930, 8, 289—300).—The hypothesis of an "evolution zone" in the dynamic equilibrium of polymerides is advanced, an increase in the number of molecules being regarded as "positive evolution" and a decrease as "negative evolution." The theory of molecular evolution is applied to lyophilic colloids, which are regarded as matter in the evolution zone. Such colloids consist of chain-like polymerides, the ends of the chains being saturated with molecules acquired from the dispersion medium; they are regarded as existing in two states, according to whether their evolution is positive or negative, *i.e.*, whether the number of particles is increasing or decreasing. A marked tendency towards positive evolution is characteristic of a peptisable colloid, the velocity of evolution being modified by temperature, pressure, and the chemical properties of the medium; under certain conditions the direction of evolution may be reversed to negative, leading to coagulation or gelation. The process of positive evolution begins with the swelling of a gel and ends with molecular dispersion. Typically lyophobic colloids, dispersed by mechanical or electrical means, are not regarded as being in the evolution zone; they neither swell nor form jellies. Colloids prepared by chemical methods, such as the

metallic hydroxides and sulphides, are in the zone of evolution, but the direction of evolution is negative.
E. S. HEDGES.

Brownian motion. G. E. UHLENBECK and L. S. ORNSTEIN (Physical Rev., 1930, [ii], **36**, 823—841).—Mathematical. The frequency distribution of the velocity and displacement of a particle in Brownian motion, and the Brownian motion of a harmonically bound particle, are investigated. N. M. BLIGH.

Cataphoretic and extinctiometric measurements with kaolin suspensions. A. REIFENBERG (Kolloid-Z., 1930, **53**, 162—170).—Measurements of the velocity of cataphoresis of kaolin particles in dilute electrolyte solutions have been compared with the amount and state of aggregation of the transmigrated portion as determined by nephelometric investigation. The results establish that small concentrations of ammonium, sodium, and calcium hydroxides and disodium hydrogen phosphate raise the charge on the particles and reduce the aggregation simultaneously, the order of effectiveness for both processes being $Ca>Na>NH_4$. Similarly, with falling electrokinetic potential the amount of kaolin transferred is reduced and the degree of aggregation is greater. At somewhat higher concentrations sodium hydroxide has the greatest charging effect, and in more concentrated solutions all the electrolytes have a discharging effect, that of calcium being very pronounced. Coagulation is considered to be due not only to discharge, but also to dehydration of the particles. E. S. HEDGES.

Cataphoresis in rotating electric fields. E. M. PUGH and C. A. SWARTZ (Physical Rev., 1930, [ii], **36**, 1495—1502).—A new method of making cataphoresis measurements on colloid particles, using a rotating electric field causing the particles to move in circles, is described. The mobilities of particles smaller than 10^{-4} cm. diameter fluctuate widely; a qualitative explanation is discussed. N. M. BLIGH.

Dielectric constant of complex colloidal systems. Adsorption by micelles in solution. Dielectric origin of forces of adsorption. C. MARIE and N. MARINESCO (J. Chim. phys., 1930, **27**, 455—470).—The dielectric constants of suspensions of carbon in water and also in the presence of gelatin, leucine, and glycine have been measured. The results are said to show that the phenomenon of protection of colloids is a simple adsorption due to the dielectric attraction between the dipoles of high moment of the protective agent and the electrically deformable adsorbent particle. Good protective colloids should therefore have high dipole moments and it is shown that this property is a special feature of some of the proteins. E. S. HEDGES.

Plasticity and viscosity as criteria of molecular aggregation. S. E. SHEPPARD (J. Rheology, 1930, **1**, 471—483).—A critical discussion of recently published work on the phenomena associated with the viscosity of colloidal solutions and the light thereby thrown on the degree of dispersion of solvated molecules. E. S. HEDGES.

Colloidal structure of egg-white as indicated by plasticity measurements. J. L. ST. JOHN and E. L. GREEN (J. Rheology, 1930, **1**, 484—504).—Egg-white from fresh eggs consists of two portions (described as thick and thin, respectively), which differ in their physical and colloidal properties. By means of a horizontal capillary-tube plastometer the difference in properties of the two portions has been examined. The mobility of the thick portion appears to increase with the time for which the egg is kept after opening, but this time factor does not affect the behaviour of the thin white, suggesting a colloidal change involving a translation of thick into thin white. The thick portion is not considered to be pseudoplastic, although the thin portion may be. Analyses of the plasticity data and especially of the inconsistencies therein lead to the view that with the thick portion a part of the total work is used to break down the gross structure before the white enters the tube, a part to deform and deflocculate the disperse phase after it enters the tube, and the remainder to cause viscous flow. The effect of the breakdown of the gross structure is probably shown by the difference in the mobility of the thick and thin portions of the white. A mathematical formula for determining the pressure necessary to break down the gross structure has been developed. A method for the accurate calibration of capillary tubes is described.
E. S. HEDGES.

Adherence and packing of microscopic particles. A. VON BUZÁGH (Kolloidchem. Beih., 1930, **32**, 114—142).—The sedimentation volume of irregular, polyhedral quartz particles of microscopic dimensions has been measured in water, electrolyte solutions, lyophilic colloidal solutions, and some organic liquids and the results have been correlated with the size, form, orientation, and adherence of the particles. In water the sedimentation volume is independent of the particle size, but in the presence of coagulating electrolytes the sedimentation volume is greater the smaller is the particle size. This relation does not hold for particles greater than 100 μ. The sedimentation volume in electrolyte solutions increases with the adherence value of the particles as measured by the angle of tilt method. This apparent contradiction is explained by supposing that when the adherence is small the particles can glide over each other and become packed in a small space, whilst when the adherence is great the particles adhere at edges and corners, thus giving an open structure and larger volume to the sediment. It follows also that the value of the sedimentation volume alone cannot in such cases give a true indication of the size of the lyospheres surrounding the quartz particles. An indication of the size of the lyospheres can be obtained, however, when the size of the particle is small in comparison with the thickness of the solvate sheath or when the particles are in the form of oriented platelets, giving a uniform method of packing. Experiments have been conducted, therefore, with plate-like particles of glass and it has been established that the sedimentation volume and therefore the thickness of the solvate sheath decreases in the presence of a coagulating electrolyte. The mechanical properties of the sediment of coarsely disperse quartz also vary with the size, form, and adherence of the particles, and the thickness of the lyospheres; in

water the sediment is dense, but can flow, whilst in electrolyte solutions it is loosely packed, but cannot flow. Aliphatic alcohols in aqueous solution raise the adherence value of the particles, the effect increasing with rising concentration and with the mol. wt. of the alcohol. The sedimentation volumes of quartz particles were also measured in ethyl ether, chloroform, carbon tetrachloride, benzene, and toluene and were found to increase with the adherence values. Carbon tetrachloride is remarkable for the high values obtained. In gelatin solutions of medium concentration the sedimentation volume and adherence value of quartz particles simultaneously vary with time, being at first greater than the values obtained in water and later falling gradually to a low value. This behaviour is due to the slow formation of a gelatin sheath round the particles, a thin layer having a coagulating influence and a thicker layer a stabilising effect. For this reason, very dilute or very concentrated gelatin sols do not show this time effect. E. S. HEDGES.

Polyhydroxy-compound method of synthesis of electronegative sols. III. Formation of ferric hydroxide sol in the presence of citric acid. A. DUMANSKI and T. P. TIASHELOVA (J. Russ. Phys. Chem. Soc., 1930, **62**, 1313—1334; cf. A., 1930, 992).—Negatively-charged colloidal suspensions of ferric hydroxide are formed from ferric chloride in the presence of alkaline citrate. The first product is a complex of ferric hydroxide with sodium citrate, which reacts with sodium hydroxide to yield the sol. The complex appears, on the basis of measurements of electrical conductivity and of the f. p. lowering, to be identical with Belloni's "ferrisodium citrate," the iron being in the anion. Measurements of the absorption spectrum sharply differentiate solutions of the complex from those of the sol, obtained by adding further alkali. Excess of alkali produces coagulation of the sol. Sols formed in the presence of citric acid are less stable than are those formed in tartaric acid solution. R. TRUSZKOWSKI.

Influence of hydrolysis temperature on some properties of colloidal ferric oxide. II. Stability. G. H. AYRES and C. H. SORUM (J. Physical Chem., 1930, **34**, 2629—2635; cf. A., 1930, 693).—The coagulation values of ferric oxide sols show no regular variation with the temperature of preparation of the sol or with the concentration of ferric chloride hydrolysed. In general, however, the flocculation value towards sodium chloride decreases with a rise in temperature. The sols become opaque and reddish-orange in colour on heating above 160° and show much settling when kept. At the higher temperatures, the sols appear to be less hydrated. The decrease in stability and the increase in turbidity are not due to an increase in particle size.

L. S. THEOBALD.

Dye sols. I. Sol formation of Congo acid by washing-out peptisation. R. TANAKA (Kolloid-Z., 1930, **53**, 200—205).—When Congo-red is precipitated by mineral acids and the precipitate washed with water the first washings are colourless, later pink, red, and finally blue, with the formation of sols by peptisation. The electrical conductivity of these sols has been measured and peptisation begins when the liquid has a conductivity of 0·0003 mho. Measurements of filtration velocity and viscosity suggest that immediately before peptisation the precipitate undergoes swelling. Directions are given for the preparation of a concentrated sol of Congo acid, containing 2·46 mg. per c.c. E. S. HEDGES.

Influence of electrolytes on colloidal sulphur. A. BONVARLET (Rev. gén. Colloid., 1930, **8**, 300—309).—When progressively increasing quantities of sodium chloride are added to colloidal sulphur the stability of the sol passes through a maximum, but the concentration of sodium chloride should not exceed 0·54%. Sodium, ammonium, and lithium salts produce a reversible precipitate of sulphur at all concentrations, whilst salts of barium, copper, calcium, potassium, and magnesium give an irreversible precipitate. The precipitation is the more rapid and complete the higher is the at. wt. of the metal concerned. Ultramicroscopical examination of the precipitates has revealed that the reversible precipitates consist of an assemblage of primary particles, which have lost their electric charge, but still preserve their individuality; on the other hand, the particles in the irreversible precipitates have coalesced and cannot redisperse when the conditions of the dispersion medium are changed. The stability of a sol containing 13·4% of sulphur is at a maximum in the presence of 0·93% of sodium chloride, being thus about 7% of the weight of sulphur. Both rise and fall of temperature decrease the stability of the sulphur sols, especially when relatively large quantities of sodium chloride are present. The stability is at a maximum over the range 12—18°. Sulphur is also deposited by the action of light, but deposits formed either by light or temperature changes are redispersed in the sol by shaking. E. S. HEDGES.

Precipitation potential of arsenious sulphide hydrosol in presence of excess of arsenious oxide. S. N. MUKHERJI (Kolloid-Z., 1930, **53**, 159—162).—The cataphoretic migration velocity of the particles of arsenious sulphide sols containing an excess of arsenious oxide decreases with increasing content of the latter and the equicoagulation and precipitation concentrations of electrolytes fall simultaneously. Although dilution of the sol increases its stability towards electrolytes, it has the effect of lowering the velocity of cataphoresis. E. S. HEDGES.

Stabilisation of colloidal systems. III. S. I. DIJATSCHKOVSKI (J. Russ. Phys. Chem. Soc., 1930, **62**, 1285—1311; cf. A., 1930, 993).—The stability of a number of sols is diminished by the addition of small quantities of methyl or propyl alcohol, but is augmented by higher concentrations of the alcohol; these effects are ascribed to dehydration of the micelles at low concentrations and to slow augmentation of the dielectric polarisation of the molecules of the lyosphere, involving increase in the dipole moment, in the case of high concentrations. The variation of surface tension of colloidal solutions with temperature attains a maximum value over the interval 30—40°. A colloidal solution can be separated into fractions of different relative dispersion by freezing; the larger micelles remain in the coagulate

on thawing, whilst the solution contains particles in a high degree of dispersion. In some cases suspensions containing ultramicrocrystalline particles are obtained on thawing. R. TRUSZKOWSKI.

Reversal and peptisation of metachromic dyes at surfaces. N. VON JANCSÓ (Kolloidchem. Beih., 1930, **32**, 143—155).—When aqueous solutions of metachromic dyes containing electrolytes are shaken with an immiscible organic liquid, the dye undergoes a colour change at the liquid–liquid interface. The colour change in the case of Congo-rubin is a particular colloid-chemical problem, which can be explained in terms of Wo. Ostwald's theory that the colour is a function of the degree of dispersion. When the liquid–liquid surface is increased by shaking, the blue, coarsely disperse substance is peptised at the interface to the red, finely-dispersed form, the phenomenon being most marked when the electrolyte used is a neutral salt having a univalent cation and an anion which falls near the beginning of the lyotropic series. Blue Congo-rubin membranes spread at a large, still surface separating an aqueous electrolyte solution from an immiscible organic liquid, and assume the red form. E. S. HEDGES.

Swelling pressure. J. J. BIKERMAN (Z. physikal. Chem., 1930, **151**, 129—134).—Theoretical. Osmotic pressure and swelling pressure differ in that the forces between solute and solvent in the former effect have their origin in points, and in the latter in surfaces. If l denotes the distance between a molecule of solute and the position of weakest attraction, both types of pressure are represented by the formula $P{-}3kT/8l^3$. In the case of gels, l is the thickness of the adsorbed layer of solvent, and on introducing this magnitude into the general formula an expression is obtained which agrees with the empirical concentration–pressure relation observed by Posnjak (A., 1912, ii, 912). F. L. USHER.

General regularities of gelatin swelling in electrolyte solutions. K. RUDSIT (Kolloid-Z., 1930, **53**, 205—218).—The results of a large number of measurements on the swelling of gelatin and the influence of the hydrogen-ion concentration of the liquid, the temperature, concentration of salts, and time are presented. The swelling curves of all the kinds of gelatin investigated have two minima at p_H 4·7 and 8·0, respectively, between which lies a "neutral" maximum, the position of which may be on either the acid or the alkaline side and depends on the kind of gelatin. The swelling curve of gelatin in solutions of sodium chloride of different concentrations is essentially similar to those obtained with hydrochloric acid and sodium hydroxide. In mixtures of salt with acid or alkali the presence of sodium chloride reduces the swelling. At higher concentrations of hydrochloric acid or sodium hydroxide this holds only for low concentrations of sodium chloride, for with more of the salt the gelatin dissolves completely. In the region of the minima of the acid–alkali swelling curve small quantities of sodium chloride increase the swelling and larger amounts have the reverse effect. In these systems and also in the presence of lithium, potassium, and calcium chlorides the position of the minimum is displaced in the direction of decreasing hydrogen-ion concentration with rising temperature. E. S. HEDGES.

Titania gel. Comparison with silica gel. S. KLOSKY (J. Physical Chem., 1930, **34**, 2621—2623; A., 1925, ii, 1057).—The preparation and properties of titania gel are discussed. Silica gel is easier to prepare, is more adsorptive, and is a better catalyst support. L. S. THEOBALD.

Morphology of chemical reactions in gels. III. V. M. SCHEMJAKIN (J. Russ. Phys. Chem. Soc., 1930, **62**, 1357—1376; cf. A., 1930, 33).—The phenomena of periodic precipitation in gels are classified. The spreading of a drop of silver nitrate solution over a gelatin surface is not a continuous process, but is made up of a series of spurts; to this phenomena is ascribed the formation of "artificial" Liesegang rings on the surface of an agar gel impregnated with potassium dichromate when drop after drop of silver nitrate solution is placed on the same spot. A number of other physical processes, such as the evaporation of water or milk, the melting of ice, and the flow of mercury, take place similarly in a series of steps. R. TRUSZKOWSKI.

Constitution of soluble proteins as reversible dissociable systems of components. II. S. P. L. SØRENSEN (Kolloid-Z., 1930, **53**, 170—199; cf. A., 1930, 1603).—The dissociation tendencies of egg-albumin, serum-albumin, serum-globulin, casein, and gliadin have been calculated from previously published data. The values are small, especially in the case of egg-albumin, and increase with dilution, particularly when the concentration falls below 1%. Previous work, supplemented in some cases by recent, unpublished data, is described on the solubility of egg-albumin and its dependence on the total protein concentration of the experimental mixture, the fractionation of egg-albumin, the preparation and fractionation of serum-albumin and serum-globulin, their solubility and dependence of solubility on the total amount of protein, the chemical composition of the fractions of serum-albumin, the solubility relations and reversible fractionation of casein and wheat-gliadin. Serum-albumin can be separated into three fractions according to solubility, and, although previous attempts to differentiate between the fractions chemically by acid degradation have failed, it is found that the fractions show differences in the amounts of nitrogen combined as humin, ammonia, cystine, and tryptophan. E. S. HEDGES.

Structure viscosity of caoutchouc solutions. B. DOGADKIN and D. PEWSNER (Kolloid-Z., 1930, **53**, 239—245).—Caoutchouc solutions show the deviations from the Hagen–Poiseuille law characteristic of colloids. The dependence of the relative viscosity on the rate of flow can be expressed by the de Waele–Ostwald formula and the structure viscosity exponent can be taken as a measure of the structural peculiarities of the particular kind of caoutchouc. With rise of temperature the viscosity of the caoutchouc solutions decreases, but the exponent of structure viscosity increases. The state of aggregation of the caoutchouc micelles is reduced by rolling the material and causes

a decrease in the value of the structure viscosity exponent. Ageing produces a similar effect.
E. S. HEDGES.

Effect of plant-lecithin on the swelling and surface tension of flour-glutin and starch. I. Binding materials in cooking. W. ZIEGELNAYER (Kolloid-Z., 1930, 53, 224—231).—The agglutinating effect of egg-yolk in cooking is due to the lecithin and can be increased by adding 1% of soya-lecithin to the flour. This corresponds with the addition of six eggs to 1 kg. of flour. The lecithin has the effect of limiting the amount of swelling through the formation of an adsorption complex. Cytolipoid lecithin produces a starch–glutin–fat adsorption complex, increasing the extensibility, elasticity, and softness of the dough. The syneresis observed in a flour–water mixture is absent when lecithin has been added.
E. S. HEDGES.

Table for kinetic gas theory. T. EDQUIST (Physikal. Z., 1930, 31, 1032).—Of the total number of N gas molecules, the number (dn) for which the kinetic energy possesses values between E and dE can be expressed according to Maxwell's distribution law. This equation has been integrated from 0 to $\sqrt{E/kT}$, and n is expressed as a function of N ($n=N\phi$). Numerical values of ϕ are tabulated for values of $\sqrt{E/kT}$ from 0·10 to 3·00. W. R. ANGUS.

Thermodynamic treatment of chemical equilibria in systems of real gases. III. Mass-action effects. Optimum hydrogen : nitrogen ratio for ammonia formation in the Haber equilibrium. L. J. GILLESPIE and J. A. BEATTIE (J. Amer. Chem. Soc., 1930, 52, 4239—4246; cf. A., 1930, 1357).—By means of the equations previously developed, optimal initial (r) and equilibrium (r_e) values of the ratio $H_2:N_2$ have been calculated for total pressures between 100 and 1000 atm. at 500°, with and without the presence of argon. Except at low total pressures the ratios are less than 3; r has a minimum value of 2·90 at 600 atm. and r_e falls to 2·68 at 1000 atm. The corresponding values are 2·91 and 2·72 when atmospheric nitrogen containing 0·012 mol. fraction of argon is used. When yields of ammonia at 500° are calculated for the $H_2:N_2$ ratios 2 and 4, deviations as great as 1·5% at 1000 atm. are found between values derived from the ordinary and the improved mass-action equations. Argon has a deleterious effect at all total pressures. J. G. A. GRIFFITHS.

Higher stages of dissociation of phosphoric and boric acids. F. L. HAHN and R. KLOCKMANN (Z. physikal. Chem., 1930, 151, 80—86; cf. A., 1930, 560).—The failure to detect a third point of inflexion in the potentiometric titration curve of phosphoric acid is shown by a simple calculation to be due to unfavourable conditions of concentration. By using a saturated solution of disodium hydrogen phosphate and concentrated alkali the third stage of neutralisation becomes apparent. By using the same formula an upper limit for the hitherto undetermined second and third dissociation constants of boric acid may be calculated, the concentrations and the accuracy of the potential measurements which fail to reveal the corresponding points of inflexion being known. The values obtained are: $K_2=1{\cdot}8\times10^{-13}(f_2/f_{OH})$, and $K_3=1{\cdot}6$ to $3\times10^{-14}(f_3/f_{OH})$, where f_2, f_3, f_{OH} are the activity coefficients of the respective acid anions and the hydroxyl ions. F. L. USHER.

Colorimetric investigations of indicators in presence of neutral salts. N. V. SIDGWICK, W. J. WORBOYS, and L. A. WOODWARD (Proc. Roy. Soc., 1930, A, 129, 579—588).—The change of colour exhibited by a definite concentration of an indicator in a solution of given p_H on the addition of a neutral salt is investigated by a colorimetric method. An optical wedge is employed in conjunction with a Lindemann electrometer and a rubidium photoelectric cell, the light absorption being measured by means of the wedge shift. The photo-electric effect enters into the method only as a null-point observation. The Tizard relation $K=[H](c_1-c)/(c-1)$ is used, where K is the apparent dissociation constant of the indicator acid, c the colour of a slightly alkaline solution of methyl-orange at a given concentration, and c_1 the relative colour, which is the ratio of the colour of any other solution to the unit colour. A correction is made for the part of the hydrogen ions combined with the indicator anions to form undissociated indicator acid. Determinations of K are made in the absence of neutral salts with varying concentrations of hydrochloric acid and a method is described for studying the possibilities (1) that the neutral salt may alter the absorption bands of the coloured forms of the indicator, and (2) that it may affect the chemical equilibrium between these forms. The first is studied independently of the second by dealing with solutions in which the indicator is completely in the yellow or the red forms. Measurements are also made of the dissociation constant of methyl-orange in the presence of varying concentrations of several salts (sodium chloride, bromide, chlorate, and nitrate, and potassium chloride and bromide), the concentration of the indicator being $N/40{,}000$. For sodium chloride K rises to a maximum between $N/20$ and $N/10$ and afterwards falls. A series of measurements was also carried out with a constant quantity of acetic acid–ammonia buffer, instead of hydrochloric acid, at an indicator concentration of $N/53{,}000$, and the results were of the same type for all salts; the value of $[H^{\cdot}_{free}]$ rises with increase of salt concentration, passing through a maximum at about $N/2$. The theoretical significance of these results is discussed. L. L. BIRCUMSHAW.

Ionisation constants of some chloro- and nitro-anilines by the partition method. G. WILLIAMS and F. G. SOPER (J.C.S., 1930, 2469—2474).—The ionisation constants of *o*-, *m*-, and *p*-chloroanilines and of *o*-nitroaniline have been determined and compared with the discordant values given in the literature. A partition method was used, in which attention was directed to the effect of unhydrolysed salt on the distribution equilibrium and to the choice of extracting solvent when dealing with certain very weak bases. The values obtained for the "concentration" basic dissociation constants of the four substances are $K_b\times10^{11}=0{\cdot}371$, 2·88, 8·45, and 0·00353, respectively, and for the "concentration" hydrolysis constants are $K_h\times10^4=27{\cdot}1$, 3·49, 1·19, and 2850, respectively. E. S. HEDGES.

Strength of weak bases and pseudo-bases in glacial acetic acid solutions. J. B. CONANT and T. H. WERNER (J. Amer. Chem. Soc., 1930, **52**, 4436—4450; cf. A., 1928, 129, 1188).—Spectrophotometric observations at wave-lengths between 470 and 680 μμ, on glacial acetic acid solutions of crystal-violet buffered with carbamide and sulphuric acid, carbamide and perchloric acid, and acetoxime and sulphuric acid at 25°, and electrometric determinations with these buffers show that the first dissociation constant of crystal-violet (Adams and Rosenstein, A., 1914, i, 1092) and the constants of carbamide and acetoxime increase greatly with increasing ionic strength, and in more concentrated solutions the salts have specific effects. In titrations it is therefore essential to keep the ionic strength constant by the presence of sufficient neutral salt.

Apparent dissociation constants of seven pseudo-bases in glacial acetic acid have been determined. The hydrogen-ion activity of solutions of the stronger pseudo-bases, half neutralised by sulphuric acid, decreases and then increases with increasing concentration of water. Very weak pseudo-bases exhibit the latter effect only. J. G. A. GRIFFITHS.

Electrolytes in mixed solvents. II. Effect of lithium chloride on the activities of water and alcohol in mixed solutions. R. SHAW and J. A. V. BUTLER (Proc. Roy. Soc., 1930, **A**, **129**, 519—536). —An air-bubbling method, in which the volume of air required is less than 2 litres, has been devised for the determination of the partial pressures of water and alcohol in mixed solutions (cf. Downes and Perman, A., 1927, 194). Measurements have been made at 25° of the partial vapour pressures of water–alcohol solutions containing 0—100% of alcohol and lithium chloride in 0·5, 1·0, and 4·0*M* concentrations. It is found that, whilst increasing concentration of lithium chloride causes a decrease in the partial pressure of water in all solutions, its effect on the alcohol varies with the composition of the solvent. In solutions containing a large proportion of alcohol, its partial pressure falls steadily as the salt concentration increases, and in solutions containing 6·4 mol.-% of alcohol it rises steadily, whilst in intermediate solutions it first falls and then rises. The fractional lowering of the vapour pressure of water is always greater than that of alcohol. An approximately linear relationship is established between the relative activities of both water and alcohol and the molar fraction of alcohol in the solvent, at constant lithium chloride concentration. It is possible to distinguish approximately the effects of the solvation of ions by alcohol molecules and the salting-out of alcohol by the interaction of the ions and water. L. L. BIRCUMSHAW.

Calculation of activity coefficients from solubility measurements. II. Thallous iodate. III. Unsymmetrical valency type effect. C. W. DAVIES (J.C.S., 1930, 2410—2421, 2421—2426; cf. A., 1930, 860).—II. From the solubility data for thallous iodate at 25° recorded by La Mer and Goldman (A., 1929, 1387) the activity coefficients have been recalculated, making allowance for the incomplete dissociation of the salts. When so corrected, certain abnormal features disappear; the activity coefficient becomes independent of the nature of the added salt at low concentrations, specific effects not appearing with uni-univalent salts until an ionic strength of 0·1 is reached. The activity coefficient of thallous iodate in the most dilute solutions is expressed by the equation −log where A=0·47. Since this A value is much greater than those derived from the most accurate data for other uni-univalent electrolytes, it is concluded that A may vary from salt to salt; it appears to be always lower than the Debye–Hückel value 0·50. The solubility data contribute no support, as stated by La Mer and Goldman, for the principle of specific interaction. In dilute solutions containing magnesium iodate allowance must be made for the $MgIO_3^{\cdot}$ ion, the dissociation constant of which is calculated to have the approximate value K=0·19. The dissociation constant of magnesium sulphate previously calculated from conductivity and f.-p. data is confirmed by the solubility data.

III. The large deviations from the Debye–Hückel theory of dilute solutions which have been described as "the electric type effect" or "the unsymmetric valency type effect" are considered to be due wholly to the incomplete dissociation of the salts concerned. Calculations based on solubility measurements with two luteocobaltic salts in potassium sulphate solutions support this view, and give closely concordant values for the dissociation constant of the luteocobaltic sulphate cation. The large deviations found with lanthanum iodate in sulphate solutions are interpreted in the same way and lead to a value for the dissociation constant of the lanthanum sulphate cation which agrees with that derived from the conductivity of lanthanum sulphate solutions. E. S. HEDGES.

Equilibrium between vapour and solution in the system acetic acid–acetic anhydride. S. I. TSCHERBOV (J. Russ. Phys. Chem. Soc., 1930, **62**, 1509—1521).—The percentage association of acetic acid is the same in acetic anhydride as in aqueous solution. Vapour-pressure measurements show that Gibbs' law of association is applicable also to the gaseous phase of the above system. R. TRUSZKOWSKI.

M.-p. curve of sodium chloride dihydrate. Incongruent melting at pressures up to twelve thousand atmospheres. L. H. ADAMS and R. E. GIBSON (J. Amer. Chem. Soc., 1930, **52**, 4252—4264). —The m. p. of $NaCl,2H_2O$ has been determined directly and from measurements of the volume changes at pressures between 1 and 12,000 bars. At the ordinary pressure, the m.-p. curve commences at 0·1° with an initial slope of 7·05° per kilobar. Th slope decreases with increasing pressure and finally becomes negative. The maximum of the curve is at 25·8° and 9500 bars. The volume is increased 0·037 c.c. by the melting of 1 g. of $NaCl,2H_2O$ at 0·1°, and hence by means of the Clapeyron–Clausius equation the latent heat of fusion, L_f, is 34·4 g.-cal. per g. L. has the value 30 when computed from solubility data. d^{01} is 1·630 at 1 bar, and the mean compressibility of the dihydrate between 6000 and 12,000 bars at about 22° is $4{\cdot}8\times10^{-6}$ per bar. When the dihydrate is under conditions close to those corre-

sponding with the maximum of the m. p.-pressure curve, a sudden increase of the applied pressure is followed by a further gradual increase. An interpretation of this abnormal behaviour is offered.

J. G. A. GRIFFITHS.

System cobalt–chromium. F. WEVER and U. HASCHIMOTO (Mitt. Kaiser-Wilh. Inst. Eisenforsch., 1929, **11**, 293—330; Chem. Zentr., 1930, i, 3482).—The equilibrium diagram has been reconstructed; on account of the small velocity of diffusion of the components complete equilibrium is attained only with difficulty. Chromium has m. p. 1705±10°. Cobalt and chromium are miscible in the fused state in all proportions. The eutectic is at 1408° and 42% Cr. Up to 38% Cr the mixed crystals are face-centred cubic, whilst above 48% Cr they are body-centred. The compounds Co_2Cr_3 and CoCr (tetragonal, with 8 mols. in the unit cell) probably exist. The temperature of polymorphic α–β transformation is maximal for 7·5% Cr, falling with a higher chromium content. The temperature of magnetic transformation falls almost proportionally to the chromium content. The hardness, tensile strength, elastic limit, elongation, and constriction up to 1000° have been determined for alloys containing up to 40% Cr. The resistance to corrosion by acid is considerable, being greatest for nitric and least for hydrochloric acid. The f.-p. curves for cobalt–chromium alloys containing up to 6·5% C or 95% Fe have been determined, and the effects of addition of silicon, manganese, aluminium, copper, nickel, molybdenum, and tungsten are recorded.

A. A. ELDRIDGE.

Phase equilibria in the system Cr_2O_3–SiO_2. E. N. BUNTING (Bur. Stand. J. Res., 1930, **5**, 325—327).—*X*-Ray study of fused mixtures of chromic oxide and silica indicates that no compounds are formed and that the two substances are practically immiscible in both the liquid and solid state. The m. p. of chromic oxide, determined with the optical pyrometer, is 2140°±25°.

H. F. GILLBE.

Equilibrium in the Fe–H_2–O_2 system. Indirect calculation of the water-gas equilibrium constant. P. H. EMMETT and J. F. SHULTZ (J. Amer. Chem. Soc., 1930, **52**, 4268—4285).—By means of a flow method and with synthetic ammonia catalysts as source of iron, the equilibrium constant, $K=P_{H_2O}/P_{H_2}$, of the reaction $FeO+H_2=Fe+H_2O$ at 600°, 700°, 800°, 900°, and 1000° is found to be 0·332, 0·422, 0·499, 0·594, and 0·669, ±0·012, respectively. Similarly, for the reaction $Fe_3O_4+H_2=3FeO+H_2O$, K is approximately 1·18 and 2·37 at 700° and 800°, respectively. These values of K are smaller than those obtained from many static investigations (*e.g.*, Eastman and Evans, A., 1924, ii, 413). The discrepancy is attributed to a "surface effect" in the latter experiments in which the superficial layers of iron oxide consume an abnormal quantity of hydrogen, thus leading to a "false" equilibrium (cf. Emmett and Brunauer, A., 1930, 1131). The "surface effect" is manifest in dynamic experiments by the abnormal ratios between the gaseous products obtained initially (*e.g.*, A., 1930, 861; Pease and Cook, A., 1926, 684).

Values of the water-gas equilibrium constant in good agreement with those of Neumann and Kohler (A., 1928, 707) are computed from the above data in conjunction with the best determinations for the reaction $FeO+CO=Fe+CO_2$.

J. G. A. GRIFFITHS.

Carburising and graphitising reactions between iron–carbon alloys, carbon monoxide, and carbon dioxide. M. L. BECKER (J. Iron and Steel Inst., 1930, **121**, 337—365).—The equilibria between steels of varying carbon content, carbon monoxide, and carbon dioxide have been investigated by maintaining a known carbon dioxide partial pressure by adjustment of the temperature of a dissociating carbonate. The composition of the gas phase in equilibrium with graphite is poorer in carbon monoxide than that in equilibrium with iron carbide and saturated solid solution at the same temperature, and thus the carbon vapour pressure of iron carbide must be greater than that of pure carbon between 650° and 1000°; graphite is therefore stable with respect to iron carbide over this temperature range, in contradiction to the views of Matsubara, and of Johansson and von Seth. Silicon up to 3% does not alter the carbide equilibrium; manganese up to 15·5% does not apparently influence the cementite equilibrium, but it may be the slowness of the reaction which prevents graphitisation. Although the gaseous equilibrium is not altered by nickel, chromium markedly diminishes the carbon vapour pressure of the solid solution. At normal pressures the gas in equilibrium with silicon irons and chromium steels may contain sufficient carbon dioxide to cause the formation of a superficial layer of oxide which protects the metal from further oxidation; such a coating on carbon steels tends to react with the metal at temperatures above 700°, and hence has little protective value.

H. F. GILLBE.

Double decomposition in the absence of a solvent. XII. N. M. WAKSBERG (J. Russ. Phys. Chem. Soc., 1930, **62**, 1259—1283).—The phase diagram for the system $NaI+KCl \longrightarrow KI+NaCl$ has been constructed. The triple eutectic at 504° corresponds with 37% NaCl, 46·5% KI, and 16·5% KCl.

R. TRUSZKOWSKI.

System Na_2SO_4–NaF–NaCl–H_2O. I. Ternary systems with water and two salts. II. Quaternary system at 25° and 35°. H. W. FOOTE and J. F. SCHAIRER (J. Amer. Chem. Soc., 1930, **52**, 4202—4209, 4210—4217).—I. Solubility isotherms in the system Na_2SO_4–NaF–H_2O have been determined at 35°, 25°, 15°, and 10°. Eutectic and transition points are recorded. Crystallographic data are given for the double salt Na_2SO_4,NaF, which yields NaF and $Na_2SO_4,10H_2O$ below the transition point, 17·5°. Solubility data at 25° and 35°, and significant points for the systems NaCl–NaF–H_2O and Na_2SO_4–NaCl–H_2O are recorded.

II. Solubility data for the quaternary system at 25° and 35° are represented graphically. The double salt, Na_2SO_4,NaF, forms solid solutions in which a small proportion of the fluoride is replaced by chloride. The mineral sulphohalite, $2Na_2SO_4$,NaF,NaCl, was not obtained in these experiments.

J. G. A. GRIFFITHS.

System $NaNO_3$–Na_2SO_4–$MgCl_2$–H_2O in the temperature range 0—100°. II, III, IV. G. LEIMBACH (Caliche, 1929—1930, **11**, 340—352, 386

394, 428—436; cf. A., 1929, 1013).—Details are given of the system at 50°, 75°, and 100°.
H. F. GILLBE.

Phase-rule studies on the proteins. V. Quinquevalent nitrogen in organic compounds. VI. W. D. BANCROFT and C. E. BARNETT (J. Physical Chem., 1930, **34**, 2433—2471; cf. A., 1930, 1604).—The addition of hydrogen chloride by compounds containing four or more atoms of nitrogen in the molecule is discussed. L. S. THEOBALD.

Heat of formation of cuprous and cupric chlorides. H. VON WARTENBERG and H. WERTH (Z. physikal. Chem., 1930, **151**, 109—112).—Direct synthesis of the chlorides in aqueous solution in a calorimeter yields $32{\cdot}1\pm0{\cdot}4$ and $50{\cdot}8\pm0{\cdot}4$ kg.-cal. for the cuprous and cupric salts, respectively. These values differ but slightly from those of Berthelot, and the value for cuprous chloride agrees with that deduced by Noyes from potential measurements.
F. L. USHER.

Heat of formation of fluorine oxide. H. VON WARTENBERG and G. KLINKOTT (Z. anorg. Chem., 1930, **193**, 409—419).—The substance KF,3HF is a definite molecular compound and has a vapour pressure of 28 mm. at 100° and of 130 mm. at 150°. Details are given of the preparation of fluorine from this salt by Lebeau's electrolytic method and of the production of fluorine oxide by passage of fluorine through dilute sodium hydroxide solution (A., 1929, 779). The oxide reacts quantitatively with potassium and sodium hydroxides according to the equation $F_2O+2MOH\longrightarrow2MF+H_2O+O_2$, and with ammonia solution with liberation of nitrogen which is, however, oxidised to nitric acid. Hydrochloric, hydrobromic, and hydriodic acids are oxidised with liberation of the halogen. Benzene and "benzine" absorb the oxide quantitatively. The heat of formation of fluorine oxide, calculated from the heat effects of the reactions with potassium hydroxide and hydrobromic and hydriodic acids, is −8 to −15 kg.-cal. per mol., the most probable value being -11 ± 2 kg.-cal. The following thermal data have been redetermined: $2(I)+2KI\,aq=2KI_3\,aq-0{\cdot}73$ kg.-cal.; $(Br)+HBr\,aq=Br\,aq+HBr\,aq+1{\cdot}5$ kg.-cal. Fluorine oxide absorbs light of wavelength below 2150 Å., but is not decomposed even after prolonged irradiation. H. F. GILLBE.

Heats of dilution of potassium chloride in sucrose and carbamide solutions as solvents below 0·1*M* at 25°. E. LANGE and A. L. ROBINSON (J. Amer. Chem. Soc., 1930, **52**, 4218—4224; cf. Lange and Robinson, A., 1930, 997).—The integral and differential heats of dilution of potassium chloride at concentrations between 0·0001 and 0·1*M* in 15 wt.-% aqueous sucrose and 5% aqueous carbamide have been determined at 25°. At concentrations, *c*, below 0·008*M*, the integral heat of dilution, V_c, is related to *c* by the equation $V_c=A\sqrt{c}$, the constant *A* having the values 386 and 332 for the sugar and carbamide solutions, respectively. The $V_c-\sqrt{c}$ curves are of the same form as those obtained with 1:1 type salts in pure water, but the observed deviations are outside experimental error and are possibly due to the different dielectric properties of the solvents rather than to concentration or association effects.
J. G. A. GRIFFITHS.

Heat of combustion of salicylic acid. P. E. VERKADE and Y. COOPS, jun. (J. Physical Chem., 1930, **34**, 2549—2553).—A reply to Keffler (A., 1929, 267), whose suggested value for the heat of combustion of salicylic acid is not accepted. L. S. THEOBALD.

Heat of hydrogenation of ethylene. H. VON WARTENBERG and G. KRAUSE (Z. physikal. Chem., 1930, **151**, 105—108).—Calorimetric measurements lead to the value $30{\cdot}0+0{\cdot}3$ kg.-cal. for the reaction $C_2H_4+H_2=C_2H_6$ at constant volume. Hydrogenation was effected with palladium sol by Skita's method. F. L. USHER.

Heats of association of acetic and heptoic acids in the vapour state. H. DOHSE and M. DUNKEL (J.C.S., 1930, 2409—2410).—The comparison of the heat of dissociation of the double molecule of acetic acid, calculated by Fenton and Garner (A., 1930, 677) from the influence of temperature on the equilibrium, with the heat of vaporisation determined calorimetrically is not permissible. The heat of dissociation should be halved and brought into relation with the heat of vaporisation as determined from the variation of vapour pressure with temperature. The heat of dissociation of acetic acid is then found to be 6900 g.-cal. per mol. The measurements of Beckmann (cf. A., 1891, 389) for the heat of dissociation of benzoic acid in benzene can be treated similarly and lead to the value 5600 g.-cal. per mol. There is no reason for supposing that such associations are concerned with "chemical" combination.
E. S. HEDGES.

Heat of hydration and energy content of *cis*- and *trans*-*cyclo*hexane-1 : 2-dicarboxylic acids and of the primary ions. A. WASSERMANN (Z. physikal. Chem., 1930, **151**, 113—128; cf. A., 1930, 524).—The heats of dissolution and of the first and second stages of ionisation of the *cis*- and *trans*-acids have been determined, and from these and other existing data the energy content of the primary anions has been calculated. The *trans*-ion is the more heavily hydrated, and the behaviour of the ions of the *cyclo*hexane-1 : 2-dicarboxylic acids therefore agrees with that of the ions of fumaric and maleic acids. Thermochemical data afford no more support to a "*meso-trans*" configuration than do the dissociation constants or the adsorption behaviour. There is no measurable difference in the hydration of the undissociated molecules. F. L. USHER.

Thermal data for organic compounds. IX. Effect of unsaturation on the heat capacities, entropies, and free energies of hydrocarbons and other compounds. G. S. PARKS and H. M. HUFFMAN (J. Amer. Chem. Soc., 1930, **52**, 4381—4391).—The following heats of fusion (g.-cal./g.) are recorded: β-methyl-Δ^{β}-butene, 25·74; *n*-pentane, 27·75; di*iso*butylene (probably βδδ-trimethyl-Δ^{β}-pentene), 16·83; *cyclo*hexene, 9·57; methyl*cyclo*hexane, 16·24. *cyclo*Hexene exhibits a solid transition at 138·7° Abs.; the heat of transition is 11·86 g.-cal./g. The specific heats of the above hydrocarbons, Δ^{β}-pentene, fumaric, maleic, and succinic acids,

stilbene, dibenzoylethane, and dibenzoylethylene have been measured over a wide range of temperature by the method previously used (A., 1925, ii, 491). The molar entropies at 25°, calculated from the heat capacity data, show that for a given unsaturated compound the value is appreciably less than that for the corresponding saturated substance. The entropies of liquid olefines agree fairly well with the values calculated from the equation $S_{298}=25\cdot0+7\cdot7n-4\cdot5r-2\cdot7e+19\cdot5p$ (cf. A., 1930, 677), where e is the number of double linkings in the acylic portions of the compounds. The free energy change (ΔF_{298}) for the conversion of maleic into fumaric acid is —6600 g.-cal. The free energy change for the formation of olefinic compounds from the corresponding saturated derivatives varies considerably. H. BURTON.

Method of measuring the resistance of electrolytes at low frequencies. J. A. C. TEEGAN (Indian J. Physics, 1930, 5, 463—471).—A new method of measuring metallic and electrolytic resistances at audio frequencies is described, using a Hartley oscillator circuit. The results obtained by this method with copper sulphate and sodium chloride solutions are the same as those measured by Dowling's method at frequencies of 10^6 cycles. When copper electrodes are substituted for the gold electrodes, however, apparent changes of the resistance with frequency are observed, but these are probably due to polarisation or chemical effects. J. W. SMITH.

Conductivity and density of chromic acid solutions. H. R. MOORE and W. BLUM (Bur. Stand. J. Res., 1930, 5, 255—264).—The density of chromium trioxide solutions from $2M$ to $10M$ is an approximately linear function of the concentration; at 25° $d=1\cdot00644+0\cdot06606c$, where c is the molar concentration. The conductivity of the solution is a maximum at 4—$5M$, and increases with rise of temperature at the rate of 1—1·5% per degree. H. F. GILLBE.

Electrical conductivity of potassium perrhenate solutions. N. A. PUSHIN and P. S. TUTUNDZIC (Z. anorg. Chem., 1930, 193, 420—424).—The conductivities of 0·0005—0·04M-potassium perrhenate solutions have been measured at 18°, 25°, 30°, and 40°; the values of   at these temperatures are 111·5, 125·7, 141·8, and 169, respectively, and the mobility of the ReO_4' ion is at 18° 46·9 and at 25° 57·3. The temperature coefficient of the conductivity between 18° and 40° is 0·0247—0·0248, and the degree of ionisation in 0·01M solution rises from 0·905 at 18° to 0·92 at 40°. H. F. GILLBE.

Conductivity of some uni-univalent salts in ethyl alcohol. E. D. COPLEY, D. M. MURRAY-RUST, and (SIR) H. HARTLEY (J.C.S., 1930, 2492—2498).—A method of preparing pure ethyl alcohol for conductivity work is described. The electrical conductivity of solutions of nine uni-univalent salts in ethyl alcohol has been measured at 25° over the concentration range 0·0001—0·002N. In each case the curve relating equivalent conductivity to the square root of the concentration consists of a straight line, and an indication of the relative amounts of ionic association is given by comparing the slopes of these lines with the theoretical slopes calculated from the Debye-Hückel-Onsager equation. In spite of its large size, the perchlorate ion has a greater mobility in ethyl alcohol than chloride, bromide, iodide, or nitrate ions. E. S. HEDGES.

Mobility of the perchlorate ion in methyl alcohol. E. D. COPLEY and (SIR) H. HARTLEY (J.C.S., 1930, 2488—2491).—The electrical conductivities of solutions of the perchlorates of lithium, sodium, and silver have been measured in methyl alcohol at 25° at concentrations varying from 0·0001N to 0·002N. The variation of conductivity with concentration is in each case in close agreement with the Debye-Hückel-Onsager theory. The mobility of the perchlorate ion is found to be 70·85, and that of the silver ion 50·3. Attention is directed to the surprisingly high mobility of the perchlorate ion, which may be due to slight solvation in consequence of the weaker electrical field in its neighbourhood, due to its large size. E. S. HEDGES.

Conductivity of very dilute solutions in antimony trichloride. Z. KLEMENSIEWICZ and Z. BALÓWNA (Rocz. Chem., 1930, 10, 481—491).—The conductivity curves for 10^{-2} to $5\times10^{-5}N$ solutions of potassium, rubidium, ammonium, thallous, and mercuric chlorides, and of ammonium, potassium, thallous, and mercuric bromides in fused antimony trichloride are of the same type as those found by Klemensiewicz (A., 1925, ii, 40) for more concentrated solutions; the results obtained are in complete conformity with Ghosh's theory (A., 1922, ii, 125) for solutions containing uni- but not multi-valent ions.
R. TRUSZKOWSKI.

Theory and technique of the thermionic valve potentiometer for the measurement of *E.M.F.* I. F. MÜLLER (Z. Elektrochem., 1930, 36, 923—934).—The general theory of the thermionic valve is given in relation to its application to the measurement of *E.M.F.* The valve potentiometer may be employed especially in those cases where difficulties are met with in the ordinary compensation method, *e.g.*, when no current must be taken from the cell studied, or if this has a very high internal resistance. Either a deflexion or a null-point method may be used. According to the first, the curve connecting grid potential and anode current must be known; the unknown potential is inserted in the grid circuit, and the new anode current determined. In the null-point method the anode current is maintained at a fixed value and the deflexion produced by the unknown potential is compensated for by a potentiometer also in the grid circuit, so that the same point of the characteristic curve is adhered to throughout. A detailed description is given of such an instrument which is capable of measuring potentials of 10^{-3} to 10^{2} volts with an accuracy of 0·5 millivolt.
J. R. I. HEPBURN.

Glass electrode studies. I. Oxy-acids of phosphorus. C. MORTON (Quart. J. Pharm., 1930, 3, 438—449).—The neutralisation curves of hypophosphorous and phosphorous acids have been determined by means of the glass electrode (Haber and Klemensiewicz, A., 1909, ii, 785) and those of glycerylphosphoric, phenylphosphoric, pyrophosphoric, and orthophosphoric acids by means of the hydrogen

electrode. The curves of phosphorous, glycerylphosphoric, and phenylphosphoric acids are similar in form to the well-known phosphoric acid curve; in each case there are inflexions at p_H 3·4—4·5 and at p_H 8·4—9·2, corresponding with mono- and di-sodium salts, respectively. The curve of hypophosphorous acid is that of a strong monobasic acid, whilst in that of pyrophosphoric acid inflexions corresponding with $Na_3HP_2O_7$ and $Na_2H_2P_2O_7$ are discernible.

The apparent dissociation constants of the six acids have been calculated by the method of the author (Trans. Faraday Soc., 1928, **24**, 1). The effect of the addition of neutral salts on the p_H changes of phenylphosphoric acid enables a mean value of 6·11 to be calculated for the thermodynamic second dissociation constant, pk_2 (cf. A., 1928, 840), of this acid.

From the results of the electrometric titrations, it is shown that phosphorous and phosphoric acids, if present, will be included in the result obtained by the B.P.C. method for the volumetric determination of hypophosphorous acid. Correct results may be obtained by titration with dimethylaminoazobenzene, and then with cresolphthalein; the extra alkali required to reach the cresolphthalein end-point represents phosphorous (and phosphoric) acid and is deducted from the titre to the first end-point.

R. Child.

Measurement of the Peltier effect at tungsten–molybdenum [junctions]. E. Blumenthal (Ann. Physik, 1930, [v], 7, 470—488).—The Peltier effect at a tungsten–molybdenum junction has been measured at the ordinary temperature by a differential calorimetric method and at temperatures up to 2000° by optical measurement of the temperature change at the junction when the current, which serves both to heat the junction and to produce the effect, is reversed in direction. At the ordinary temperature the Peltier coefficient π is $4·69\times10^{-3}$ g.-cal., in fair agreement with that calculated from thermoelectric data. At 1290° Abs. π is $29·3\times10^{-3}$ g.-cal., and rises to about 59×10^{-3} g.-cal. at 1600° Abs.; thereafter the coefficient diminishes slowly, in accordance with earlier thermoelectric data. For molybdenum–tantalum junctions the coefficient at 1100° is about four times as great as for tungsten–molybdenum, but exact measurements are difficult owing to the considerable difference of resistance of the two metals.

H. F. Gillbe.

Gaseous combustion in electric discharges. VI. Effect of diluents on the cathodic combustion of carbon monoxide "detonating gas." VII. Effect of dilution with hydrogen on the cathodic combustion of carbon monoxide–oxygen mixtures. G. I. Finch and W. L. Patrick (Proc. Roy. Soc., 1930, **A**, **129**, 656—671, 672—685; cf. Finch and Hodge, A., 1929, 890, 1401).—VI. An electric discharge can be passed through a dry or moist carbon monoxide–oxygen mixture diluted with nitrogen, helium, argon, carbon monoxide, or oxygen so that the rate of combustion of carbon monoxide is determined solely by and is directly proportional to the current passed by the discharge. At a non-sputtering cathode (tantalum) the rate is only slightly affected by dilution of the dry "detonating gas" with either of its constituents, between the limits of 88% CO_2 and 83% O_2, a slight decrease being shown with increasing oxygen concentration. The rate at a freely sputtering cathode (gold) is inversely proportional to the amount of dilution with nitrogen, helium, or argon, and increases on dilution with oxygen up to 70—80% O_2. For moist "detonating gas" the rate at a non-sputtering cathode increases on dilution with carbon monoxide (up to 80%), but decreases with increasing pressure, whilst at a freely-sputtering cathode the rate is independent of pressure, but increases on dilution with either carbon monoxide (negative pressure effect) or oxygen (positive pressure effect). Both hydrogen and hydrogen peroxide have been detected in the cathodic combustion of moist "detonating gas," the amount of the former being greater at a sputtering cathode, and of the latter at a non-sputtering cathode. It is concluded that auto-oxidation of carbon monoxide occurs, the carbon formed being burnt directly by oxygen. The fundamental mechanism of the direct oxidation of carbon monoxide by oxygen consists in the union of carbon monoxide molecules with oxygen atoms in either pure or (chiefly) indirect triple collisions. Sputtered metal atoms also interact with oxygen molecules to form loose complexes, which readily oxidise carbon monoxide.

VII. Mixtures of carbon monoxide with oxygen and hydrogen containing just sufficient oxygen for complete combustion burn cathodically at either tantalum or gold, so that the relative proportion of carbon dioxide to steam in the combustion products is greater than the corresponding proportion of carbon monoxide to hydrogen in the original mixture. This preferential combustion of carbon monoxide becomes more marked with decreasing pressure and at a freely sputtering cathode. The rate of combustion of dry detonating gas at a non-sputtering cathode is less than one sixth of that of dry electrolytic gas. When electrolytic gas, or a $(CO+O_2+H_2)$ mixture, or moist detonating gas is burnt cathodically, at least three times as much hydrogen peroxide can be recovered from the products leaving a non-sputtering cathode as when a freely-sputtering cathode is used. From these and a number of further experimentally established facts it is concluded that in the cathodic combustion of carbon monoxide–oxygen–hydrogen mixtures hydrogen first burns to active steam and hydrogen peroxide, both of which then oxidise carbon monoxide more readily than does oxygen; active steam is thereby reduced to an active form of hydrogen and hydrogen peroxide to inactive steam. Increasing pressure and/or oxygen concentration favours the combustion of hydrogen to hydrogen peroxide, whilst decreasing pressure and/or decreasing oxygen concentration and/or increasing hydrogen concentration favours its combustion to active steam.

L. L. Bircumshaw.

Ignition of carbon monoxide–oxygen mixtures: effect of impurities. A. K. Brewer and W. E. Deming (J. Amer. Chem. Soc., 1930, **52**, 4225—4233).—In an extension of previous work (Brewer, A., 1927, 1147) it is found that for mixtures of oxygen with ethyl alcohol, ether, or carbon disulphide vapours the product of the ignition voltage, V, and

the total pressure, P, is a constant which is different for each mixture. Hence the voltage, V, or the quantity of electricity, Q ($Q \propto V$ in this investigation), required to ignite an explosive mixture is inversely proportional to the number of molecules in the path of the spark. In all cases, the relation between V and $1/P$ leads to $V=15$—20 volts when $1/P=0$. This indicates that ionisation is necessary for ignition.

Impurities may increase (negative catalysis) or decrease (positive catalysis) V for carbon monoxide–oxygen mixtures. The relative inhibiting effects are almost directly proportional to the number of atoms composing each molecule of impurity. Ether and ethyl alcohol, and to a smaller extent hydrogen, may be positive or negative catalysts, according as to whether or not sufficient additional oxygen is added for their complete combustion. The positive catalysis is attributed to the formation of water (Bone and Weston, A., 1926, 480) which precedes the general ignition of the mixture. The efficiency of a positive catalyst is, over a wide range, proportional to the number of catalyst molecules in the path of the discharge. J. G. A. Griffiths.

Slow combustion of ethane. W. A. Bone and S. G. Hill (Proc. Roy. Soc., 1930, A, **129**, 434—457).—The "hydroxylation" and "peroxidation" theories of hydrocarbon combustion are discussed. Experiments have been carried out to determine if a peroxide is formed during the slow combustion of ethane, and if so, at what stage in the process. The investigation covered a temperature range of 290—323° and initial pressures between 440 and 780 mm. The results indicate that the oxidation proceeds homogeneously throughout the medium, being greatly retarded by increasing the surface exposed to the gases, that it is preceded by a well-marked induction period, during which no oxidation occurs, and that it is accompanied by a steady pressure rise and the production chiefly of aldehydes, steam, and oxides of carbon, but of neither hydrogen nor free carbon. The induction period can be considerably reduced by the addition of small amounts (say 1%) of moisture, iodine, nitrogen peroxide, ethyl alcohol, formaldehyde, etc. to a dry $C_2H_6+O_2$ medium without altering the non-explosive nature of the combustion. The addition of 1% of acetaldehyde, however, causes an instantaneous inflammation of the medium. A rise of temperature or an increase of pressure shortens the induction period. A rise of temperature also shortens the reaction period," and an increase in pressure tends to shorten it. Both the induction and the reaction periods are much shorter for a $(2C_2H_6+O_2)$ than for a $(C_2H_6+O_2)$ mixture, and are rapidly lengthened by an increase in oxygen content beyond an equimolecular proportion. This is consistent with the hydroxylation," but not with the "peroxidation," theory. Although inconsiderable amounts of a "peroxide" appear to be formed at the acetaldehyde stage of the combustion, no evidence was obtained of any earlier peroxide formation. Indirect experimental evidence supports the view that ethyl alcohol or some lower "oxyethane," rather than $C_2H_6O_2$, is primarily formed in the slow combustion of ethane.

L. L. Bircumshaw.

Combustion of carbon disulphide in oxygen. H. W. Thompson (Z. physikal. Chem., 1930, B, **10**, 273—295).—The curve showing the relationship between the ignition temperature and pressure for mixtures of carbon disulphide vapour and oxygen in the volume ratio 1 : 3 resembles closely that for hydrogen–oxygen mixtures; the temperature minimum is 140° at 100 mm., and at higher temperatures the pressure interval becomes increasingly greater. The transition from the slow reaction which takes place at low temperatures or outside the critical pressure range to explosive combustion is abrupt at both pressure limits. As with hydrogen–oxygen mixtures, the explosion is initiated at the walls of the vessel; if streams of the two gases impinge in a free space combustion does not take place at temperatures below 250—290°, but on contact with a glass rod combustion occurs at much lower temperatures.

H. F. Gillbe.

Velocity of polymerisation. I. Polymerisation of diethylenic hydrocarbons. II. Polymerisation of isoprene. E. N. Gapon (J. Russ. Phys. Chem. Soc., 1930, **62**, 1385—1393, 1395—1406).—I. A theoretical consideration of the polymerisation of diethylenic compounds leads to the assumption that the activation of substrate molecules depends on the opening of a double linking with the formation of tervalent carbon; the energy necessary for this process represents the energy of activation. The polymeride is formed by combination of active with inactive molecules.

II. The ratios of the values of the velocity coefficients of the reaction of polymerisation of isoprene to dipentene, to 1 : 3-dimethyl-3-ethenyl-Δ^6-*cyclo*hexene, and to the polymeride are 530 : 41 : 1. Three types of activated molecules may be formed in the polymerisation of isoprene, explaining the variety of products. The temperature coefficients of the above reactions of polymerisation diminish in the order given, as do also the heats of activation and the activity constants of the active molecules.

R. Truszkowski.

Influence of neutral salts on reaction velocity in alcoholic solution. A. Kailan and A. Irresberger (Monatsh., 1930, **56**, 428—446).—The effect of lithium, calcium, and mercuric chlorides on the velocity of esterification of benzoic acid with alcoholic hydrogen chloride has been studied. With alcohol containing 0·05 mol. of water per litre, addition of the salts causes a retardation; the differences in the individual salts are small. When the alcohol contains 1 mol. of water per litre, addition of the salts causes an increase in the coefficient (except with mercuric chloride in concentrations below 0·668N); calcium chloride has the greatest accelerating action, probably owing to its greater capacity for hydrate formation.

H. Burton.

Velocity of intramolecular transformation of β-naphthylacetylchloroamine. A. P. J. Hoogeveen (Rec. trav. chim., 1930, **49**, 1093—1106).—β-Acetnaphthalide is converted by the action of bleaching-powder solution and a small amount of acetic acid on its solution in 96% alcohol at 0° into N-*chloroacet*-β-*naphthylamide*, m. p. 80°. Similar chlorination in glacial acetic acid at 20° yields 1-chloro-

2-acetnaphthalide (cf. Franzen and Stäuble, A., 1922, i, 450), complete isomerisation of the chloroamine taking place under these conditions. The velocity of conversion of the chloroamine into 1-chloro-2-acetnaphthalide was determined by a method similar to that employed in the case of the corresponding α-compound (A., 1930, 866). In aqueous alcohol containing 100 c.c. of *N*-hydrochloric acid per litre, the mean value of the unimolecular coefficient $k\times10^4$ at 25° in 5, 10, 20, 30, 40, 50, 60, and 70% alcohol is, respectively, 46, 40, 39, 45, 70, 124, 233, and 500, the corresponding value when the concentration of hydrochloric acid is doubled being —, 94, 102, 146, 245, 423, 808, and 1670, respectively. The values of $k\times10^4$ in the corresponding series, water–acetic acid containing 100 c.c. of *N*-hydrochloric acid (no value for 5% acetic acid), are, 39, 38, 56, 92, 185, 489, and 1832, respectively. The occurrence of a minimum reaction velocity observed in the case of the α-compound with 50% of the organic solvent (*loc. cit.*) is thus also observed, but to a much smaller extent, with the β-compound, minimum values being obtained in 20% alcohol or acetic acid. In the alcohol series, doubling the concentration of the acid increases the reaction velocity 3·5 times except in 10 and 20% mixtures, when the velocity is only doubled. Comparison of these results with those obtained for the velocity of conversion of *N*-chloroacetanilide and *N*-chloroacet-β-naphthylamide shows that the velocity with the β-compound is approximately 50% greater than that observed in the other two cases. Similar migrations from the β- to the α-position in β-naphthylamine derivatives are discussed. J. W. Baker.

Phenomena of corrosion. XVII. A. Thiel (Z. physikal. Chem., 1930, **151**, 103—104; cf. A., 1928, 376).—The explanation of the "difference effect" by Straumanis (A., 1930, 1125) is considered unsatisfactory. F. L. Usher.

Quartz. R. Weil (Compt. rend., 1930, **191**, 935—937).—Contrary to the results obtained with *L*-quartz (A., 1930, 1240) the action of hydrofluoric acid on a slip of *S*-quartz normal to the ternary axis produces numerous "hairs" over the entire surface which, at the limits of the regions of birefringence, appear as stellar tufts or fissures in the planes normal to the prism faces. Similar hairs are formed at 150° by the action of sulphuric acid on calcium fluoride, but at 300° they are shorter. A detailed study has been made, enabling the corrosion figures to be distinguished from those of *L*-quartz. Corrosion parallel or perpendicular to the ternary axis is obtained by the production of a cylindrical hole by the action of acid on a portion of the crystal surrounded by paraffin wax, the acid being renewed at intervals over several weeks. *L*-Quartz then shows true negative crystals with the rounded (10$\bar{1}$0) prism below two rounded rhombohedra (10$\bar{1}$1 and 01$\bar{1}$1), 2—3 mm. long. The *S*-quartz, however, shows complete disaggregation resulting from accentuation of the corrosion phenomena observed for a section normal to A^3. J. Grant.

Passivity of metals. W. J. Müller (Korrosion u. Metallschutz, 1929, **5**, 8—15; Chem. Zentr., 1930, i, 3483).—A discussion. A. A. Eldridge.

Effect of amount of catalyst on combination of hydrogen and oxygen. C. Kroger (Z. anorg. Chem., 1930, **194**, 73—88).—The rate of formation of water when a mixture of hydrogen and oxygen in the stoicheiometric ratio is passed over various catalysts at a fixed rate has been studied with the object of finding the connexion between the percentage reaction, *Y*, and the weight of catalyst, *m*. With silver as catalyst the experimental data can be represented satisfactorily by the equation $\log\{100/(100-Y)\}=km$, where *k* is a constant for a fixed temperature. This equation can also be deduced theoretically on the assumption that the hydrogen reacts only with adsorbed oxygen free from adsorbed water (cf. Benton and Elgin, A., 1929, 274). For a given weight of catalyst the Arrhenius equation is valid for the effect of temperature on the velocity coefficient, but the heat of activation, *Q*, increases as *m* decreases. When antimony is the catalyst, on the other hand, *Q* does not vary with *m*, which is taken as indicating that here the mechanism of catalysis is chemical, probably consisting in alternate oxidation and reduction of the metal. The effect of variations in *m* when nickel or copper is the catalyst is qualitatively similar to that observed with silver, but is ascribed to the equilibrium ratio of oxide to metal in the catalyst being dependent on the amount of catalyst initially taken (cf. Smith, A., 1928, 719). In the case of nickel, however, it seems that the reaction is not entirely heterogeneous; a homogeneous reaction is probably brought about by reaction chains propagated from the catalyst. Reaction over a nickel oxide catalyst seems to depend on the rate of reduction and oxidation of a higher oxide, and with increase in *m* the amount of this oxide, and therefore *Y*, increases. At the same time, however, the water vapour exerts a retarding influence, and the net result can be represented by the equation $\log\{100/(100-Y)\}=a\log m+\log(100/k)$, where *a* and *k* are constants, the former depending on the temperature. When copper oxide is the catalyst, *Y* is only slightly affected by variations in *m*, apparently because the equilibrium ratio of metal to oxide in the catalyst varies very little with *m* (cf. Pease and Taylor, A., 1922, ii, 148). R. Cuthill.

Effect of water on the decomposition of ethyl alcohol at the surface of nickel. W. W. Russell and R. F. Marschner (J. Physical Chem., 1930, **34**, 2554—2566).—The addition of water to ethyl alcohol reacting at a nickel surface at 200±2° increases the amount of alcohol undergoing reaction and decreases the percentage of aldehyde decomposed over a wide concentration range. At 80 mol.-% of water a dilution effect begins to predominate. The 10% nickel catalyst was prepared by igniting and reducing at 350° the nitrate supported on pumice. The deactivation of such catalysts is reduced by the presence of water in the alcohol and reactivation is achieved by treatment with hydrogen at 350°. An approximately linear relationship between time of contact and amount of reaction exists for a certain range of space velocities. An explanation of the observed results is discussed. L. S. Theobald.

Nickel as a catalyst for hydrogenation. H. Adkins and H. I. Cramer (J. Amer. Chem. Soc.,

1930, **52**, 4349—4358).—Details, for which the original must be consulted, are given for the reduction of 45 compounds by hydrogen in presence of a nickel catalyst, prepared by a modification of the method of Rather and Reid (A., 1915, i, 933), at 100—200° and pressures up to 200 atm. The reductions are carried out both in absence and presence of solvents such as ether, alcohol, heptane, or methyl*cyclo*hexane. Aldehydes and ketones usually furnish the corresponding alcohols; cyanides give the corresponding amines; aromatic compounds are usually hydrogenated completely (or in distinct stages at different temperatures). The alcoholic hydroxyl group is not replaced by hydrogen except when it is on a carbon atom attached directly to a benzenoid ring. Quinoline is reduced to the 1 : 2 : 3 : 4-tetra- and deca-hydro-derivatives at 150°/160 atm. and 175°/175 atm., respectively.

H. BURTON.

Inversion of sucrose by platinised charcoal saturated with hydrogen. B. BRUNS and M. WANJAN (Z. physikal. Chem., 1930, **151**, 97—102; cf. Miller and Bandemer, A., 1927, 821).—When charcoal (2 g.) containing 0·2—1·0% Pt and saturated with hydrogen is introduced into 50 c.c. of a 5% solution of sucrose at 50°, about 97% of the sucrose is inverted in 48 hrs., whilst no detectable inversion occurs under the same conditions with degassed platinised charcoal. The presence of oxygen leads to oxidation of the sucrose. The result is attributed to catalytic action of the hydrogen ions of the double layer.

F. L. USHER.

Cathodic separation forms of tin. F. FOERSTER and H. DECKERT (Z. Elektrochem., 1930, **36**, 901—923; cf. B., 1929, 685).—The influence of crude *m*-cresolsulphonic acid in determining the form of tin separating at the cathode during electrolysis of sulphuric acid solutions (0·15*M*) of stannous sulphate (0·25*M*) is due to the presence of small quantities of by-products, more especially a resin (0·4%), which exerts a specific influence, being adsorbed at the metal surface. With small adsorption there is a tendency towards the formation of needle-like aggregates or slimes, changing to white tin, and finally to a milky-white structureless deposit, with maximum adsorption. The action of the purely adsorbed material is prolonged, whilst that of the colloidal by-products formed when the *m*-cresolsulphonic acid is prepared above 120° is transitory, the colloid being deposited on the cathode through electrophoresis. Pure *m*-cresol gives in high concentrations separation forms similar to those of the resin by-product, and is itself adsorbed at the cathode. The effect is diminished with rise of temperature and increased with fall of temperature in accordance with the adsorption law, whilst other adsorbable materials, including other phenols, sulphates of aniline and pyridine, and gelatin, are also active. Experiments on electrodeposition of cadmium from ammoniacal solution in presence of pyridine indicate the occurrence of a similar effect with this metal corresponding that of phenols on tin in acid solution. Stannous chloride in hydrochloric acid solution shows the same effect as the sulphate in a very much smaller degree, having a greater tendency to the formation of the needle-like aggregates. A large number of photographs illustrating the forms of the metal which are obtained under varying conditions is given. It is suggested that the polarisation effect in electrodeposition is connected with changes in the hydration of ions at the moment of deposition, rather than with electric forces in the formation of the crystal lattice. In agreement with this it is shown that the observed adsorption effect is at a maximum at the points and edges of the crystals, and at a minimum on the plane surfaces. It is concluded that the tendency of tin to form needle-like aggregates, and the small polarisation value, make the metal particularly sensitive to adsorption effects.

J. R. I. HEPBURN.

Theory of the lead accumulator. L. JUMAU.—See B., 1930, 1116.

Effect of anodic impurities on the electrodeposition of gold. R. W. HARBISON.—See B., 1930, 1114.

Variations in thickness of metal electrodeposits. E. L. GRANT and V. E. GRANT.—See B., 1930, 1114.

Displacement by ultra-violet light of the explosion limit in a chain reaction. C. N. HINSHELWOOD and K. CLUSIUS (Proc. Roy. Soc., 1930, **A**, **129**, 589—598).—At atmospheric temperatures mixtures of oxygen and phosphine explode within a sharply defined pressure region, above or below which reaction is negligibly slow. This can be explained on the assumption that the oxidation is a chain reaction. Both limits are affected by exposing the gas mixture to ultra-violet light, and the present work deals with the lower limit. The apparatus used was similar to that described by Dalton and Hinshelwood (A., 1929, 1243), the reaction tube being of fused silica coated internally with a thin layer of phosphoric acid. When illuminated, the gases explode at a lower limit than normally, and the increased sensitiveness persists for a time when the light is extinguished. The increased explosibility appears to be due to the formation of a definite substance which exists for an appreciable time. Its formation was observed experimentally in two ways: (*a*) by exposing the mixture to radiation and then compressing to the explosion point, the total time of illumination, including the time required for compression, being measured, and (*b*) by compressing the gases to some suitable pressure and then illuminating, when explosion occurs after a definite time-interval. The decay curves for mixtures which had been illuminated for 1·5 and 3 min., respectively, show that a stationary state is set up in the light, the action of the substance produced being comparable with that of a trace of nitrogen peroxide in the combination of hydrogen and oxygen. The value for the maximum concentration in the photostationary state is deduced, and the efficiency of collisions with the vessel wall in destroying this substance is calculated. It is considered that the oxidation provides an example of "material" rather than "energy" chains.

L. L. BIRCUMSHAW.

Photochemical combination of chlorine and hydrogen. II. T. ICHIKAWA (Z. physikal. Chem.,

1930, **B**, **10**, 299—336).—The photochemical reaction between hydrogen and chlorine has been studied under various conditions of pressure and time of illumination. The total reaction velocity does not immediately fall to zero when the illumination is removed, and on re-illumination after a short interval the resulting increase of velocity commences apparently instantaneously from a higher value than that to which it had fallen. The velocities of the primary and secondary reactions have been calculated, and the kinetics of the reaction are discussed. A suggested new type of mechanism for the combination involves the formation of a complex molecule H_2O,Cl_2, which is decomposed by light, yielding H_2O,Cl groups and chlorine atoms; the reactions $H_2O,Cl+H_2=HCl+H_2O+H$, and $H+Cl_2=HCl+\mathit{Cl}$ ensue, where *Cl* is a high-velocity chlorine atom capable of causing dissociation on collision with a chlorine molecule, and thus aiding the further formation of H_2O,Cl groups. H. F. GILLBE.

Photochemical formation of chlorine dioxide from chlorine monoxide in carbon tetrachloride solution. R. G. DICKINSON and C. F. P. JEFFREYS (J. Amer. Chem. Soc., 1930, **52**, 4288—4297).—The absorption coefficients of chlorine, chlorine monoxide, and chlorine dioxide in carbon tetrachloride are recorded for light of wave-lengths 4358 and 4047 Å. The photo-decomposition of chlorine monoxide in carbon tetrachloride by light of λ 4358 Å. is accompanied by the formation of considerable quantities of chlorine dioxide. For 0·014—0·054*M* solutions of chlorine monoxide, the initial rate of formation of chlorine dioxide is 0·35 mol. per quantum absorbed, and the yield of chlorine dioxide for a given number of quanta absorbed is greater the higher is the initial concentration of chlorine monoxide. The rate of decomposition of the latter falls slightly, with increasing exposure, from an initial value greater than 1·8 mols. per quantum absorbed by the monoxide.

J. G. A. GRIFFITHS.

Directional distribution of the relative velocity of the decomposition products in the optical dissociation of sodium iodide. A. C. G. MITCHELL (Physical Rev., 1929, [ii], **33**, 279).—Sodium iodide can be dissociated by ultra-violet light of wave-length 2450 Å. into an excited sodium and a normal iodine atom. With wave-lengths less than 2450 Å. the excess energy goes into relative kinetic energy of the two atoms as they part, and the excited sodium atom emits *D*-lines with a corresponding Doppler broadening. The atoms fly apart in either direction to that of the electric vector with equal probability.

L. S. THEOBALD.

Decomposition of thiocyanates in ultra-violet light. K. JABŁCZYNSKI and H. JABŁCZYNSKA (Rocz. Chem., 1930, **10**, 579—600).—Ammonium, sodium, or potassium thiocyanate is decomposed in aqueous solution on irradiation with wave-lengths of less than 3000 Å.; the reaction products are cyanide and sulphur. The reaction is in all cases exothermic. It is autocatalysed by sulphur, the velocity coefficient K being expressed by $K=\log(x+d)/d(1-x)/(1+d)t$, where x represents the relative opacity of the liquid at time t and d is a constant for the given system. The velocity–concentration curves exhibit a maximum at 0·991*N* for ammonium, 1·09*N* for potassium, and 0·271*N* for sodium thiocyanate. The equilibrium point is displaced in the direction of disintegration by raising the temperature, and for this reason the velocity of reaction is greater at higher temperatures. The addition of hydrochloric acid has the same effect, as a result of the greater instability of free thiocyanic acid. The velocity of reaction is retarded by the addition of potassium chloride or zinc or nickel sulphate to potassium thiocyanate solutions.

R. TRUSZKOWSKI.

Action of light on silver hydrosols containing particles of uniform size. A. GAŁECKI and R. SPYCHALSKI (Rocz. Chem., 1930, **10**, 492—500).—The velocity of decolorisation of silver hydrosols conforms to that of a unimolecular reaction. The temperature coefficient is 1·3. R. TRUSZKOWSKI.

Photochemistry of the associated state. F. WEIGERT (Z. physikal. Chem., 1930, **B**, **10**, 241—263). —Franck's views of the photochemical dissociation of non-polar molecules is applied to the consideration of possible changes in associated systems produced by the action of light, and the conditions under which excitation of the electron systems of individual molecules of the associated complexes and micelles can lead to partial opening up are discussed. On examination of the influence of light on silver chloride emulsions it is shown that the lack of proportionality between the energy absorbed and the effect produced, and the anomalous additive effect of radiations of different wave-lengths, are evidence for the occurrence of photomicellary processes, as opposed to photomolecular processes, in which a large number of energy quanta are absorbed by one micelle. Other systems discussed are those of gelatin and collodion films containing light-sensitive dyes, the visual purple of the retina, and systems in which it is impossible directly to observe the nature of the phenomena which take place, such as highly mobile gaseous and liquid associated systems, systems containing solid micelles dispersed in gaseous or liquid media, and certain types of solid micro-crystalline media. The occurrence of primary and induced photodichroism is an indication that the form of the "opened" particles within the micelles is dependent on the wave-form of the exciting radiation, and although the physical significance of such a phenomenon is obscure, it appears that a quantitative study of photodichroism, by revealing the nature of the opening-up process, would give much information relating to the structure of associated systems and to many biological problems.

H. F. GILLBE.

Laying bare of ripening centres. LUPPO-CRAMER (Z. wiss. Phot., 1930, **29**, 5—7).—The surface centres on the grains of a series of layers of negative (bromide) and chloride emulsions were removed by treatment with chromic acid, and the internal centres were then revealed by physical development after opening up the grains by treatment with a solution of potassium iodide. A much greater number of internal centres was found in the grains of the chloride emulsion, which is in agreement with the easy reducibility of silver chloride, and the ready formation and

comparatively greater stability of the silver–silver chloride adsorption complexes. J. W. GLUSSETT.

Photochemical polymerisation of acetylene. S. C. LIND and R. S. LIVINGSTON (J. Amer. Chem. Soc., 1930, **52**, 4613—4614; cf. Reinicke, A., 1928, 1340).—The polymerisation of acetylene at pressures less than 30 cm. in the complete radiation of a quartz mercury lamp is proportional to the pressure. The velocity approaches a constant value at higher pressures. The 10° temperature coefficient between 12° and 39° is 1·25, but this may be due to a temperature coefficient of light absorption. Light of wavelength 2537 Å. or longer is inactive; the quantum efficiency for shorter wave-lengths is about $7 \cdot 4 \pm 2 \cdot 5$. Mercury vapour was excluded from the reaction system. J. G. A. GRIFFITHS.

Composition of deposit forming on zinc immersed in cupric sulphate solutions. II. A. GAŁECKI and J. TOMASZEWSKI (Rocz. Chem., 1930, **10**, 601—629; cf. B., 1930, 822).—The copper content of the deposit diminishes with rise of temperature from 18° to 50°; this effect is most marked in dilute solutions (0·02—0·1N). The appearance of the deposits is unaffected by temperature. The addition of zinc sulphate to the solution similarly depresses the copper content of the deposits; at the same time these become less coherent in stirred systems. The copper content of the deposits diminishes as the concentration of zinc in solution increases. Zinc is present in the deposits probably exclusively as oxide or hydroxide. R. TRUSZKOWSKI.

Cupriammines. II. Ammines of cupric perchlorate. R. PORTILLO (Anal. Fís. Quím., 1930, **28**, 1125—1144).—*Pentamminoaquocupric perchlorate* has been prepared as a blue crystalline powder by addition of ammonia solution to a solution of cupric perchlorate; it has d_4^{25} 1·657 and molecular heat of dissolution −17·9 kg.-cal. At the ordinary temperature it readily passes into the violet tetramminocupric perchlorate, which has d_4^{25} 1·952, mol. heat of dissolution −18·30 kg.-cal. (480 mols. of water), −20·95 kg.-cal. (1600 mols. of water), heat of formation 181·7 kg.-cal. On hydration this compound yields the pale blue *tetramminodiaquocupric perchlorate*. *Tetramminoaquocupric perchlorate*, blue, d_4^{25} 1·83, mol. heat of dissolution −17·9 kg.-cal., results from the recrystallisation of tetramminocupric perchlorate dihydrate; the last-named compound has no definite m. p. but commences to liquefy at 50—54°, and when heated at 100—105° it solidifies to a greenish-black mass of *triamminocupric perchlorate*, which is produced also by heating any of the other complexes at 180°. The dihydrated tetrammine has d 1·60, mol. heat of dissolution −20·38 kg.-cal., and decomp. 82°. *Hexamminocupric perchlorate*, which has been prepared, although not in a pure state, by the action of ammonia on the tetrammine, has d_4^{25} 1·60, mol. heat of dissolution −20·38 kg.-cal.

H. F. GILLBE.

Cupric perchlorate. R. PORTILLO and L. ALBEROLA (Anal. Fís. Quím., 1930, **28**, 1117—1124).—Pure *cupric perchlorate*, $Cu(ClO_4)_2,7H_2O$, has been prepared by dissolution of copper carbonate in 30% perchloric acid solution, and concentration of the solution. Dehydration over phosphorus pentoxide at the ordinary temperature yields the hexahydrate, which is more stable than the heptahydrate; when heated at 70° in a current of dry air it yields the tetrahydrate. The almost colourless *dihydrate* is produced by heating at 80—100°, but further dehydration causes decomposition with evolution of perchloric acid. The heptahydrate forms pale blue, extremely deliquescent triclinic crystals, m. p. 82°; the hexahydrate has d_4^{25} 2·2255, mol. heat of dissolution −4·6 kg.-cal., and heat of formation in solution 64·7 kg.-cal. The saturated solution at 0° contains 54·3% of anhydrous salt. The classical degree of ionisation falls from 1·02 in 0·024M solution to 0·93 in 0·198M solution. H. F. GILLBE.

Ammonium, potassium, and sodium cuprous thiosulphates. I. G. SPACU and I. G. MURGULESCU (Bull. Soc. Stiinte Cluj, 1929, **5**, 61—107; Chem. Zentr., 1930, i, 3422—3423).—In the titration of 0·1—0·2M-cupric nitrate with ammonium thiosulphate the addition of alcohol (75—86%) affords a yellow, crystalline precipitate, or (with more alcohol) a white, amorphous precipitate; the potentiometric curve indicates the formation of the *compound* $(NH_4)_2[Cu_2(S_2O_3)_2]$, and in a 0·5M-solution with more than 50% of alcohol, the *compound* $(NH_4)_4[Cu_2(S_2O_3)_3]$ results. Other cupric *salts*, similarly obtained, are $(NH_4)_7[Cu(S_2O_3)_4],2NH_4NO_3$, $(NH_4)_5[Cu(S_2O_3)_3]$, and $(NH_4)_7[Cu(S_2O_3)_4],2NH_4ClO_3$. A. A. ELDRIDGE.

Metallic hydroxy-acid complexes. V. Neutral α-cupritartrates. E. E. WARK and I. W. WARK (J.C.S., 1930, 2474—2478).—Dumanski and Chalisev (A., 1929, 259) have questioned the existence of the α-cupritartrates described by Packer and Wark (J.C.S., 1921, **119**, 1348), suggesting that the supposed compounds are merely colloidal solutions of copper hydroxide in neutral or alkaline tartrate solutions. Copper tartrate is completely soluble in sufficient sodium tartrate and it is claimed that lack of appreciation of this fact has led to the criticism, incorrect stoicheiometric relationships for the action of sodium hydroxide on copper tartrate being obtained. As the end-point of the reaction is difficult to determine, a potentiometric method has now been applied and the results confirm the existence of the α-cupritartrates. Similar results were obtained for the copper salts of salicylic, lactic, and glycollic acids.

E. S. HEDGES.

Extraction of rubidium and cæsium from carnallite. III. G. JANDER and F. BUSCH (Z. anorg. Chem., 1930, **194**, 38—46; cf. A., 1930, 435).—The cæsium in a mixture containing rubidium chloride and a little cæsium chloride, such as is obtained in working up carnallite for these metals, may be concentrated by taking advantage of the fact that if silicomolybdic acid is gradually added to the solution precipitation of the cæsium is practically complete when considerably less precipitant than would be required for complete precipitation of the mixture has been added. At the same time, therefore, a considerable proportion of the rubidium compound can be obtained in a state of purity. The mixed precipitate is then boiled with barium hydroxide to eliminate the silicomolybdic acid as barium silicate

and molybdate, and the excess of barium is removed as carbonate by saturating the filtrate with carbon dioxide and boiling. By boiling the barium molybdate with sodium carbonate solution, the molybdic acid is recovered as the sodium salt. R. CUTHILL.

Rubidium and cæsium nitrides. K. CLUSIUS (Z. anorg. Chem., 1930, **194**, 47—50).—The residues obtained on heating rubidium and cæsium azides contain the nitrides Rb_3N and Cs_3N, respectively. R. CUTHILL.

Thermal decomposition of mixtures of calcium sulphide and sulphate. J. ZAWADZKI and I. KOWALCZEWSKI (Rocz. Chem., 1930, **10**, 501—509).—Calcium sulphite is converted into sulphide and sulphate only at very high temperatures, and even then very slowly, whence it follows that sulphite is not one of the products of the thermal decomposition of gypsum. The reaction $CaS+3CaSO_4 \longrightarrow 4CaO+4SO_2$ is complicated by secondary reactions occurring between the products of this reaction, and leading to the liberation of sulphur. The partial pressure of sulphur rises from 2·3 mm. at 820° to 115·1 mm. at 1060°; over the same range that of sulphur dioxide rises from 8·8 to 149·0 mm. R. TRUSZKOWSKI.

Formation and composition of bleaching powder. B. NEUMANN (Z. Elektrochem., 1930, **36**, 934—936).—Polemical against Ditz (A., 1930, 1138). The assumption of Ditz that his formulæ for bleaching powders types I and II correspond with those for the hydrates of bleaching powder established experimentally by Neumann and Haebler (*ibid.*, 176) is incorrect. J. R. I. HEPBURN.

Röntgenographic study of the products obtained by the action of the halogen acids on mercuric sulphates, and fusion diagram of the system HgI_2–$HgSO_4$. M. PAIC (Compt. rend., 1930, **191**, 941—943).—The halogen acids in the gaseous state or in aqueous solution react with the compounds $HgSO_4$ and $3HgO,SO_3$ to form sulphuric acid and the corresponding mercuric halide. Neither concentrated sulphuric acid nor H_2SO_4,H_2O reacts with mercuric chloride or bromide, but at 300—350° the former reacts with mercuric iodide, forming mercuric sulphate and hydriodic acid. The compound $HgSO_4,HgI_2$ (pale yellow crystals) was shown by *X*-ray, chemical, and thermal analysis to be formed under the latter conditions. Contrary to the results of previous workers, no evidence was obtained of the existence of the compounds $HgSO_4,2HCl$, $HgSO_4,2HBr$, $3HgO,SO_3,6HCl$, $3HgO,SO_3,6HBr$, $HgSO_4,HCl$, $HgSO_4,2HCl,H_2O$, and $HgSO_4,HBr$. J. GRANT.

Boron hydrides. XIV. B_4H_{10}. A. STOCK, E. WIBERG, and H. MARTINI (Ber., 1930, **63**, [*B*], 2927—2937).—The stability of the compound B_4H_{10} varies within wide limits and appears to be influenced by the glass of the apparatus. In the presence of hydrogen chloride, a part of the hydride remains unchanged; a small proportion is decomposed into boron trichloride and a similar amount to non-volatile chlorinated derivatives. The remainder decomposes in the usual manner mainly into B_2H_6 and $(B_5H_4)_n$. The auto-decomposition is not impeded by the presence of an excess of hydrogen chloride in spite of neutralisation of the alkali of the glass. With deficiency of sodium amalgam, the hydride B_4H_{10} yields the non-volatile substance $B_4H_{10},2Na$, decomposed by water into hydrogen and a sodium hypoborate. Treatment of the hydride with an excess of sodium amalgam and subsequently with hydrogen chloride or diborane affords evidence of the production of compounds richer in sodium than $B_4H_{10},2Na$. With an excess of ammonia at −70° the hydride B_4H_{10} yields a colourless, non-volatile *compound*, $B_4H_{10},4NH_3$, which decomposes at the ordinary temperature with evolution of ammonia and hydrogen and without production of recognisable intermediate compounds. At 180° the product $B_3H_6N_3$ is formed, and is thus conveniently obtained. It appears doubtful whether the addition of hydrogen chloride to the compound $B_3H_6N_3$ is a simple case of salt formation. With ammonia and an excess of B_4H_{10} products poorer in ammonia than $B_4H_{10},4NH_3$ appear to be formed, but their precise nature has not been ascertained. Apart from unimportant side reactions, the interaction of $B_4H_{10},4NH_3$ and hydrogen chloride proceeds according to the scheme $B_4H_{10},4NH_3+8HCl=7H_2+B_4H_4Cl_8,4NH_3$. Electrolysis of solutions of the substance $B_4H_{10},4NH_3$ in liquid ammonia between platinum electrodes at −70° is accompanied by evolution of nitrogen and hydrogen at the cathode and a substance, $B_4H_{15·5}N_{5·5}$, is produced. It is therefore probable that the initial material is a salt, $(B_4H_6)''''4(NH_4)^{\cdot}$. In the hydride B_4H_{10} it is certain that four hydrogen atoms differ in their behaviour from the remaining six. H. WREN.

Peraluminates of the alkali and alkaline-earth metals. J. PRÁŠEK (Coll. Czech. Chem. Comm., 1930, **2**, 653—664).—*Sodium* and *potassium peraluminates*, $M_2Al_2O_5,8H_2O$ and $M_2Al_2O_6,8H_2O$, have been prepared as soluble white crystalline powders by addition of hydrogen peroxide to a cold solution of the corresponding aluminate, and precipitation by alcohol; by heating at 105° the normal aluminates are formed. The stability of the solutions, which readily undergo hydrolysis and deposit aluminium hydroxide, decreases with increase of the active oxygen content. Normal lithium peraluminate has not been prepared, but the *compound* $Li_2Al_4O_9,28H_2O$ separates on addition of hydrogen peroxide to a solution of lithium aluminate; dehydration causes decomposition to hydrated acid aluminates. By the action of potassium aluminate on a solution of lithium chloride and hydrogen peroxide the *compound* $Li_2Al_8O_{17},25H_2O$ is formed. Insoluble *magnesium, calcium, strontium*, and *barium peraluminates*, of the general formula $MAl_2O_6,10H_2O$, are precipitated on addition of potassium aluminate solution to a solution containing the appropriate chloride and hydrogen peroxide, whilst $Ca_4Al_2O_9,15H_2O$, $Sr_3Al_2O_8,20H_2O$, and $Ba_3Al_2O_8,20H_2O$ are formed by shaking these compounds with the hydroxide of the metal and water. The magnesium and alkaline-earth peraluminates are relatively stable, but at temperatures above 100° they decompose, yielding aluminates. The reactions of all these substances are typical of per-compounds; concentrated sulphuric acid liberates oxygen, whereas dilute acids liberate hydrogen per-

oxide. Consideration of the structure of the peraluminates based on f.-p. determinations indicates that the anions formed in solution are $[Al(OH)_3{\cdot}O{\cdot}OH]'$ and $[Al(OH)_4]'$. H. F. GILLBE.

Halides of the rare earths. IV. Samarium di-iodide and the thermal decomposition of samarium tri-iodide. G. JANTSCH and N. SKALLA (Z. anorg. Chem., 1930, **193**, 391—405).—Reduction of completely anhydrous samarium tri-iodide in a current of hydrogen, which must be free from oxygen and water, commences at 350°; by raising the temperature gradually to 760° pure samarium di-iodide has been prepared. If the tri-iodide is heated in a vacuum at 800° for 50 min. and then at 900° for 15 min., a 90% yield of pure samarium di-iodide is obtained, but if the tri-iodide is heated slowly decomposition commences at 560°. Since at about 680° the di-iodide begins to decompose according to the equation $3SmI_2 \longrightarrow 2SmI_3 + Sm$, the initial rate of heating should be as high as possible. The compound forms dark green, nearly black, very hygroscopic crystals, m. p. 840° (decomp.), which dissolve in water to a deep red solution with evolution of hydrogen and gradual deposition of a basic salt: the solution is more stable than that of samarium dichloride, but on shaking with air or on addition of acid hydrogen is rapidly evolved and the solution becomes colourless. The equivalent conductivity of the solution at 0° falls with time according to a linear law, until complete decolorisation and formation of the basic salt has occurred. Sulphate, chromate, or phosphate ions precipitate from a neutral solution of samarium di-iodide stable orange-yellow crystals of the corresponding salt; the sulphate, which has been isolated in the solid form, is sparingly soluble in water, and its solution in acid rapidly decomposes with evolution of hydrogen. Samarium tribromide, m. p. 665±2° when heated in a vacuum, commences to decompose at 700°, and at 800—850° the dibromide formed decomposes with separation of metallic samarium, but even with rapid heating only a poor yield of impure samarium dibromide is obtained.

H. F. GILLBE.

Rare earths. XXXVI. Separation of ytterbium by electrolytic reduction. R. W. BALL [with L. F. YNTEMA] (J. Amer. Chem. Soc., 1930, **52**, 4264—4268).—Ytterbium sulphate, $YbSO_4,xH_2O$, containing only 1—2% of other rare-earth metals, is precipitated as greenish-white crystals from a sulphuric acid solution of the mixed chlorides of the metals of the yttrium group by prolonged electrolytic reduction with a current of density 0·025 amp. per cm.² at the mercury cathode. The solution becomes green during the reduction, but on stopping the current hydrogen is evolved throughout the solution, colourless, probably owing to the reaction – + $\longrightarrow 2Yb^{\cdot\cdot\cdot} + H_2$. The precipitate dissolves in dilute acid with the evolution of hydrogen and in nitric acid with the evolution of oxides of nitrogen.

J. G. A. GRIFFITHS.

Preparation of lanthanum from cerite from Suecia. Separation of ammonium lanthanum nitrate, and spectral analysis of the lanthanum oxide produced. R. LLORD Y GAMBOA (Anal. Fís. Quím., 1930, **28**, 1145—1152).—Details are given of the separation of lanthanum from cerite by extraction with nitric acid, conversion into the double ammonium nitrate, fractional crystallisation of the salt, and ignition to oxide. The method is reported to be very satisfactory, especially as regards the quantity of material which can be handled. Spectroscopic analysis of the product shows it to be entirely free from metals of the yttrium group, although containing traces of cerium, praseodymium, neodymium, europium, and samarium. H. F. GILLBE.

Reduction of zinc oxide by carbon monoxide in a gaseous cycle, and the mechanism of the reaction. O. DONY (Bull. Acad. roy. Belg., 1930, [v], **16**, 881—892).—The reduction has been investigated at about 1000°. When the zinc oxide is mixed with carbon, the only function of the latter is to reduce the carbon dioxide formed.

C. W. GIBBY.

Anhydrous lower bromides of titanium. R. C. YOUNG [with W. C. SCHUMB] (J. Amer. Chem. Soc., 1930, **52**, 4233—4239).—By applying the hot-cold tube technique to a mixture of hydrogen and titanium tetrabromide vapour, *titanium tribromide* is obtained as bluish-black needles and plates which have been examined crystallographically. The tribromide decomposes at 400° into a mixture of titanium tetrabromide and a black powder, *titanium dibromide*. The reaction is reversed by passing the tetrabromide over the dibromide at 280—380°. Titanium dibromide decomposes slowly at 500° and more rapidly at 650° into titanium and titanium tetrabromide; the dibromide ignites when exposed to moist air, and dissolves in water with the evolution of hydrogen.

Titanium tetrabromide and hydrogen are produced by passing hydrogen bromide over titanium tribromide at 250—350°. Similarly, at 160° the dibromide is converted into the tribromide and some tetrabromide. A mixture of the bromides containing a higher proportion of the non-volatile substances is produced at 300° than 450° by the action of hydrogen bromide on metallic titanium. Titanium tetrabromide at 300° is reduced to the tribromide by titanium metal, mercury, and silver. J. G. A. GRIFFITHS.

Oxides of lead and their reduction by charcoal. E. J. RODE (J. Russ. Phys. Chem. Soc., 1930, **62**, 1419—1442).—Two types of lead dioxide exist; one gives three breaks on the temperature–time curve, viz., with absorption of heat at 275—409°, with evolution of heat at 525—535°, and with absorption of heat at 602—620°, whilst the other type gives only two breaks, both of an endothermic character. The first break is due to loss of oxygen, with production of litharge, the second to formation of Pb_3O_4, and the third to loss of oxygen by the latter oxide. Oxides of type I (α) are solid solutions of monoxide and dioxide, whilst the second type consists of the β form, of composition $PbO—PbO_{1\cdot 01}$, and γ form, $PbO_{1\cdot 31}—PbO_{1\cdot 93}$; the character of combination with oxygen is of the zeolite type. Up to 1·01% of water may also be present in solid solution. Reduction of oxides of lead by sugar or wood charcoal takes place in two stages, the first probably corresponding with reduction to a suboxide, and the second to metal.

The transformation of red to yellow lead dioxide does not involve any thermal effect.

R. TRUSZKOWSKI.

Structure of nitroamide and Hantzsch's arguments. A. ANGELI (Gazzetta, 1930, **60**, 665—668).—Hantzsch's abandonment (A., 1930, 1032) of his view that nitroamide and hyponitrous acid are stereoisomerides is discussed. T. H. POPE.

Interaction between nitrogen trichloride and nitric oxide at $-150°$. II. Further evidence for formation of nitrogen dichloride and mono-oxygen dinitrogen dichloride. W. A. NOYES (J. Amer. Chem. Soc., 1930, **52**, 4298—4301; cf. A., 1929, 158).—The reaction at $-150°$ in chloroform and carbon tetrachloride is represented, approximately, by the equation $NCl_3+3NO=2NOCl+N_2O+Cl$. It is thought that the reaction proceeds in four stages: (i) $NCl_3+NO=ClNO+NCl_2$, (ii) $NCl_2+NO=Cl_2N_2O$, (iii) $Cl_2N_2O+NO=ClNO+ClN_2O$, (iv) $2ClN_2O=Cl_2+2N_2O$, although the intermediate compounds could not be isolated. The difference between the reaction at $-80°$ (*loc. cit.*) and $-150°$ is attributed to the occurrence of stage (iii) which is made possible by the greater stability of the unstable mono-oxygen dinitrogen dichloride at the lower temperature. Attempts to carry out the reaction at $-185°$ to $-191°$ were not successful. J. G. A. GRIFFITHS.

Quadrivalent vanadium cyanide complex. A. YAKIMACH (Compt. rend., 1930, **191**, 789—790).—*Potassium vanadicyanide*, $K_4V(CN)_6$, was prepared as netted green prisms by slowly mixing concentrated solutions of potassium cyanide and vanadium tetra-acetate and stirring (cf. A., 1930, 558). It decomposes in air or water, in excess of either reagent and at 150°, and should be washed rapidly with alcohol and recrystallised from a dilute solution of potassium cyanide. Cyanogen was determined by distillation (Liebig–Deniges), vanadium by titration with potassium permanganate solution before and after reduction with sulphur dioxide, and by precipitation with cupferron, and the potassium was weighed as sulphate. J. GRANT.

Displacement of "metallic" arsenic from alkaline solutions of arsenic acid by hydrogen at a high pressure and temperature. II. V. N. IPATIEV, G. A. RAZUBAIEV, and V. S. MALINOVSKI (Ber., 1930, **63**, [*B*], 2812—2817; cf. A., 1930, 306).—Reduction of arsenic acid by hydrogen in the presence of alkali occurs in two stages, $Na_2HAsO_4+2H\longrightarrow Na_2HAsO_3+H_2O$ and $Na_2HAsO_3+3H\longrightarrow As+2NaOH+H_2O$. After 24 hrs. at 200° only the first change has occurred, whereas under similar conditions at 250° the separation of "metallic" arsenic also commences. At 350°, the maximum separation of arsenic (96%) is observed. At this temperature, displacement of "metallic" arsenic occurs most completely in the absence of alkali. With increase in the amount of the latter, between 0·0 and 0·3 mol. per 50 c.c., the yield of precipitated arsenic decreases, but between 0·3 and 0·4 mol. there is a marked increase in yield. Variation between 43 and 47 atm. in the initial pressure of hydrogen has no effect. The production of arsine is not observed.

H. WREN.

Preparation and physical properties of sulphur hexafluoride. W. C. SCHUMB and E. L. GAMBLE (J. Amer. Chem. Soc., 1930, **52**, 4302—4308).—Monel metal is used in place of magnesium in the construction of the fluorine generator (cf. Bancroft and Jones, A., 1929, 658). Sulphur hexafluoride is prepared by passing fluorine over sulphur in a copper tube, and the subsequent purification of the gas is described. The vapour pressure has been determined at temperatures between $-72°$ and $-46°$, and is 760 mm. at $-63·8°$. The vapour density (air=1) is 5·106. The m. p., $-50·8\pm0·2°$, is higher than values previously recorded. J. G. A. GRIFFITHS.

Preparation of tetra- and tri-thionate from thiosulphate and sulphurous acid. A. KURTENACKER and K. MATEJKA (Z. anorg. Chem., 1930, **193**, 367—384).—By passing sulphur dioxide into a mixture of 25 g. of ammonium thiosulphate and 15 c.c. of water at 13·5° crystals of ammonium tetrathionate of 99·1% purity separate; they contain only small quantities of the trithionate and of hydrogen sulphite. The mother-liquor retains about 24% of tetrathionate and 34% of trithionate. With mixtures containing less thiosulphate sulphur alone separates, whilst at higher concentrations the precipitate contains decreasing quantities of tetra- and increasing quantities of tri-thionate. The reaction proceeds largely, although not entirely, in accordance with the equation $2S_2O_3''+3SO_2=S_3O_6''+S_4O_6''$. The precipitate obtained from mixtures of potassium thiosulphate with water by the action of sulphur dioxide contains not more than 40% of tetrathionate, but from relatively dilute mixtures the precipitate contains up to 91% of trithionate; the mother-liquor contains varying proportions of thiosulphate, and tri-, tetra-, and penta-thionate. Sodium thiosulphate solutions yield precipitates containing up to 90% of tetrathionate, but by addition of a small quantity of arsenious acid solution both the yield and the quality of the product are improved; a 98% pure tetrathionate, containing tri-thionate but no free sulphur, may be obtained by this procedure. For the preparation of tetra- and tri-thionate the following procedure is recommended: 200 g. of sodium thiosulphate and 1 c.c. of saturated arsenious acid solution are added to 40 c.c. of saturated sulphur dioxide solution, and the cooled mixture is saturated with sulphur dioxide; the clear solution is alternately shaken and treated with the gas, and the resulting precipitate of sodium tetrathionate is separated and washed with ether. The mother-liquor, after passage of sulphur dioxide for a few minutes, is treated with a solution of 100 g. of potassium acetate in 120 c.c. of water, and after a short time the crystalline precipitate of potassium trithionate is removed and washed with a mixture of alcohol and ether. Both products are 95—98% pure, and may be further purified by dissolving in warm water, filtering the solution from sulphur, and precipitating the salt with alcohol. H. F. GILLBE.

Action of fluorine on wood charcoal. M. p. and b. p. of carbon tetrafluoride. P. LEBEAU and A. DAMIENS (Compt. rend., 1930, **191**, 939—940).—The mixture of fluorides of carbon obtained from purified wood charcoal by the authors' method (A.,

1926, 710) was freed from oxygen by the action of white phosphorus, washed with dilute alkali, dried, liquefied at $-190°$, and the pure carbon tetrafluoride (about 50% of the total yield) obtained by repeated fractional evaporations at a low pressure. The revised b. p. is $-126°$ (760 mm.) and m. p. $-191°$ (cf. *loc. cit.*, and Ruff and Keim, A., 1930, 1387). The residue after fractional evaporation contained hexafluoroethane and octafluoropropane. J. GRANT.

Preparation of pure rhenium compounds. F. KRAUSS and H. STEINFELD (Z. anorg. Chem., 1930, **193**, 385—390).—Potassium per-rhenate solution is not reduced by sulphur dioxide or by hydrogen with simultaneous short-wave irradiation. By the action of zinc and hydrochloric acid, sodium amalgam, or hydrazine hydrate, a brownish-black precipitate is produced; this after being dried at 105° consists of metallic rhenium containing oxide. Although hydrazine yields a product free from other metals, the yield is poorer and the substance contains volatile material. Rhenic acid may be prepared by dissolving the brown precipitate in hydrochloric or nitric acid and evaporating the solution to dryness, but the purity is greatly increased if the precipitate is first heated in a current of hydrogen.

H. F. GILLBE.

Oxides of iron and their reduction by hydrogen and charcoal. E. J. RODE (J. Russ. Phys. Chem. Soc., 1930, **62**, 1453—1466).—A halt, ascribed to the formation of an allotrope, occurs on the heating curves of ferric oxide at 745°, whilst above 1280° fluctuations in the curve, due probably to elimination of oxygen, appear. The temperature–time curves of ferric oxide and of various iron ores heated in an atmosphere of hydrogen exhibit two breaks; one, at 300—325°, corresponds with the formation of triferric tetroxide, and the second, at 350—370°, indicates further reduction of the latter to metallic iron. Ferrous oxide does not appear to exist as an intermediate reduction product. Three breaks are found on the temperature–time curves of mixtures of iron oxide or iron ores with charcoal; the first occurs at 400—650°, and is due to the exothermic reaction of reduction to magnetite, whilst the remaining two, occurring at 750—830° and 875—995°, respectively, are ascribed to the endothermic reactions of reduction of magnetite to ferrous oxide, and of the latter to metallic iron. R. TRUSZKOWSKI.

Hydrates of iron oxide. E. J. RODE (J. Russ. Phys. Chem. Soc., 1930, **62**, 1443—1452).—Hydrated ferric oxide is converted when heated into an unstable modification of ferric oxide; this reaction is endothermic. The unstable modification is converted at 320—340° into crystalline oxide, with evolution of heat, and the crystalline oxide undergoes further transformation at 450°. The results obtained for ferric hydroxide gel are substantially the same as those obtained for such natural products as bog iron ore, xanthosiderite, hetite, etc.

R. TRUSZKOWSKI.

Atomic hydrogen occluded in iron nitride. S. SATOH (Bull. Chem. Soc. Japan, 1930, **5**, 292—303).—Iron nitride prepared by the action of nitrogen on iron previously reduced with hydrogen contains atomic hydrogen, as shown by potential measurements on iron nitride in ferrous sulphate solution, and other tests. C. W. GIBBY.

Decomposition of potassium ferrocyanide and ferricyanide by autoclave treatment. T. KATSURAI and T. WATANABE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, **14**, 189—192; cf. A., 1930, 289).—*N*-Potassium ferrocyanide when heated for 1 hr. in an autoclave at 120° or 140° becomes alkaline owing to the formation of ammonia, and deposits hydrated ferric oxide. At 160° or 180° the precipitate is a mixture of ferric oxide and Prussian-blue. *N*-Potassium ferricyanide gives rise to an ammoniacal liquid and hydrated ferric oxide (hæmatite) at all four temperatures. F. L. USHER.

Isomerism of radicals. C. DUVAL and (MME.) DUVAL (Compt. rend., 1930, **191**, 843—845).—Persulphatopentamminocobaltic sulphate, $[Co(SO_4)^I(NH_3)_5](SO_4)^{II},H_2O$ (*a*), is prepared by keeping a mixture of solutions of aquopentamminocobaltic hydroxide and excess of ammonium persulphate for 2 days, and then treating the filtered solution with excess of ammonium persulphate. The compound is precipitated as orange crystals by alcohol. This is compared with the red sulphatopentamminocobaltic sulphate, $[Co(SO_4)^{II}(NH_3)_5]HSO_4$ (*b*) (cf. Job, Diss., Paris, 1921), the cation of which is isomeric with that of (*a*). The densities are, respectively, 2·1, 1·7, and magnetic susceptibilities ($\chi \times 10^6$), -588, -212, giving for the susceptibilities of the cations -537, -80. The absorption spectra of solutions of high concentration of the two salts are different, but greater dilution converts both alike into aquopentamminocobaltic sulphate. It is also concluded that persulphuric acid is HSO_4, and not $H_2S_2O_8$. C. A. SILBERRAD.

Univalent palladium. W. MANCHOT and H. SCHMID (Ber., 1930, **63**, [*B*], 2782—2786).—Dilute aqueous solutions of potassium palladocyanide react vigorously with sodium amalgam. The solution, which contains cyanide, has more energetic reducing properties than the corresponding platinum solution (following abstract). When shaken with air it yields hydrogen peroxide. When preserved at the ordinary temperature the initially colourless solution becomes pale yellow and hydrogen is noticeably evolved. The colour gradually deepens and finally black particles of metal separate which slowly increase in number. If the solution is boiled, the metal is deposited copiously and hydrogen vigorously evolved. If the alkaline solution is boiled before or after addition of acetic acid, hydrochloric acid, or potassium cyanide, hydrogen free from carbon monoxide is evolved in amount varying from 0·22 to 0·72 equivalent. A portion of the liberated hydrogen is utilised in other ways, since methylamine is present in the acetic acid solution. Titration with potassium ferricyanide or iodine requires amounts of reagent less than 1 equivalent, thus corresponding sharply with the transformation of univalent into bivalent palladium.

H. WREN.

Univalent platinum. W. MANCHOT and G. LEHMANN (Ber., 1930, **63**, [*B*], 2775—2782).—Treatment of a 1% aqueous solution of potassium platino-

cyanide with 3% sodium amalgam yield a colourless solution which reduces ammoniacal silver, Nylander's bismuth reagent, cadmium salt solution, mercuric chloride, and, if more concentrated, litmus, anthraquinonesulphonate, and acid indigotin solution. If the solution is exposed to air, its reducing power slowly disappears. Reduction can also be effected by potassium amalgam, calcium filings, electrolytically, or by aluminium and potassium hydroxide. Barium platinocyanide may be used or potassium chloroplatinite or chloroplatinate in presence of the equivalent amount of potassium cyanide. The reduced solution contains free cyanide, but colloidal platinum is not present. The boiling solution slowly evolves hydrogen, the maximum amount observed being 0·83 equivalent. In the presence of acids hydrogen is much more rapidly evolved in quantity much exceeding one equivalent per atom of platinum; a similar result is obtained after addition of potassium cyanide. Possibly the platinum passes into the quadrivalent state and also disproportionation of the univalent metal occurs to multivalent and free metal which dissolves in the potassium cyanide with evolution of hydrogen. Addition of the reduced solution to a strongly acidic iodine solution results in the production of iodoplatinic acid, H_2PtI_6, and titration of it with potassium ferricyanide requires more than one equivalent of the oxidising agent. The potential of the reduced solution measured at a platinised platinum electrode differs from that of a solution containing the same amounts of potassium platinocyanide, sodium hydroxide, and potassium cyanide. In course of time the potential of the second solution approaches that of the first, probably due to dissolution of the electrode in the cyanide with production of univalent platinum. Attempts to concentrate the reduced solution on the water-bath or in a vacuum are accompanied by evolution of gas; potassium platinocyanide separates. H. WREN.

Complex ions. III. Relative stabilities of halogenoplatinates. H. I. SCHLESINGER and R. E. PALMATEER (J. Amer. Chem. Soc., 1930, 52, 4316—4331).—Light accelerates the attainment in aqueous solution of the equilibrium $6NaY+Na_2PtX_6$—$6NaX+Na_2PtY_6$, where X and Y are different halogens. It is found colorimetrically that the concentration of chloride ion must be 660 times that of bromide ion for the equilibrium to be shifted 99% in the direction $PtBr_6''+6Cl'\longrightarrow PtCl_6''+6Br'$, and the concentration of bromide ion must be 25×10^3 times that of iodide ion to cause a like shift in the reaction $PtI_6''+6Br''\longrightarrow PtBr_6''+6I'$. These results indicate the relative order of the tendency of halogen ions to enter into co-ordination in the platinates. Molecular extinction coefficients are recorded and the existence of intermediate compounds in solution is demonstrated. The solid intermediate compounds previously reported are mixtures. J. G. A. GRIFFITHS.

Colorimetric analysis. F. F. HAHN and R. KLOCKMANN (Z. angew. Chem., 1930, 43, 993—995).—The error of a colorimetric determination may be reduced to 1—2% by the following procedure. Two comparison standards are prepared, both of a lighter shade than the solution under test; the latter is diluted with water until its colour lies between those of the standards, and after further dilution is brought back to approximately its original colour by addition of a further quantity of the original solution. By repetition of this cycle a series of figures may be obtained for the volume of water necessary to bring the colour to the intermediate point; the optical mean value should not be regarded as a sinple mathematical mean, but must be obtained by calibration with solutions of known concentration. H. F. GILLBE.

Analysis of mixtures of hydrogen, methane, and ethane. (MLLE.) E. M. J. MULDERS and F. E. C. SCHEFFER (Rec. trav. chim., 1930, 49, 1057—1065).—A phase-rule study of the system hydrogen–methane–ethane at the temperature of liquid air (−190°), which is above the critical temperature of hydrogen, shows that separation of the mixture of these three gases into a solid phase (ethane) and a gaseous phase (hydrogen+methane) is effected at this temperature under diminished pressure, and an apparatus for the accurate analysis of such mixtures on this principle is described in detail. Some methane is occluded by the solid ethane, the quantity being smaller when hydrogen is present, but larger in the absence of hydrogen, since condensation is more rapid in this case. The two fractions obtained in this manner are then separately analysed by oxidation with hot copper oxide, the water and carbon dioxide formed are condensed in liquid air, and the volume of any inert gas is determined. The water is then absorbed by phosphoric oxide and the carbon dioxide collected and measured. From the data thus obtained the composition of the original mixture may be calculated. In the apparatus described the whole determination may be effected in 2 hrs. and the accuracy of the method is proved by analysis of mixtures of known composition. J. W. BAKER.

Diphenylamine and diphenylbenzidine as oxidation–reduction indicators. I. M. KOLTHOFF and L. A. SARVER (J. Amer. Chem. Soc., 1930, 52, 4179—4191).—The velocity of the oxidation of diphenylamine and diphenylbenzidine to diphenylbenzidine-violet by dichromate is accelerated markedly by rise of temperature and increase of acidity, and is approximately proportional to the quantity of dichromate (indicator constant) and to that of indicator (dichromate constant). Mercuric chloride has a large inhibiting effect which is only partly eliminated by ferrous ion. The mechanism suggested for the oxidation (A., 1930, 706) receives further support. In 0·1—2·0*N*-acid, diphenylamine is oxidised quantitatively to diphenylbenzidine if the potassium dichromate is added slowly. The absorption spectra of oxidised diphenylamine and diphenylbenzidine solutions (diphenylbenzidine-violet) are identical; the maxima of the curves are nearly flat between 5400 and 5700 A. and are shifted towards longer wave-lengths by increase of acidity (cf. Thiel, A., 1929, 836). In electrometric titration of diphenylbenzidine-violet to diphenylbenzidine-green with ferrous sulphate, the colour change, violet to green, occurs at a potential of about 0·51 volt with reference to the saturated calomel electrode, independently of hydrogen-ion concentration

and almost independently of temperature. An explanation is offered. J. G. A. GRIFFITHS.

Separation of alkali chlorides, bromides, and iodides; analysis of mixtures. COUSIN and DUFOUR (J. Pharm. Chim., 1930, [viii], **12**, 439—444).—In a solution containing equal quantities of chloride, bromide, and iodide the total halogen is determined by titration with silver nitrate and ammonium thiocyanate. The iodine and bromine are then liberated successively from a second sample by distillation with ferric ammonium sulphate and with acetic acid and lead dioxide, respectively. Mixtures of chlorates, bromates, and iodates are first reduced by zinc dust in boiling neutral solution, or, when the last two only are present, by sulphur dioxide. H. E. F. NOTTON.

Bromo-iodometry. VI. J. H. VAN DER MEULEN (Chem. Weekblad, 1930, **27**, 618—619; cf. A., 1930, 1542).—In mixtures containing bromate, iodate, and iodide the three anions are determined simultaneously by oxidising the iodide with bromine water in presence of carbonate or borate, reducing the excess of bromine, and titrating the iodine liberated on addition of potassium iodide to the acidified solution; bromate and iodate are determined iodometrically in a second portion of the original solution, and in a third portion the bromate is reduced by hydrobromic acid, the iodide being simultaneously oxidised to iodate, and the total iodate is determined. By appropriate manipulation of the results the quantity of each anion may be calculated. H. F. GILLBE.

Rapid detection and determination of fluorine in mineral waters. J. CASARES and R. CASARES Anal. Fís. Quím., 1930, **28**, 1159—1162).—Fluorine in mineral waters may be detected by evaporating 15 c.c. to dryness on the water-bath in a porcelain basin, and adding to the residue solid silver sulphate, powdered glass, and concentrated sulphuric acid; the basin is covered with a glass plate from which is suspended a drop of barium acetate solution acidified with acetic acid, and the crystals of barium fluosilicate are observed under the microscope. The fluorine may be determined colorimetrically after acidification of the solution with hydrochloric acid, with a solution composed of equal volumes of 0·17% sodium alizarin-sulphonate solution and 0·87% zirconium nitrate solution. H. F. GILLBE.

Volumetric determination of active oxygen in mixtures of hydrogen peroxide and persulphuric acid. G. O. LUBARSKY and M. G. DIKOVA.—See B., 1930, 1108.

Optical determination of atmospheric ozone. A. I. DUNINOWSKI (Compt. rend., 1930, **191**, 859—861). By focussing a narrow portion of the solar spectrum on a thermo-element, recording photographically the resulting current, and by means of a clockwork arrangement, energy–wave-length curves are obtained for the whole solar spectrum from 4860 to 12,000 Å. A series of such curves for varying thicknesses of air traversed is obtained, whence the value of Δ in the relation (m=mass of air traversed) is deduced for various wave-lengths. Thence by the method of Cabannes and Dufay (A., 1926, 1080) the equivalent thickness of ozone (at normal temperature and pressure) is determined, without the necessity for the special arrangements required for observations on ultra-violet light. In this way the thickness of ozone at Montpellier in the autumn of 1929 was found to have varied from 0·20 to 0·36 cm. C. A. SILBERRAD.

Colorimetric micro-determination of sulphur in sulphides, sulphates, etc. I. S. LORANT (Z. physiol. Chem., 1930, **193**, 56—58; cf. A., 1930, 181).—Minor improvements in the method are described. J. H. BIRKINSHAW.

Determination of nitrous and nitric acids in concentrated sulphuric acid. H. A. J. PIETERS and M. J. MANNENS.—See B., 1930, 1149.

Reaction of diphenylamine and sulphuric acid with nitrates in the presence of chlorides, with especial reference to its use in the determination of nitrates in arable soil. H. RIEHM.—See B., 1930, 1149.

Analysis of red phosphorus. S. A. TOLKATSCHOV and M. A. PORTNOV.—See B., 1930, 1108.

Determination of phosphorus in aluminium. STEINHÄUSER.—See B., 1930, 1157.

Volumetric determination of the orthophosphate ion. A. DEL CAMPO (Anal. Fís. Quím., 1930, **28**, 1153—1158).—The orthophosphate ion, in dilute acetic acid solution, may be determined by precipitation with a 1% solution of benzidine acetate. To 50—150 c.c. of the solution is added with stirring a slight excess of the reagent; the white precipitate is collected after about 20 min., and washed until the water is but feebly acid. The precipitate is then titrated with $0·1N$-sodium hydroxide, using phenolphthalein as indicator. If there is more than 10% of free acetic acid in the solution during the precipitation low results are obtained. Sulphates interfere, but sucrose is without influence and the method is therefore well suited to the determination of phosphate in pharmaceutical preparations. H. F. GILLBE.

Precipitation and ignition of magnesium ammonium phosphate. J. I. HOFFMAN and G. E. F. LUNDELL (Bur. Stand. J. Res., 1930, **5**, 279—293).—Details of the precipitation and ignition of magnesium ammonium phosphate for the gravimetric determination of phosphorus and of magnesium have been studied, and the procedure recommended in each case is described. The temperature of ignition is of particular importance; for accurate work ignition at 1100° is advisable, since at 1000° constancy of weight is attained only slowly, and at 1200° there is a slow loss of weight. Constancy of weight is more readily obtained in determinations of phosphorus than of magnesium. Data are given relative to the loss of weight of platinum crucibles when heated at various temperatures, for which corrections should be made. H. F. GILLBE.

Cap for holding Gutzeit mercuric chloride papers. T. J. WARD (Analyst, 1930, **55**, 630).—The cap consists of a piece of glass 2 in. square coarsely ground on the lower surface and cemented to a cardboard cylinder. The cap fits loosely over a

flat red rubber bung with one hole over which is placed the mercuric chloride paper; the bung serves to close the upper end of the purifying tube and the gases, after traversing the paper and producing uniformly coloured stains with sharp edges, escape through the interstices of the ground glass surface.

A. R. POWELL.

Volumetric determination of silicic acid in silicates. N. A. TANANAEV and A. K. BABKO.—See B., 1930, 1110.

Micro-determination of potassium in [potable] waters. M. H. GRIFFON and A. BERNARD.—See B., 1930, 1132.

Direct determination of sodium in presence of aluminium and chromium. E. R. CALEY and D. V. SICKMAN (J. Amer. Chem. Soc., 1930, **52**, 4247—4251; cf. Caley and Foulk, A., 1929, 900).—Improved methods for washing the precipitate of magnesium sodium uranyl acetate are described. Aluminium and chromium do not interfere in the determination of sodium, but if the sulphate ion is also present it is desirable to keep the concentration of ammonia low.

J. G. A. GRIFFITHS.

Adsorption indicators for argentometry, together with comparison of their limits of sensitiveness. A. G. BERRY and P. T. DURRANT (Analyst, 1930, **55**, 613—617).—Tartrazine and safranine (or phenosafranine) are shown to be suitable indicators for the titration of chloride or bromide with silver nitrate or *vice versa*. In the first case the precipitate of silver halide is coloured deep yellow as long as an excess of silver ions is present in solution but immediately all the silver is precipitated the solution becomes greenish-yellow and the precipitate assumes its normal colour. With safranine the precipitate is red until the end-point is reached, when it suddenly becomes blue. Lead does not interfere in either case. Proteins interfere only in so far as they have a protective colloid action; addition of strontium nitrate, however, causes flocculation.

A. R. POWELL.

Quantitative precipitation of calcium oxalate in presence of arsenate ion. J. T. DOBBINS and W. M. MEBANE (J. Amer. Chem. Soc., 1930, **52**, 4285—4288).—It is recommended that the calcium solution ($<0{\cdot}1N$) at 90—100° be made slightly alkaline with ammonia and after the addition of excess of ammonium oxalate maintained at about 95° for 10 min. After 1 hr. the precipitate is collected and washed with very dilute ammonia solution. A large excess of ammonia or a lower temperature delays the formation of calcium oxalate.

J. G. A. GRIFFITHS.

Application of the filtration method in volumetric analysis, especially in the analysis of Portland cement. H. T. BUCHERER and F. W. MEIER.—See B., 1930, 1153.

Determination of calcium and magnesium by titration of the same solution. K. L. MALIAROV (J. Russ. Phys. Chem. Soc., 1930, **62**, 1529—1531).—Calcium is precipitated as oxalate, and magnesium as hydroxide; the precipitates are collected and washed together, and heated with a known quantity of $0{\cdot}1N$-sulphuric acid, the excess of which is determined by titration. The calcium oxalate is then treated with 10% sulphuric acid and titrated with 0·05—$0{\cdot}1N$-permanganate solution. This method gives accurate results provided that the joint concentration of calcium and magnesium oxides does not exceed 0·03% in the original solution. R. TRUSZKOWSKI.

Test papers for detecting magnesium. I. STONE (Science, 1930, **72**, 322).—One drop of slightly acid solution is allowed to dry on dry filter-paper which has been treated with 0·01% alcoholic *p*-nitrobenzeneazoresorcinol. In the presence of magnesium a blue spot in a reddish field develops when the paper is immersed in 1% sodium hydroxide solution. The reaction is sensitive to 1 drop of a solution containing 0·1 mg. of magnesium per c.c. L. S. THEOBALD.

Separation of magnesium from sodium and potassium. G. KALIKINSKI (J. Russ. Phys. Chem. Soc., 1930, **62**, 1355—1356).—The solution, after the elimination of barium, strontium, and calcium, may contain magnesium, sodium, and potassium. Ammonia is added, with sufficient ammonium chloride to prevent precipitation, the solution is heated at 30°, and phosphoric acid is added to complete precipitation of magnesium, the reaction being maintained alkaline. The solution is filtered, and the filtrate is evaporated to one third of its original volume, when excess of calcium carbonate is added to remove excess of phosphoric acid. The solution is then filtered, the filtrate evaporated to dryness, and the residue ignited, sodium and potassium being detected by the usual tests in the solution of the residue. R. TRUSZKOWSKI.

Iodometric determination of thallium in cadavers. R. FRIDLI (Magyar Gyo. Tarsas. Ert., 1929, **5**, 479—488; Chem. Zentr., 1930, i, 3470—3471).—Thallous ion in the solution is first oxidised with bromine water and the excess of bromine removed with phenol. Sodium monohydrogen phosphate and phosphoric acid are then added, followed by potassium iodide, and the iodine liberated is treated with $0{\cdot}01N$-sodium thiosulphate. Excess of potassium iodide causes the precipitation of thallous iodide, which may be collected and weighed or reoxidised with chlorine water to iodate and thallic ions which are determined iodometrically. Portions of cadaver are first treated with dilute hydrochloric acid and potassium chlorate; the filtered solution is evaporated, treated with sodium hydroxide, and ashed together with the residue. The ash of the solid matter is extracted several times with dilute sulphuric acid, the solution being used to extract the other ash also. Bromine water is then added to the acid solution and the above method employed.

A. A. ELDRIDGE.

Gravimetric determination of aluminium, chromium, and iron by means of potassium cyanate. B. J. F. DORRINGTON and A. M. WARD (Analyst, 1930, **55**, 625—628).—Precipitation of aluminium hydroxide by boiling neutral aluminium chloride solution gives good results only when the precipitate is collected next day and washed with feebly ammoniacal ammonium nitrate solution; contrary to Ripan's statement (A., 1928, 499) the precipitate is always gelatinous. Chromic and ferric

hydroxides produced in a similar way from slightly acid chloride solutions are, however, granular and filter readily, but the method does not separate these elements from zinc and manganese even in the presence of ammonium chloride, and there is a tendency for a thin film of precipitate to adhere tenaciously to the beaker. A. R. POWELL.

Activity of iron. V. Benzidine reaction. A. SIMON and T. REETZ (Z. anorg. Chem., 1930, **194**, 89—112; cf. A., 1928, 147).—The benzidine reaction for "active" iron may be used in alcoholic solution just as well as in aqueous solution, and is most sensitive at p_H 3·95; in strongly acid or strongly alkaline solutions the reaction is not obtained. The reaction mechanism of ferrous ions with benzidine-blue is quite similar to that of hæmoglobin and complex ferrous salts, the duration of the blue colour being solely a function of the intensity and velocity of reaction. Complex salts, however, have a stabilising effect on the blue colour. Petow and Kosterlitz's method for comparing the activity of iron compounds by determining the amount of benzidine-blue formed (A., 1929, 1486) is to be rejected, since there are always formed at the same time as benzidine-blue brown oxidation products which are not reduced by hydrogen iodide. Satisfactory results can, however, be obtained by determining the amount of unchanged benzidine by precipitating as sulphate and titrating while hot with alkali. R. CUTHILL.

Compound of phosphoric and stannic acids and its precipitation in analysis. A. KRUGER (Z. anal. Chem., 1930, **82**, 62—68).—On boiling with fuming nitric acid a solution of stannous nitrate and an excess of phosphoric acid a voluminous precipitate of *stanniphosphoric acid*, $2SnO_2,P_2O_5,8H_2O$, is obtained. The precipitate is insoluble in nitric acid but readily soluble in alkali hydroxides and ammonia, showing it to be a derivative of α-stannic acid. For the removal of phosphoric acid from a chloride solution the chlorides are converted into nitrates by evaporation with nitric acid and the solution is boiled with nitric acid and stannous nitrate in excess until a syrupy liquor is obtained; on dilution with boiling water all the phosphoric acid separates as stanniphosphoric acid together with most of the excess of tin as metastannic acid. The presence of more than 5% of iron prevents precipitation; in this case the iron should previously be separated by the ether method. A. R. POWELL.

Iodometric determination of vanadium in special steels and in ferrovanadium. W. WERZ. —See B., 1930, 1156.

Electrolytic separation of antimony and copper in hydrochloric acid solution. H. HOLEMANN (Z. anal. Chem., 1930, **81**, 161—207).—The deposition potentials of antimony and copper from chloride solutions are so close together that a satisfactory separation of the two metals by electrolysis is not to be expected. Addition of hydroxylamine or hydrazine hydrochloride makes the deposition potential of both metals more negative; increase in the concentration of hydrochloric acid has the same effect, but to a much greater extent. In either case the addition has a more pronounced effect on the copper potential, so that by varying the acidity etc. of the solution either one or the other metal may be deposited first. Measurements of the deposition potentials of copper and antimony at various temperatures from solutions of several compositions are tabulated. A. R. POWELL.

Analytical chemistry of tantalum, niobium, and their mineral associates. XVIII. Separation of titanium from zirconium and hafnium. A. R. POWELL and W. R. SCHOELLER (Analyst, 1930, **55**, 605—612).—Dittrich and Freund's method (A., 1908, ii, 134) for the separation of zirconia from titania gives fair results in two treatments only by a compensation of errors, some titania being co-precipitated with the zirconia and a corresponding amount of zirconia remaining in solution. An accurate separation may be effected by precipitation of the titania with tannin from a boiling neutral solution of the double oxalates half saturated with ammonium chloride. The mixed oxides obtained from thiosulphate hydrolysis are fused with potassium hydrogen sulphate and the mass is leached with a hot saturated solution of 2—3 g. of ammonium oxalate. The solution is neutralised with dilute ammonia solution, avoiding a permanent turbidity, diluted to 200—250 c.c. with a 15% solution of ammonium chloride, heated to boiling, and treated dropwise with a solution containing tannin equal to twelve times the weight of titania present. The precipitate is collected by suction, using a platinum cone, washed with hot 12% ammonium chloride solution, and ignited to titania. Reprecipitation is advisable when much zirconia is present. The filtrate is made feebly ammoniacal and treated at 100° with more tannin to recover the zirconia, which should be purified by fusion with potassium hydrogen sulphate and subsequent thiosulphate hydrolysis. Alumina and thoria follow the zirconia. A. R. POWELL.

Radiation thermopile design. F. A. FIRESTONE (Rev. Sci. Instr., 1930, [ii], **1**, 630—649).—Existing formulæ for the design of thermopiles for use with a Thomson galvanometer are summarised, and new formulæ for designs to be used with d'Arsonval galvanometers developed. A type of thermopile in which the cold almost entirely surround the hot junctions to reduce drifts is described. The whole fits an evacuated case of 10 mm. edge, and can be used in front of an elliptical mirror, which forms a small hot image. By a slight modification of the spectrometer, a thermopile having adjustable compensation can be used, theoretically eliminating drifts due to temperature changes of the optical parts and surroundings. N. M. BLIGH.

Comparator for spectroscopic work. E. BACKLIN (Rev. Sci. Instr., 1930, [ii], **1**, 662—666).—An improved comparator for use with both eyes, and suitable for measuring small spectral plates, is described. A magnified real image of the object plate is formed on a screen with the aid of a photographic objective. N. M. BLIGH.

Constricted mercury arc. R. H. CRIST (J. Amer. Chem. Soc., 1930, **52**, 4337; cf. Forbes and Harrison, A., 1925, ii, 1194).—The air-cooled quartz capillary lamp described may be used at 4—5·5 amp.

and 20—25 volts per. cm.^{2} for about 30 hrs. and yields a constant high light intensity. J. G. A. GRIFFITHS.

Colorimetry without comparative standards by means of the Bloch leukometer. L. HOCK and H. T. MÜLLER (Z. wiss. Phot., 1930, 29, 262—266).—The leukometer consists of the photometer head of a Marten polarisation photometer fitted with a series of coloured filters which may be interposed to cover the two comparison fields. A calibration curve is prepared for each particular substance to be determined by measuring the percentage of light transmitted by a standard thickness of solutions of known concentration, a suitably coloured light being used by interposition of one of the filters. Fairly accurate results were obtained with nickel sulphate, cobalt nitrate, and copper sulphate solutions by measuring the red light transmission. J. W. GLASSETT.

Measurement of hardness and absorption of *X*-rays by a photographic method. L. GREBE and W. SCHMITZ (Z. wiss. Phot., 1930, 29, 129—133).—A photographic plate is exposed to the *X*-ray source behind an aluminium wedge of known gradation and then, in another part of the plate, given a series of time exposures in the ratio 1 : 2 : 3 etc., which corresponds with a series of intensity exposures varying in the same ratio for a standard time. From the latter series a curve can be plotted from which the intensities corresponding with each density in the wedge exposure may be obtained. By substitution of these values in the absorption law $I/I_0=e^{-\mu d}$ (d being the wedge constant) a series of values for μ, the absorption coefficient, can be obtained for each pair of consecutive steps, and from these values the mean effective wave-length can be calculated. J. W. GLASSETT.

Immersion refractometer. A. DOLINEK.—See B., 1930, 1095.

Double-pole double-throw mercury switch. G. H. DAMON (J. Physical Chem., 1930, 34, 2627—2628).—A mercury switch eliminating the difficulties attendant on the use of the usual knife-edge switch is described. The contact resistance is constant, and a unique feature is the possession of neutral or no contact position. The switch can be used for small or relatively large currents and can be operated automatically. L. S. THEOBALD.

Photographing of cooling curves. H. D. CROCKFORD and A. E. HUGHES (J. Physical Chem., 1930, 34, 2624—2626).—An apparatus for photographing cooling curves is described. The method is accurate to 0·1° and the curves are better than the usual thermometric ones for showing the mechanism of supercooling. L. S. THEOBALD.

Condenser for low-temperature evaporation of water. H. M. EVANS, R. E. CORNISH, and J. C. ATKINSON (J. Amer. Chem. Soc., 1930, 52, 4334—4335).—By means of the arrangement described, 2—3 c.c. per min. of water may be evaporated from biological fluids (700 c.c.) at 7°. The condenser is a 12-litre flask, filled with a mixture of ice and salt, and kept below −10°; the neck of the flask is closed by a stopper pierced by two concentric tubes, the wider of which makes immediate connexion with the "retort" (1- or 2-litre flask) and the other communicates with a large-capacity high-vacuum oil pump by which the condenser and "retort" are evacuated. A slow stream of air bubbles admitted to the "retort" facilitates distillation and assists the maintenance of ice in the biological fluid. Apparatus for larger-scale operations is discussed. J. G. A. GRIFFITHS.

Inorganic lubricants. III. Mixtures of aqueous liquids with non-reacting solids. W. A. BOUGHTON (J. Amer. Chem. Soc., 1930, 52, 4335—4336).—Evaporation of water from such mixtures may be prevented by the use of concentrated aqueous solutions of a deliquescent salt or acid. Of the many mixtures tested, the most successful lubricants consisted of kaolin or graphite with calcium chloride solution. J. G. A. GRIFFITHS.

Short manometer. L. CHUDOZILOV (Z. anal. Chem., 1930, 82, 68—69).—The closed end of the tube is replaced by a stopcock provided with a short bent funnel to facilitate re-filling with mercury. A. R. POWELL.

Extracting liquids which form emulsions. W. WEINBERGER (Amer. J. Pharm., 1930, 102, 594—595).—A review of laboratory methods. H. E. F. NOTTON.

Apparatus for the determination of extraction residues. ANON. (Chem.-Ztg., 1930, 54, 881).—The apparatus comprises a glass-stoppered weighing bottle with a hemispherical bottom supported on three glass legs and provided with an external siphon connecting with the bottom of the hemisphere. The substance to be extracted is placed in a dried and weighed extraction thimble in the tube and, after weighing, the stopper is removed and the tube placed inside a wide glass tube fitting into the neck of a boiling flask and surmounted by a reflux condenser which returns the condensed solvent into the thimble. A. R. POWELL.

Applications of the differential ebullioscope fitted with a condenser. W. SWIENTOSŁAWSKI (Rocz. Chem., 1930, 10, 570—578).—A differential ebullioscope intended for the analysis of liquid reagents and eutectic and azeotropic systems is described, with examples of its use for the determination of the purity of samples of benzene, toluene, etc., and of the water content of an azeotropic mixture of acetone and carbon disulphide. R. TRUSZKOWSKI.

Vacuum tube potentiometer applicable for use with glass electrodes of high resistance. D. DUBOIS (J. Biol. Chem., 1930, 88, 729—741).—A full description, with diagrams, is given of a potentiometer employing a screen grid valve suitable for use in determining p_H values by means of the glass electrode. The plate current is so reduced by lowering the screen grid voltage that it can be carried directly through a sensitive galvanometer. As, when the apparatus is properly adjusted, the grid current is extremely low (less than 5×10^{-15} amp.), there is no drift of glass electrode voltage. Readings can be taken within 5 min. of switching on the batteries and high accuracy is obtainable. W. O. KERMACK.

Corrections for Redwood viscosimeters. G. BARR (J. Sci. Instr., 1930, 7, 359—361).—The equations $\nu=AT-B/T$ and $\nu=A'T'-B'/T'$ are assumed to hold

for the standard Redwood viscosimeter and the instrument to be tested respectively (ν—kinematic viscosity, T, T' times of flow for the usual 50 c.c.). Parallel flow tests are made with two oils, and the results are used in a simple graphic method to estimate the corrections, $T'-T$, which should be applied at several stated values of T. C. A. SILBERRAD.

Oil viscosimeter. H. SCHAFFER.—See B., 1930, 1095.

Micro-balance of new design. G. R. STANBURY and N. TUNSTALL (J. Sci. Instr., 1930, **7**, 344—349).—The essential difference from the ordinary torsion micro-balance lies in the replacement of the wire by a strip of spring steel which can be stretched by a varying tension. C. A. SILBERRAD.

Apparatus for experiments with gases at pressures of 6000 kg. per cm.^{2} J. BASSET (Compt. rend., 1930, **191**, 928—931; cf. A., 1927, 849).—The gas is compressed in a small cylinder by means of a piston, the reaction on which is supported by means of a larger auxiliary piston moving in a larger cylinder and activated by a glycerin pump. The ratio of the surfaces of the two cylinders gives the ratio of the pressures, 500—1000 kg. per cm.^{2} being attainable. Apparatus for continuous experiments with one or more gases at 5000 kg. per cm.^{2} and 1000° is also described; the gases are compressed in two stages and passed through an electrically-heated reaction vessel. J. GRANT.

Platinum resistance thermometry. I. Calibration of the bridge and annealing of the platinum bulb. II. Determination of constants of the platinum bulb and accuracy of resistance thermometry. M. MATSUI and S. KAMBARA (J. Soc. Chem. Ind. Japan, 1930, **33**, 401—403B, 403—407B).—I. Details of the calibration and temperature coefficient determination of a Müller bridge are given. A platinum resistance thermometer was found to vary in resistance after being heated at 400—600° until it had been annealed fourteen times.

II. The error of temperature determinations with the platinum resistance thermometer is discussed and the maximum permissible variations in the quantities measured, in order to obtain a given accuracy, are given for temperatures of from 0° to 1000°. The limit of accuracy is 0·01° up to 500°, and 0·1° at higher temperatures. H. F. GILLBE.

Determination of the m. p. of platinum alloys. L. MÜLLER (Ann. Physik, 1930, [v], **7**, 9—47).—A new method of measuring temperatures above 1500°, applicable especially to m.-p. determinations with metals and alloys, has been developed. Emission from the heated material, between certain limits of the spectrum, is measured with a photo-electric cell, calibrated by means of the emission from a similar substance. The method has been applied to the determination of the liquidus curves of alloys of platinum with rhodium, iridium, tungsten, and chromium, with an error of less than 5°, the pure metals being used for calibration. Series of mixed crystals exist for alloys containing 0 to 100% Rh, 0 to 100% Ir, 0 to 50% W, and 0 to 10—30% Cr. These results have been confirmed by photomicrographs, and by measurements of the electrical conductivity and of the temperature coefficient of the conductivity. H. F. GILLBE.

Determination of the m. p. of chromium by a thermo-element. L. MÜLLER (Ann. Physik, 1930, [v], 7, 48—53).—The method previously described (cf. preceding abstract) is not applicable to the determination of the m. p. of chromium on account of the ease with which the metal oxidises. The m. p. has been determined using an iridium–rhodium/iridium–ruthenium thermo-element, the chromium being melted in a zirconia crucible in a high-frequency furnace; a single observation gave the m. p. as 1805°. This was not confirmed as the apparent m. p. changes owing to interaction between the crucible material and the chromium; the latter also dissolves iridium from the thermo-element. H. F. GILLBE.

Test-tube. A. KUHN (Chem.-Ztg., 1930, **54**, 908).—An unflanged, robust test-tube is preferred. D. F. TWISS.

Geochemistry.

Amount of ozone in the earth's atmosphere, and its relation to other geophysical conditions. IV. G. M. B. DOBSON (Proc. Roy. Soc., 1930, **A**, **129**, 411—433; cf. Dobson, Harrison, and Lawrence, A., 1929, 419).—A year's observations have been made of the distribution of ozone at Arosa (Switzerland), Table Mountain (California), Helwan (Egypt), Kodaikanal (India), and Christchurch (N.Z.). The results are tabulated, and curves are drawn showing the general distribution and annual variations over the greater part of the earth. The low and uniform value of the ozone content throughout the autumn hemisphere is of importance in connexion with the theory of the variation of ozone with pressure conditions. The ozone value in India appears to be unaffected by the setting in of the monsoon. There is fairly clear evidence that the same relationship exists between ozone content and pressure conditions in Egypt and New Zealand as that previously found in N.W. Europe (*loc. cit.*). In Chile and S. India the meteorological conditions are very constant, and no important variations of the ozone value were observed. Reports are submitted by H. H. KIMBALL and E. KIDSON on the relation of variations in the ozone values obtained at Table Mountain to the meteorological conditions, and on the relation between weather and the amount of ozone above Christchurch, respectively. L. L. BIRCUMSHAW.

Carbonates in the sediments of the Lake of Geneva. J. ROMIEUX (Arch. Sci. Phys. Nat., 1930, [v], **12**, 244—254; cf. A., 1930, 1155).—In some samples of the sediments of the lake of Geneva sulphate has been found to the extent of 1% SO_3. The distribution of carbonates depends principally

on material deposited by rivers, then on currents, and thirdly on the action of organisms. The micaceous muds of the Rhone are the poorest in carbonates and the whitish muds of the Petit Lac the richest. In a horizontal section the variations are small provided the deposits are far enough from the shore. The variations in a vertical section are greater in the Petit Lac than in the Grand Lac, increasing with increasing depth in the deposit near the coast and in shallow water; far from the coast and in deep water the reverse is the case. C. W. GIBBY.

Presence of vanadium in Spanish rocks and minerals. S. PINA DE RUBIES (Anal. Fís. Quím., 1930, **28**, 1110—1116).—Vanadium has been detected spectroscopically in a great variety of rocks and minerals, as well as in sea-sand and meteorites. Titanium appears always to be associated with vanadium, and the greater is the titanium content the more pronounced is the vanadium spectrum; rocks free from titanium show no trace of the presence of vanadium. H. F. GILLBE.

Crystals of gold, titanite, and garnet. H. BUTTGENBACH (Bull. Acad. roy. Belg., 1930, [v], **16**, 874—880).—Detailed crystallographic descriptions of gold from Kibali (Congo), titanite from Tavetsh, and of garnet from Ala (Piedmont) are given. C. W. GIBBY.

Tectites of Indo-China. A. LACROIX (Compt. rend., 1930, **191**, 893—899; cf. A., 1929, 288).—The tectites, which are identical in character, are usually found on the surface of the soil mixed with round quartz pebbles and grains of limonite. Samples from three different portions of the belt were also similar in chemical composition (approximately: SiO_2 71, Al_2O_3 13·2, FeO 5, MgO 1·9, CaO 3, Na_2O 1·5, K_2O 2·7, TiO_2 1, MnO 0·15, Fe_2O_3 0·2, free SiO_2 38%; *d* 2·440—2·422). The artificial glass and volcanic hypotheses of origin are dismissed as doubtful, whilst the presence of grains of quartz in the neighbourhood of the tectites, although not in the tectites themselves, suggests decomposition by laterisation, *i.e.*, by the more or less complete elimination of certain elements (silica, alkalies, lime, magnesia) from the silicated rocks and their replacement by others (iron, titanium, aluminium). There is also strong evidence of meteoric origin; they date probably to Pleistocene times, and must certainly have existed before the 7th century. J. GRANT.

"Fibrous lignites" ("fibrous coal") in brown coal and "fibrous coal" in general. W. GOTHAN and BENADE (Braunkohle, 1930, **29**, 274; Fuel, 1930, **9**, 482—488).—Samples of the fibrous lignites which have been known for some time to occur in German brown coals of different localities have been examined microscopically and chemically. They are distinguished by the readiness with which they split into fibres, and by the very tough nature and flexibility of the cells. With few exceptions they are evidently portions of the bark bast of conifers, the rows of bast cells of which, when the specimens fall to pieces, are weathered and split off in the form of very thin bast lamellæ, so that the general appearance is often almost like that of tow. The cork portions of the bark may also exhibit a similar state of preservation. The remarkable toughness and flexibility of the cells is probably due to the large amount of cellulose, more than 30%, still left in the material. These true fibrous coals should be distinguished from fusain, which yields splinters and not fibres. A. B. MANNING.

Occurrence of resin in Ruhr coals. E. HOFFMANN and H. KIRCHBERG (Brennstoff-Chem., 1930, **11**, 389—394).—Numerous resin inclusions one or more mm. in thickness and 5—20 cm. long have been found in the coal seams of the Brassert mine, and have been examined chemically and microscopically. From their occurrence it may be concluded at once that the coal has never been subjected to any considerable rise of temperature. The resins are sparingly soluble in alcohol, but readily soluble in warm benzene. Under the microscope they have a streaky appearance, and in transmitted light exhibit an irregular net-like structure. The frequent occurrence of particles of fusain in the resins is regarded as supporting the "forest fire" theory of the origin of fusain. The microstructure of the resins is discussed from the viewpoint of colloid chemistry; the original colloidal material must have undergone a differential coagulation or coacervation (cf. de Jong and Kruyt, A., 1930, 158) to produce the observed structure. A similar theory is applied to other banded coal constituents. A. B. MANNING.

Organic Chemistry.

Effect of electrical discharge on gaseous hydrocarbons. V. Condensation of hydrocarbons by electrical discharge. Comparison with condensation by α-rays. S. C. LIND and B. GLOCKLER (J. Amer. Chem. Soc., 1930, **52**, 4450—4461).—When methane, propane, butane, and ethylene are submitted to a silent discharge in an ozoniser, the condensations taking place are similar in all respects to those caused by α-rays (A., 1926, 1077). The results previously obtained (A., 1927, 1039) with ethane are confirmed. The mechanisms of the reactions are discussed. H. BURTON.

Production of liquid hydrocarbons from propylene. A. MAILHE and RENAUDIE (Compt. rend., 1930, **191**, 851—854).—When ethylene is passed over silica gel at 700° (A., 1930, 1157) the production of a deposit of carbon is due to the presence of metallic iron. When this is removed the liquid products, consisting, besides ethylenic hydrocarbons, chiefly of benzene and toluene, are obtained in high yields, methane and its homologues being produced only in small quantities. Some naphthalene and anthracene have been isolated from the tar. When propylene is passed over silica gel at 650° under similar

conditions there are formed a liquid condensate, which contains low-boiling olefines together with aromatic hydrocarbons, and a tar in which toluene, *m*-xylene, naphthalene, and anthracene have been detected.

T. H. MORTON.

Auto-oxidation of pentenes. J. HYMAN and C. R. WAGNER (J. Amer. Chem. Soc., 1930, **52**, 4345—4349).—Oxidation of Δ^{α}- and Δ^{β}-pentenes, β- and γ-methyl-Δ^{α}-butenes, and β-methyl-Δ^{β}-butene with oxygen in presence of cobalt oleate as a catalyst in the dark at 15° shows that a double linking in the αβ-position is the least readily oxidised; the amount of oxidation is determined by the liberation of iodine from potassium iodide by the peroxidic oxygen. Δ^{α}-Pentene, prepared from allyl bromide and magnesium ethyl bromide, has b. p. 30° (corr.) (cf. Kirrmann, A., 1926, 934; Norris and Joubert, A., 1927, 440); an unsaturated hydrocarbon, b. p. 20—24°, is formed as a by-product. H. BURTON.

Pyrolysis of allene and propinene. R. N. MEINERT and C. D. HURD (J. Amer. Chem. Soc., 1930, **52**, 4540—4549).—The gases are decomposed by passing through pyrex glass tubes at about 1—2 c.c. per sec. The main reaction with allene at 500° is polymerisation; 80% of the allene reacts when the contact time is 86 sec. and 90% of the products formed consist of liquid polymerides which are essentially the same as those obtained by Lebedev (A., 1913, i, 1285). Reaction proceeds very slowly below 500°, but at 600° (contact time 50 sec.) there is a marked increase in the amount of gaseous products formed; these consist of hydrogen, methane, ethane, ethylene, and small amounts of acetylenes. There is no indication of the formation of aromatic hydrocarbons.

The optimum yield of liquid products obtained from propinene is at 575° and a contact time of 48 sec.; the liquids formed resemble those from allene. At 650°, increased amounts of hydrogen, ethylene, and methane are produced. Pure propinene, prepared from sodium acetylide and methyl sulphate, undergoes pyrolysis at 555°/74·5 sec. yielding some allene, which may be an intermediate in the pyrolysis of propinene. The name "keteno-ynol" is suggested for the tautomeric change CH⋮CMe ⟵ C(CH$_2$)$_2$.

H. BURTON.

Preparation of substituted acetylenic hydrocarbons. R. TRUCHET (Compt. rend., 1930, **191**, 854—856).—The interaction of a sodium derivative of an acetylenic hydrocarbon and an ester of benzene- or *p*-toluene-sulphonic acid gives 45—60% of the theoretical yield: CR⋮CNa+Ph·SO$_3$R′=CR⋮CR′+Ph·SO$_3$Na. The reaction is complete in 3 hrs. at 80°. In this way there are obtained: Δ^{γ}-*noninene*, b. p. 155—157°, d^{20} 0·763, n_D^{20} 1·429, from ethyl *p*-toluenesulphonate and Δ^{α}-heptinene; Δ^{γ}-*decinene*, b. p. 175—176°, d^{21} 0·765, n_D^{21} 1·433, from ethyl benzenesulphonate and Δ^{α}-octinene; Δ^{ϵ}-*undecinene*, b. p. 195—196°, d^{20} 0·785, n_D^{20} 1·437, from butyl benzenesulphonate and Δ^{α}-heptinene; and the *hydrocarbon* C_5H_{11}·C⋮C·CH$_2$·CH⋮CH$_2$, b. p. 74·5—75·5°/12 mm., d 0·788, n_D^{20} 1·445, from allyl benzenesulphonate and Δ^{α}-heptinene. T. H. MORTON.

Preparation of anhydrous alcohol and the detection and determination of water in alcohol. F. ADICKES [with W. BRUNNERT and O. LUCKER] (Ber., 1930, **63** [*B*], 2753—2760).—The process consists in dissolving sodium in the alcohol, addition of ethyl formate, and boiling the mixture under a reflux condenser until carbon monoxide ceases to be evolved: H·CO$_2$Et+NaOEt+H$_2$O=2EtOH+H·CO$_2$Na and H·CO$_2$Et=CO+EtOH. The product is distilled, the final portion of the distillate being rejected. The alcohol thus prepared contains 0·03% of water and 0·00015% of ethyl formate. For the detection of water, an ethoxide–ester solution (about 50 c.c. of alcohol, 1 g. of sodium, and 10 g. of ester preserved in an Erlenmeyer flask until subsidence is complete) is filtered into the alcohol; if more than 0·013% of water is contained therein, a precipitate of sodium formate is produced at 0°. Gravimetric determination of water is effected by means of the sodium formate produced. If 2·5—3·0% of water is present, this can be effected directly, since the slight solubility of the salt is unimportant. With a smaller proportion of water, the alcohol and undecomposed ester are distilled from the sodium formate and excess of sodium ethoxide, finally in a vacuum. With very small amounts of water the acid or water content of the ester must be taken into account. The weight of sodium formate is determined from that of the mercurous chloride which it forms by reduction of mercuric chloride; the method is not applicable in presence of alcohol, which slowly reduces mercuric chloride. With larger amounts, the oxidimetric–volumetric process is applicable. If the alcohol contains more than 4—5% of water it must be mixed with a suitable proportion of absolute alcohol of known water content.

A gas-volumetric method, based on the measurement of the carbon monoxide evolved from the unused ethyl formate, is described; it is sufficiently accurate only with alcohol containing at least 1% of water. H. WREN.

Decomposition of ethylene glycol in presence of catalysts. I. Vanadium pentoxide as catalyst. N. L. DRAKE and T. B. SMITH (J. Amer. Chem. Soc., 1930, **52**, 4558—4566).—When ethylene glycol vapour is passed over vanadium pentoxide at 250—400°, the main decomposition products are acetaldehyde and ethylene; small amounts of carbon oxides and acetic acid (from the acetaldehyde) are also formed. At temperatures up to about 320°, ethylene is the major product; the minimum amount of ethylene is found at about 360°, at which temperature aldehyde formation is at a maximum. Considerable reduction of the vanadium pentoxide occurs during the decomposition. The use of the partly reduced oxide causes a considerable variation in the proportions of the decomposition products.

H. BURTON.

Derivatives of propylene glycol. A. DEWAEL (Bull. Soc. chim. Belg., 1930, **39**, 395—401).—α-Chloro*iso*propyl alcohol (propylene α-chlorohydrin) and methyl sulphate react at 100° affording a mixture of *methyl α-chloro*iso*propyl ether*, b. p. 103—104°/760 mm., d_4^{20} 1·009, n_D^{20} 1·41372, and *di-α-chloro*iso*propyl ether*, b. p. 187—188°/761 mm., d_4^{20} 1·103, n_D^{20} 1·45046. The last-named ether is converted by treatment with potassium acetate and a little acetic acid into *di-α-*

acetoxyisopropyl ether, b. p. 248°/761 mm., d_4^{20} 1·050, n_D^{20} 1·42654. Propylene α-chlorohydrin and ethyl sulphate give *ethyl α-chloroisopropyl ether*, b. p. 117°/760 mm., d_4^{20} 0·9965, 1·41902, also obtained from allyl chloride, alcohol, and sulphuric acid. Treatment of propylene oxide with an alcohol and a small amount of sulphuric acid furnishes *propylene glycol α-alkyl ethers*, of which the following are described: *ethyl*, b. p. 136°, d_4^{20} 0·9028, n_D^{20} 1·4 (*acetate*, b. p. 158—160°, d_4^{20} 0·9461, n_D^{20} 1·40968); *methyl*, b. p. 126—127°/760 mm., d_4^{20} 0·9260, n_D^{20} 1·40696 (*acetate*, b. p. 147°/762 mm., d_4^{20} 0·9709, n_D^{20} 1·40449); iso*propyl*, b. p. 142—143°/765 mm., d_4^{20} 0·9059, and *β-chloropropyl ethers*, b. p. 204—205°/762 mm., d_4^{20} 1·059. Ethyl α-chloro*iso*propyl ether and potassium acetate in presence of small amounts of acetic acid and potassium iodide afford *β-ethoxypropyl acetate*, b. p. 160—161°, d_4^{20} 1·025, hydrolysed by concentrated potassium hydroxide solution to *propylene glycol β-ethyl ether*, b. p. 140—141°/761 mm., d_4^{20} 0·9044, n_D^{20} 1·41223. *β-Chloropropyl butyrate* has b. p. 184°/741 mm., d_4^{20} 1·031, n_D^{20} 1·42875. Propylene glycol diacetate, b. p. 190—191°/762 mm., d_4^{20} 1·059, n_D^{20} 1·4173, prepared from propylene dibromide and potassium acetate or by acetylation of the glycol, when saturated with hydrogen chloride (or bromide) gives a mixture of chloro(or bromo)propyl acetates. H. BURTON.

New form of two enantiomorphous rhamnitols. F. VALENTIN (Coll. Czech. Chem. Comm., 1930, **2**, 689—696).—Reduction of rhamnose with 3% sodium amalgam and crystallisation of the product from water gives l-*rhamnitol trihydrate*, m. p. 69°, $[\alpha]_D$ +8·83° in water, dehydrated at 100° in a vacuum to *l*-rhamnitol, m. p. 123°, $[\alpha]_D$ +12·4°. d-*Rhamnitol trihydrate* has m. p. 69°, $[\alpha]_D$ −8·89° in water, whilst r-*rhamnitol*, prepared by crystallising equal quantities of the enantiomorphs from water, has m. p. 117° and is anhydrous. Crystallographic data for the *d*- and *l*-rhamnitol trihydrates are given; the crystals exhibit enantiomorphous facets. C. W. SHOPPEE.

Pentachloromethyl ether. I. RABCEWICZ-ZUBKOWSKI and S. CHWALINSKI (Rocz. Chem., 1930, **10**, 686—689).—*Pentachloromethyl ether*, b. p. 158·5—159·5°, $d^{17·3}$ 1·6496, n_D 1·4825, is prepared by chlorinating *s*-dichloromethyl ether under the influence of ultra-violet light. When heated with water it decomposes to yield carbon monoxide and dioxide, hydrogen chloride, and hexachloroethane, whilst with aqueous aniline the product is *s*-diphenylcarbamide. R. TRUSZKOWSKI.

"Ring contraction" during the formation of internal ethers (oxides) from glycols. αε-Oxidododecane from dodecane-αμ-diol. A. FRANKE and A. KROUPA (Monatsh., 1930, **56**, 331—346; cf. A., 1923, i, 530; 1929, 1422).—ακ-Dibromodecane is converted by aqueous alcoholic potassium cyanide into the dinitrile of decamethylene-ακ-dicarboxylic acid and the methyl ester of this is reduced by sodium and alcohol to dodecane-αμ-diol (57% yield), also obtained in 21% yield from trioxymethylene and the Grignard reagent from ακ-dibromodecane. Treatment of this diol with 50% sulphuric acid and distillation with superheated (180°) steam yields *αε-oxidododecane*, b. p. 235—237°, in 22% of the theoretical amount. This is oxidised by 1% potassium permanganate solution at 50° mainly to succinic and octoic acids; similar oxidation of the diol affords no fatty acids. αε-Oxidodecane (*loc. cit.*) is also obtained when decane-ακ-diol is heated with 89% phosphoric acid to 200°. H. BURTON.

Unsaponifiable matter from oils of elasmobranch fish. VII. Synthesis of α-glyceryl ethers and its bearing on the structure of batyl, selachyl, and chimyl alcohols. G. G. DAVIES, I. M. HEILBRON, and W. M. OWENS (J.C.S., 1930, 2542—2546).—The following *alkyl α-glyceryl ethers* are prepared from α-monochlorohydrin and the requisite sodium alkoxide: α-ethyl, b. p. 118—121°/21 mm. (*diphenylcarbimide* derivative, m. p. 103—104°); *α-propyl*, b. p. 118—122°/15 mm., d_4^{18} 1·074, n_D^{18} 1·4400 (*diphenylcarbimide* derivative, m. p. 116°); and *α-butyl*, b. p. 138—140°/22 mm., d_4^{18} 1·002, n_D^{18} 1·4463 (*diphenylcarbimide* derivative, m. p. 94—95°). Higher alkyl α-glyceryl ethers could not be prepared by this method or from sodium glyceroxide and the alkyl chloride. Sodium allyloxide and cetyl chloride in allyl alcohol give *cetyl allyl ether*, m. p. 25°, oxidised by hydrogen peroxide in acetic acid to *α-cetyl glyceryl ether*, m. p. 64—65° (*diphenylcarbimide* derivative, m. p. 93—94°). This ether appeared to be identical with a specimen of chimyl alcohol (cf. Toyama, A., 1924, i, 604; 1925, i, 4) isolated from a Japanese shark liver-oil, but it is stated that the chimyl alcohol is a mixture of batyl alcohol and an unidentified substance. *Octadecyl allyl ether*, m. p. 27·5—28·5°, is converted similarly into *α-octadecyl glyceryl ether*, m. p. 70—71° (*diphenylcarbimide* drivative, m. p. 95—96°), which is not identical with batyl alcohol (A., 1928, 616). This alcohol must, therefore, be β-octadecyl glyceryl ether. Since selachyl alcohol is hydrogenated to batyl alcohol, it must, by analogy, be β-oleyl glyceryl ether. H. BURTON.

Dipentaerythritol [di-γ-hydroxydi-ββ-hydroxymethylpropyl ether]. W. FRIEDERICH and W. BRÜN (Ber., 1930, **63**, [*B*], 2681—2690).—Pentaerythritol, obtained by the condensation of acetaldehyde with formaldehyde in presence of alkali hydroxide, contains dipentaerythritol, from which it cannot be separated by crystallisation. Nitration of the crude product affords a mixture of pentaerythritol tetranitrate and *dipentaerythritol hexanitrate*, m. p. 75°, d^{15} 1·630 or 1·617 after fusion, which can be separated from one another by means of acetone. Hydrolysis of the hexanitrate by zinc and hydrochloric acid or, preferably, with alkaline sodium sulphide gives *dipentaerythritol*, $O[CH_2{\cdot}C(CH_2{\cdot}OH)_3]_2$, m. p. 221°. Homogeneous pentaerythritol has m. p. 260°. Examination of the f.-p. curves of pentaerythritol and dipentaerythritol shows that the technical "pure" alcohol, m. p. 235°, contains 10% of the ether. The m.-p. curve of mixtures of tetranitroerythritol and hexanitrodipentaerythritol is given. *Dipentaerythritol hexaformate*, m. p. 56°, from the ether and boiling concentrated formic acid, *hexaacetate*, m. p. 73°, prepared by use of acetic anhydride and sodium acetate, and *hexabenzoate*, m. p. 183°, according to Schotten–Baumann, are described.

With triphenylmethyl chloride in pyridine, *dipentaerythritol hexatriphenylmethyl ether*, m. p. 173°, is prepared in 97·3% yield. Attempts to increase the yield of dipentaerythritol from acetaldehyde and formaldehyde by use of potassium, barium, lead, or zinc hydroxides or sodium carbonate were unsuccessful and conversion of pentaerythritol into the ether could not be effected by prolonged ebullition with sodium or calcium hydroxide, sodium or calcium formate, or potassium carbonate, or by heating alone or in presence of water at 300°. Condensation of mixtures of glyceraldehyde and dihydroxyacetone does not give a crystalline product. Pentaerythritol is obtained in 64% yield from crotonaldehyde and formaldehyde (1 : 8) in presence of 1 mol. of calcium oxide or in 63·5% yield from acraldehyde and formaldehyde (1 : 3) in presence of 0·5 mol. of calcium hydroxide. The purest specimens of pentaerythritol, m. p. 258°, are obtained in 73·5% yield from acetaldehyde and formaldehyde (1 : 5), whereas those containing most dipentaerythritol (15%) are derived from the aldehydes in the ratio 1 : 3 in presence of 0·5 mol. of calcium hydroxide.

The constitution of dipentaerythritol is established as follows. The formate decomposes almost quantitatively at 270° into carbon monoxide and dipentaerythritol, thus resembling pentaerythritol tetraformate. Oxidation of dipentaerythritol with nitric acid (*d* 1·13) gives a polymerisation product of diglycollaldehyde $O(CH_2{\cdot}CHO)_2$, hydrolysed by 20% sulphuric acid to diglycollaldehyde, isolated as the phenylhydrazone, m. p. 123°. Pure pentaerythritol under similar conditions is not oxidised to an aldehyde, the previous observation of which is due to the presence of dipentaerythritol in the mixture. The action of hydrobromic acid or hydriodic acid (*d* 1·7) on dipentaerythritol does not give crystalline products, whereas hydriodic acid, red phosphorus, and acetic anhydride give a *dipentaerythritol di-iodohydrin*, $C_{10}H_{20}O_5I_2$, m. p. 106—107°. With hydriodic acid (*d* 3·0) in presence of a little red phosphorus and acetic anhydride at 140° α-iodo-αα-di-iodomethylpropane, m. p. 154°, is produced, hydrolysed to pentaglycerol, m. p. 191·5°. H. WREN.

Structure of synthetic mixed triglycerides. R. BHATTACHARYA and T. P. HILDITCH (Proc. Roy. Soc., 1930, **A**, **129**, 468—476; cf. Collin and Hilditch, A., 1930, 260).—Mixtures of saturated (lauric, palmitic, or stearic) and unsaturated (85% of oleic and 15% of linoleic) fatty acids have been esterified with about 85% of the theoretical amount of glycerol and 0·5% of naphthalene-2-sulphonic acid at 135—145°/about 1 mm. for 6 hrs. The product is examined by the acetone–permanganate process. Under these conditions the whole of the glycerol retained in the product was in the form of triglycerides. A smooth curve was obtained by plotting the molecular proportion of fully-saturated glycerides in the synthetic fats against the molecular percentage of saturated acids present in the mixture of fatty acids esterified. The corresponding values for a number of animal fats and vegetable pericarp fats tend to follow, although they are not coincident with the experimental curve; the animal fats contain as a rule rather more, the pericarp fats rather less, fully-saturated glycerides than the synthetic fats for a given ratio of saturated to unsaturated fatty acids. Vegetable seed fats, on the other hand, are assembled on entirely different principles, the glyceride structure being determined by a tendency to " even distribution " of the fatty acids amongst the glycerol molecules.

L. L. BIRCUMSHAW.

Hexosemonophosphates. Dextrose 3-phosphate, dextrose 6-phosphate, and their bearing on the structure of Robison's ester. P. A. LEVENE and A. L. RAYMOND (J. Biol. Chem., 1930, **89**, 479—499).—Di*iso*propylideneglucose was treated with phosphoryl chloride and pyridine at a low temperature and the crude product was partly hydrolysed with hydrochloric acid; the resulting hexosemonophosphate, $[\alpha]_D$ +39·5° (*brucine* salt, $[\alpha]_D$ −42·3° in pyridine; *barium* salt, $[\alpha]_D^{27}$ +26·5°), forms both a stable and an unstable methylglucoside; the aldonic acid prepared from it by oxidation with hypoiodite forms 1 : 4 and 1 : 5 lactones. The previously-suggested structure of dextrose 3-phosphate (A., 1929, 1278) for this ester is therefore confirmed. Treatment of *iso*propylideneglucose with phosphoryl chloride and pyridine followed by partial hydrolysis afforded *dextrose 6-phosphate*, $[\alpha]^{25}$ +25·9° [*brucine* salt, $[\alpha]_D^{25}$ −49·3° in pyridine; *barium* salt, $[\alpha]^{25}$ +13·0° in water; *phenylosazone*, m. p. 151—152°, $[\alpha]_D$ −31·4° (equilibrium in pyridine–alcohol)]. When hydrolysed with intestinal phosphatase both the dextrose 3-phosphate and the hexosemonophosphate of Robison (A., 1923, i, 86) give dextrose (isolated as glucosazone). Differences in the rates of fermentation of these esters and in the physical properties of their derivatives, however, preclude their identity (cf. King and Morgan, Chem. and Ind., 1929, 296). On the other hand, the dextrose 6-phosphate is fermented at the same rate as Robison's ester, but differs from the latter in the m. p. of the phenylosazone. This last discrepancy may be due to insufficient purity of Robison's ester. C. R. HARINGTON.

Decomposition of mercaptans in alkali solutions. E. C. BILLHEIMER and E. E. REID (J. Amer. Chem. Soc., 1930, **52**, 4338—4344).—When aliphatic mercaptans are heated with sodium hydroxide solution at 250—270°, decomposition occurs in the following ways: $SHR + 2NaOH = R{\cdot}OH + Na_2S + H_2O$; $2SHR + 2NaOH = SR_2 + Na_2S + 2H_2O$; $SH{\cdot}CH_2{\cdot}CH_2R + 2NaOH = CH_2{:}CHR + Na_2S + 2H_2O$. The amount of *n*-butyl mercaptan decomposed at 260° increases almost as a linear function of the normality of the alkali, and is 50% with 3*N*-sodium hydroxide after 2 hrs. Under these conditions the amount of *n*- and *sec.*-alkyl mercaptans reacting decreases gradually with increasing number of carbon atoms; the values for the *sec.*-compounds are, however, somewhat higher than those for the *n*-derivatives. The amount of dialkyl sulphide produced is usually of the order of 5 and 10% for the *sec.*- and *n*-mercaptans, respectively. The decompositions are carried out in an apparatus similar to that described by Herndon and Reid (A., 1929, 46). H. BURTON.

Oxidation of sulphides by perbenzoic acid. IV. β-Chloroethyl β-chlorovinyl sulphide and

β-chloroethyl α-chlorovinyl sulphide. L. N. Levin and J. Tschulkov (J. pr. Chem., 1930, [ii], **128**, 171—179).—β-Chloroethyl β-chlorovinyl (I) and β-chloroethyl α-chlorovinyl (II) sulphides (Lawson and Dawson, A., 1928, 153) have b. p. 99°/4 mm. and 92°/4 mm., respectively (*loc. cit.*, 77—77·7°/4 mm. and 69·5—70·5°/4 mm.; values recorded for d_4^{20} and n agree with Lawson and Dawson's, *loc. cit.*). I and II have been oxidised by means of the perbenzoic acid method previously described (cf. A., 1928, 505, 999; 1930, 1161).

β-*Chloroethyl* α-*chlorovinyl sulphoxide* (from II) has b. p. 104°/6 mm., d_4^{20} 1·4068, n^{20} 1·5511; the corresponding *sulphone* (from II or, better, from the sulphoxide) has b. p. 108—109°/2—2·5 mm. (slight decomp.), d_4^{20} 1·4366, 1·5238. β-*Chloroethyl* β-*chlorovinyl sulphoxide*, d_4^{20} 1·3924, n^{20} 1·5416 (prepared similarly from I), cannot be distilled at 4 mm. without decomposition; it solidifies at −14° to −16°; the *sulphone* has b. p. 125—127°/2 mm., d_4^{20} 1·4384, n^{20} 1·5306 (by-products, two crystalline *substances*, m. p. 109—111° and decomp. 160°). R. Child.

Organic sulphonic and sulphinic acids. J. von Braun and K. Weissbach (Ber., 1930, **63**, [*B*], 2836—2847).—The action of phosphorus pentachloride on benzenesulphonethylamide at 100° proceeds sluggishly, leading to a difficultly-separable mixture of non-crystalline products in which chlorination has occurred partly outside the $\cdot SO_2\cdot NH\cdot$ group. With similar compounds which do not contain an aromatic group reaction occurs less readily than with the amides of non-aromatic carboxylic acids, but, without use of extreme measures, leads to the production of the expected compounds $R'\cdot S(:O)Cl:NR''$. These are stable towards heat and retain chlorine so firmly that they react only very slowly with water and alcohol and not with amines. With excess of phosphorus pentachloride and under more drastic conditions they yield substances, $R'\cdot SCl_3:NR''$, in which two of the chlorine atoms are so mobile that they are removed by cold water. The unexpected behaviour of the chloride is explicable on the supposition that the sulphonamides contain the ring $:S\overset{O}{\frown}N\cdot$; measurements of the parachor afford no evidence, since the customary parachor constants do not apply with these substances. The amides of the sulphinic acids are converted by phosphorus pentachloride into liquid chloro-compounds which cannot be distilled without decomposition in a high vacuum, react violently with water, and thus completely resemble the imido-chlorides of carboxylic acids.

Non-aromatic sulphinic acids undergo disproportionation when heated into sulphonic acids and thiosulphonic esters, $2R\cdot SO_2H + R\cdot SO_2H = R\cdot SO_2\cdot SR + R\cdot SO_3H + H_2O$. The sulphinic acid molecule which undergoes oxidation can be replaced by thiol compounds ($2R\cdot SO_2H + 2HSR' = R\cdot SO_2\cdot SR + 2H_2O + R'S\cdot SR'$), but not by pyrocatechol or quinol. Sulphinic esters and chlorides are relatively stable, but with the last-named substance the role of oxygen acceptor can be played by sodium mercaptides or, more conveniently, by salts of dithiocarbamic acid, $2NR_2\cdot CS\cdot SH,NHR_2 + 2R'\cdot SOCl = NR_2\cdot CS\cdot S\cdot S\cdot CS\cdot NR_2 + 2NHR_2,HCl + R'\cdot SO_2\cdot SR'$. With chlorothiols reaction occurs according to the scheme $2NR_2\cdot CS\cdot SH,NHR_2 + 2R'SCl = NR_2\cdot CS\cdot S\cdot S\cdot CS\cdot NR_2 + 2NHR_2,HCl + R'S\cdot SR'$.

The following compounds are described: *butyl* n-*butylthiosulphonate*, b. p. 126—128°/0·2 mm.; n-*butylsulphonic acid*, b. p. 145°/0·2 mm.; n-*butylsulphinyl chloride*, b. p. 38°/0·1 mm., 78°/12 mm., transformed by dry air into n-*butylsulphonyl chloride*, b. p. 90°/11 mm.; *ethyl* n-*butylsulphinate*, b. p. 85°/13 mm.; n-*butylsulphinethylamide*, b. p. 108—110°/10 mm.; iso*amyl* iso*amylthiosulphonate*, b. p. 176—180°/13 mm.; iso*amylsulphonic acid*, b. p. 176—178°/0·2 mm.; iso*amylsulphinyl chloride*, b. p. 60—62°/0·1 mm., 91—92°/13 mm.; *ethyl* iso*amylsulphinate*, b. p. 98°/13 mm.; iso*amylsulphinethylamide*, b. p. 120°/high vac.; cyclo*hexylsulphinic acid monohydrate*, m. p. 33—35°, completely decomposed by distillation in a high vacuum; cyclo*hexyl* cyclo*hexylthiosulphonate*, b. p. 184—186°/0·1 mm.; cyclo*hexylsulphonic acid*, b. p. 178—180°/0·1 mm. [monohydrate, m. p. 92° (cf. Borsche and Lange, A., 1905, i, 765)]; n-*butylsulphonethylamide*, b. p. 120—122°/0·1 mm., and the corresponding chloride, $Bu^{\alpha}\cdot ClS\overset{O}{\frown}NEt$, b. p. 124—126°/0·2 mm.; iso*amylsulphonethylamide*, b. p. 130—132°/0·2 mm., and the *chloride* $C_7H_{16}ONSCl$, b. p. 128—130°/0·3 mm.; cyclo*hexylsulphonethylamide*, b. p. 183—185°/18 mm., m. p. 72°, and the corresponding *chloride*, b. p. 131—132°/0·7 mm., m. p. 73—74°, converted by more drastic treatment with phosphorus pentachloride into the *substance* $C_8H_{15}NCl_4S$, b. p. 140—150°/1 mm., from which the *compound* $C_8H_{15}ONCl_2S$, m. p. 156°, is derived by the action of water. cyclo*Hexylsulphonpropylamide*, m. p. 78°, and cyclo*hexylsulphon*-n-*heptylamide*, m. p. 72°, are attacked with difficulty by phosphorus pentachloride. H. Wren.

Methanetrisulphonic acid. H. J. Backer [with R. H. Klaassens] (Rec. trav. chim., 1930, **49**, 1107—1117).—The following methods, described in the literature, for the preparation of methanetrisulphonic acid have been re-investigated: (1) sulphonation of methionic (methanedisulphonic) acid with sulphur trioxide in a sealed tube at 170°; (2) sulphonation of acetanilide (Bagnall, J.C.S., 1899, **75**, 278), a similar result being obtained by sulphonation of succinanilide; (3) oxidation of thiolmethanetrisulphonic acid with bromine (A., 1930, 1556); (4) the action of potassium sulphite on potassium nitromethionate (solubility in water at 25° 1·6; *strychnine* $+3·5H_2O$, *sodium*, and *thallous* salts; free *acid* $+2H_2O$), which is prepared by the action of potassium sulphite on chloropicrin in aqueous solution at 80°, and (5) by the action of potassium hydrogen sulphite (as potassium pyrosulphite) on potassium diazomethionate in aqueous solution at 60° (cf. Fantl and Fisch, *ibid.*, 320). Methods 3 and 5 are to be preferred, the former giving a 90% yield. The following salts of methanetrisulphonic acid $+2·5H_2O$, m. p. 156°, are described: potassium $+H_2O$ (solubility in water at 25°, 1·126; crystallographic data), *thallous* $+H_2O$ (crystallographic data); *silver* $+H_2O$; *barium* $+9H_2O$ (solubility in water at 25°, 0·107); *calcium* $+12H_2O$, and *lanthanum* $+6H_2O$, and the *potassium barium*, $CHO_9S_3KBa,3H_2O$, salt $+3H_2O$, the last-named being obtained by addition of a hot, concentrated solution of barium chloride to a hot, saturated solution of

potassium methanetrisulphonate. Potassium diazomethionate is decomposed by water in accordance with the scheme $N_2C(SO_3K)_2+H_2O \longrightarrow CH(OH)(SO_3K)_2+N_2 \longrightarrow KHSO_3+SO_3K\cdot CH{:}O$; $SO_3K\cdot CH{:}O+H_2O \longrightarrow KHSO_3+H\cdot CO_2H$, the potassium hydrogen sulphite reacting with more diazomethionate to give potassium methanetrisulphonate. Concentrated hydrochloric acid at 0° converts potassium diazomethionate into potassium chloromethanetrisulphonate with evolution of nitrogen. J. W. BAKER.

Solubility of ethylenic stereoisomerides in solvents themselves ethylenic stereoisomerides. I. LEBRUN (Bull. Soc. chim. Belg., 1930, **39**, 423—433).—The solubilities of maleic, fumaric, citraconic, mesaconic, crotonic, *iso*crotonic, β-chlorocrotonic, β-chloro*iso*crotonic, oleic, elaidic, and cinnamic acids in *cis*- and *trans*-dichloroethylenes, *cis*- and *trans*-β-bromo-Δ^{β}-butenes, ethyl β-chloro*iso*crotonate, crotononitrile, and *iso*crotononitrile have been determined at 0—50°. β-Chloro*iso*crotonic, oleic, *iso*crotonic, citraconic, and maleic acids are more soluble in all the solvents than their isomerides; they are the more fusible isomerides. H. BURTON.

Unsaturation phenomena of acetylenic acids and esters. III. Constitution of mercury derivatives. W. W. MYDDLETON, A. W. BARRETT, and J. H. SEAGER (J. Amer. Chem. Soc., 1930, **52**, 4405—4411).—The triacetoxymercuri-derivatives obtained by the action of mercuric acetate on acetylenic compounds containing the $\cdot C{:}CH$ group are probably best represented as $\cdot C(O\cdot HgOAc){:}C(HgOAc)_2$. Treatment of these compounds with hydrochloric acid affords methyl ketones, formed through the enol, $\cdot C(OH){:}CH_2$, whilst the action of bromine in chloroform at 40° affords tribromomethyl ketones, viz., $\cdot C(OBr){:}CBr_2 \longrightarrow \cdot CBr(OBr)\cdot CBr_3 \xrightarrow{-Br_2} \cdot CO\cdot CBr_3$. Thus, the *triacetoxymercuri*-derivative of Δ^{α}-heptinene furnishes methyl *n*-amyl ketone and *tribromomethyl* n-*amyl ketone*, b. p. 120°/0·5 mm.; the *triacetoxymercuri*-derivative of Δ^{α}-octinene affords methyl *n*-hexyl ketone and *tribromomethyl* n-*hexyl ketone*, b. p. 137°/0·5 mm.; the *triacetoxymercuri*-derivative of phenylacetylene gives acetophenone, and the *triacetoxymercuri*-derivative of Δ^{ι}-undecinoic acid yields (with chlorine) *κκκ-trichloro-ι-ketoundecoic acid*. The last-named compound decomposes on attempted distillation and is reduced by aqueous-alcoholic hydriodic acid to (probably) the corresponding dichloroketo-acid.

The diacetoxymercuri-derivatives obtained from acetylenes containing the $\cdot C{:}C\cdot$ group are probably best represented as $\cdot C(O\cdot HgOAc){:}C(HgOAc)\cdot$. These are converted by treatment with hydrochloric acid and halogens into keto-derivatives and monohalogenoketo-derivatives, respectively. Thus, the diacetoxymercuri-derivatives of stearolic and behenolic acids are converted into *θ-chloro-* and *-bromo-ι-ketostearic acids* and *μ-chloro-* and *-bromo-ξ-ketobehenic acids*, respectively. The *diacetoxymercuri*-derivative from methyl Δ^{α}-noninoate is converted by hydrochloric acid into methyl β-ketononoate, b. p. 137·5°/28 mm., which is shown by Meyer's method (A., 1911, i, 832) to contain 13·5% of the enol form; the action of bromine causes the formation of a *methyl dibromoketononoate*, b. p. 169°/14 mm. Phenylpropiolic acid yields a *diacetoxymercuri*-derivative convertible into acetophenone and ωωω-tribromoacetophenone (?ωω-dibromoacetophenone). The formation of the dibromo-compounds in these cases probably occurs thus: $\cdot C(O\cdot HgOAc){:}C(HgOAc)\cdot \longrightarrow \cdot C(OBr){:}CBr\cdot \longrightarrow \cdot CBr(OBr)\cdot CBr_2\cdot \xrightarrow{-Br_2} \cdot CO\cdot CBr_2$.
H. BURTON.

Synthesis of nervonic acid. J. B. HALE, W. H. LYCAN, and R. ADAMS (J. Amer. Chem. Soc., 1930, **52**, 4536—4539).—Treatment of erucyl alcohol with phosphorus tribromide in toluene, first at −5° and then at 100°, affords erucyl bromide, b. p. 203—207°/1 mm., which reacts with ethyl sodiomalonate, forming *ethyl erucylmalonate*, b. p. 203—207°/0·001 mm. The corresponding acid decomposes when heated at 175° into a mixture of cis-, m. p. 39—39·5°, and trans-*erucylacetic* (Δ^{ξ}-*tetracosenoic*) *acids*, m. p. 61°; the former of these is identical with the nervonic acid of Klenk (A., 1927, 691). The *cis*-acid is converted into the *trans*-modification when it is melted over nitric acid containing a small amount of nitrous acid. Both isomerides are reduced catalytically (Adams) in alcohol to tetracosoic acid, m. p. 83—84°. Similar reduction of *ethyl* Δ^{ξ}-*tetracosenoate*, b. p. 233—234°/1 mm., affords ethyl tetracosoate, m. p. 55—56° (corr.). H. BURTON.

Transformation of pyruvic acid as a function of time and temperature. M. GARINO, G. BALLETTO, F. DE THIERRY, and C. BECCHI (Gazzetta, 1930, **60**, 592—605).—The published physical data for pyruvic acid vary considerably, and earlier experiments (A., 1923, i, 11, 23, 24) showed that the yields of derivatives prepared from the acid are increased if the acid used is of recent preparation. Numerous fractional distillations of the freshly-prepared acid yield ultimately an acid, m. p. 13·62°, showing 100% purity on titration. Its electrolytic dissociation constant K is 0·00593 and its dilute solutions conduct normally. At about 0° the solid acid is stable, but when kept at 10°, with repeated fusion and recrystallisation, it undergoes change, its electrical conductivity becoming irregular and its m. p. lower, although for some time its titratable acidity remains constant. At 25° the m. p. falls markedly in 24 hrs., owing apparently to the formation of the condensation product, $CO_2H\cdot CO\cdot CH_2\cdot CMe(OH)\cdot CO_2H$, but its acidimetric value remains unchanged; in 20—25 days, it begins to undergo a series of more complex alterations, becoming uncrystallisable and losing about 11% of its titratable acidity and yielding a fluorescent compound not yet identified. In contact with dry air, it gives rise to carbon dioxide. At 40° these changes are accelerated, and contact of the acid with moist air still further accelerates them and sometimes introduces complications into the process of decomposition.
T. H. POPE.

Halogenated derivatives of pyruvic acid. M. GARINO, A. CERESOTO, M. BERNI, and M. BRAMBILLA (Gazzetta, 1930, **60**, 582—592; cf. A., 1923, i, 11, 23, 24).—Chlorine replaces one hydrogen atom of pyruvic acid readily and a second with difficulty, whilst it has

not been found possible to replace the third. Bromine replaces either two or three of the hydrogen atoms. Iodine immediately replaces all three hydrogen atoms.

Chloropyruvic acid in anhydrous crystals remains unchanged below 15° and the freshly-prepared acid forms highly dilute solutions without undergoing hydrolysis, but these gradually decompose with formation of hydrogen chloride and carbon dioxide, probably according to the scheme: $2CH_2Cl\cdot CO\cdot CO_2H =$ $CH_2Cl\cdot C(OH)(CO_2H)\cdot CHCl\cdot CO\cdot CO_2H \xrightarrow{-H_2O}$ $\begin{matrix}CO\cdot CHCl\\CO\cdot O\text{---}\end{matrix}\!\!>C(CH_2Cl)\cdot CO_2H \xrightarrow{+H_2O}$ $\begin{matrix}CO\cdot CHCl\\CO\cdot O\text{---}\end{matrix}\!\!>C(CH_2\cdot OH)\cdot CO_2H + HCl \longrightarrow$ $\begin{matrix}CCl\text{—}CH(OH)\\C(CO_2H)\cdot CH_2\end{matrix}\!\!>O$. Its dissociation constant has the value 0·00626. Dichloropyruvic acid is unstable when freshly crystallised, but if kept dry at 10—12° for 10—15 days it becomes more stable and may then be repeatedly crystallised at 20—25° without great loss; its dissociation constant is 0·0078. Dibromopyruvic acid, dissociation constant 0·1527, is moderately stable, but gradually undergoes change in the solid or dissolved state (cf. Grimaux, A., 1874, 887). Chlorobromopyruvic acid, dissociation constant 0·01076, has properties intermediate between those of the dichloro- and dibromo-acids. Tribromopyruvic acid (cf. Grimaux, *loc. cit.*) readily undergoes hydrolysis and above 60—65° is decomposed by water, to form bromoform and oxalic acid. *Chlorodibromopyruvic acid* decomposes without melting and, in aqueous solution, forms chlorodibromomethane at about 80° and lachrymogenic substances at higher temperatures. Dichlorobromopyruvic acid (cf. Hantzsch, A., 1890, 132) melts indefinitely owing to decomposition and becomes more stable if kept, as crystals, in a fairly dry atmosphere. T. H. POPE.

Preparation of δ-ketonic esters. (MLLE.) S. GRATEAU (Compt. rend., 1930, **191**, 947—949).—The chloride of ethyl hydrogen adipate reacts with benzene in presence of aluminium chloride, forming 80% of the theoretical amount of ethyl δ-benzoylvalerate, b. p. 164°/3 mm. This is reduced by the Clemmensen method to ethyl ε-phenylhexoate, b. p. 162—164°/12 mm. [free acid, b. p. 186—188°/11 mm., m. p. 11 (anilide, m. p. 80°; *p*-toluidide, m. p. 78°)]. H. BURTON.

Bacterial oxidation of oxalates. R. SCHOLDER and C. F. LINSTROM (Ber., 1930, **63**, [*B*], 2730—2737).—The titre of 0·01*N*-sodium oxalate solutions is diminished greatly but somewhat irregularly on exposure to air. The effect is independent of light and the material of the vessel. Since under similar conditions the concentration of sterile solutions remains unchanged, the effect is due to micro-organisms gained from the air. The preparation of cultures from the deposit in an extensively decomposed solution is described, but the pure culture thus obtained does not contain the bacteria responsible for the action. The oxalate is decomposed according to the equation $Na_2C_2O_4 + H_2O + O = 2NaHCO_3$. In an atmosphere of nitrogen or carbon dioxide the change does not occur. Formate, carbon monoxide, or hydrogen peroxide could not be detected. Sterilisation of solutions by addition of sulphuric acid is not effective unless exposure to bright light is avoided. Mercuric chloride sterilises solutions preserved in brown glass. Sterilised aqueous suspensions of the oxalates of barium, strontium, calcium, zinc, cadmium, manganese, cobalt, or nickel after addition of culture or deposit from a decomposed sodium oxalate solution generally contain carbonate after some months. Copper, mercury, and silver oxalates act bactericidally and remain free from carbonate. An apparatus for the determination of small amounts of carbon dioxide is described. H. WREN.

Partial replacement of the oxalate residue in oxalato-anions of bivalent metals. II. R. SCHOLDER and C. F. LINSTROM (Ber., 1930, **63**, [*B*], 2828—2831; cf. A., 1927, 854).—The compounds are usually prepared by addition of the oxalate of the heavy metal to hot, very concentrated solutions of potassium nitrite, thiocyanate, or thiosulphate. In contrast to the simple oxalato-compounds of bivalent metals, the mixed-complex substances dissolve transitorily in cold water, but the sparingly soluble oxalate separates more or less rapidly from the cold solution; decomposition occurs instantaneously in hot solution. The following *salts* are described: $[Mn(C_2O_4)(NO_2)_2]K_2,H_2O$; $[Zn(C_2O_4)_2]K_2,[Zn(C_2O_4)(NO_2)(H_2O)]K,5H_2O$; $[Mn(C_2O_4)_2]K_2,[Mn(C_2O_4)(CNS)_2]K_2$; $[Zn(C_2O_4)_2]K_2[Zn(C_2O_4)(CNS)(H_2O)]K,5H_2O$; $[Co(C_2O_4)(S_2O_3)]K_2$; $[Mn(C_2O_4)(S_2O_3)]K_2,H_2O$; $[Zn(C_2O_4)_2]K_2$. H. WREN.

Auto-complex formation with oxalates of bivalent, heavy metals. III. Preparation of lead oxalate hydrate; determination of solubility and conductivity of manganese oxalate. R. SCHOLDER and C. F. LINSTROM (Ber., 1930, **63**, [*B*], 2831—2835; cf. A., 1927, 855).—*Lead oxalate dihydrate* is prepared by mixing dilute solutions of lead nitrate and ammonium oxalate at 0°, slowly and with thorough agitation, and preserving the mixture for at least 12 hrs. It loses its water of crystallisation when exposed to air at the ordinary temperature. Its existence tends to explain the abnormal conductivity of saturated and dilute solutions of lead oxalate. Manganese oxalate dihydrate is prepared from manganese chloride and ammonium oxalate in boiling aqueous solution, whereas at 0° the trihydrate is obtained. The solubilities of the di- and tri-hydrate in water at 18° are respectively 0·270 and 0·537 g. per litre. The equivalent conductivity of the two hydrates changes abnormally with increasing dilution. The two curves coincide within the limits of experimental error, showing that the hydrates have the same complex arrangement in solution. H. WREN.

"Superfluous" isomerides. IV. Supposed existence of isomerides of cyclic oxalic esters. E. BERGMANN and H. A. WOLFF (J. pr. Chem., 1930, [ii], **128**, 229—232; cf. A., 1930, 902, 912).—Ethylene oxalate, $O\!<\!\begin{matrix}CO\text{—}CO\\CH_2\cdot CH_2\end{matrix}\!>\!O$ (I) (from methyl or ethyl oxalate and ethylene glycol), has m. p. 143° (cf. Bischoff and Walden, A., 1895, i, 17). The alleged isomeride, m. p. 162°, of Tilitschéev (A., 1923, i, 1173) is

probably identical with *methyl β-hydroxyethyl oxalate*, m. p. 166° (obtained by the interaction of ethylene glycol and methoxalyl chloride), which on distillation in a vacuum is converted into I. R. CHILD.

Preparation of α-alkylpimelic acids from αε-oxido-decane and -dodecane. A. FRANKE and A. KROUPA (Monatsh., 1930, 56, 347—357).—αε-Dibromodecane, b. p. 146—147°/9 mm., prepared from αε-oxidodecane and hydrobromic acid at 100° (cf. A., 1929, 1422), is converted by aqueous-alcoholic potassium cyanide into the corresponding *dinitrile*, b. p. 185—189°/9 mm., which when hydrolysed with aqueous-alcoholic potassium hydroxide solution affords impure α-amylpimelic acid together with *α-amylpimelamic acid*, m. p. 149·5°. The last-named acid is hydrolysed by concentrated potassium hydroxide solution to *α-amylpimelic acid*, m. p. 68° (*amide*, m. p. 186°). αε-Oxidododecane (this vol., 62) is converted as above into *αε-dibromododecane*, b. p. 171°/9 mm., and thence into the corresponding *dinitrile*, b. p. 203—204°/9 mm., which is hydrolysed to *α-heptylpimelamic* and *α-heptylpimelic acids*, m. p. 150·3° and 75°, respectively. H. BURTON.

Course of addition of sodium enol alkylmalonates to αβ-unsaturated esters. A. MICHAEL and J. ROSS (J. Amer. Chem. Soc., 1930, 52, 4598—4609).—Ethyl crotonate and ethyl methylmalonate react in presence of ether containing $\frac{1}{6}$ mol. of sodium ethoxide, forming mainly *ethyl β-methylbutane-αγγ-tricarboxylate*, b. p. 160°/9 mm., also obtained from ethyl sodio-β-methylpropane-αγγ-tricarboxylate and methyl iodide. When the initial condensation is effected with 1 mol. of sodium ethoxide, a 60% yield of *ethyl β-methylbutane-ααγ-tricarboxylate*, b. p. 148—150°/3 mm. (free *acid*, m. p. 145°), is obtained; the same ester is also produced from ethyl tiglate and ethyl sodiomalonate. Methylation of this affords *ethyl γ-methylpentane-ββδ-tricarboxylate*, b. p. 164°/3 mm. (the free *acid*, an oil, when heated, gives *cis*- and *trans*-αβγ-trimethylglutaric acids), whilst similar treatment of its isomeride causes fission to ethyl crotonate and sodiomethylmalonate. When ethyl β-methylbutane-αγγ-tricarboxylate is treated with sodium ethoxide in ether about 50% is isomerised to ethyl β-methylbutane-ααγ-tricarboxylate; the remainder undergoes fission as above. Ethyl tiglate and ethyl sodiocyanoacetate afford ethyl γ-cyano-αβ-dimethylglutarate, methylated to *ethyl γ-cyano-αβγ-trimethylglutarate*, b. p. 160°/2 mm. Conversion of this nitrile into the corresponding tricarboxylic acid, an oil (lit. m. p. 144—145°), and thermal decomposition of this yields a mixture of trans- (oily) and cis-*αβγ-trimethylglutaric acids*, m. p. 125° after softening at 115° (*anhydride*; *imide*, m. p. 90°) (cf. Ray, A., 1928, 394). *β-Methylpropane-αγγ-tricarboxylic acid*

Ethyl methylmalonate condenses with ethyl cinnamate in ether containing 0·2 mol. of sodium ethoxide, furnishing *ethyl β-phenylbutane-αγγ-tricarboxylate*, b. p. 194—195°/3 mm. [the free *acid* exists in two forms, m. p. 148° (labile) and 188°], also produced by methylation of ethyl β-phenylpropane-αγγ-tricarboxylate, b. p. 187°/4 mm. (free *acid*, m. p. 137°). In presence of 1 mol. of sodium ethoxide the above condensation gives *ethyl β-phenylbutane-ααγ-tricarboxylate*, b. p. 185—188°/3 mm. (the free *acid* exists in two forms, m. p. 145° and 171°). Ethyl sodiocyanoacetate and ethyl α-methylcinnamate furnish *ethyl γ-cyano-β-phenyl-α-methylglutarate*, b. p. 185—187°/3 mm., hydrolysed by potassium hydroxide solution to the above β-phenylbutane-ααγ-tricarboxylic acids.

These results confirm Thorpe's explanation (J.C.S., 1900, 77, 923) of the course of the addition of ethyl sodio-cyanoacetate and -α-cyanopropionate to αβ-unsaturated esters. H. BURTON.

Composition and structure of mesquite gum. E. ANDERSON and L. OTIS (J. Amer. Chem. Soc., 1930, 52, 4461—4470; cf. B., 1927, 152).—The gum is shown to consist of a salt of a complex acid, *M* 1222, [α] +70·8°, derived from 4 mols. of *l*-arabinose, 3 mols. of *d*-galactose, 1 mol. of *d*-glycuronic acid, and 1 mol. of methyl alcohol by loss of 8 mols. of water; the acid is obtained pure by acidification of an aqueous solution of the gum with hydrochloric acid and repeated precipitation of the acid from its aqueous solution by alcohol. Hydrolysis of the gum with 3% sulphuric acid at 80° for 11 hrs. affords *l*-arabinose, *d*-galactose, and a mixture of methoxydi- and methoxytri-galactosidoglycuronic acids (purified through the *calcium* salts, [α] +16·8° and +38·5°, respectively). The methoxy-group is attached to the acid and not to the sugar residue. Oxidation of the above calcium salts with barium hypoiodite solution gives the corresponding dibasic acids (*calcium* salts, [α] +2·7° and +12·8°, respectively). More prolonged hydrolysis of the gum with 3% sulphuric acid affords, in addition to the above products, a methoxygalactosidoglycuronic acid (*calcium* salt). A structural formula for the complex acid is given. H. BURTON.

Cobalt complexes of thiolacetic acid. L. MICHAELIS and M. P. SCHUBERT (J. Amer. Chem. Soc., 1930, 52, 4418—4426).—When cobalt chloride (1 mol.) is treated with potassium thiolacetate (2 mols.) in alkaline phosphate buffer solutions in absence of oxygen, a green complex is produced. This is oxidised readily to a brown *substance*, $[Co(S{\cdot}CH_2{\cdot}CO_2)_2KH]_2O,5H_2O$, formed as the result of the uptake of 0·5 atom of oxygen per atom of cobalt. Treatment of this with barium chloride solution furnishes the *complex* $Ba[Co(S{\cdot}CH_2{\cdot}CO_2)_2H]_2O,5H_2O$, whilst acidification with hydrochloric acid affords the *complex* $KH[Co(S{\cdot}CH_2{\cdot}CO_2)_2H]_2O,4H_2O$, converted by further acidification into the *substance* $[Co(S{\cdot}CH_2{\cdot}CO_2H)_2]_2O,3{\cdot}5H_2O$. Various structures are suggested for the above complexes. H. BURTON.

α-Oxidation of acetaldehyde and the mechanism of the oxidation of lactic acid. J. B. CONANT and C. O. TONGBERG (J. Biol. Chem., 1930, 88, 701—708).—The main products identified in the oxidation of acetaldehyde by ceric sulphate in dilute acid solutions at 80° are formic acid, carbon dioxide, glyoxylic acid, and glycollaldehyde. When lactic acid is oxidised by ceric sulphate under similar conditions acetaldehyde is formed, but if the acetaldehyde is not allowed to escape from the acid mixture, formic acid, formaldehyde, glyoxylic acid, and glycollaldehyde may be identified. It appears that acetaldehyde is

an intermediate in the oxidation of lactic acid in this reaction. The bearing of these results on the oxidation of lactic acid and acetaldehyde in living tissue is discussed. W. O. KERMACK.

Production of solutions of methylglyoxal. E. HOFMANN and C. NEUBERG (Biochem. Z., 1930, **226**. 489—491; cf. A., 1930, 1409).—When oximinoacetone, in aqueous solution, is oxidised first at 0—3°, then at the ordinary temperature, and finally at 30—40° with an equimolecular amount of nitrosylsulphuric acid, unchanged material being then removed by extraction with ether, a solution containing methylglyoxal and sulphuric acid is obtained. When this solution is distilled at 140—150° with occasional addition of water the distillate is an aqueous solution of methylglyoxal. The yield is 56·5% of the theoretical. W. MCCARTNEY.

Cracking of acetone under pressure and in presence of zinc chloride. V. N. IPATIEV, A. PETROV, and I. IVANOV (Ber., 1930. **63**, [*B*], 2806—2812; cf. A., 1927, 449, 1172).—Acetone is heated at 300—320° under pressure in the presence of zinc chloride, whereby a very complex mixture of hydrocarbons, b. p. 40—340°, is obtained which is freed from oxygenated compounds by repeated distillation over metallic sodium. Unsaturated hydrocarbons in the mixture are determined by the iodine value, also by treatment with 80% and 100% sulphuric acid. Aromatic hydrocarbons are determined by nitration and by treatment with fuming sulphuric acid. Unsaturated hydrocarbons and mesitylene predominate in the product, whereas naphthenes are present only in minor amount. In the "light petroleum" fraction the unsaturated hydrocarbons belong to the ethylenic series and in the "kerosene" fraction they are polymerised products of diethylenic hydrocarbons and secondary compounds derived therefrom. Attempts to separate the unsaturated hydrocarbons from one another by means of mercuric acetate were unsuccessful; the more volatile portions yield mercury compounds volatile with steam, but partly decomposed during the process, and are also somewhat oxidised by the reagent. The olefines have mainly the *iso*-structure. The question of the structure of the hydrocarbons of the fraction of b. p. 200—300° is provisionally left open. H. WREN.

Polymerisation and condensation. VI. αβ-Dihydroxyhexan-ε-one. P. A. LEVENE and A. WALTI (J. Biol. Chem., 1930, **88**, 771—790).—αβ-Dihydroxyhexan-ε-one, b. p. 120°/0·3 mm., d^{25} 1·118, n^{25} 1·4673, $[M]_D$ 32·81, appears to be a mixture of open-chain and cyclic forms. When the compound is treated with acetic anhydride and pyridine a *diacetyl* derivative is obtained, b. p. 112—114°/0·6 mm. (*semicarbazone*, m. p. 112° decomp.), which predominantly exists in the open-chain form. Treatment of αβ-dihydroxyhexan-ε-one with dry methyl alcohol containing 0·5% of hydrogen chloride yields a *methyl* derivative, b. p. 66—69°/1·5 mm., d^{25} 1·0614, n^{25} 1·4496, apparently possessing the ring structure and giving a *monoacetyl* derivative, b. p. 102—104°/16 mm.; it may be further methylated with silver oxide and methyl iodide to yield *dimethoxycyclohexan-ε-one*, b. p. 74°/17 mm., d^{25} 0·9922, n^{25} 1·4302. A viscous residue the composition of which corresponded with an anhydrodihydroxyhexan-ε-one was also obtained from the methylation; this when acetylated gave a non-distillable product, the analysis of which corresponded with *hydroxyacetoxyanhydrohexan-ε-one*. When redistilled dihydroxyhexan-ε-one is preserved at 25° or sometimes even at 0° more than 50% may be converted into a *compound*, b. p. 175—180°/0·3—0·4 mm., possessing the composition of a *dihydroxyhexoyldihydroxyhexanone*, $C_{12}H_{22}O_5$ (*diacetyl* derivative, b. p. 170—180°/0·2—0·3 mm.), which when treated with dry methyl alcohol containing 0·5% of hydrogen chloride is apparently hydrolysed with the formation of dihydroxymethyl*cyclo*hexan-ε-one, b. p. 101—103°/15 mm. When dihydroxyhexan-ε-one is allowed to polymerise at 155° in presence of sulphuric acid as catalyst (Hibbert and Timm, A., 1924, i, 16) the product $(C_6H_{10}O_2)_x$ yields a *monoacetate*, $(C_8H_{12}O_3)_x$, and therefore cannot have the formula postulated by Hibbert and Timm, which contains no free hydroxyl group. When αβ-dihydroxyhexan-ε-one is heated intermittently at 150° for 9 hrs. an *anhydride*, $C_6H_{10}O_2$, b. p. 40°/20 mm., 55°/42 mm., d^{25} 1·0423, n^{25} 1·4356, parachor 259·2, apparently containing two oxygen bridges, results. If the condensation product is acetylated before distillation a *monoacetyl* derivative, b. p. 58°/2 mm., d_4^{25} 1·0575, n^{25} 1·4490, parachor 352·6, is obtained probably containing a double linking and an oxygen bridge. Further, when acetylanhydro-αβ-dihydroxyhexan-ε-one is hydrogenated in presence of Adams' catalyst it absorbs 1 mol. of hydrogen to form a *compound*, $C_8H_{14}O_3$, b. p. 95°/12 mm. The hard brown resin sometimes obtained on heating αβ-dihydroxyhexan-ε-one intermittently at 150° for 10½ hrs. lost only water at 230° under reduced pressure to yield a solid *polymerised anhydrodihydroxyhexan-ε-one*, $(C_6H_{10}O_2)_x$, which when acetylated yielded an *acetyl* derivative, $(C_8H_{12}O_3)_x$, indicating that the hydroxyl group of the anhydride is not involved in the polymerisation. The substance $(C_6H_{10}O_2)_x$ is unchanged by 0·5% of hydrogen chloride at the ordinary temperature and on refluxing is methylated only to the extent of one methyl group to five groups of the ketone. In presence of Adams' catalyst it absorbed 1 mol. of gas for every 7 mols. of anhydride. It is therefore probable that the double linking is involved in the polymerisation. The conclusion of Hibbert and Timm (*loc. cit.*) that polymerised αβ-dihydroxyhexan-ε-one is analogous to the polymerisation of hexoses to form polysaccharides is adversely criticised. When the solid polymeric anhydride was heated in a bath at 230—290°/high vac., a small quantity of yellow viscous distillate, $(C_6H_{10}O_2)_x$, b. p. 130—180°/0·5 mm., was obtained which yielded an ill-defined monoacetyl derivative, $(C_8H_{12}O_3)_x$. When freshly-distilled αβ-dihydroxyhexan-ε-one in acetic acid solution is reduced by hydrogen in presence of Adams' catalyst, a *compound*, $C_6H_{12}O_2$, b. p. 70—73°/14 mm. (*monoacetyl* derivative, $C_8H_{14}O_3$, b. p. 88°/13 mm., d^{25} 1·0175, n^{25} 1·4321), is formed, the most probable structure of which is that of a tetrahydrofuran or a tetrahydropyran derivative.

W. O. KERMACK.

Osazonogenic groups. E. VOTOCEK (Coll. Czech. Chem. Comm., 1930, **2**, 681—688).—The following groups by treatment with phenylhydrazine under ordinary conditions yield osazones: $\cdot CO\cdot CH_2Cl$, $\cdot CO\cdot CHCl\cdot$. $\cdot CO\cdot CHCl_2$ (cf. Nastvogel, A., 1889, i, 237), and chloroacetaldehyde, chloroacetone, and α-monochlorodiethyl ketone give respectively the osazones of glyoxal, methylglyoxal, and acetylpropionyl. The corresponding reaction with $\cdot CO\cdot CH_2\cdot NH_2$ or $\cdot CO\cdot CH(NH_2)\cdot$ is prevented by alkylation, and no osazone could be obtained from diethylaminoacetone. The known replacement in oximes by treatment with phenylhydrazine $\cdot C{:}NOH \longrightarrow \cdot C{:}N\cdot NHPh$ also occurs with glyoximes, dimethylglyoxime giving the osazone of diacetyl. Oximes and semicarbazones of reducing sugars with phenylhydrazine yield osazones under the same conditions as the free sugars. α-Ketol ethers and tertiary α-ketols do not give osazones. Secondary α-ketols, $\cdot CO\cdot CH(OH)\cdot$, react readily with secondary hydrazines, $NRR'\cdot NH_2$, to form osazones; thus acetoin with phenylmethyl-, phenylbenzyl-, and diphenyl-hydrazine gives *diacetylphenylmethylosazone*, m. p. 96—97°, *diacetylphenylbenzylosazone*, m. p. 110—111°, both also obtained from diacetyl, and *diacetyldiphenylosazone*, m. p. 187°. C. W. SHOPPEE.

Synthesis of a methoxyketose. E. F. HERSANT and W. H. LINNELL (Nature, 1930, **126**, 844).—A 5-methoxyketose has been prepared by the condensation of dihydroxyacetone and α-methoxyglyceraldehyde. The method of synthesis proves the position of the methoxyl group, and such a structure cannot form a furan ring. The *acetal* of α-methoxyglyceraldehyde has been obtained as a colourless liquid, b. p. 100—102°/6 mm. Osazones considered to be r-5-*monomethoxyfructosazone*, m. p. 183° and r-5-*monomethoxysorbosazone*, m. p. 130°, have been prepared. Experiments which show that the synthesised 5-methoxyhexose and its derivatives have properties similar to those of the methylated derivatives of normal fructose and that the hexose is the racemic form of 5-monomethoxyfructose are described. Normal fructose and its derivatives cannot possess a furanose structure and the accepted pyranose constitution is supported. L. S. THEOBALD.

Alcoholysis of αγ-diketones and β-ketonic esters. W. M. KUTZ and H. ADKINS (J. Amer. Chem. Soc., 1930, **52**, 4391—4399).—When a mixture of sodium ethoxide (0·5 mol.) and ethyl acetate (6 mols.) is boiled for 10—96 hrs., approximately the same amount of ethyl acetoacetate is produced as that remaining when ethyl acetoacetate (0·5 mol.) is heated with alcohol (0·5 mol.), sodium ethoxide (0·5 mol.), and ethyl acetate (6 mols.). Attempts to obtain similar equalities in the synthesis and alcoholysis of αγ-diketones have been unsuccessful owing to the non-homogeneous reaction conditions.

The rates of alcoholysis of diacetyl-, diacetylethyl-, benzoylacetyl-, diacetylbenzyl(?)-, benzoylacetylbenzyl-, and dibenzyldiacetyl-methane, ethyl acetoacetate, ethyl ethyl-, benzyl-, diethyl-, and dibenzylacetoacetate have been measured in alcohol containing varying amounts of sodium ethoxide at 60°. The esters undergo slower alcoholysis than the diketones for a given ratio ethoxide : reactant. The rates for both esters and diketones are increased by introducing ethyl or benzyl groups into the molecule (on the carbon atom between the carbonyl groups). The rates of alcoholysis of diacetyl- and dibenzoyl-methanes are approximately the same; these are increased by 100% when the ratio ethoxide : diketone is changed from 1 : 5 to 1 : 2. The order of increasing reactivity of the above αγ-diketones towards sodium ethoxide is as quoted; this is the reverse order of their reactivity towards alcoholic hydrogen chloride (A., 1930, 1273), except in the case of benzoylacetylmethane. These results support Bradley and Robinson's hypothesis that alkaline fission of diketones occurs through the keto-form. H. BURTON.

Action of methylglyoxal on acetoacetic acid. II. M. HENZE and R. MÜLLER (Z. physiol. Chem., 1930, **193**, 88—96; cf. A., 1930, 1022).—Hexan-γ-ol-βε-dione exists in two modifications, b. p. 113·5°/12 mm. and m. p. 95°. When oxidised by alkaline hypobromite, it yields bromoform and malic acid. Derivatives were obtained: di-*p*-bromophenylhydrazone, m. p. 181°; *p-di-p-nitrophenylhydrazone*, m. p. 198°, dehydrated by boiling nitrobenzene to form a *pyrazole* compound, $C_{18}H_{18}O_4N_6$, m. p. 254°; *disemicarbazone*, $C_8H_{16}O_3N_6$, m. p. 210° (*anhydride*, m. p. 254°, decomp.). J. H. BIRKINSHAW.

Dextrose and the structure of the cycloses. A. L. PATTERSON (Nature, 1930, **126**, 880—881).—The assumption that the cycloses and their methyl derivatives have their origin in dextrose or at least are closely related to it structurally is discussed. L. S. THEOBALD.

Carbazole reaction for carbohydrates and related compounds. J. S. HEPBURN and M. LAZARCHICK (Amer. J. Pharm., 1930, **102**, 560—564).—The colours given under standard conditions by 1 c.c. of 1—0·0001% solutions of typical monosaccharides, disaccharides, polysaccharides, glucosides, and hydroxy-acids with 0·1 c.c. of 0·5% alcoholic carbazole and 2 or 4 c.c. of sulphuric acid (cf. Dische, A., 1927, 1213) are tabulated. The limiting concentration at which a positive reaction is obtained varies from 0·01% with maltose and β-hydroxybutyric acid to 0·0001% with salicin and calcium gluconate, and both the sensitivity and the colour obtained sometimes vary considerably with slight changes in technique. The reaction forms a useful general test, but none of the compounds examined gives a sufficiently characteristic colour to permit its identification. H. E. F. NOTTON.

Sugar anhydrides. II. Action of trimethylamine on acetobromo-*l*-rhamnose. F. MICHEEL and H. MICHEEL (Ber., 1930, **63**, [*B*], 2862—2866; cf. A., 1929, 543).—Acetobromo-*l*-rhamnose is slowly converted by trimethylamine in alcohol and benzene into *diacetylrhamnose anhydride*, $C_{10}H_{14}O_6$, m. p. 124—125°, $[\alpha]_D$ −21° in chloroform, which reduces boiling Fehling's solution slowly, very rapidly after hydrolysis by acids, and is stable towards bromine and permanganate. Under apparently identical conditions, β-triacetylrhamnose, m. p. 108—115°, $[\alpha]_D^{18}$ −26·7° in chloroform, is sometimes the main product of the reaction. A strongly-reducing syrup is always

formed as by-product. Formation of the anhydride appears to be preceded by loss of acetyl bromide from acetobromorhamnose, since, in benzene solution, the unstable additive *compound*, $CH_3 \cdot COBr,NMe_3$, m. p. about 100° (decomp.), is precipitated. H. WREN.

Composition of Salkovski's araban. C. L. BUTLER and L. H. CRETCHER (J. Amer. Chem. Soc., 1930, 52, 4509—4511).—The araban of Salkovski (A., 1902, i, 593) is not a simple polymeride of arabinose, since it contains arabinose, galactose, rhamnose, and glycuronic acid. H. BURTON.

Sugars with branched carbon chains. II. Constitution and configuration of apiose. O. T. SCHMIDT (Annalen, 1930, 483, 115—123).—Crude apiose is obtained by hydrolysis of apiin (Vongerichten, A., 1901, i, 646) with dilute sulphuric acid and removing admixed dextrose from the partly purified sugar by fermentation. Decomposition of apiosephenylbenzylhydrazone, m. p. 137—138°, $[\alpha]_{5461}^{0}$ −94° in pyridine (cf. Vongerichten, A., 1906, i, 143), with aqueous-alcoholic formaldehyde affords pure apiose, $[\alpha]_D^{15}$ +5·6° in water. This is oxidised by Goebel's method (A., 1927, 647) to apionic acid, $[M]_{5461}^{10}$ −33·2° in water [calcium salt (+$2H_2O$); potassium salt, −2·45° in water; *phenylhydrazide*, m. p. 127°, $[M]_{5461}^{25}$ +76·8° in water]; the calcium salt is reduced by phosphorus and hydriodic acid (*d* 1·9) to *iso*valeric acid. The optical data for apionic acid show that it possesses the same configuration as *d*(—)-lactic acid. Apiose has, therefore, the constitution $(CH_2 \cdot OH)_2C(OH) \cdot CH(OH) \cdot CHO$. *p*-Bromophenacyl *n*-valerate has m. p. 74° (lit. 63·5°). H. BURTON.

Anhydro-sugars. I. Constitution of anhydro-sugars. II. Action of superheated water on anhydro-sugars. C. TANAKA (Mem. Coll. Sci. Kyoto, 1930, A, 13, 239—263, 265—280).—I. From comparative observations of ultra-violet absorption spectra and heats of combustion of simple and anhydro-sugars, modified formulæ are proposed for the latter. The following heats of combustion (g.-cal. per g.) have been determined: lævan, 4300; lævulosan, 4183; α-, 4186, β-glucosan, 4184; chitose, 4148; triacetyl-1 : 2-glucosan, 4593; triacetylglucal, 4949; tetra-acetyl-1 : 2-glucosen, 4647; triacetyl-β-glucosan, 4527; glycerol, 4312; glycide, 5610; allyl alcohol, 7626; glycide acetate, 5490; allyl acetate, 6549. The absorption spectra of some acetylated simple and anhydro-sugars are described, the general effect of acetylation being to displace the absorption end towards the red.

II. Lævulosan, α-glucosan, and lævan are gradually hydrolysed by water in a closed vessel at 100°; progress of hydrolysis leads to increasing reducing power, increasing amounts of humus and hydroxymethylfurfuraldehyde, and decreasing rotatory power and p_H value of the solution. β-Glucosan is not hydrolysed at 120°, but at 150° about 50% is converted into dextrose in 24 hrs., whereas heterolævulosan is unaffected. It is suggested that the p_H of the original sugar may determine the rate of hydrolysis. Chitose is easily hydrolysed to hydroxymethylfurfuraldehyde, which is simultaneously polymerised to humus and degraded to acids. With water at 150°, chitose, β-glucosan, and lævulosan give formic and lævulic acids and hydroxymethylfurfuraldehyde; lævulosan also gives lævulose, and β-glucosan dextrose (no trace of γ-glucose). The humus obtained from anhydro-sugars, dextrose, lævulose, and hydroxymethylfurfuraldehyde under the same conditions is similar in composition. It is suggested that the anhydro-sugars examined (except chitose, hydrolysed directly) give hydroxymethylfurfuraldehyde by way of a hexose and, subsequently, a chitose-like intermediate.

The absorption spectra of furfuraldehyde, its hydroxymethyl and methyl derivatives, and hydroxymethylpyromucic acid are formally similar; the heats of combustion (g.-cal. per g.) of furfuraldehyde and hydroxymethylfurfuraldehyde are 5816 and 5320, respectively. C. W. SHOPPEE.

Degradation of sugars in alkaline medium and with simultaneous action of oxidising agents. F. FISCHLER and J. REIL (Biochem. Z., 1930, 227, 140—155).—When the ratio of cuprous oxide to dextrose is plotted against the mg. of sugar in determinations of sugars by Ost's method, a curve and not a straight line is obtained, due to the sensitivity of the methylglyoxal formed to alkali. If an alkaline solution containing sugar is distilled in presence of sufficient oxygen, acet- and form-aldehydes and acetic and formic acids are obtained, and if methylglyoxal is treated in the same way, the same products are obtained. Distillation in presence of oxidising agents (hydrogen peroxide, hypochlorite, hypoiodite, and permanganate) also gives the same results, and it appears probable that alkaline oxidative degradation of sugars proceeds by way of the formation and further oxidation of methylglyoxal. P. W. CLUTTERBUCK.

Relationship of methylglyoxal to alkaline degradation of dextrose. F. FISCHLER, H. HAUSS, and K. TAUFEL (Biochem. Z., 1930, 227, 156—170).—Solutions of pure methylglyoxal, obtained by distilling solutions of crude methylglyoxal over barium carbonate under reduced pressure, show an absorption maximum at 2840 and minimum at 2400 Å. Pure dextrose solutions show no absorption, but after treatment with very dilute alkali show absorption characteristic for methylglyoxal. The formation of caramel does not account for the absorption. The absorption is lost almost completely on adding small amounts of acid. Addition of alkali to pure methylglyoxal solutions causes an immediate formation of caramel together with lactic, acetic, and formic acids. These results are followed quantitatively.

P. W. CLUTTERBUCK.

Action of animal charcoal on dextrose in the presence of dehydrogenated intermediate products. F. ZUCKERKANDL and L. MESSINER-KLEBERMASS (Biochem. Z., 1930, 226, 395—400).—Although dextrose in aqueous solution is not decomposed when boiled with animal charcoal, if the hydrochloride of an aromatic amine such as *p*-phenylenediamine or aniline (but not dimethylaniline) or an amino-acid such as tyrosine, alanine, phenylalanine, or histidine is also present, decomposition both of the sugar and of the amino-compound or amino-acid takes place, and in the case of *p*-phenylenediamine a sparingly soluble condensation product can be obtained. The process

can be explained by supposing that the amines or amino-acids are converted by loss of hydrogen into intermediate imino-compounds which then attack the dextrose molecule, and it is possible that a similar process occurs in the animal organism.

W. McCartney.

Carbohydrates. X. 1 : 2-Derivatives of dextrose. P. Brigl and R. Schinle (Ber., 1930, **63**, [*B*], 2884—2887; cf. A., 1929, 1043).—Tetrabenzoylglucose diethylmercaptal (cf. Brigl and Mühlschlegel, A., 1930, 1022) is very readily transformed by silver oxide and methyl iodide into the corresponding 2-*methyl* derivative, m. p. 88—89°, $[\alpha]_D^{18}$ +64·57° in acetone, from which sodium ethoxide removes the benzoyl groups, giving 2-methylglucose diethylmercaptal, m. p. 178°, $[\alpha]_D^{20}$ −25·0° in pyridine, identical with the product described by Papadakis (A., 1930, 1274). Treatment of the mercaptal with aqueous mercuric chloride affords 2-*methylglucose*, m. p. 158° after softening, $[\alpha]_D^{20}$ +56·6° to +65·6° in water, which reduces Fehling's solution very slowly when freshly prepared, but normally after repeated crystallisation. With phenylhydrazine in cold acetic acid it gives 2-methylglucosephenylhydrazone, m. p. 177°, whereas in hot solution glucosephenylosazone, m. p. 205°, is produced.

H. Wren.

Acetone [*iso*propylidene] compounds of the sugars and their derivatives. XVII. Conversion of *iso*propylideneglucose into a new amino- and anhydro-hexose; acyl migration. H. Ohle and R. Lichtenstein (Ber., 1930, **63**, [*B*], 2905—2912).—The action of methyl-alcoholic ammonia on 5-*p*-toluenesulphonyl-6-benzoylglucose *iso*propylidene ether proceeds very slowly at the ordinary temperature and is incomplete after 3 weeks. If the change is interrupted after 14 days, the main products are 1 : 2-iso*propylideneidosyl*-6-*amine* p-*toluenesulphonate*, m. p. 173—174° (decomp.), $[\alpha]^{20}$ −23·49° in water, and a nitrogen-free material (see later). Removal of the *iso*propylidene group leaves a material which does not give a crystalline phenyl-hydrazone or -osazone, but affords *idosyl*-6-*amine*-p-*nitrophenylosazone*, m. p. (indef.) 227° [*phenylhydrazine* p-*toluenesulphonate*, m. p. 183—184° (decomp.), is incidentally described]. With benzoyl chloride in pyridine at 37°, the *p*-toluenesulphonate affords *tribenzoylidosyl*-6-*amine* iso*propylidene ether*, m. p. 192°, $[\alpha]^{20}$ −19·30° in chloroform; the corresponding acetyl and *p*-toluenesulphonyl derivatives have not been obtained crystalline. Sodium nitrite transforms the *p*-toluenesulphonate into 3 : 6-*anhydroidose* iso*propylidene ether*, m. p. 105°, $[\alpha]_D^{20}$ +24·94° in water, hydrolysed by *N*-sulphuric acid to 3 : 6-*anhydroidose*, m. p. 105—106°, $[\alpha]_D^{20}$ +25·36° in water. For purposes of comparison the following derivatives of dextrose have been prepared: *triacetylglucosyl*-6-*amine* iso*propylidene ether*, m. p. 86°, $[\alpha]_D^{18}$ +18·35° in chloroform, from *iso*propylideneglucosyl-6-amine *p*-toluenesulphonate, pyridine, and acetic anhydride at 37°; *tribenzoylglucosyl*-6-*amine* iso*propylidene ether*, m. p. 198—199°, $[\alpha]_D^{20}$ −76·43° in chloroform; *di*-p-*toluenesulphonylglucosyl*-6-*amine* iso*propylidene ether*, m. p. 172° (decomp.), $[\alpha]_D^{19}$ −2·54° in chloroform; *hexabenzoylglucosyl*-6-*amine*, (+C_6H_5Me), m. p. 188°, $[\alpha]_D^{20}$ +22·89° in chloroform.

Acetylation of the nitrogen-free syrup (see above) yields an *acetyldi*-p-*toluenesulphonylhexose* iso*propylidene ether*, m. p. 112°, $[\alpha]_D^{19}$ −28·76°, which is not identical with 3-acetyl-5 : 6-di-*p*-toluenesulphonylglucose *iso*propylidene ether. It is remarkably resistant to dilute mineral acid. Its constitution is not established, but its formation is accompanied by the wandering of a *p*-toluenesulphonyl group.

H. Wren.

Ring structure of methylglucodesoside. P. A. Levene and L. A. Mikeska (J. Biol. Chem., 1930, **88**, 791—798; cf. Bergmann and Breuers, A., 1929, 797).—2-Deoxy-*d*-glucose (glucodesoside; cf. Bergmann, Schotte, and Lechinsky, A., 1922, i, 227) was oxidised according to the method of Goebel (A., 1927, 647) to yield 2-*deoxy*-d-*gluconic acid*, $C_6H_{12}O_6$, m. p. 145°, $[\alpha]_D$ +2·4° in water (*barium* salt), converted in aqueous solution at 100° into the *lactone*, m. p. 95—97°, $[\alpha]^{25}$ +68·0° in water, which when methylated with methyl iodide and silver oxide yields *trimethyl*-d-*glucodesonolactone*, m. p. 62°, $[\alpha]^{25}$ +21·5° in benzene. Methyl-2-deoxy-*d*-glucoside (Bergmann, Schotte, and Lechinsky, *loc. cit.*) was methylated with methyl sulphate and sodium hydroxide to yield *trimethyl*-d-*methylglucodesoside*, b. p. 86—90°/0·35 mm., $[\alpha]^{25}$ varying from +64° to +97° in chloroform from which *trimethyl*-d-*glucodesose*, m. p. 58—61°, $[\alpha]_D$ +59·5° to +33·1° in water, was obtained by treatment with 0·1*N*-hydrochloric acid at 100°. *Trimethyl*-d-*glucodesonic acid* (*barium* salt, $[\alpha]_D^{25}$ +18·1° in water), obtained from the last compound by oxidation by the method of Goebel, yields a *lactone*, b. p. about 137°/0·02 mm., $[\alpha]_D$ +87·5° in chloroform, $[\alpha]^{29}$ +88·2° in benzene. From the non-identity of these two trimethyl-*d*-glucodesonic lactones it is concluded that as the one formed by direct methylation of *d*-desonolactone probably has the 1 : 4 ring structure, a 1 : 5 ring structure is to be assigned to the other and therefore to the 2-deoxyglucoside from which it was formed. The instability of this compound is therefore to be attributed, not to its possessing a furanose structure, but to the reduced state of carbon atom 2.

W. O. Kermack.

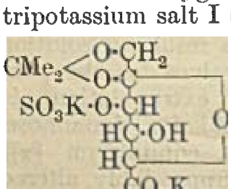
α-*d*-Gulose calcium chloride, its rotation and mutarotation in aqueous solution. H. I. Isbell (Bur. Stand. J. Res., 1930, **5**, 741—755).—The solution of crude *d*-gulose from reduction of gulonolactone (Fischer and Stahel, A., 1891, 667) is purified through the phenylhydrazone (cf., Blanksma and van Ekenstein, A., 1908, i, 951); treatment of the pure syrup so obtained with calcium chloride affords α-d-*gulose calcium chloride* (+H_2O), decomp. 205°, initial $[\alpha]_D$ +37·7° (by extrapolation), mutarotation constant k_1+k_2, 0·0193, equilibrium $[\alpha]^{20}$ −15·4°+0·78*c* (*c*=concentration in g. per 100 c.c.).

Calcium chloride is rapidly and quantitatively removed from solutions of the above compound by means of silver oxalate, and the resulting solution of *d*-gulose gives the following values for the pure sugar: initial $[\alpha]_D^{20}$ +61·6° (by extrapolation), k_1+k_2 0·0206 (cf. the value found for *d*-mannose, 0·019, by Dale, A., 1929, 1280), equilibrium $[\alpha]_D^{20}$ −26·4°. The last value is not appreciably altered by variations in the concentration of the sugar itself, although the equilibrium rotation of the calcium chloride compound is greatly altered by variations

in concentration (cf. the equation above, which may be modified to express the equilibrium rotation of *d*-gulose in presence of calcium chloride to $[\alpha]^{20}$ $-26{\cdot}4°+3{\cdot}73m$, where m=g. of anhydrous calcium chloride per 100 c.c. of solution); concentrated solutions of the compound on dilution with water show a mutation rate approximately equal to that of *d*-gulose. A different equilibrium is reached in alcoholic solution.
R. CHILD.

Individualities of anhydrofructose and difructose anhydride. R. F. JACKSON and S. M. GOERGEN (Bur. Stand. J. Res., 1930, 5, 733—734).—Difructose anhydride, m. p. 162—164° (A., 1929, 1280) has the mol. wt. required for a double hexose molecule, and is thus not identical with the anhydrofructose of Irvine and Stevenson (A., 1929, 1046); the latter is deliquescent, whilst the former will crystallise from aqueous solutions at the ordinary temperature.
R. CHILD.

Model experiments based on the theory of alcoholic fermentation. III. Degradation of α-di*iso*propylidenefructose sulphate. H. OHLE and G. COUTSICOS (Ber., 1930, 63, [*B*], 2912—2927; cf. A., 1929, 913; 1930, 70).—The constitution of the potassium salt, $CMe_2{<}^{O\cdot C(OH)\cdot CH_2\cdot O\cdot SO_3K}_{O\cdot CH\cdot CH(CO_2K)_2}$, obtained by the oxidation of β-di*iso*propylidenefructose hydrogen 1-sulphate by potassium permanganate in neutral, aqueous solution is confirmed by determination as the basic lead salt of glycollic acid produced by its hydrolysis. The observations are extended to *potassium di*iso*propylidenefructose 3-sulphate*, $C_{12}H_{19}O_9SK,0{\cdot}5H_2O$, decomp. about 165°, $[\alpha]_D^{20}$ $-124{\cdot}3°$ in water, which causes alcohol to gelatinise markedly; the corresponding *sodium* salt ($+H_2O$), decomp. about 170°, has $[\alpha]^{20}$ $-128{\cdot}3°$ in water. The oxidation graph shows that the substance is completely degraded to optically inactive compounds when 12 atoms of oxygen are used. The graph of hydrolysis shows that the maximum possibility of isolating intermediate products containing sulphur occurs when 6 atoms of oxygen are used, and under these conditions, the *potassium* salt (I), $^{CMe_2\cdot O}_{O-CH_2}{>}C(OH)\cdot CH(O\cdot SO_3K)\cdot CH(CO_2K)_2$, prisms ($+3H_2O$), $[\alpha]_D^{20}$ $-1{\cdot}78°$, or long needles, $4{\cdot}5H_2O$, $[\alpha]_D^{20}$ $-2{\cdot}72°$, is obtained. It is decomposed by dilute mineral acid into acetone, sulphuric acid, methylglyoxal, glycollic acid, and carbon dioxide. Partial hydrolysis of potassium α-di*iso*propylidenefructose 3-sulphate affords *potassium* α-*iso*propyl*idenefructose* 3-*sulphate*, decomp. about 150°, $[\alpha]_D^{20}$ $-112°$ in water (corresponding *sodium* salt, decomp. 140°, $[\alpha]_D^{20}$ $-118{\cdot}6°$ in water). When oxidised with 5 atoms of oxygen it yields large amounts of the tripotassium salt I (see above) and smaller quantities of the *fructuronate* II ($+4H_2O$), $[\alpha]_D^{20}$ $-45{\cdot}68°$ in water, which is hydrolysed to acetone, carbon dioxide, and sulphuric acid. The oxidation graph of β-di*iso*propylidenefructose resembles in some respects that of the corresponding 1-sulphate and indicates a possibility of isolating intermediate compounds by use of 6 atoms of oxygen. Since an optically inactive product is not obtained when 12 atoms of oxygen are employed, it appears that a portion of the liberated acetone must be oxidised. This is also the case with α-di*iso*propylidenefructose, with which also the reproducible scattering of the experimental values around the graph indicates the production of a series of intermediate compounds formed along different lines, some of which are closed by the introduction of the sulphuric acid residue. α-*iso*Propylidenefructose with 2—9 atoms of oxygen appears mainly to suffer direct conversion into acetone, carbon dioxide, and water without marked accumulation of intermediate compounds.



(II.)

The selective influence of the sulphuric acid residue is most apparent in the case of α-*iso*propylidenefructose and its 3-sulphate, and obviously depends on its proximity to the masked ketonic group, the hydrate form of which is stabilised by the strongly electronegative character of the acid residue. This stabilisation strengthens the union of the acetone residue and thus withdraws the upper half of the molecule from attack by the oxidising agent. The conclusion is reached that degradation of dextrose in the sense of Neuberg's fermentation scheme is possible only by a detour through lævulose. H. WREN.

Action of mercury salts on acetohalogenosugars. IV. Direct preparation of alkylbiosides of the α-series. G. ZEMPLÉN and A. GERECS (Ber., 1930, 63, [*B*], 2720—2729; cf. A., 1929, 683; 1930, 456, 1167).—Re-examination of the action of mercuric acetate and ethyl alcohol on acetobromocellobiose in benzene shows that α-ethylcellobioside hepta-acetate is obtained with certainty when about 100% excess of ethyl alcohol is used; with a 200% excess the product is reasonably homogeneous, but the yield is unsatisfactory. The reducing power of the products increases sharply when more than about a 300% excess of ethyl alcohol is used, and with between 300 and 400% excess there is marked transition to the production of the β-form. With *iso*propyl alcohol α-*iso*propylcellobioside hepta-acetate is obtained in good yield and excellent optical purity by the use of a 40—200% excess of the alcohol; with increase in the amount of the alcohol a maximum in the reducing power of the product is observed. With *n*-propyl, *n*-butyl, *iso*butyl, *sec.*-butyl, *sec.*-amyl, *n*-hexyl, and β-phenylethyl alcohols the highest observed specific rotation of the α-forms is attained with an approximate excess of 100% of the alcohol. For the production of the β-alkylcellobioside hepta-acetates a large excess of the requisite alcohol is advisable. With the lower members it is advantageous to use alcohol as solvent, whereby completely non-reducing products which are optically homogeneous only after repeated crystallisation are obtained. In benzene the majority of the β-alkylcellobioside hepta-acetates can be obtained provided that a sufficiently large excess of the alcohol is used. They may also be prepared from acetobromocellobiose in the necessary alcohol or in benzene with the aid of mercury cyanide, which is not very successful in the production of the α-compounds. The following α-alkylcellobioside hepta-acetates are described. The

rotations are the highest observed, all being measured in chloroform: ethyl, $[\alpha]_D^{23}$ $+57.23°$; n-*propyl*, $[\alpha]_D$ $+58.79°$; iso*propyl*, $[\alpha]^{22}$ $+59.29°$; n-*butyl*, m. p. 172°, $[\alpha]^{23}$ $+52.40°$; iso*butyl*, m. p. 174°, $[\alpha]_D^{21}$ $+45.51°$; sec.-*butyl*, m. p. 193°, $[\alpha]^{25}$ $+55.76°$; sec.-*amyl*, m. p. 193°, $[\alpha]^{25}$ $+52.23°$; n-*hexyl*, m. p. 182°, $[\alpha]_D^{21}$ $+53.42°$; β-*phenylethyl*, m. p. 207°, $[\alpha]_D^{21}$ $+54.16°$. The following β-alkylcellobioside hepta-acetates are described: *methyl*, $[\alpha]_D^{20}$ $-25.0°$; iso*propyl*, $[\alpha]_D^{25}$ $-22.7°$; n-*butyl*, $[\alpha]_D^{21}$ $-24.60°$; iso*butyl*, $[\alpha]_D^{23}$ $-23.04°$; sec.-*butyl*, $[\alpha]_D^{22}$ $-23.20°$; *hexyl*, $[\alpha]_D^{23}$ $-24.37°$; β-*phenylethyl*, $[\alpha]_D^{23}$ $-25.28°$.

H. WREN.

Preparation and m. p. of β-maltose anhydride. J. GILLIS (Natuurwetensch. Tijds., 1930, **12**, 193—199).—Contrary to the results obtained by de Bruyn and van Leent (A., 1895, i, 7), β-maltose hydrate may be dehydrated below 100° in a vacuum; the m.-p. curves show that the anhydride melts at 108°, and the hydrated form at 102—103°. The product obtained by de Bruyn and van Leent is probably a supercooled mixture of about 56% of β- and 46% of α-maltose.

S. I. LEVY.

Thio-sugars and their derivatives. XV. Nature of the sugars of mustard oil glucosides. W. SCHNEIDER, H. FISCHER, and W. SPECHT (Ber., 1930, **63**, [*B*], 2787—2793; cf. A., 1929, 913).—Aqueous solutions of sinigrin are smoothly and rapidly decomposed by silver nitrate in presence of barium or silver carbonate (to neutralise the liberated nitric acid) in accordance with the equation $C_{10}H_{16}O_9NS_2K+H_2O+2AgNO_3$ —— $C_4H_5O_4NS_2Ag_2+C_6H_{12}O_6+KNO_3+HNO_3$. The liberated dextrose exhibits downward mutarotation attaining the equilibrium value, $[\alpha]_D^{20}$ $+53.3°$. Similar results are obtained with sinalbin. Precisely analogous results are obtained when mercury salts are used with the glucosides, thus apparently confirming the conclusion of Wrede (A., 1923, i, 589) that these are α-glucosides. Since, however, α-glucose is liberated by the action of silver nitrate in presence or absence of barium carbonate on the sodium compound of β-glucothiose, it appears that in all cases the reaction is accompanied by a Walden inversion and that the glucosides are β-compounds. Experimental confirmation of this view is found in the production of octa-acetyl-ββ-diglucosyl disulphide, m. p. 142—143°, $[\alpha]^{21}$ $-158.7°$ in *s*-tetrachloroethane (cf. A., 1928, 872) from sinigrin and $0.1N$-aqueous sodium hydroxide with subsequent treatment of the neutralised solution with iodine, evaporation to dryness, and treatment of the residue with pyridine and acetic anhydride.

H. WREN.

Chellol glucoside. P. FANTL and S. I. SALEM (Biochem. Z., 1930, **226**, 166—179).—Kellin, $C_{14}H_{12}O_5$, the supposed glucoside of *Ammi Visnaga* (A., 1897, 1041), is not a single substance. Alcoholic extraction of the seeds (in the absence of lime) gave β-d-*chellol glucoside*, $C_{19}H_{20}O_{10},2H_2O$, m. p. 175°, α_D^{20} $-31.88°$, containing one methoxyl group and giving a *tetra-acetyl* derivative, m. p. 153°. Hydrolysis of the glucoside with hydrochloric acid gave dextrose and *chellol*, $C_{13}H_{10}O_5$, m. p. 179°, which contains one methoxyl group and gives a *monoacetyl* derivative, m. p. 105°. Hydrolysis of the glucoside with dilute alkalis gave β-*d*-glucosidoglycollic acid, $C_8H_{14}O_8$, m. p. 163°, together with a *substance*, $C_{11}H_{10}O_4$, m. p. 111° (*methyl* derivative, m. p. 136—137°; *benzoyl* derivative, m. p. 115°; *oxime*, m. p. 144°).

P. W. CLUTTERBUCK.

Natural glucosides. II. Constitution of æsculin. F. S. H. HEAD and A. ROBERTSON (J.C.S., 1930, 2434—2444; cf. Glaser and Kraus, A., 1923, i, 820).—Prolonged treatment of æsculin with methyl iodide in presence of acetone and potassium carbonate affords 7-O-*methylæsculin* ($+2H_2O$), m. p. 230° (decomp.), hydrolysed by 5% sulphuric acid to 7-*O*-methylæsculetin, m. p. 185° (Tiemann and Will, A., 1883, 199; Bargellini and Monti, A., 1915, i, 84). This is converted by treatment with ethyl iodide in presence of acetone and potassium carbonate into 7-*methoxy*-6-*ethoxycoumarin*, m. p. 120°, which on repeated treatment with methyl sulphate and 20% sodium hydroxide solution gives the *methyl* ester, m. p. 80°, of 2 : 4-*dimethoxy*-5-*ethoxycinnamic acid*. When this acid is heated it passes (at 117—118°) into a yellow solid, m. p. 128°, which when kept in contact with benzene reverts to the original colourless form. 5-Nitro-2-ethoxyanisole is reduced by aqueous sodium sulphide to the corresponding amine, convertible by the usual method into 3-*methoxy*-4-*ethoxyphenol*, m. p. 58°. When a solution of this in ether containing hydrogen and zinc cyanides is saturated with hydrogen chloride and the resulting product hydrolysed, 2-*hydroxy*-4-*methoxy*-5-*ethoxybenzaldehyde*, m. p. 112—113°, is obtained. Methylation of this with methyl iodide in presence of acetone and potassium carbonate affords 2 : 4-*dimethoxy*-5-*ethoxybenzaldehyde*, m. p. 110°, which could not be converted into the above cinnamic acid but into a pale yellow *modification*, m. p. 132—133°, by condensation with malonic acid in presence of pyridine and a small amount of piperidine. Oxidation of both cinnamic acids with aqueous potassium permanganate in acetone furnishes the above dimethoxyethoxybenzaldehyde, which is oxidised further to 2 : 4-*dimethoxy*-5-*ethoxybenzoic acid*, m. p. 137°. 7-Methoxy-6-ethoxycoumarin could not be prepared from 2-hydroxy-4-methoxy-5-ethoxybenzaldehyde.

4-Aminoveratrole is converted by the usual method into 3 : 4-*dimethoxyphenol* ($+H_2O$), m. p. 46°, and thence by Gattermann's reaction into 2-*hydroxy*-4 : 5-*dimethoxybenzaldehyde*, m. p. 105°, which is methylated to asarylaldehyde. Methoxyquinol, m. p. 89° (lit. 82—84°), affords similarly 2 : 5-*dihydroxy*-4-*methoxybenzaldehyde*, m. p. 209° (slight decomp.) (also methylated to asarylaldehyde), which with acetic anhydride and sodium acetate at 120—180° gives a small amount of 7-*O*-methylæsculetin. Æsculin, therefore, contains the glucose residue in the 6- and not the 7-position as suggested by Glaser and Kraus (*loc. cit.*).

4-*Methoxy*-3-*ethoxyphenol* ($+H_2O$), m. p. 92—93° after sintering at 85°, is converted into 2-*hydroxy*-5-*methoxy*-4-*ethoxybenzaldehyde*, m. p. 91° (*phenylhydrazone*, m. p. 157—158°), and thence by the usual methods into 2 : 5-*dimethoxy*-4-*ethoxy-benzaldehyde*, m. p. 110°, -*benzoic acid*, m. p. 130°, and -*cinnamic acid*, m. p. 178—179° after sintering at 170°.

H. BURTON.

***Digitalis* glucosides. II. Digoxigenin, the aglucone of digoxin.** S. SMITH (J.C.S., 1930, 2478—2482).—When digoxigenin (A., 1930, 583) [*diacetyl* derivative, m. p. 221°, $[\alpha]^{20}_{5461}$ +61·3° (all rotations are in methyl alcohol)], is heated with aqueous-alcoholic sulphuric acid, *anhydrodigoxigenin*, $C_{23}H_{32}O_4$, m. p. 182°, $[\alpha]^{20}_{5461}$ +16·3° (*diacetyl* derivative, m. p. 199°, $[\alpha]^{20}_{5461}$ +38·6°), is obtained. These results indicate that digoxigenin contains three hydroxyl groups; the remaining oxygen atoms are present in a lactone group as shown by hydrolysis and titration. Reduction of digoxigenin with hydrogen in presence of palladium-black and 80% alcohol affords *dihydrodigoxigenin*, $C_{23}H_{36}O_5$, m. p. 215°, $[\alpha]^{20}_{5461}$ +20·5° (*diacetyl* derivative, m. p. 222°, $[\alpha]^{20}_{5461}$ +29·8°), and since digoxigenin gives a red colour with alkaline sodium nitroprusside (cf. Jacobs, Gustus, and Hoffmann, A., 1926, 430, 1250), it is probably a trihydroxy-$\Delta^{\beta\gamma}$-unsaturated lactone. When digoxigenin is treated with 10% methyl-alcoholic potassium hydroxide solution, iso*digoxigenin* (+C_5H_5N), m. p. 280°, m. p. (solvent-free) 260° (decomp.), $[\alpha]^{20}_{5461}$ +13·6° [*diacetyl* derivative, m. p. 280° (all m. p. except this are corr.)], is produced. This does not give Legal's test, is not reduced under the above conditions, and is converted by successive treatment with warm 10% sodium hydroxide solution and acetic acid into iso*digoxigeninic acid*, $C_{23}H_{36}O_6$, m. p. 228° (decomp.). H. BURTON.

Digitalinum verum. H. KILIANI (Ber., 1930, **63**, [*B*], 2866—2869).—To avoid the formation of ethylated sugars during the hydrolysis of digitalinum verum, the ethyl-alcoholic hydrochloric acid is replaced by a mixture of glacial acetic acid, water, and concentrated hydrochloric acid (vol. ratio 35 : 55 10). Digitaligenin is readily isolated in satisfactory yield, but the digitalose could not be caused to crystallise. It is therefore oxidised with bromine, thus giving digitalonolactone (yield 40%) and *d*-gluconic acid isolated as the barium salt. H. WREN.

Constitution of starch. Critical review. M. SCHOEN (Bull. Soc. Chim. biol., 1930, **12**, 1033—1099).

Action of hydrofluoric acid on starch. B. HELFERICH, A. STARKER, and O. PETERS (Annalen, 1930, **482**, 183—188).—When hydrofluoric acid is allowed to interact with anhydrous potato-starch under the conditions described in the case of cellulose (cf. A., 1930, 72) *amylan*, $[\alpha]^{16}_{D}$ +145° in water, is produced. It resembles cellan in all properties except that it is precipitated from an aqueous solution by alcohol. When heated with acetic anhydride and pyridine, an *acetyl* derivative $(C_6H_7O_5Ac_3)_x$, $[\alpha]^{17}_{D}$ +141·5° in chloroform, results, from which the amylan can readily be regenerated in a state of purity, $[\alpha]^{17}_{D}$ +144·2° in water, +110° in hydrofluoric acid. Identical treatment of anhydrous maltose gives *maltan*, $[\alpha]^{17}_{D}$ +145° (*acetyl* derivative, $[\alpha]^{17}_{D}$ +141·3° in chloroform), indistinguishable in all its properties from amylan. Mercerised cotton has $[\alpha]^{14}_{D}$ +1·2°, +0·4° in hydrofluoric acid, as has raw cotton.

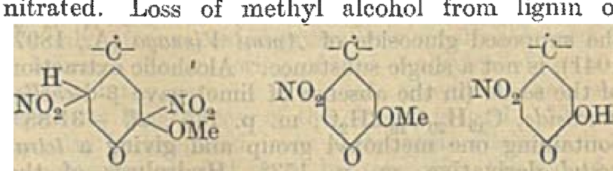
H. A. PIGGOTT.

Supposed depolymerisation of glycogen. E. BERNER (Ber., 1930, **63**, [*B*], 2760—2764; cf. A., 1930, 1025).—Glycogen, $[\alpha]^{20}_{D}$ +194·5°, ash content less than 0·02%, causes depressions of the f. p. of water which become smaller as the substance is more completely dried, thus indicating the probable presence of alcohol. Complete dehydration of glycogen requires heating at 100—110°/vac. Dried glycogen precipitated by alcohol from solutions in anhydrous solvents such as acetamide, formamide, and ethylene glycol retains the substances, the amount of amide depending on that of alcohol employed. The precipitates lose alcohol slowly over calcium chloride in a vacuum; when exposed to air the loss is more rapid, owing to the absorption of atmospheric moisture. Cryoscopic determinations of the mol. wt. of the glycogen precipitates in water gives values corresponding with those observed by Reilly, Pringsheim, and Donovan (A., 1930, 895). Analysis discloses the presence of amide and alcohol in amount sufficient to explain the low values. Addition of alcohol to solutions of glycogen in ethylene glycol yields a product giving, after desiccation for 2 days, a high depression of the f. p. It contains 9·4% of alcohol. The observation of Reilly, Pringsheim, and Donovan (*loc. cit.*) that its aqueous solution exhibits opalescence and gives the same colorations with iodine as pure glycogen solutions is in harmony with the author's view that depolymerisation has not occurred. H. WREN.

Constitution of cellulose nitrates and acetates and their passage to colloidal film. J. J. TRILLAT. —See this vol., 27.

Cellulose xanthate. III. T. LIESER (Annalen, 1930, **483**, 132—139).—Treatment of methylcellulose (A., 1929, 799) with a mixture of acetic acid and anhydride containing sulphuric acid at 25—30° for 7—20 days gives about 50% of cellobiose octa-acetate, indicating that some of the glucose anhydride units in the original product are not methylated. No methylcellobiose acetate could be detected; it is probably decomposed during acetolysis. H. BURTON.

Lignin and cellulose. XV. Lignin and nitrogen dioxide. K. FREUDENBERG and W. DURR (Ber., 1930, **63**, [*B*], 2713—2720).—Lignin reacts very rapidly with gaseous nitrogen dioxide and, after a short period, the initial absorption is succeeded by evolution of nitric oxide due to a secondary oxidation. With methyl-lignin only the initial, rapid absorption is observed. During the reaction the lignin becomes partly demethylated with production of methyl alcohol. The observations are most readily explained on the assumption that substitution has occurred. Under favourable conditions the ratio of nitrogen introduced to original aromatic methoxyl approaches 1 : 1. Double linkings are not involved to an important extent, since nitrolignin and nitromethyl-lignin can be brominated and bromomethyl-lignin can be nitrated. Loss of methyl alcohol from lignin or



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methyl-lignin is considered due to addition of nitrogen dioxide, yielding the compound I, which in part loses

nitric acid to give the substance II and in part eliminates methyl nitrite giving a quinol derivative passing into the nitrophenol III.

Dehydrodivallin is very violently attacked by nitrogen dioxide owing to the presence of free phenolic hydroxyl groups. Its dimethyl ether resembles lignin in being nitrated with loss of about 2% of methyl as methyl alcohol. Veratric acid is nitrated with production of traces of methyl alcohol, and veratryl-cellulose behaves similarly. H. WREN.

Two syntheses of heptamethyleneimine. A. MÜLLER and P. BLEIER (Monatsh., 1930, **56**, 391—406).—Reduction of suberone*iso*oxime (α-ketoheptamethyleneimine) with sodium and alcohol (cf. A., 1929, 194) affords 1·5% of the theoretical amount of slightly impure heptamethyleneimine, b. p. 162—164°, d_4 0·869, 1·5262 (*chloroaurate*, m. p. 188° after sintering at 173° and slight decomp. at 183—185°; *picrate*, m. p. 147—148°), together with high-boiling products. Oxidation of N-*benzoylheptamethylene-imine*, b. p. 196—197°/13 mm., with aqueous potassium permanganate at about 65° furnishes 41·3% of ζ-benzamido-*n*-heptoic acid, dimorphous, m. p. 86° and 90° (lit. 81—82°), prepared also by Zemplen and Csürös' method (A., 1929, 1283) and by benzoylating ζ-amino-*n*-heptoic acid [hydrochloride, m. p. 112° (lit. 97—99°)]. The last-named acid is obtained when suberone*iso*oxime is heated with 20% hydrochloric acid at 150°.

Hydrolysis of the reaction product from αη-dibromo-*n*-heptane and *p*-toluenesulphonamide in presence of alcoholic potassium hydroxide with hydrochloric acid at 160° yields slightly impure heptamethyleneimine (0·8% yield) and αη-diamino-*n*-heptane.

Improved methods of preparation of suberic acid, suberone, and suberone*iso*oxime are given. All m. p. are corr. H. BURTON.

Asymmetric nitrogen atom. LVIII. Decomposition of active and inactive quaternary ammonium nitrates under the influence of amines; solvate formation by ammonium salts. E. WEDEKIND and F. FEISTEL (Ber., 1930, **63**, [*B*], 2743—2753; cf. Wedekind and Uthe, A., 1925, i, 536, 1059).—Examination by the conductivity method of a number of quaternary ammonium halides and the corresponding nitrates shows that the halides which are stable in chloroform solution are stable also after addition of aniline. Decomposition of the halides takes place only if a phenyl or benzyl or an allyl group is present. With phenylmethylallylammonium nitrate decomposition occurs in chloroform in presence of aniline or methylaniline, but not of dimethylaniline, the secondary base having the more profound influence. Triethylamine and methylethylaniline are ineffective. The action of the various bases is shown by the half period in minutes for drop in activity and mean velocity coefficient as deduced from the conductivity: *iso*amylamine, 25, 0·0182: *iso*butylamine, 45, 0·0072; *n*-propylamine, 47, 0·0065; *n*-butylamine, 88, 0·0064; benzylamine, 90, 0·0037; aniline, 250, 0·0032; diethylamine, 26, 0·0259: benzylethylamine, 4–, 0·01,6 dibenzylamine, 80, 0·0077; methylaniline, 90, 0077; ethylaniline, 150, 0055: benzylaniline, 195, 0·0014; diphenylamine, ∞. Confirmation of the hypothesis that reaction occurs in accordance with the scheme $NR^1R^2R^3R^4{\cdot}NO_3+H{\cdot}NHX=NR^1R^2R^3+R^4{\cdot}NHX+HNO_3$, is found in the isolation of *p*-toluidine nitrate, decomp. 199°, from phenylmethylallylammonium nitrate in molten *p*-toluidine. The possible preliminary formation of solvates is examined by placing weighed amounts of amine, nitrate, and amine +nitrate in a high vacuum at a temperature not exceeding 36° until the solvent is removed, and then raising the temperature in stages until, at 111°, constancy in weight is observed. A final weight lower than the original weight (owing to removal of volatile bases formed as shown above) is observed with those nitrates which are known by the decrease in conductivity to decompose in chloroform solution after addition of aniline. The method does not indicate solvate formation with tertiary bases. Further evidence of solvate formation is deduced from measurements of specific rotation, the lowest values being observed in "indifferent" solvents, the highest in those which cause decomposition. In indifferent media the specific rotation is affected slightly by variation in concentration, but shows great dependence thereon in "active" solvents. Cryoscopic measurements of the mol. wt. of phenylbenzylmethylallylammonium nitrate in bromoform show only that the salt is associated in this medium. In *p*-toluidine decomposition of the nitrate appears to occur, a constant minimum value being reached when the solution has been preheated at 45—50° for a lengthy period. With the non-decomposing phenyldimethylethylammonium perchlorate in *p*-toluidine, the apparent mol. wt. diminishes with increasing concentration, thus indicating solvate formation. H. WREN.

Purely aliphatic *strepto*pentamethine dyes. W. KONIG and W. REGNER (Ber., 1930, **63**, [*B*], 2823—2827; cf. A., 1926, 522).—ε-Methylanilino-pentadienal is converted by dimethylamine in presence of alcohol and perchloric acid into methylaniline and *αε-tetramethyldiaminopentamethinium perchlorate*, m. p. 165°, obtained similarly from ethylanilino- or tetrahydroquinolino-pentadienal; it may be prepared in poor yield and accompanied by much other substance by addition of dimethylamine followed by perchloric acid to a mixture of piperidine and cyanogen bromide in alcohol and ether. *αε-Dipiperidinopentamethinium perchlorate*, m. p. 111°, is described. The new compounds give yellowish-green solutions in water or alcohol and give shades on mordanted cotton similar to those of auramine G. The absorption curves of the aliphatic dyes are nearly identical with one another. The shades on cotton are as fast to light as those of the auramines and superior in resistance to acids and alkalis. The solid compounds exhibit very marked luminescence when exposed to the Hanau lamp. H. WREN.

Reaction of choline and lecithin. J. A. SANCHEZ (Semana méd., 1930, i, 1416).—When heated with iodine and sodium hydroxide, choline and lecithin (the latter after saponification with sodium hydroxide) afford iodoform. CHEMICAL ABSTRACTS.

Glycine and its neutral salt additive products. J. V. DUBSKY and A. RABAS (Pub. Fac. Sci. Univ. Masaryk, 1930, No. 123, 1—18).—The zinc salt of

glycine, $ZnX_2,2HX,4H_2O$ ($X=NH_2{\cdot}CH_2{\cdot}CO_2$) (cf. Kraut, A., 1892, 294), is hydrolysed under special conditions to the normal *salt*, ZnX_2,H_2O, decomp. 319°, a neutral *salt*, $ZnX_2,3HX,H_2O$, decomp. 245°, being simultaneously produced. The following neutral salts are described: $ZnCl_2,2HX,2H_2O$, m. p. 100°, decomp. 230°; $ZnCl_2,3HX,2H_2O$, decomp. 228°; $ZnBr_2,2HX,2H_2O$, m. p. 98°, decomp. 335°; $ZnSO_4,HX,5H_2O$, m. p. 82°, decomp. 320°; $CuCl_2,CuX_2,2H_2O$, decomp. 195°; $CuCl_2,CuX_2,HCl$, decomp. 190°; $CuCl_2,(HCl,HX)_2,2H_2O$, m. p. 96°, decomp. 120°. Analogous compounds with cobalt, nickel, or stannic chlorides were not obtained.

R. CHILD.

Preparation of ω-amino-acids. B. FLASCHENTRAGER. **I. κ-Benzenesulphonylmethylaminoundecoic acid from κ-undecenoic acid.** B. FLASCHENTRAGER, F. HALLE, and T. HOSODA. **II. Degradation of sebacic acid to δ-aminononoic acid by the Jeffreys–Hofmann method.** B. FLASCHENTRAGER and F. GEBHARDT. **III. Degradation of normal dicarboxylic acids of high mol. wt. to ω-amino-acids by the Naegeli–Curtius method. Degradation of sebacic acid to δ-aminononoic acid.** B. FLASCHENTRAGER and F. HALLE. **IV. Degradation of αϕ-heneicosanedicarboxylic acid to ϕ-aminobehenic acid.** B. FLASCHENTRAGER, B. BLECHMAN, and F. HALLE (Z. physiol. Chem., 1930, **192**, 245—248, 249—252, 253—257, 257—263).—I. κ-Bromoundecoic acid when heated with alcoholic methylamine at 90—110° (under pressure) yields *κ-methylaminoundecoic acid*, m. p. 136—137°, which forms *κ-benzenesulphonylmethylaminoundecoic acid*, m. p. 47—48°.

II. When sebacamic acid is treated with bromine in methyl alcohol followed by sodium methoxide, it forms *θ-carbomethoxyaminononoic acid*, m. p. 77°. The latter when heated with concentrated hydrochloric acid furnishes *θ-aminononoic acid hydrochloride*, which is isolated as *θ-benzenesulphonamidononoic acid*, m. p. 85°.

III. θ-Carbethoxynonoyl chloride when heated with sodium azide in xylene yields *ethyl θ-carbimidononoate*. The latter when boiled with concentrated hydrochloric acid furnishes *ethyl θ-aminononoate hydrochloride*. Hydrolysis of the ester and removal of the by-product, *carbamido-NN′-di-θ-nonoic acid*, m. p. 158° (corr.), gives θ-aminononoic acid, isolated as the benzenesulphonyl compound.

IV. *Ethyl hydrogen heneicosanedicarboxylate*, m. p. 83·3° (corr.), obtained by heating together in alcohol the free acid and the normal ester, yields successively by the Naegeli–Curtius method *α-carbethoxyheneicosane-ϕ-carboxyl chloride*, m. p. 59·9° (corr.); *ϕ-aminobehenic acid*, m. p. 167° (corr.); *ϕ-benzenesulphonamidobehenic acid*, m. p. 114·5° (corr.). *Carbamido-NN′-di-ϕ-behenic acid*, m. p. about 110°, is obtained as by-product.

J. H. BIRKINSHAW.

N-Alkylation of β-amino-esters. J. DECOMBE (Compt. rend., 1930, **191**, 945—947).—Treatment of β-amino-esters with alkyl iodides causes decomposition to ammonia and αβ-unsaturated esters. When an equimolecular mixture of αβ-amino-ester and acetaldehyde is reduced catalytically (Adams) in alcohol, the ethylamino-ester is obtained together with resinous material. The following are prepared: *ethyl β-ethylaminobutyrate*, b. p. 74—75°/12 mm. (*hydrochloride*, m. p. 125°; free *acid*, m. p. 169—170°); *ethyl β-ethylaminohexoate*, b. p. 110—111°/20 mm. (*hydrochloride*, m. p. 79°); *ethyl β-ethylamino-octoate*, b. p. 130—132°/20 mm. (*hydrochloride*, m. p. about 60°; free *acid*, m. p. 140—141°). Similar treatment of a mixture of butaldehyde and ethyl β-ethylaminobutyrate gives a small amount of *ethyl β-ethylbutylaminobutyrate*, b. p. 118—119°/15 mm.

Ethyl β-aminobutyrate has b. p. 68—69°/17 mm., and not 82°/20 mm., as previously reported (A., 1930, 328).

H. BURTON.

Synthesis of *dl*-aspartic acid. M. S. DUNN and B. W. SMART (J. Biol. Chem., 1930, **89**, 41—50).—Ethyl sodiophthalimidomalonate (conveniently prepared by the action of sodium on ethyl phthalimidomalonate in boiling toluene) was condensed with ethyl chloroacetate to give *ethyl ethane-α-phthalimido-ααβ-tricarboxylate*, which was hydrolysed with aqueous-alcoholic hydrochloric acid to *dl*-aspartic acid (33%) together with a small amount of glycine. β-Chloropropionitrile and other halogen compounds (except trimethylene bromide) failed to condense with ethyl sodiophthalimidomalonate.

C. R. HARINGTON.

Reduction of cystine in liquid ammonia by metallic sodium. V. DU VIGNEAUD, L. F. AUDRIETH, and H. S. LORING (J. Amer. Chem. Soc., 1930, **52**, 4500—4504).—Cystine (1 mol.) is reduced to cysteine when a solution in liquid ammonia is treated with sodium (4 atoms). The resulting solution is evaporated, the residue extracted with alcoholic hydrochloric acid, the cysteine hydrochloride crystallised from 20% hydrochloric acid, and then decomposed with ammonia in alcohol, whereby practically pure cysteine is obtained. Treatment of the liquid ammonia solution with benzyl chloride affords α-amino-β-benzylthiolpropionic acid.

H. BURTON.

Reduction of *l*-cystine to *l*-cysteine. E. GEBAUER-FULNEGG (J. Amer. Chem. Soc., 1930, **52**, 4610—4611).—Cystine is reduced by 1—1·5 parts of aluminium amalgam (Wislicenus, A., 1896, i, 671) in carbon dioxide-free aqueous solution to *l*-cysteine, which is isolated in the usual manner.

H. BURTON.

Action of alkali on cystine and cysteine. H. T. CLARKE and J. M. INOUYE (J. Biol. Chem., 1930, **89**, 399—419).—When cystine or cysteine is boiled in alkaline solution in presence of lead acetate and of phenylhydrazine or of phenylhydrazine-4-carboxylic acid, the phenylhydrazone or *p*-carboxyphenylhydrazone (m. p. 259°) of pyruvic acid is formed in a yield of about 60% from cystine and 80% from cysteine. Pyruvic acid given an orange colour when warmed with salicylaldehyde in alkaline solution; the same colour is obtained by interaction of salicylaldehyde with alkaline solutions of cystine, cysteine, αβ-dibromopropionic acid, and β-chlorolactic acid. When boiled in alkaline solution in presence of lead cystine yields 75% (larger amounts in presence of reducing agents, *e.g.*, stannite and arsenite) and cysteine the whole of its sulphur as sulphide; the remainder of the cystine

sulphur appears as thiosulphate. Deamination of cystine tends to lag behind desulphurisation.

C. R. HARINGTON.

Optical rotation of *l*-cystine. G. TOENNIES and T. F. LAVINE (J. Biol. Chem., 1930, **89**, 153—166).—Cystine, after careful purification by fractional precipitation, has, in 1% solution in *N*-hydrochloric acid, $[\alpha]_{5461}$ −241·87° ±0·15° and $[\alpha]^{20}$ −205·1° ±0·2°. Over the temperature range 20—30° the relationships, $[\alpha]^{t}_{5461}$ — (2·431*t*—312·37) ±0·2° and $[\alpha]^{t}_{D}$ —(2·061*t*—264·84) ±0·2° hold good. C. R. HARINGTON.

***N*-Carbomethoxyformamide.** I. J. RINKES (Rec. trav. chim., 1930, **49**, 1126).—When methyl carbamate is refluxed with 100% formic acid and the product is distilled at 90° in a vacuum *N*-carbomethoxyformamide, identical with the product obtained by ozonolysis of methyl styrylcarbamate (A., 1929, 1296), is obtained. J. W. BAKER.

Action of magnesium ethyl bromide on chloroacetdiethylamide. S. P. TI (Compt. rend., 1930, **191**, 943—945).—Decomposition of the reaction product from chloroacetdiethylamide (1 mol.) and magnesium ethyl bromide (3 mols.) with alkali furnishes diethylamine, 20% of *α-diethylamino-α-ethylbutyl alcohol*, b. p. 90°/18 mm. [*picrate*, m. p. 99°; *chloroplatinate*, m. p. 140—141°; *acetate*, b. p. 97—98°/13 mm. (*picrate*, m. p. 130—131°)], together with small amounts of an unsaturated *base*, $C_{10}H_{21}N$, b. p. 169° (*picrate*, m. p. 74°; *chloroplatinate*, m. p. 142—143°), diethylaminoacetdiethylamide, b. p. 125—126°/20 mm. [picrate, m. p. 121° (lit. 133°); *chloroplatinate*, m. p. 164—165°], and a basic *compound*, $C_{16}H_{34}O_2N_2$, b. p. 160—162°/14 mm. H. BURTON.

Derivatives of *dl*-asparagine. II. S. BERLINGOZZI and G. CAROBBI (Gazzetta, 1930, **60**, 573—582; cf. A., 1928, 158).—Although it has not been found possible to prepare the racemic modification of asparagine, such modifications are obtainable for various derivatives of asparagine. Chloroacetyl-*d*(or *l*)-asparagine, m. p. 150°, d^{15} 1·538, forms monoclinic crystals, $a:b:c$—0·7876 : 1 : 0·4281, 96° 22′. *Chloroacetyl*-dl-*asparagine*, m. p. 105°, d^{15} 1·560, forms triclinic (pinacoidal) crystals (+H_2O), $a\cdot b\cdot c$= 0·9068 : 1 : 0·8617, α 63° 29′, β 113° 20′, γ 117° 15′. *Benzoyl*-dl-*asparagine*, m. p. 184°, d^{15} 1·433, forms monoclinic crystals, $a:b:c$=0·8865 : 1 : 0·5929, β 92 12′. *Benzenesulphonyl*-d(or l)-*asparagine*, m. p. 163 , d^{15} 1·434, forms monoclinic crystals, $a:b:c$= 0·7557 : 1 : 0·7105, 104° 42′, and is optically inactive as sodium salt in aqueous solution. *Benzenesulphonyl*-dl-*asparagine*, m. p. 172°, d^{15} 1·559, forms monoclinic crystals. T H POPE.

Adipheptadecylamic acid and sebacheptadecylamic acid. B. FLASCHENTRAGER and H LACHMANN (Z. physiol. Chem., 1930, **192**, 268—273).—Heptadecylamine hydrochloride, m. p. 163° (corr.), is converted into the following compounds; *heptadecylamine*; *heptadecyl carbamate*, m. p. 99·5—102·5°; *benzenesulphonylheptadecylamine*, m. p. 64·7°; *heptadecylamine gluconate*, m. p. 140° (decomp.) after softening at 105°; *adipheptadecylamic acid*, m. p. ·0 (*ethyl* ester, m. p. 77—77·5°; *barium* salt, decomp. 198°); *sebacheptadecylamic acid*, m. p. 115° (*ethyl* ester, m. p. 82°; *barium* salt, decomp. 204°).

J. H. BIRKINSHAW.

Biuret reaction. II. Di-acid amides. M. M. RISING, J. S. HICKS, and G. A. MOERKE (J. Biol. Chem., 1930, **89**, 1—25).—Biuret, malonamide, and oxamide, together with certain mono- and *s*-dialkyl derivatives of these amides give the biuret reaction with formation of coloured compounds having the general formula $Na_2Cu(amide)_2,nH_2O$. That the copper of these compounds is contained in an electronegative ionic complex is proved by the fact that electrolysis of the alkaline solution leads to the accumulation of the colour in the anodic region and only after long periods to the cathodic deposition of copper. The same applies to the previously described (A., 1929, 196) sodium copper diethylbarbiturate, and structural formulæ are now given which represent the complex ions as consisting of copper united by auxiliary valencies with the nitrogen atoms of four imide or amide groups, respectively; this accounts for the fact that 4 mols. of imide (*loc. cit.*) and only 2 mols. of diamide take part in the formation of the coloured compounds. By treatment of the appropriate amide in aqueous solution with sodium hydroxide (4 mols.) and cupric acetate (1 mol.) the following *compounds* were obtained: *sodium copper biuret*, $Na_2Cu(C_2H_3O_2N_3)_2,2H_2O$; *sodium copper malonamide*, $Na_2Cu(C_3H_4O_2N_2)_2,2H_2O$; *sodium copper oxethylamide*, $Na_2Cu(C_4H_6O_2N_2)_2,4H_2O$; *sodium copper oxdiethylamide*, $Na_2Cu(C_6H_{10}O_2N_2)_2$. The last-named compound is blue, whilst the hydrated salts are pink; those of them, however, which lose their water over phosphoric oxide (*e.g.*, sodium copper oxethylamide) become blue during dehydration. Using nickel acetate, there was obtained *sodium nickel oxethylamide*, $Na_3Ni_2C_{12}H_{37}O_{14}N_6$. *Malonethylamide*, obtained by treatment of ethyl malonamate with ethylamine, had m. p. 122°; it gave the biuret reaction, but the coloured product could not be isolated. C. R. HARINGTON.

Interaction between alkyl Grignard reagents and arsenic trichloride. W. J. C. DYKE and W. J. JONES (J.C.S., 1930, 2426—2430).—Magnesium alkyl halides react with arsenic trichloride forming trialkylarsines; free arsenic is always produced owing to the reducing action of the arsine. The paraffin formed during the preparation of the Grignard reagent can be isolated by shaking the pre-arsine fraction in the final distillation with sulphuric acid. The following are prepared: trimethylarsine; triethylarsine; tri-*n*-butylarsine; *triisobutylarsine*, b. p. 119°/31 mm., d^{25}_{4} 0·9590, n^{25}_{D} 1·4627; *tri*-dl-*β-methylbutylarsine*, b. p. 160°/28 mm., d^{25}_{4} 0·9563, n^{25}_{D} 1·4696; *tri-γ-methylbutylarsine*, b. p. 167—168°/28 mm., d^{25}_{4} 0·9504, n^{25}_{D} 1·4694, and *tri-δ-methylamylarsine*, b. p. 158—160°/5 mm., d^{25}_{4} 0·9309, n^{25}_{D} 1·4669. The mean value for the atomic refractivity of arsenic is calculated from these values to be 11·84 for the *D* line.

No arsine could be obtained from magnesium *tert.*-butyl chloride. H. BURTON.

Boron. II. Action of lithium on ethylamminoboron trifluoride. C. A. KRAUS and E. H. BROWN (J. Amer. Chem. Soc., 1930, **52**, 4414—4418).—Ethylamminoboron trifluoride (A., 1929

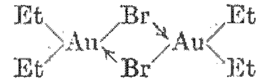
1250) is completely aminolysed in ethylamine solution. Treatment of such a solution with lithium affords hydrogen, lithium fluoride, and *boron triethylimine*, $BF_3+3NH_2Et+3Li=1{\cdot}5H_2+3LiF+B(NHEt)_3$. Boron triethylimine is a liquid which is volatile at the ordinary temperature and readily hydrolysed by water vapour. H. BURTON.

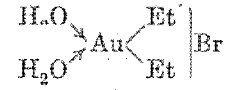
Tin methyl derivatives. VI. Reaction between chloroform and tin sodium trimethyl in liquid ammonia. C. A. KRAUS and A. M. NEAL (J. Amer. Chem. Soc., 1930, 52, 4426—4433).—Tin sodium trimethyl and chloroform react in liquid ammonia forming tin trimethyl and s-*di(trimethylstannyl)ethylene*, $SnMe_3{\cdot}CH{:}CH{\cdot}SnMe_3$, b. p. 194—195°, separable by successive treatment of an ethereal solution of the mixture with iodine and ammonia whereby the tin trimethyl is precipitated as the compound $SnMe_3I,NH_3$. The ethylene derivative is not affected by bromine at the ordinary temperature, but in boiling carbon tetrachloride tin dimethyl dibromide is produced slowly. When treated with sodium in liquid ammonia it furnishes methane, sodamide, and a mixture of tin sodium trimethyl and sodium dimethylvinylstannide, $CH_2{:}CH{\cdot}SnMe_2Na$. The last-named compound is produced by the action of sodium and ammonia on the intermediately formed trimethylvinylstannane according to the equation $CH_2{:}CH{\cdot}SnMe_3+2Na+NH_3 \longrightarrow CH_4+NaNH_2+CH_2{:}CH{\cdot}SnMe_2Na$. Treatment of the above mixture with methyl iodide affords tin tetramethyl and trimethylvinylstannane; the latter has not been obtained pure.

Carbon tetrachloride reacts with sodium tin trimethyl and triethyl forming mainly tin trimethyl and triethyl, respectively. H. BURTON.

Thermal decomposition of gaseous germanium tetraethyl. R. L. GEDDES and E. MACK, jun. (J. Amer. Chem. Soc., 1930, 52, 4372—4380).—Decomposition of germanium tetraethyl, usually in quartz vessels at 420—450°, is followed by measurement of pressure changes; quartz and pyrex glass membrane manometers are used. The reaction is almost wholly homogeneous and is unimolecular at pressures above 80 mm. The velocity coefficient increases with rise of temperature and in presence of 0·1—0·2% of oxygen; the rate is decreased by carbon dioxide, but nitrogen, helium, and argon have little or no effect. Added hydrogen and ethylene enter into hydrogenation and polymerisation reactions, respectively. The products formed by the decomposition are germanium and the pyrolysis compounds of butane (Hurd and Spence, A., 1930, 58). The reactions $GeEt_4 \longrightarrow Ge+4Et$ and $2Et \longrightarrow C_4H_{10}$ may occur. H. BURTON.

Organic compounds of gold. I. Diethylgold bromide and derivatives. C. S. GIBSON and J. L. SIMONSEN (J.C.S., 1930, 2531—2536).—Determinations of the mol. wt. of diethylgold bromide (Pope and Gibson, J.C.S., 1907, 91, 2061) (complete details given for its preparation from magnesium ethyl bromide and gold tribromide) by the cryoscopic method in benzene show that it has the composition $(AuEt_2Br)_2$; it is represented as (I). The bromide is acted on slowly by water with the production of ionisable bromine, probably owing to the tendency of formation of the salt (II). Treatment of the bromide with methyl-alcoholic pyridine furnishes *pyridinodiethylgold bromide*


(I.)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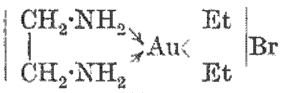
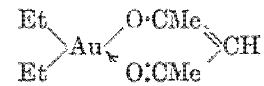
$[AuEt_2Br,C_5H_5N]$, m. p. 59—60° (decomp.; explosive decomp. at about 79°), which, like the ammino-derivative (*loc. cit.*), darkens rapidly when exposed to light. With ethylenediamine in light petroleum, *ethylenediaminodiethylgold bromide* (III), becomes red at 182° and then decomposes gradually, is obtained. Thallous acetylacetone and diethylgold bromide in alcohol give *diethylgold acetylacetone* (IV), m. p. 9—10°, which with bromine in carbon tetrachloride regenerates the bromide. Treatment of IV with sodium iodide in alcohol furnishes


(III.)


(IV.)

diethylgold iodide, m. p. 67—68° (vigorous decomp. at 70—71°), which with ethylenediamine in light petroleum gives *ethylenediaminodiethylgold iodide*, m. p. 162° (decomp.). In all the above compounds gold has a co-ordination number of 4.

H. BURTON.

Distillation of Grignard reagents. H. GILMAN and R. E. BROWN (J. Amer. Chem. Soc., 1930, 52, 4480—4483).—Magnesium alkyl halides (or their equivalents MgR_2+MgX_2) can be distilled by the method previously used for organoberyllium compounds (A., 1928, 50). Magnesium phenyl bromide could not be distilled; during the process, some diphenyl is formed (possibly by the change $RMgX \longrightarrow R{\cdot}+{\cdot}MgX$). High-vacuum sublimation of magnesium alkyl halides gives magnesium dialkyls.

H. BURTON.

Determination of constitution by the displacement of groups from the benzene nucleus. J. W. DIENSKE (Rec. trav. chim., 1930, 49, 1096—1081).—A theoretical paper in which cases of the replacement of one substituent in an aromatic compound by another are systematically summarised. The structure of *p*-thiocyanoaniline (cf. A., 1927, 454) is confirmed by the fact that *p*-chloro(or bromo)thiocyanobenzene is obtained by the appropriate Sandmeyer reaction on either *p*-thiocyanoaniline or *p*-chloroaniline. The observation of Challenger and Collins (A., 1924, i, 953) that *p*-iodothiocyanobenzene is not obtained by the action of cuprous thiocyanate on diazotised *p*-iodoaniline is confirmed. J. W. BAKER.

Behaviour of benzenoid hydrocarbons in the Tesla discharge. J. B. AUSTIN and I. A. BLACK (J. Amer. Chem. Soc., 1930, 52, 4552—4557).—When vapours of aromatic hydrocarbons are excited by the Tesla discharge (cf. A., 1930, 660) two types of compounds are produced: (*a*) shellac-like substances containing oxygen, probably condensed molecules of a phenolic type and (*b*) simple crystalline products. The crystalline products formed from the following substances are quoted in parentheses: benzene

(diphenyl), toluene (dibenzyl and di-*o*-tolyl), *p*-xylene (di-*p*-tolylethane), and chlorobenzene (diphenyl; in this case benzene and chlorine are also produced). The low and high refractive indices of dibenzyl are 1·53 and 1·74, respectively. H. BURTON.

Action of sodium methoxide on derivatives of o-dichlorobenzene. G. M. KRAAY (Rec. trav. chim., 1930, 49, 1082—1092).—The action of sodium methoxide at 180° on the following halogenobenzene derivatives has been investigated: 1 : 2-dichloro-4-nitrobenzene, 3 : 4-dichloroaniline, 3 : 4-*dichlorofluorobenzene* (A., 1929, 1170), 1 : 2 : 4-trichlorobenzene, 3 : 4-dichlorobromobenzene (best obtained by the Sandmeyer reaction from 3 : 4-dichloroaniline), 3 : 4-*dichloroiodobenzene*, b. p. 117°/15 mm., m. p. 30·5° (obtained in 83% yield from 1 : 2-dichloroaniline by the Sandmeyer reaction), 3 : 4-dichlorobenzenesulphonic acid, 3 : 4-*dichlorobenzonitrile*, m. p. 71·8—72·1° (obtained by the action of cuprous cyanide on 3 : 4-dichlorobenzenediazonium chloride), 3 : 4-dichlorophenol (converted by dissolving in concentrated sulphuric acid into its 6(?)-*sulphonic acid*, m. p. 75—76°), 3 : 4-dichlorotoluene, 3 : 4-*dichloronitrosobenzene*, m. p. 88° (prepared by oxidation, with potassium dichromate and sulphuric acid, of 3 : 4-dichlorophenylhydroxylamine, the latter being converted, in alcoholic solution, by atmospheric oxidation into 3 : 4 : 3′ : 4′-*tetrachloroazoxybenzene*, m. p. 139—139·5°), 3 : 4-dichlorobenzophenone, 3 : 4-dichlorobenzaldehyde, m. p. 38° (lit. m. p. 77°), and 3 : 4-dichlorobenzoic acid, m. p. 208—209° (lit. m. p. 204·1—206·5°). The product of the action of sodium methoxide on these compounds is, respectively, I 1-chloro-group replaced, II a resin, III 3 : 4-dichloroanisole, converted into the phenol by prolonged action, IV 2 : 5-dichlorophenol (Holleman, A., 1916, i, 22), V 2-*chloro-5-bromophenol*, m. p. 57°, identical with a specimen obtained by the diazo-reaction from 2-chloro-5-bromoaniline, prepared by reduction of the corresponding nitro-compound, VI 3 : 4-dichlorophenol and 2-*chloro-5-iodophenol*, m. p. 56·5°, identical with a specimen synthesised by the action of potassium iodide on diazotised 4-chloro-3-nitroaniline to yield 1-*chloro-4-iodo-2-nitrobenzene*, m. p. 74·5°, reduction of this with titanous chloride to 2-*chloro-5-iodoaniline*, m. p. 61·6°, and conversion into the phenol by diazotisation; VII 2-chlorophenol-4-sulphonic acid, converted by nitric acid (*d* 1·52) into 2-chloro-4 : 6-dinitrophenol; VIII hydrolysis of the nitrile group; IX no action; X 4-chloro-*m*-cresol, m. p. 46° (Gibson, A., 1926, 832, gives m. p. 57°), identical with a specimen obtained from 4-chloro-*m*-toluidine by the diazo-reaction; XI 3 : 4 : 3′ : 4′-tetrachloroazoxybenzene; XII—XIV, chlorine partly replaced, but the products were not identified. Under comparable conditions the amount of the halogen replaced is as follows: I 83(F) and 4(Cl); II 72; III 83(Cl) and a trace of bromine; IV 94(Cl+I); V 79; VI 3; VII 20; and VIII 0%, respectively.

J. W. BAKER.

Direct *meta*-substitution in the toluene nucleus. J. B. SHOESMITH and J. F. MCGECHEN (J.C.S., 1930, 2231—2236).—*tert.*-Butyl chloride reacts with toluene in presence of aluminium chloride at 0—5° forming 46% of the theoretical amount of a mixture of *m*- (6·5—7 parts) and *p*-*tert.*-butyltoluenes (3—3·5 parts); in presence of nitrobenzene the yield is improved to 70% without affecting the ratio. Baur's statement (A., 1891, 1464) that only the *m*-derivative is produced is, therefore, incorrect. A similar mixture is produced from *sec.*-butyl bromide and toluene in presence of aluminium chloride or from the above reactants in presence of ferric chloride (cf. Bialobrzeski, A., 1897, i, 514, who states that only the *p*-compound is formed). The amounts of isomerides produced are determined either by treating the mixture with sulphuric acid at the ordinary temperature, extracting the unaffected *p*-derivative, and regenerating the *m*-*tert.*-butyltoluene from its sulphonic acid by distillation with superheated steam, or by complete sulphonation of the mixture at 100° and fractional crystallisation of the *barium* salts of the sulphonic acids produced. Toluene and *n*-butyl chloride in presence of aluminium chloride give 45% of the theoretical amount of a mixture of *m*- (75 parts) and *p*-*sec.*-butyltoluenes (25 parts); the latter is unaffected by sulphuric acid at the ordinary temperature.

Magnesium *m*- and *p*-tolyl bromides react with methyl ethyl ketone forming the corresponding carbinols, which are dehydrated with boiling acetic anhydride to β-*m*- and β-*p*-tolyl-Δ^{β}-butenes, respectively. The former of these is reduced with sodium and alcohol to *m*-*sec.*-butyltoluene, b. p. 194—198° (*sulphonyl chloride*, b. p. 164—165°/11 mm.; *sulphonanilide*, m. p. 119·5—120·5°), and the latter with red phosphorus and hydriodic acid (b. p. 127°) to *p*-*sec.*-butyltoluene (*sulphonyl chloride*, b. p. 162—164°/12 mm.; *sulphonanilide*, m. p. 124·5—125°). These unoriented sulphonic acid derivatives were also prepared from the hydrocarbons obtained in the Friedel–Crafts reaction.

The observations (lit.) that toluene and acetyl chloride in presence of aluminium chloride give *p*-tolyl methyl ketone are confirmed. H. BURTON.

Diphenyl-2 : 2′-disulphonic acid. VIII. W. M. STANLEY and R. ADAMS (J. Amer. Chem. Soc., 1930, 52, 4471—4476).—Reduction of azobenzene-3 : 3′-disulphonic acid with stannous chloride and hydrochloric acid gives 4 : 4′-diaminodiphenyl-2 : 2′-disulphonic acid [*strychnine* salt, m. p. 310—318° (decomp.), $[\alpha]_D^{20}$ −22·4° in water; *brucine* salt, m. p. 311—314° (decomp.), $[\alpha]_D^{20}$ −24·6° in water], convertible by the usual method into diphenyl-2 : 2′-disulphonic acid [*brucine* salt, m. p. 245—248°, $[\alpha]_D^{20}$ −33·2° in chloroform; *quinine* salt, m. p. 189—192°, $[\alpha]^{20}$ −83·5° in chloroform; *morphine* salt, m. p. 261—267° (decomp.), $[\alpha]_D^{20}$ −75·1° in water]. No evidence of resolution was obtained, although the size of the sulphonic acid group is sufficiently large to interfere with the 6(6′)-hydrogen atom.

H. BURTON.

Reaction between triphenylmethyl, magnesium, and a small amount of magnesium halide. Composition of the Grignard reagent. W. E. BACHMANN (J. Amer. Chem. Soc., 1930, 52, 4412—4413).—Magnesium reacts with triphenylmethyl in presence of a small amount of magnesium iodide (not in its absence) in ethereal benzene in an atmosphere of nitrogen forming magnesium triphenylmethyl,

which is hydrolysed to triphenylmethane. The reactions taking place are: $2CPh_3+Mg+MgI_2 \longrightarrow 2CPh_3{\cdot}MgI \rightleftharpoons (CPh_3)_2Mg+MgI_2$, *i.e.*, a small amount of magnesium iodide causes continuous reaction. Magnesium triphenylmethyl is also produced when triphenylmethyl and magnesium react in presence of a small amount of triphenylmethyl bromide; in this case, the bromide is converted into triphenylmethyl and magnesium bromide with subsequent reaction as above. H. Burton.

s-Diphenyldi-*n*-alkylethanes and their stereoisomerism. A. Leepin (Latvij. Univ. Raksti, 1930, 1, 145—232).—α-Bromoethylbenzene is converted by treatment with magnesium into a mixture of *dl*-, b. p. 283—284°/752 mm., 140°/10 mm., m. p. 8°, d_4^{20} 0·9757, 1·55516, and *meso*-, m. p. 126°, -βγ-diphenyl-*n*-butanes. Sodium reacts with α-halogenoalkylbenzenes, $CHXPh{\cdot}CH_2Alk$, forming mixtures of *s*-diphenyldi-*n*-alkylethanes, $(CHPh{\cdot}CH_2Alk)_2$, structural isomerides of these, the ethylenes, $CHPh{:}CHAlk$, and the alkylbenzenes, $CH_2Ph{\cdot}CH_2Alk$. The following *s*-diphenyldi-*n*-alkylethanes are described: *dl*-, b. p. 297—298°/767 mm., d_4^{20} 0·9591, n^{20} 1·54622, and *meso*-, m. p. 90°, -γδ-diphenyl-*n*-hexanes; *dl*-, b. p. 178—179°/13 mm., d_4^{20} 0·9452, 1·53663, and *meso*-, m. p. 98°, -δε-diphenyl-*n*-octanes; *dl*-, b. p. 183—184°/10 mm., d_4^{20} 0·9337, n^{20} 1·52857, and *meso*-, m. p. 79·5°, -εζ-diphenyl-*n*-decanes; *dl*-, b. p. 223—224°/10 mm., d_4^{20} 0·9174, n^{20} 1·51770, and *meso*-, m. p. 59°, -ηθ-diphenyl-*n*-tetradecanes. The m. p. of the *meso*-forms decrease (with alternation) with increasing length of the carbon chain, whilst for the *dl*-modifications, the density decreases with increased carbon content. Both *dl*- and *meso*-forms are oxidised to phenyl *n*-alkyl ketones; the m. p. of the semicarbazones decrease (with alternation) with the length of the alkyl group. The same equilibrium mixture is obtained when either modification is heated at 230—300° in presence of a catalyst such as iodine.

The mechanism of the formation of the structural isomerides of the above stereoisomeric hydrocarbons is discussed and various observations are made regarding the Wurtz–Fittig reaction. An explanation of the mechanism of racemisation is made from the viewpoint of the chemical theory of catalysis. Racemisation and the Walden inversion are considered from a common viewpoint as two phenomena identical in principle. H. Burton.

Synthesis of alkylnaphthalenes. II. 1:3:5- and 1:3:8-Trimethylnaphthalenes. I. M. Heilbron and D. G. Wilkinson (J.C.S., 1930, 2537—2542).—2:4-Dimethylbenzaldehyde condenses with ethyl acetate in presence of sodium wire forming *ethyl* 2 : 4-*dimethylcinnamate*, b. p. 135—137°/5 mm., reduced by sodium and alcohol to γ-2 : 4-*dimethylphenylpropyl alcohol*, b. p. 126°/5 mm. (*phenylcarbimide* derivative, m. p. 81°). This is converted by way of the *bromide*, b. p. 147°/18 mm., and nitrile, b. p. 175—177°/23 mm., into γ-2 : 4-*dimethylphenylbutyric acid*, m. p. 78—79° (*amide*, m. p. 128—129°, formed as a by-product during the preparation of the nitrile); the *acid chloride*, b. p. 136—138° 9 mm., is then converted by treatment with aluminium chloride under the conditions previously described (A., 1930, 593) into 5-*keto*-1 : 3-*dimethyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, b. p. 160°/14 mm. [*semicarbazone*, m. p. 243—246° (decomp.)]. The carbinol from this ketone and magnesium methyl iodide is dehydrated by boiling acetic anhydride to 1 : 3 : 5-*trimethyl*-7 : 8-*dihydronaphthalene*, b. p. 143—145°/18 mm., which is dehydrogenated by selenium to 1 : 3 : 5-*trimethylnaphthalene*, m. p. 47° (*picrate*, m. p. 141—142°; *styphnate*, m. p. 138°).

2 : 4-Dimethylacetophenone and ethyl bromoacetate react in presence of zinc and benzene forming mainly impure *ethyl* β-*hydroxy*-β-2 : 4-*dimethylphenylbutyrate*, b. p. 170—180°/20 mm. (free *acid*, m. p. 70—72°), dehydrated by treatment with phosphoryl chloride in benzene to *ethyl* β-2 : 4-*dimethylphenylcrotonate*, b. p. 160—170°/20 mm. Reduction of this gives a mixture of γ-2 : 4-*dimethylphenylbutyl alcohol*, b. p. 152—153°/19 mm. (*bromide*, b. p. 143°/17 mm.), and β-2 : 4-*dimethylphenylbutyric acid*, m. p. 69°, the *ethyl* ester, b. p. 168—170°/25 mm., of which is reduced by sodium and propyl alcohol at 130° to the alcohol. The *chloride*, b. p. 157—160°/18 mm., of γ-2 : 4-*dimethylphenylvaleric acid*, b. p. 175°/9 mm. (*amide*, m. p. 91—92°), when treated with aluminium chloride in light petroleum (b. p. 90—100°) affords 5-*keto*-1 : 3 : 8-*trimethyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, b. p. 174—176°/20 mm. (*semicarbazone*, m. p. 220—222°), reduced by Clemmensen's method to 1 : 3 : 8-*trimethyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, b. p. 133—136°/18·5 mm. This is dehydrogenated by selenium at 300° to 1 : 3 : 8-*trimethylnaphthalene*, m. p. 48° (*picrate*, m. p. 125°; *styphnate*, m. p. 140·5°). H. Burton.

Unsaponifiable matter from oils of elasmobranch fish. VIII. Structure of the naphthalene hydrocarbon derived from squalene. I. M. Heilbron and D. G. Wilkinson (J.C.S., 1930, 2546—2554).—The naphthalene hydrocarbon previously obtained (A., 1927, 130) by dehydrogenation of tetra*cyclo*squalene with sulphur or, better, with selenium at 300° is 1 : 2 : 5-trimethylnaphthalene, since it is not identical with the 1 : 3 : 8-isomeride (preceding abstract) and is oxidised to a series of products which can arise only from either the 1 : 2 : 5- or 1 : 3 : 8-derivatives. Prolonged oxidation of the hydrocarbon with potassium ferricyanide in potassium hydroxide solution at 60° affords *naphthalene*-1 : 2 : 5-*tricarboxylic acid*, m. p. 270—272° (*methyl* ester, m. p. 89°), whilst oxidation with chromic acid in 80% acetic acid at 60° furnishes a mixture of the following substances: a 1 : 2 : 5-*trimethyl*-β-*naphthaquinone*, decomp. 130—135°, isolated in appreciable amount only when oxidation is arrested before completion; 1 : 6-dimethyl-α-naphthaquinone, m. p. 94° (*phenylhydrazone*, m. p. 226°); (?)5 : 8-*diacetoxy*-1 : 6-*dimethylnaphthalene*, m. p. 70—71°; 3-*methylacetophenone-2-carboxylic acid*, m. p. 126° {*semicarbazone*, m. p. 177° (decomp.); *methyl* ester, m. p. 47—48° [*semicarbazone*, m. p. 215° (decomp.)]}, oxidised by sodium hypobromite to 3-methylphthalic acid; 4-*methylacetophenone-2-carboxylic acid*, m. p. 125—126° [*semicarbazone*, m. p. 182° (decomp.); *methyl* ester, m. p. 71—72°]; 3 : 4-*dimethylacetophen*-

one-2-carboxylic acid, m. p. 105° [*semicarbazone,* m. p. 217° (decomp.); *methyl* ester, m. p. 78—79°]. 3-Methylacetophenone-2-carboxylic acid crystallises from the acid fraction; the other acids are separated from the residue by fractionation of the mixed methyl esters. During the oxidation with chromic acid scission of the hydrocarbon occurs in both rings.

The formation of 1 : 2 : 5-trimethylnaphthalene from a sesquiterpene of the farnesene type can be formulated; two methyl groups must be eliminated on passing from the hydroaromatic to the aromatic condition. H. BURTON.

Purification of phenanthrene. F. L. COHEN and U. CORMIER (J. Amer. Chem. Soc., 1930, **52**, 4363—4364).—Crude phenanthrene is crystallised from 95% alcohol and this material (1 kg.) heated with alcohol (6 litres) and concentrated nitric acid (120 g.). The resultant solution (freed, if necessary, from insoluble oxidation products) is cooled, the crystalline material distilled in portions of 500 g., and finally crystallised from alcohol. The overall yield of pure phenanthrene, m. p. 99—99·5°, is 30—45% of the crude product. H. BURTON.

Pyrolysis of allylanilines. F. L. CARNAHAN and C. D. HURD (J. Amer. Chem. Soc., 1930, **52**, 4586—4595).—When allylaniline [p-*toluenesulphonyl* derivative, m. p. 69·3° (corr.)] is heated at 275°, aniline, propylene, and resinous material are produced (cf. Dains and others, A., 1923, i, 62). At 600°, propylene, ethylene, hydrogen, carbon monoxide, nitrogen, gaseous paraffin hydrocarbons, a small amount of benzene, aniline, and unidentified products are formed; at 700°, a small amount of quinoline is also obtained. Diallylaniline decomposes at 275° to a mixture of products similar to that obtained from allylaniline. *Diallyl*-p-*phenetidine*, b. p. 164—165°/23 mm., d_4^{23} 0·9921, n_D^{23} 1·5458, affords similarly mainly propylene, *p*-phenetidine [p-*toluenesulphonyl* derivative, m. p. 110° (corr.)], and resinous material. Various mechanisms are suggested for the changes; allene is not a product of the pyrolysis. H. BURTON.

Rhythmic phenomena in the combination of methylethylaniline with ethyl iodoacetate. P. FREUNDLER and (MLLE.) PILAUD (Bull. Soc. chim., 1930, [iv], **47**, 1151—1157).—When equimolecular quantities of ethyl iodoacetate and diethyl- or methyl-*iso*butyl-aniline are mixed the clear mixture gradually becomes turbid and a coloured syrup accumulates at the bottom of the vessel which in some cases has the consistency of a gel. The surface of separation is sharp and after a rapid initial increase the volume of syrup gradually becomes constant, the syrup then containing, in the case of diethylaniline, the quaternary iodide with about 20% of iodoacetate, whilst the supernatant liquid consists of nearly pure tertiary amine.

With methylethylaniline turbidity first appears after about 2 hrs. 20 min. and the limit is reached in 4 days, the rate of combination decreasing rapidly after 12 hrs. No sensible heat of reaction is observed and there is a final contraction of about 6% by volume, the viscosity of the suspended drops increasing as the volume of syrup increases. A periodic stratification of coloured zones appears at intervals of 24 hrs. and persists for 1—2 months until diffusion gradually renders the surface of separation less sharp. The stratification is intensified when the tube is surrounded with silver. The phenomenon is regarded as due to the nature of the material, in particular the nitrogen atom, and not to external factors. R. BRIGHTMAN.

Reduction of Schiff's bases. L. ZECHMEISTER and J. TRUKA (Ber., 1930, **63**, [*B*], 2883—2884).—The Schiff's base is dissolved in nearly anhydrous methyl alcohol and treated with at least five times the theoretical quantity of magnesium; the mixture is heated or cooled as required. After disappearance of the metal, the alcohol is mainly recovered by distillation; the residue is treated with ice-water and sufficient 30—50% acetic acid to dissolve the magnesium hydroxide. The following bases are obtained in 70—90% yield: benzylaniline, m. p. 37—38°; *p*-methoxybenzylaniline, m. p. 64·5°; γ-phenylpropylaniline, b. p. 193—195°; *o*-hydroxybenzylaniline, m. p. 108°; phenylpiperonylamine, m. p. 78°; *p*-dimethylaminobenzylaniline, m. p. 62°; benzyl-*p*-toluidine, b. p. 318—320°; methoxybenzyl-*p*-toluidine, m. p. 65°; benzyl-α-naphthylamine, m. p. 67°; methoxybenzyl-α-naphthylamine, m. p. 80°; benzyl-β-naphthylamine, m. p. 68°; methoxybenzyl-β-naphthylamine, m. p. 104·5°. H. WREN.

$\alpha\gamma$-Migration of [aryl]amino-groups. Mechanism. Applications to other analogous reactions. J. ROBIN (Compt. rend., 1930, **191**, 1013—1015; cf. A., 1930, 1571).—In addition to that named in the title, two mechanisms are suggested for the transformation $NHPh\cdot CPh_2\cdot C{:}CPh \longrightarrow CPh_2{:}CH\cdot CPh{:}NPh$; the first, involving $\alpha\gamma$-migration of a phenyl group and subsequent rearrangement, is disproved, since $NHPh\cdot CPh_2\cdot C{:}C\cdot C_7H_7(p)$ yields, not $NPh{:}CPh\cdot CH{:}CPh\cdot C_7H_7(p)$, but $CPh_2{:}CH\cdot C({:}NPh)\cdot C_7H_7(p)$. The second mechanism involves addition of hydrogen chloride to the triple linking followed by simultaneous elimination of aniline and condensation with an external aniline molecule. In support, it is found that compounds $CAr_2Cl\cdot C{:}CAr$ give unstable but well-defined hydrochlorides, which are very sensitive to water, being converted into unsaturated ketones, $CAr_2Cl\cdot CH{:}CClAr \longrightarrow CAr_2{:}CH\cdot COAr$. This mechanism is adopted (the aniline and water acting similarly) and the $\alpha\gamma$-migration of arylamino-groups is therefore only apparent. It is suggested that a similar mechanism should apply to other transformations, apparently involving $\alpha\gamma$-migration, of acetylenic compounds. The *hydrochlorides* of diphenyl-β-naphthyl- and diphenyl-*p*-bromophenyl-ethinyl chloride have m. p. 155° and 100°, respectively. C. W. SHOPPEE.

Acenaphthene series. V. G. T. MORGAN and H. A. HARRISON (J.S.C.I., 1930, **49**, 413—421T).—The substances previously described as 1-nitro- and 1-amino-acenaphthene and derivatives (A., 1925, i, 1144) are impure forms of the 3-nitro-compounds (cf. J.S.C.I., 1928, **47**, 16T). Nitration of acenaphthene with benzoyl nitrate or diacetylorthonitric acid under carefully regulated conditions does, how-

ever, give 1-*nitroacenaphthene*, m. p. 151°, characterised by the greyish-blue colour of its solution in cold concentrated sulphuric acid, which rapidly changes to bright red; this test serves for its detection in the products of nitration under ordinary conditions. On oxidation it gives 1-*nitro*-7 : 8-*dihydroxyacenaphthene*, orange-red, m. p. 137—139°, and 2-*nitronaphthalic acid*, m. p. 173—175° (as anhydride, m. p. 190—200°). 1-*Aminoacenaphthene*, m. p. 81·5° (*hydrochloride*; *sulphate* (+1H_2O), m. p. 235°; *picrate*, decomp. 221°: *formyl*, m. p. 151—152°; *acetyl*, m. p. 192—193°; *benzoyl*, m. p. 209—210°; *benzylidene*, m. p. 65—66°; o-*nitrobenzylidene*, m. p. 143·5—144·5°; m-*nitrobenzylidene*, m. p. 142·5—143·5°; and p-*nitrobenzylidene*, m. p. 157—158°, derivatives) is formed on reduction, accompanied by a little 1 : 6-*diaminoacenaphthene*, m. p. 167—168°, when the crude 3-nitro-compound is employed. 1-*Chloro-*, m. p. 76—77°, 1-*bromo-*, m. p. 78°, 1-*iodo-*, m. p. 87°, and 1-*hydroxy-acenaphthene*, m. p. 151—151·5°, are prepared through the diazo-compound, and 1-*aminoacenaphthenemono-*, -di-, and -tri-sulphonic acids by direct sulphonation.

Nitration of 1-formamidoacenaphthene in acetic acid at 12° gives 3-*nitro-*, m. p. 260—262° (decomp.), and 2(?)-*nitro*-1-*formamidoacenaphthene*, m. p. 193—196°; the former is readily hydrolysed to 3-*nitro*-1-*aminoacenaphthene*, m. p. 199—200° (*hydrochloride*, decomp. 235°). No similar product was obtained from 1-acetamidoacenaphthene, but 1-benzamidoacenaphthene gave the 3(?)-*nitro*-derivative, m. p. 215—216°. 1 : 4-*Dinitro-*, decomp. 205—206°, and a little 1 : 6-*dinitro-acenaphthene*, m. p. 155—156°, are obtained by dissolving the 1-nitro-compound in nitric acid; the latter is more readily prepared by use of diacetylorthonitric acid; this reagent with 3-nitroacenaphthene appears to give a mixture of 1 : 4- and 3 : 4-dinitroacenaphthenes. Partial reduction of the appropriate dinitro-compound with stannous chloride and hydrochloric acid in glacial acetic acid gives 4-*nitro*-1-*aminoacenaphthene*, m. p. 181°. The action of excess of nitric acid, followed by hydrochloric acid at 70°, on acenaphthene dissolved in glacial acetic acid gives 4-chloro-3-nitro- and the 4-chloronitro-acenaphthene of Farnell (J.C.S., 1923, **123**, 60); from the reduction product of the former 3 : 4-*dichloroacenaphthene*, m. p. 169—170°, may be obtained by the Sandmeyer reaction. It is more conveniently prepared from 3-chloroacenaphthene and sulphuryl chloride, and is converted by fuming nitric acid at 10° into a *mono-*, m. p. 157—160°, and *di-nitro*-derivative, m. p. 248—250°. Reduction of 3-nitro- with zinc dust and alcoholic calcium chloride gives 3-*azoxy-acenaphthene*, m. p. 180°. *Di*-3-*acenaphthenyl ether*, m. p. 210—215°, is prepared by heating 3-chloroacenaphthene with methyl-alcoholic alkali at 200—210°, or from the sodium 3-sulphonate with aqueous alkali under identical conditions. The following also are described: *acenaphthene*-3-*diazonium chloroaurate*; 3-*acenaphthenylazoimide*, m. p. 66—68° (from sodium azide and the diazonium salt): 3′-*acenaphthene*-2-*azo*-3-*acenaphthenol*, m. p. above 305° (by diazotisation of 3-aminoacenaphthene under special conditions); 3 : 3′-*diamino*-2 : 2′-*diacenaphthenylmethane*, brick-red, m. p. 226—229°, and an *acenaphtheneacridine*, m. p. above 300° (from 3-aminoacenaphthene hydrochloride and formaldehyde in alcoholic solution); 2-*iodoacenaphthene*, m. p. 88—90°; p-*nitrobenzenediazo*-1-*amino-*, m. p. 140—142°, and -3-*amino-acenaphthene*, m. p. 170—173°. The oxidation of acenaphthene and its 3-nitro- and 3-chloro-derivatives by a variety of agents to the quinone and naphthalic acid, and the preparation of resins from acenaphthene or its 3-chloro- (but not 3 : 4-dichloro-)derivative and formaldehyde are described. The acenaphthene resin can be oxidised to a tricarboxylic acid, probably $C_{13}H_8O_6$, m. p. 265—268°.

H. A. PIGGOTT.

p-Aminophenylguanidine hydriodide. C. E. BRAUN (J. Biol. Chem., 1930, **89**, 97—108).—Equimolecular proportions of *S*-methyl*iso*thiocarbamide hydriodide and *p*-phenylenediamine, when heated together in aqueous or alcoholic solution, yield p-*aminophenylguanidine hydriodide*, m. p. 209—210°. Solubility data are given for this salt. In doses of 5—10 mg. per kg. the compound exercised a definite hypoglycæmic effect in rabbits without apparent toxic action.

C. R. HARINGTON.

Constitution and reactions of isomeric diazohydroxides. A. ANGELI (Atti R. Accad. Lincei, 1930, [vi], **11**, 923—929).—Polemical against Hantzsch (A., 1930, 1032).

T. H. POPE.

Double linking. II. Spatial configuration of aromatic azo-compounds. E. BERGMANN, L. ENGEL, and S. SANDOR (Ber., 1930, **63**, [*B*], 2572—2575).—The dipole moments of azobenzene and 4 : 4′-dibromoazobenzene are zero, whereas 4-chloro- and 4-bromo-azobenzene have exactly the dipole moments of chlorine and bromine as deduced from chloro- and bromo-benzene. The azo-hydrocarbons have therefore the *trans* structure.

H. WREN.

Group influence on the colours of substituted benzeneazophenols, including o-azophenols. H. H. HODGSON and W. ROSENBERG (J.S.C.I., 1930, **49**, 405—408T; cf. B., 1929, 1008; A., 1930, 906).—The results obtained are discussed from the viewpoint of modern electronic theory under five headings. (*a*) Differences between the isomeric *o*- and *p*-hydroxy-azo-dyes. Here in all the cases investigated, coupling in *o*-position produces a deeper (redder) dye than does coupling in *p*-position. (*b*) Influence of groups on the colours of substituted *o*-hydroxyazo-dyes. (*c*) Influence of halogeno-substitution in *o*-position to the hydroxyl group in the *p*-hydroxyazo-dyes. Each of the aniline⟶*o*-halogenophenol dyes is found to be redder than unsubstituted benzeneazophenol, which establishes that in all cases ionisation has been promoted by the general effect of the halogen. The order of electronic restraint being Cl>Br>I, the consequent order of electronic mobility with attendant ease of photo-activation will be I>Br>Cl as observed. (*d*) Influence of the nitro- and sulphonic acid groups when in the aniline (first) component. An electronic explanation is given for the effect of the nitro-group in *p*-position greatly exceeding that in the *o*- and *m*-positions, respectively. (*e*) Influence of chlorine, especially in positions adjacent to the azo-group. Here certain additive relationships are indicated and

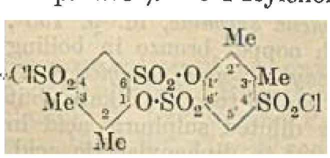
an explanation is given for the greater effect of two chlorine atoms *ortho*- to the azo-group when in the phenolic than when in the other nucleus.

Action of ferric chloride on acyl esters of phenol. H. Huber and K. Brunner (Monatsh., 1930, **56**, 322—330).—When phenyl acetate is heated with an equal weight of anhydrous ferric chloride at 100° (bath), *p*-hydroxyacetophenone is obtained in 10% yield (on ester used); at 65° the yield is improved to 25%. Similar treatment of phenyl *iso*butyrate affords p-*hydroxyphenyl* iso*propyl ketone* (16% yield), m. p. 56°, and a small amount of the o-*isomeride*, an oil, b. p. about 110°/10 mm. (*oxime*, m. p. 129°; *dibromo*-derivative, m. p. 97°), whilst phenyl benzoate gives a mixture of 2- and 4-hydroxybenzophenone (28% yield; *phenylhydrazone*, m. p. 144°; *semicarbazone*, m. p. 194°). Diphenyl derivatives were not isolated in any of the above experiments. H. Burton.

Action of aromatic alcohols on aromatic compounds in presence of aluminium chloride. V. Benzylation of *o*-cresol. R. C. Huston, H. A. Swartout, and G. K. Wardwell (J. Amer. Chem. Soc., 1930, **52**, 4484—4489).—Benzyl alcohol (1 part) reacts with *o*-cresol (1 part) in presence of aluminium chloride (0·65 part) and light petroleum (2 parts) at 30—35°, forming mainly 5-*benzyl*-o-*cresol*, b. p. 167—169°/5 mm., m. p. 49·5—50·5° (*benzoate*, m. p. 54—55°; 3-*bromo*-derivative, b. p. 182—184°/5 mm.), together with small amounts of 3-benzyl-*o*-cresol, b. p. 150—152°/5 mm., m. p. 49·5—50·5° (*benzoate*, b. p. 216—218°/5 mm.; 5-*bromo*-derivative, b. p. 187—189°/5 mm., m. p. 63—64°, prepared also from benzyl chloride and sodium 5-bromo-*o*-tolyloxide in toluene), and 3 : 5-*dibenzyl*-o-*cresol*, b. p. 225—227°/5 mm. Benzyl chloride and sodium *o*-tolyloxide in toluene afford the above 3-benzyl-*o*-cresol (cf. Schorigin, A., 1925, i, 1404). 5-Benzyl-*o*-cresol, zinc ammonium chloride, and ammonium chloride at 330° give a small amount of 4-amino-3′-methyldiphenylmethane, which after elimination of the amino-group and subsequent oxidation with potassium dichromate and sulphuric acid yields *m*-benzoylbenzoic acid. H. Burton.

Action of chlorosulphonic acid on phenols. VI. Xylenol-sulphonyl chlorides and -sulphonylides. E. Katscher (Monatsh., 1930, **56**, 381—390).—The action of chlorosulphonic acid on five xylenols is investigated.

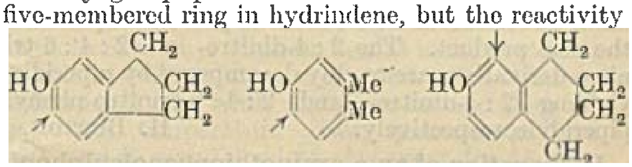
[With H. Lehr, A. Harnisch, and L. Steinhardt.] Treatment of *vic.-o*-xylenol with 10 parts of chlorosulphonic acid at −5° to 0° (bath) gives water-soluble products; at 110° a mixture of approximately equal amounts of the 4 : 6-*disulphonyl chloride*, m. p. 104—105° (*disulphonanilide*, m. p. 232°), and 2 : 3 : 2′ : 3′-*tetramethyldiphenyl*-1 : 6 : 1′ : 6′-*sulphonylide*-4 : 4′-*disulphonyl chloride* (I), decomp. 295° (*disulphonanilide*, m. p. 273°). *o*-4-Xylenol is converted similarly at the ordinary temperature into probably the 3 : 5-*disulphonyl chloride*, m. p. 72° (*disulphonanilide*, m. p. 160°), since the corresponding acid couples with diazotised *p*-nitroaniline in neutral or alkaline solution. *p*-



(I.)

Xylenol and chlorosulphonic acid at 110—150° give p-*xylenol*-3 : 6-*disulphonyl chloride*, m. p. 58° (*disulphonanilide*, m. p. 173°; the free acid couples with diazotised *p*-nitroaniline), together with an unidentified substance, m. p. 104—105°. Two *disulphonyl chlorides*, m. p. 89—91° and 117—119° (corresponding *disulphonanilides*, m. p. 160—161° and 205—207°), are obtained from *m*-5-xylenol and 10 parts of chlorosulphonic acid at the ordinary temperature; when the reaction is carried out with a mixture of chlorosulphonic acid and sulphur trioxide at 60—70°, the former chloride is the sole product. *m*-4-Xylenol and chlorosulphonic acid at the ordinary temperature yield a mixture of probably m-4-*xylenol*-5-*sulphonyl chloride*, m. p. 93—95°, and 3 : 5 : 3′ : 5′-*tetramethyldiphenyl* 1 : 6 : 1′ : 6′-*sulphonylide*, decomp. above 300°. The former of these derivatives gradually changes to a water-soluble oil; an aqueous solution contains free sulphuric acid and gives a colour with ferric chloride. It is suggested that the chloride may be *m*-4-xylenol-*O*-sulphonyl chloride. H. Burton.

Stereochemical influences on aromatic substitution. Substitution derivatives of 5-hydroxyhydrindene. W. H. Mills and I. G. Nixon (J.C.S., 1930, 2510—2524).—It is argued, on stereochemical grounds, that of the two possible configurations of hydrindene required by the Kekulé formula, I is the more stable, and that 5-hydroxyhydrindene should be substituted by bromine and diazonium salts mainly in the 6-position. For details of the reasoning the original should be consulted. Application of these criteria to *o*-4-xylenol (II; cf. Diepolder, A., 1909, i, 786) and 4-acetamido-*o*-xylene indicates that the *o*-methyl groups produce an effect similar to that of the five-membered ring in hydrindene, but the reactivity



(I.) (II.) (III.)

of the 1-position in *ar*-tetrahydro-β-naphthol (cf. Schroeter, A., 1922, i, 123; Smith, J.C.S., 1904, **85**, 730) is in favour of the alternative configuration (III) for this.

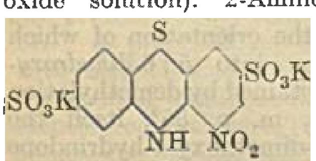
5-Hydroxyhydrindene (cf. Moschner, A., 1900, i, 344) is obtained by reduction of 5-hydroxy-1-hydrindone (A., 1917, i, 37) by Clemmensen's method. 6-p-*Chlorobenzeneazo-5-hydroxyhydrindene*, m. p. 155—156°, is formed in 90% yield, mixed (presumably) with 10% of 4-isomeride. 6-p-*Tolueneazo-5-hydroxyhydrindene*, m. p. 132·5°, is reduced by alcoholic stannous chloride to 6-*amino-5-hydroxyhydrindene*, m. p. 185—186° (described by Borsche and John, A., 1924, i, 723, as the 4-amino-compound), the orientation of which follows from its conversion into 5 : 6-*dihydroxyhydrindene*, m. p. 116°, also obtained by demethylation of 5 : 6-*dimethoxyhydrindene*, m. p. 55°, itself the reduction product of 5 : 6-dimethoxy-1-hydrindone (J.C.S., 1907, **91**, 1079). 6-*Bromo-5-hydroxyhydrindene*, m. p. 37·7°, b. p. 143°/14 mm., is the product of direct bromination of the hydroxy-compound, and may also be obtained from 6-amino-5-hydroxyhydrindene by the Sandmeyer reaction.

Bromination of 4-acetamido-*o*-xylene in acetic acid gives the 5-*bromo*-derivative, m. p. 164°, hydrolysed by 50% sulphuric acid to 5-*bromo*-o-4-*xylidine*, m. p. 84·5°, converted by Sandmeyer's reaction into 4 : 5-dibromo-*o*-xylene (A., 1885, 142). H. A. PIGGOTT.

β-Naphthol-3-sulphonic acid. S. HOLT and F. A. MASON (J. Soc. Dyers and Col., 1930, **46**, 270—271).—The synthesis of β-naphthol-3-sulphonic acid, hitherto the only one of the seven possible β-naphtholsulphonic acids not prepared, is announced but not described. It couples smoothly with diazo-components to give dyes of slightly redder shade than the corresponding dyes from Schaeffer acid, and having similar dyeing properties. The *aniline* and *α-naphthylamine* salts of the 2 : 3-acid prepared by the method of Forster and Keyworth (J.S.C.I., 1924, **43**, 166T, 299T) have m. p. 241—242° and 247—248°, respectively. A. J. HALL.

Nitration of substituted diaryl ethers. Phenyl *p*-tolyl ether. J. REILLY, P. J. DRUMM, and T. GRAY (Sci. Proc. Roy. Dublin Soc., 1930, **19**, 461—465).—Nitration of phenyl *p*-tolyl ether with nitric acid (*d* 1·51) at $-20°$ to $-10°$ affords (?) 4-*nitrophenyl* 3-*nitro*-p-*tolyl ether*, m. p. 101—102°, which when treated with boiling piperidine does not undergo appreciable scission. Nitration of the ether in presence of acetic acid gives a *nitro*-derivative, b. p. 204°/21 mm. Partial scission of the ether occurs during nitration (cf. A., 1927, 239). *Phenyl* 3-*nitro*-p-*tolyl ether*, b. p. 224—225°/24 mm., 2 : 4-*dinitrophenyl* p-*tolyl ether*, m. p. 93°, and *phenyl* 3 : 5-*dinitro*-p-*tolyl ether*, m. p. 70°, are synthesised by the usual methods. 2 : 4 : 6-*Trinitrophenyl* p-*tolyl ether*, m. p. 103°, is obtained from picryl chloride and potassium *p*-tolyloxide in cold alcohol; in the hot, potassium picrate is the sole product. The 2 : 4-dinitro- and 2 : 4 : 6-trinitro-derivatives are readily decomposed by piperidine yielding 2 : 4-dinitro- and 2 : 4 : 6-trinitro-phenylpiperidine, respectively. H. BURTON.

Preparation of an *o*-aminothiophenolsulphonic acid. J. POLLAK and K. DEUTSCHER (Monatsh., 1930, **56**, 365—380).—When potassium 4-chloro-3-nitrobenzenesulphonate is heated with an aqueous solution of potassium hydrogen sulphide, the resulting solution evaporated to dryness, and the residue reduced with tin and hydrochloric acid, 2-*aminothiophenol*-4-*sulphonic acid* is obtained in 75% of the theoretical amount. This reacts with potassium 4-chloro-3 : 5-dinitrobenzenesulphonate in presence of aqueous sodium acetate, forming *potassium* 5-*nitrophenthiazine*-3 : 8-*disulphonate* (I) ($+2H_2O$) (isolated by treating the reaction mixture with potassium hydroxide solution). 2-Aminothiophenolsulphonic acid and sodium nitrite afford a phenylenediazosulphidesulphonic acid (or its sodium salt) which does not couple with β-naphthol. Numerous attempts to prepare the above acid using other sulphur-containing salts were unsuccessful.


(I.)

Potassium 4-chloro-3-nitrobenzenesulphonate and sodium disulphide in 96% alcohol give *potassium* 2 : 2′-*dinitrodiphenyl disulphide*-4 : 4′-*disulphonate*; in aqueous solution reduction occurs with either sodium sulphide or disulphide. Barium 4-chloro-3-nitrobenzenesulphonate and potassium xanthate react in aqueous solution according to Blanksma's scheme (A., 1902, i, 281), forming alcohol, ethyl xanthate, carbon disulphide, barium carbonate, and *barium* 2 : -*dinitrodiphenyl sulphide*-4 : 4′-*disulphonate* (II) ($+5H_2O$). In presence of ammonium acetate only a small amount of the sulphide is produced. Treatment of II with phosphorus pentachloride gives 2 : 2′-*dinitrodiphenyl sulphide* 4 : 4′-*disulphonyl chloride* ($+0·5C_6H_6$), m. p. (solvent-free) 195°, oxidised by fuming nitric acid to 2 : 2′-*dinitrodiphenylsulphone*-4 : 4′-*disulphonic acid* [*lead* salt ($+3H_2O$); *barium* salt ($+3H_2O$), obtained by similar oxidation of II]. Reduction of II with tin and hydrochloric acid affords 2 : 2′-*diaminodiphenyl sulphide*-4 : 4′-*disulphonic acid* ($+3H_2O$), which oxidises readily in air. Treatment of the reaction product from sodium 4-chloro-3-nitrobenzenesulphonate and aqueous sodium thiosulphate with phosphorus pentachloride also furnishes the above chloride; when the potassium sulphonate is treated similarly *sodium* 2 : 2′-*dinitrodiphenyl sulphide*-4 : 4′-*disulphonate* is produced [in one case a modification (?) of potassium 4-chloro-3-nitrobenzenesulphonate was produced].

2 : 2′-Diaminodiphenyl disulphide is decomposed by chlorosulphonic acid at $-20°$ and by fuming sulphuric acid under various conditions. Phenylenediazosulphide is unaffected by fuming sulphuric acid (25—70% SO_3) at 160—170°, and *o*-aminothiophenol could not be sulphonated. H. BURTON.

Characteristic colour reactions of certain diamino- and nitroamino-diphenyl-mono- and -di-sulphides. H. H. HODGSON and W. ROSENBERG (J. Soc. Dyers and Col., 1930, **46**, 267—270).—Characteristic colour reactions are tabulated for the identification of a number of products obtained in the thionation of aniline (B., 1924, 901) and related substances, including 2 : 2′-diaminodiphenyl disulphide, 4 : 4′-diaminodiphenyl disulphide, 2 : 2′-diaminodiphenyl sulphide, 2 : 4′-diaminodiphenyl sulphide, 4 : 4′-diaminodiphenyl sulphide, 2′-nitro-2-aminodiphenyl sulphide, 2′-nitro-4-aminodiphenyl sulphide, 4′-nitro-2-aminodiphenyl sulphide, 4′-nitro-4-aminodiphenyl sulphide. The preparation of these substances from *p*-aminothiophenol and the requisite chloronitrobenzene is described. A. J. HALL.

Action of compounds of the diazomethane series on thio-esters. Synthesis of ketenmercaptols, -acetal chlorides, and -thioacetal chlorides. Diphenyldiazomethane as a "free radical." A. SCHONBERG and L. VON VARGHA (Annalen, 1930, **483**, 176—189).—Diphenyldiazomethane reacts with diphenyl trithiocarbonate in ether at the ordinary temperature, forming ββ-*diphenylthiol*-αα-*diphenylethylene sulphide*, m. p. 135°, which on treatment with copper bronze in boiling benzene affords ββ-*diphenylthiol*-αα-*diphenylethylene*, m. p. 112°. This is very stable towards alkalis, but is hydrolysed by slightly diluted sulphuric acid in acetic acid solution at 100° to diphenylacetic acid. Di-*p*-tolyldiazomethane and di-*p*-tolyl trithiocarbonate give similarly ββ-*di*-p-*tolylthiol*-αα-*di*-p-*tolylethylene*

sulphide, m. p. 134—135°, which when heated at 200° or acted on by copper bronze passes into ββ-*di*-p-*tolylthiol*-αα-*di*-p-*tolylethylene*, m. p. 122—123°. Diphenylenediazomethane and phenyl chlorodithioformate furnish β-*chloro*-β-*phenylthioldiphenylene-ethylene sulphide*, m. p. 110°, convertible as above into β-*chloro*-β-*phenylthioldiphenylene-ethylene*, m. p. 133°, which is hydrolysed by sulphuric and acetic acids to fluorene-9-carboxylic acid. Diphenylenediazomethane and phenyl chlorothioformate, Cl·CS·OPh, react slowly in benzene at the ordinary temperature, yielding β-*chloro*-β-*phenoxydiphenylene-ethylene*, m. p. 114—115°, also hydrolysed to fluorene-9-carboxylic acid. Diphenyldiazomethane and 2 : 4 : 6-*trichlorophenyl chlorothioformate*, b. p. 146—147°/12 mm., prepared from 2 : 4 : 6-trichlorophenol and thiocarbonyl chloride in presence of chloroform and aqueous sodium hydroxide, react in ether forming β-*chloro*-β-2 : 4 : 6-*trichlorophenoxy*-αα-*diphenylethylene*, m. p. 91°.

The self-decomposition of diphenyldiazomethane and its reactions with diphenyl disulphide, oxygen, sulphur dioxide, and iodine are compared with the similar reactions of triphenylmethyl. The results are readily explicable on the assumption that diphenyldiazomethane reacts as the di-radical, $^-CPh_2 \cdot N_2^-$.

H. BURTON.

Structure of *iso*anethole. G. D. GOODALL and R. D. HAWORTH (J.C.S., 1930, 2482—2487).—Oxidation of *iso*anethole with potassium permanganate gives anisic acid and α-*p*-methoxyphenyl-*n*-propyl methyl ketone; the constitution *p*-$MeO \cdot C_6H_4 \cdot CH$:$CMe \cdot CHEt \cdot C_6H_4 \cdot OMe$-*p*′ is therefore assigned to it. The ketone was identified by comparison with the synthetic product and with the isomeric α-*p*-methoxybenzyl ethyl ketone: its structure is confirmed by oxidation with sodium hypobromite to give (probably) α-3-*bromo*-4-*methoxyphenyl*-n-*butyric acid*, m. p. 123—125°.

Ethyl p-*methoxybenzylacetoacetate*, b. p. 172°/0·25 mm., and di-*p*-methoxybenzylacetoacetate, prepared from *p*-methoxybenzyl bromide and ethyl sodioacetoacetate, are hydrolysed by 10% aqueous potassium hydroxide to p-*methoxybenzylacetone*, b. p. 177°/25 mm. (*semicarbazone*, m. p. 172—173° : *oxime*, m. p. 77°), and *di*-p-*methoxybenzylacetone*, m. p. 96—97°. *Ethyl* p-*methoxybenzylmethylacetoacetate*, b. p. 180°/0·5 mm., is similarly hydrolysed to α-p-*methoxybenzylethyl methyl ketone*, b. p. 175°/20 mm. (*semicarbazone*, m. p. 135°). *p*-Methoxyphenylacetonitrile (*benzylidene* compound, m. p. 96°) condenses with ethyl acetate in presence of sodium ethoxide to *acetyl*-p-*methoxyphenylacetonitrile*, m. p. 80°, hydrolysed by 50% sulphuric acid to p-*methoxybenzyl methyl ketone*, b. p. 150°/20 mm. (*semicarbazone*, m. p. 173°), which with ethyl iodide and sodium ethoxide gives α-p-*methoxyphenyl*-n-*propyl methyl ketone*, b. p. 125—128°/0·7 mm. (*semicarbazone*, m. p. 189° : *oxime*, m. p. 84—85°).

H. A. PIGGOTT.

Hydrogenation of α-phenylethyl and α-phenyl-*n*-propyl alcohol. Reduction of aromatic carbinols. P. A. LEVENE and P. G. STEVENS (J. Biol. Chem., 1930, **89**, 471—477; cf. A., 1930, 1178).—*l*-α-Phenylethyl alcohol yields, with hydrogen and platinum oxide, *cyclo*hexylethane together with d-α-cyclo*hexylethyl alcohol*, b. p. 88°/11 mm., $[\alpha]_D^{22}$ +4·7°; α-phenyl-*n*-propyl hydrogen phthalate was resolved with brucine, the d-*hydrogen phthalate*, $[\alpha]_D^{22}$ +41·5° in alcohol, giving the d-*carbinol*, b. p. 105·5—107°/15 mm., $[\alpha]_D^{22}$ +28·3°, which was hydrogenated to d-α-cyclo*hexyl*-n-*propyl alcohol*, b. p. 105—106°/18 mm., $[\alpha]_D^{22}$ +20·0°. It follows that *l*-α-phenylethyl and *d*-α-phenyl-*n*-propyl alcohols are configuratively related. When reduced with hydrogen and platinum oxide, benzyl alcohol yields chiefly *cyclo*hexylmethane, benzhydrol 60% of di*cyclo*hexylcarbinol together with di*cyclo*hexylmethane, and triphenylcarbinol almost exclusively diphenyl*cyclo*hexylmethane; aliphatic *tert*.-carbinols are not reduced under these conditions.

C. R. HARINGTON.

Methylation of alcoholic hydroxyl groups on the basis of the electronic theory. J. VON BRAUN, E. ANTON, and K. WEISSBACH (Ber., 1930, **63**, [*B*], 2847—2861).—Attempts are made to explain the varied behaviour of the hydroxyl groups towards methylation on the basis of the electronic theory from which the following consequences are deduced. The inductive action of a benzene nucleus or double linking must diminish greatly with its distance from the hydroxyl group, since it is distributed over each intermediate carbon atom. An effect equal to or more pronounced than that of the benzene nucleus or double linking must be exerted by each dipole with the + side directed towards the hydroxyl group, for example, O—C<, N≡C—. The effect must be most marked when hydroxyl is attached to a chain in which an element is present with the character of a positively charged ion.

The compound to be methylated is dissolved or suspended in ten times its weight of water at 5° and 6 mols. of methyl sulphate and 14 mols. of sodium hydroxide in 10% solution are added. The mixture is shaken for 5 min. while cooled in ice and then set aside. The temperature rises spontaneously to 50—55° and is maintained at this point for 15 min. With the simpler alcohols the mixture is extracted with ether; after removal of solvent and distillation, the product is analysed, particularly according to Zerewitinov. With more complex products individual methods are used for isolation. With the following alcohols, the percentage of methyl ether produced is placed within parentheses; benzyl (64); β-phenylethyl (19); γ-phenylpropyl (5); ε-phenylamyl (0); phenyldimethylcarbinol (0); cinnamyl (53); furfuryl (70); allyl (more than 20); *n*-propyl (0); *iso*amyl (0); *n*-heptyl (0). The marked influence of the cyano- and sulpho-groups is shown by the production of more than 50% and 100% of methyl ether from β-cyanoethyl alcohol and β-ethylsulphonylethyl alcohol, respectively. In compounds with basic nitrogen the influence is stronger than in the fatty-aromatic alcohol, as shown by the data: β-piperidinoethyl alcohol (100); γ-dimethylaminopropyl alcohol (100); γ-methylanilinopropyl alcohol (almost 100); δ-piperidinobutyl alcohol (about 50); ε-piperidinoamyl alcohol (0); ε-dimethylaminoamyl alcohol (0); 2-dimethylamino-3-hydroxy-1 : 2 : 3 : 4-tetrahydronaphthalene (100); 2-β-hydroxyethylpiperidine (100); 2-dimethylamino-5-methylbenzyl alcohol (60); di-

hydrocodeine (almost 100). Tropine and γ-dimethylamino-β-hydroxy-γ-methylbutane are almost unaffected. With hydroxy-acids the following percentages of methyl ether are obtained: lactic (?15); mandelic (70); tropic (40).

The following observations appear new: N-β-hydroxyethylpiperidine methiodide, m. p. 238° (corresponding *chloroplatinate*, m. p. 228; and *chloroaurate*, m. p. 243°), transformed by methylation into a non-crystalline *methiodide* [corresponding *chloroplatinate*, $C_{18}H_{40}O_2N_2Cl_6Pt$, m. p. 234° (decomp.), and *chloroaurate*, m. p. 108° after softening at 100°]; *methyl γ-dimethylaminopropyl ether methiodide*, m. p. 221° (corresponding *chloroplatinate*, m. p. 222°; *chloroplatinate* of the non-methylated compound, decomp. 235°); N-*methyl*-N-*γ-hydroxypropylaniline methiodide*, m. p. 132°, and N-*methyl*-N-*γ-methoxypropylaniline methiodide*, m. p. 119—121°; 2-dimethylamino-3-hydroxy-1 : 2 : 3 : 4-tetrahydronaphthalene, m. p. 31°, and 2-*dimethylamino*-3-*methoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene methiodide*, m. p. 223° (corresponding *methochloride*, m. p. 230°, and *chloroplatinate*, m. p. 229°); 1-*methyl*-2-β-*methoxyethylpiperidine chloroplatinate*, $C_{20}H_{44}O_2N_2Cl_6Pt$, m. p. 212°; 1-*methyl*-2-β-*hydroxyethylpiperidine methiodide*, decomp. about 235°, and the corresponding *chloroplatinate*, m. p. 204°; *methyl 2-dimethylamino-5-methylbenzyl ether*, m. p. 120—125°/12 mm. [*picrate*, m. p. 155°; *chloroplatinate*, m. p. 172°; *methiodide*, m. p. 115° (decomp.)]; *γ-dimethylamino-γ-methylbutan-β-ol methiodide*, m. p. 172° (decomp.); *benzenesulphonmethyl-γ-hydroxypropylamide*, b. p. 167°/0·3 mm.; *methylephedrine*, OMe·CHPh·CHMe·NMe₂, b. p. 116°/16 mm. (*picrate*, m. p. 166—168°; *methiodide*, m. p. 190°); *methyldihydrocodeine methiodide*, m. p. 207—209°; β-*methoxy-α-dimethylamino-α-methylenedioxyphenylpropane methiodide* and the corresponding *chloride* and *chloroplatinate*, m. p. 216°, and the *methiodide* of the corresponding β-hydroxy-compound, m. p. 190° (corresponding *chloroplatinate*, m. p. 198°); β-*ethylsulphonylethyl alcohol*, b. p. 193—195°/12 mm., m. p. 40°, and *methyl β-ethylsulphonylethyl ether*, b. p. 142—144°/12 mm.; *dimethyl-β-hydroxyethylsulphonium iodide*, m. p. 60—62° (*platinum* salt, m. p. 80—81°); *dimethyl-γ-hydroxypropylsulphonium iodide*, m. p. 52—55° (corresponding *platinum* salt, m. p. 115°); β-*methoxy-α-phenylpropionic acid*, b. p. 134—136°/0·3 mm., m. p. 62°, and the corresponding *chloride*, b. p. 88°/0·5 mm.; *phenyl β-methoxy-α-phenylethyl ketone*, b. p. 139—141°/0·2 mm. (non-crystalline *oxime* and *semicarbazone*); *phenyl β-chloro-α-phenylethyl ketone*, b. p. 139—140°/0·5 mm. (slight decomp.); o-*methoxymethylbenzoic acid*, b. p. 121—125°/0·5 mm., m. p. 93—94°, converted by thionyl chloride into phthalide; *α-methoxybenzylsuccinic anhydride*, b. p. about 155°/0·5 mm., m. p. 95—96°, and *α-methoxybenzylsuccinic acid*, m. p. 140°.

H. WREN.

Quinonoid structure of triphenylmethyl salts. L. C. ANDERSON (J. Amer. Chem. Soc., 1930, **52**, 4567—4572; cf. A., 1928, 219, 285; 1929, 977).—Curves are given for the absorption spectra of solutions of triphenylcarbinol, triphenylmethyl chloride, sulphate, and perchlorate in methyl sulphate, triphenylmethyl hydrogen sulphate in sulphuric acid, and triphenylmethyl perchlorate in perchloric acid. These show that all the above solutions (except triphenylcarbinol and triphenylmethyl chloride in methyl sulphate) are similar, probably because they are present in solution as quinonoid compounds.

H. BURTON.

Action of hydrogen sulphide on acid chlorides. I. Hydrogen sulphide and benzoyl chloride. L. SZPERL [with A. SMOLANSKA] (Rocz. Chem., 1930, **10**, 510—522).—The following products are found after passing hydrogen sulphide through benzoyl chloride at 180—185°: hydrogen chloride, sulphur, benzoic acid, dibenzoyl disulphide, ethylidene dithiobenzoate, and an unidentified, sulphur-containing *substance*, m. p. 28—30°. The last-named substance was not found when the reaction was carried out in decalin solution, whilst in xylene solution at 145° the products are hydrogen chloride, benzoic acid, and dibenzoyl mono- and di-sulphide. Dibenzoyl disulphide gives an intense red coloration on fusion in the presence of traces of sodium silicate or sodium, lithium, or strontium carbonates, whilst with cadmium or silver carbonates sulphides of the metal are precipitated. Attempts to isolate the red product from the former reaction were not successful, the only product identified being thiobenzoic acid. Dibenzoyl sulphide can be prepared by adding thiobenzoic acid to benzoyl chloride in ethereal solution. A violet coloration is obtained by fusing the monosulphide with the above salts. R. TRUSZKOWSKI.

Hydrolysis of benzoylated amino-acids and polypeptides. S. GOLDSCHMIDT and W. FUNER (Annalen, 1930, **483**, 190—216).—The hydrolysis of various benzoylated mono- and di-amino-acids, aminohydroxy-acids, and polypeptides with sodium hydroxide solution (2% unless stated otherwise) at 25° and 100° and sulphuric acid at 100° is studied (cf. A., 1929, 1188). The rate of the alkaline hydrolysis of the benzoylated monoamino-acids increases with rise in temperature and hydroxyl-ion concentration; for a definite hydroxyl-ion concentration, the coefficient decreases with increasing length of the carbon chain. Alkaline hydrolysis of hippuric acid is increased both at 25° and 100° by the addition of sodium chloride, but is decreased by added glycine. The *O*-benzoyl group is eliminated from *ON*-dibenzoylserine and -tyrosine at 25°; at 100°, both benzoyl groups are readily eliminated from the former compound. Alkaline hydrolysis of dibenzoylarginine causes the very ready elimination of one benzoyl group with the production of α-benzoylornithine; the velocity of hydrolysis of the second benzoyl group is measurable when 8% sodium hydroxide solution is used. Similarly, αε-dibenzoyl-lysine is first hydrolysed to the α-benzoyl derivative. With benzoylated glycyl-, diglycyl-, and alanylglycylglycines, the peptide linkings are rapidly broken; during this hydrolysis little benzoic acid is produced.

The rate of hydrolysis of benzoylated monoamino-acids by 70% sulphuric acid at 100° increases with the length of the carbon chain. Dibenzoylarginine behaves similarly with acidic hydrolytic agents as with alkaline, but the behaviour of αε-dibenzoyllysine is reversed, *i.e.*, the α-benzoyl group is elimin-

ated first. The peptide linkings are first broken when the above benzoylated peptides are hydrolysed with 70% sulphuric acid. The velocity of hydrolysis of benzoylproteins is greater with 30% sulphuric acid than with more concentrated acid; the rate corresponds with the specific conductivity of the acid. The velocity of hydrolysis of hippuric acid by 70% sulphuric acid at 100° is increased by the addition of glycine. H. BURTON.

Dynamic isomerism involving hydrocarbon radicals. II. Intramolecular character of the amidine rearrangement. A. W. CHAPMAN. **III. Effects of substitution on velocity of interchange and position of equilibrium of isomeric triarylbenzamidines.** A. W. CHAPMAN and C. H. PERROTT (J.C.S., 1930, 2458—2462, 2462—2468).—II. The interconversion of isomeric triarylbenzamidines (cf. A., 1929, 1294) is shown by velocity measurements (see below) to follow a unimolecular course; it does not need a catalyst, and is not accompanied by side reactions. Thus symmetrical amidines, *e.g.*, triphenyl- and tri-*p*-tolyl-benzamidines, are unchanged when heated (at 345° for 2 hrs., and 335° for 1 hr., respectively). Further evidence for the intramolecular nature of the change is afforded by the absence of phenyl-*p*-tolylamine from the hydrolysis products of a mixture of triphenyl- and tri-*p*-tolyl-benzamidines after rearrangement by heating. *Triphenyl-*, m. p. 168—169°, *tri-*p*-tolyl-*, m. p. 188—189°, and *tri-*p*-chlorophenyl-benzamidine*, m. p. 147—148°, are prepared by the method previously described (*loc. cit.*). The product of chlorination of benzoyldiphenylamine (Claus and Schaare, A., 1882, 1060) is *pp'*-dichlorodiphenylamine, as is proved by its preparation from N-p-*chlorophenylbenzimino*-p-*chlorophenyl ether*, m. p. 68—69°.

III. A kinetic study of the reaction RN:CPh·NRR' (I) R'N:CPh·NR_2 (II) indicates that its mobility is affected by the nature of R' in the order *p*-tolyl<phenyl<*p*-chlorophenyl, and by R in the order *p*-tolyl>*p*-chlorophenyl. The proportions of I in the equilibrium mixtures are estimated as 69% [R=Ph, R'=$C_7H_7(p)$], 53% [R=$C_7H_7(p)$, R'=Ph], 59% [R=Ph, R'=$C_6H_4Cl(p)$], and 71% [R=$C_6H_4Cl(p)$, R'=Ph]. In view of its similarity to this change, a modified explanation of the rearrangement of imino-ethers into amides, based on these results, is advanced (cf. A., 1927, 874). *NN'-Di-*p*-tolyl-*N*-phenyl-*, m. p. 133°; *N-di-*p*-tolyl-N'-phenyl-*, m. p. 149·5—150°; *NN'-diphenyl-N-*p*-chlorophenyl-*, m. p. 150—152°; *N-diphenyl-N'-*p*-chlorophenyl-*, m. p. 167·5—168·5°; *NN'-di-*p*-chloro-diphenyl-N-phenyl-*, m. p. 132—133°, and *N-di-*p*-chlorodiphenyl-N'-phenylbenzamidine*, m. p. 101—103°, are described.

H. A. PIGGOTT.

Esterification of 3 : 5-diamino- and iodobenzoic acids with alcoholic hydrogen chloride. A. KAILAN and A. IRRESBERGER (Monatsh., 1930, 56, 407—427).—The unimolecular velocity coefficients of esterification of 3 : 5-diamino-, and *o*-, *m*-, and *p*-iodo-benzoic acids with alcoholic hydrogen chloride in absence and presence of water have been determined at 25°. With alcohol containing little water, the coefficients for all the acids are proportional to the concentration of the hydrogen chloride; in moist alcohol, the coefficients increase much more rapidly. The values for 3 : 5-diaminobenzoic acid show that the introduction of a second *m*-amino-group into benzoic acid has a much smaller effect than the first (cf. A., 1907, ii, 158). The retarding action of the halogen atom is most marked with the *o*-iodobenzoic acid and least with the *m*-isomeride. For the *o*-halogenobenzoic acids, the coefficient decreases with increasing atomic weight of the halogen atom (cf. A., 1929, 1244). All the *m*-halogenobenzoic acids have approximately the same coefficient, which is less than that for benzoic acid. H. BURTON.

Di- and tri-arylamine derivatives. R. JOSZT and W. LESNIANSKI (Rocz. Chem., 1930, **10**, 523—540).—A number of attempts to synthesise *4-nitro-2-diphenylaminobenzoic acid*, m. p. 200°, by condensation were unsuccessful. Thus condensation of 5-nitro-2-anilinobenzoic acid or its ethyl ester with iodobenzene yielded either the original products or 5-nitrotriphenylamine, and similar reactions took place with 5-nitro-2-aminobenzoic acid and iodobenzene and with *2-iodo-5-nitrobenzoic acid*, m. p. 197—198°, and diphenylamine. The required acid is produced by oxidation with chromic acid of *4-nitro-2-methyltriphenylamine*, m. p. 130·5—131·5°, prepared by the condensation of diphenylamine with 2-iodo-4-nitrotoluene or of 4-nitro-2-methyldiphenylamine with iodobenzene. The following compounds have been prepared: *4-nitro-2-methyldiphenylamine*, m. p. 140—141°, by the condensation of 5-nitro-*o*-toluidine with nitrobenzene and iodobenzene, *6-diphenylamino-*m*-toluidine*, m. p. 94—99° (*hydrochloride*, m. p. 217°; *acetyl* derivative, m. p. 144—145·5°), and *4-amino-2-methyldiphenylamine*, m. p. 49—50° (*hydrochloride*, m. p. 185—187°; *acetyl* derivative, m. p. 139—140·5°), by the reduction of the corresponding nitro-derivatives; the former amine yields, on diazotisation and coupling with β-naphthol, a red *dye*, m. p. 186—188°. R. TRUSZKOWSKI.

Behaviour of condensation products of *p*-dimethylaminobenzaldehyde towards bromine and nitrous acid. K. H. BAUER and M. SEYFARTH (Ber., 1930, **63**, [*B*], 2691—2695).—Addition of bromine to α-phenyl-*p*-dimethylaminocinnamonitrile in chloroform affords *α-phenyl-3-bromo-4-dimethylaminocinnamonitrile*, NMe_2·C_6H_3Br·CH:CPh·CN, m. p. 102°, identical with the substance obtained by condensing 3-bromo-4-dimethylaminobenzaldehyde with phenylacetonitrile in alcohol containing a little potassium hydroxide. Similarly, treatment of α-phenyl-*p*-dimethylaminocinnamonitrile with sodium nitrite in glacial acetic acid yields *α-phenyl-3-nitro-4-dimethylaminocinnamonitrile*, m. p. 128°, also derived from 3-nitro-4-dimethylaminobenzaldehyde and phenylacetonitrile. *Ethyl α-cyano-3-bromo-4-dimethylaminocinnamate*, m. p. 107°, is prepared from 3-bromo-4 dimethylaminobenzaldehyde and ethyl cyanoacetate or from bromine and ethyl α-cyano-*p*-dimethylaminocinnamate. *Ethyl α-cyano-3-nitro-4-dimethylaminocinnamate*, m. p. 172—173°, is obtained by analogous methods, which are also applied in the production of *3-bromo-4-dimethylaminobenzylidenemalononitrile*, NMe_2·C_6H_3Br·CH:C$(CN)_2$, m. p. 123—124°, and

3-*nitro*-4-*dimethylbenzylidenemalononitrile*, m. p. 147—148°. In these compounds the introduction of a basic group into the phenyl residue does not so far neutralise the accumulation of negative groups that addition occurs, but facilitates substitution in the phenyl nucleus. Similarly, phenyl 4-dimethylaminostyryl ketone and bromine yield *phenyl 3-bromo-4-dimethylaminostyryl ketone*, m. p. 82° (*hydrochloride*, m. p. 145—146°), obtained also from 3-bromo-4-dimethylaminobenzaldehyde and acetophenone, whereas methyl *p*-dimethylaminostyryl ketone and bromine give *methyl α-bromo-4-dimethylaminostyryl ketone*, m. p. 92°. The constitution of the last-named compound follows from the conversion of its *phenylhydrazone*, m. p. 127°, into 1-*phenyl*-5-p-*dimethylaminophenyl*-3-*methylpyrazole*, m. p. 148—150°. In this instance, therefore, reaction consists in addition of bromine followed by loss of hydrogen bromide.

H. WREN.

Preparation of α-naphthonitrile from α-naphthylamine. J. A. McRAE (J. Amer. Chem. Soc., 1930, **52**, 4550—4552).—Contrary to the statement of Whitmore and Fox (A., 1930, 99), a 25—35% yield of α-naphthonitrile can be obtained by the Sandmeyer reaction from α-naphthylamine. The yield is improved to 58—65% when potassium nickel cyanide solutions containing sufficient sodium hydroxide to neutralise the diazonium solution are used (cf. Korczynski and others, A., 1920, i, 643; 1926, 1037).

H. BURTON.

Reactions of salicylic acid and salol. L. EKKERT (Pharm. Zentr., 1930, **71**, 744).—Superposition of a solution of sodium nitrite and salicylic acid, salicylates, or *o*-acetoxybenzoic acid on sulphuric acid gives a red ring and, after mixing, a blood-red solution, becoming green when basified with sodium hydroxide. Phenyl salicylate gives a red ring and, on mixing, a green solution which becomes red when diluted with water and greenish-blue and bluish-green with sodium hydroxide and ammonia, respectively.

H. E. F. NOTTON.

Keto-enol equilibrium of ethyl α-phenylacetoacetate. H. W. POST and G. A. MICHALEK (J. Amer. Chem Soc., 1930, **52**, 4358—4362).—The enol content of ethyl α-phenylacetoacetate, prepared by a modification of the method of Beckh (A., 1899, i, 211), is found to be 28·6% in pyrex glass vessels at 20°, by the indirect method of Meyer (A., 1911, i, 832). The electronegative phenyl group facilitates ionisation of the α-hydrogen atom. Abnormal results are obtained when the amount of enol is calculated from refractometric data.

H. BURTON.

Minjak pelandjau, the exudation from the wood of *Pentaspadon motleyi*, Hook f. III. P. VAN ROMBURGH, A. G. VAN VEEN, and A. J. H. SMIT (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 690—693).—When the phenol (A., 1930, 1434), obtained by the decarboxylation of pelandjauic acid, is hydrogenated in the presence of a large amount of acetic acid, with palladium-black as the catalyst, a *tetrahydrophenol*, $C_{24}H_{42}O$, m. p. 58—59°, is obtained, which when distilled with zinc dust yields a small quantity of 1-methylnaphthalene. If the original phenol is distilled in the same manner with zinc, a mixture of naphthalene and 1-methylnaphth ene is produced in a larger yield. A sample of de hydropelandjauic acid, obtained from crystall pelandjauic acid, m. p. 25°, after decarboxylation 330—350°, and vigorous reduction in acetic acid wi platinum oxide as the catalyst, yields a hydrocarb identical with rationally synthesised heptadecyl*cyc*hexane. The decahydrophenol (*loc. cit.*), after tre ment with zinc chloride to remove water, and hydroge ation with platinum oxide in acetic acid, yields t same hydrocarbon. It is therefore suggested that t crude pelandjauic acid is a mixture of a least t similar substances; the crystalline acid, m. p. 25°, formulated as 3-hydroxy-2-heptadecadienylbenz acid, and the liquid acid as 3-hydroxy-2-heptade dienyl-*p*-toluic acid.

T. H. MORTON.

Action of hydrogen sulphide on acid chlor anhydrides. II. Hydrogen sulphide and phthalyl chloride. L. SZPERL. **III. Hydrog sulphide and naphthalyl chloride.** L. SZPE and H. MORAWSKI (Rocz. Chem., 1930, **10**, 652 656, 657—666).—II. *o*-Phthalyl chloride reacts wi hydrogen sulphide at 195—200° to yield hydrog chloride, phthalic acid, *o*-phthalyl sulphide, and *di-phthalyl disulphide*, m. p. 330—331·5°.

III. Naphthalyl chloride in benzene solution rea with hydrogen sulphide at 80° to yield hydrog chloride, naphthalic acid, and *naphthalic thioanhydri* m. p. 205—206° (decomp.).

R. TRUSZKOWSKI.

Naphthalene-2 : 3-dicarboxylic acid. H. WAL MANN (J. pr. Chem., 1930, [ii], **128**, 150—152).—T preparation of 3-*cyano*-2-*naphthoic acid*, m. p. 273 274°, from the corresponding amino-acid by San meyer's method, and its hydrolysis to naphthaler 2 : 3-dicarboxylic acid, are described.

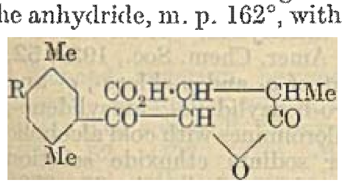
H. A. PIGGOTT.

Resolution of γ-truxillic hydrogen esters in their optical components. F. SCHENCK (Be 1930, **63**, [*B*], 2706—2712; cf. Stoermer and Fr wurst, A., 1926, 291).—Treatment of γ-truxil anhydride with the requisite boiling alcohol in t presence of a small amount of anhydrous sodiu carbonate affords *methyl*, m. p. 183·5—184°, *eth* m. p. 173—174·5°, n-*propyl*, m. p. 170—171°, a n-*butyl hydrogen* dl-γ-*truxillates* (*hydrated sodiu* n-*butyl γ-truxillate* is described). The optically acti hydrogen esters are obtained by successive treatme of the racemic compounds with morphine and bruci and from the active γ-truxillamic acids by the acti of nitrous fumes in glacial acetic acid. The followi compounds are described, all rotations being measur in acetone: *methyl* d-γ-*truxillamate*, m. p. 153—154 ethyl *d*-γ-truxillamate, m. p. 168°; n-*propyl* d-*truxillamate*, m. p. 159—160°, $[\alpha]^{20}$ −17·70°; n-*bu* l-γ-*truxillamate*, m. p. 141·5—143°, $[\alpha]_D^{20}$ +18·33 *di*-n-*butyl γ-truxillate*, m. p. 85—86°; *methyl hydrog* l(—)-γ-*truxillate*, m. p. 145·5—147°; *methyl hydrog* d-(+)-γ-*truxillate*, m. p. 145·5—147°, $[\alpha]_D^{18}$ +6·48 *ethyl hydrogen* l-(—)-γ-*truxillate*, m. p. 142·5—14 $[\alpha]_D^{17}$ −16·48°; *ethyl hydrogen* d(+)-γ-*truxillate*, m. 142·5—143°, $[\alpha]_D^{19.3}$ +19·14°; *n*-propyl hydrogen l(— γ-*truxillate*, m. p. 148—149°, $[\alpha]_D^{21}$ −21·35°; n-*pro hydrogen* d(+)-γ-*truxillate*, m. p. 148—149°; n-*bu hydrogen* l(—)-γ-*truxillate*, m. p. 151—152°, [α]

$-25{\cdot}70°$, and d(+)-γ-*truxillate*, m. p. 151—152°, $[\alpha]_D^{21}$ $+26{\cdot}14°$. H. WREN.

Chlorophenol-red. W. C. HARDEN (J. Amer. Chem. Soc., 1930, **52**, 4611).—Pure chlorophenol-red is obtained by repeated dissolution of the dye in water, acidifying with hydrochloric acid, and evaporating until crystallisation begins. The colour of the pure product with alkali is more blue and less red than that with a commercial sample. H. BURTON.

Syntheses of santonin derivatives. A. E. TSCHITSCHIBABIN and M. N. SCHTSCHUKINA (Ber., 1930, **63**, [*B*], 2793—2806).—Ethyl methylsuccinate condenses with ethyl oxalate in ether under the influence of sodium ethoxide to ethyl oxalylmethylsuccinate, which is completely decomposed into ethyl propanetricarboxylate and carbon dioxide when distilled under diminished pressure. Reduction of the crude ester by aluminium amalgam in moist ether affords three stereoisomeric lactonic *esters*, $CO<\begin{matrix}CHMe\cdot CH\cdot CO_2Et\\ O\text{———}CH\cdot CO_2Et\end{matrix}$, (i) b. p. 182—183°/13 mm., d^{20} 1·1717, n_D 1·4498, (ii) b. p. 186—187°/13 mm., d^{20} 1·1747, n_D 1·4507, and (iii) b. p. 200—204°/13 mm., m. p. 70°. Hydrolysis of the ester (i) with hydrochloric acid affords an *acid*, $C_7H_8O_6$, m. p. 181—182°, which is transformed by acetyl chloride into a mixture of dimethylmaleic anhydride and *methylbutanolidedicarboxylic anhydride*, m. p. 162°. The *anilide* of acid i has m. p. 212—214°. The ester, b. p. 186—187°/13 mm., is hydrolysed to an *acid*, m. p. 186°, mainly unchanged by warming with acetyl chloride, but to a small extent isomerised to the anhydride of acid i. The *acid* from the solid ester has m. p. 185° and passes into an *anhydride*, m. p. 201° (with a small amount of anhydride, m. p. 162°), from which the original acid is regenerated by water. Isomerisation of the anhydride, m. p. 201°, to anhydride, m. p. 162°, is caused by distillation. Both anhydrides yield the same anilide with boiling aniline. Condensation of the anhydride, m. p. 162°, with *p*-xylene in presence of aluminium chloride gives the *ketolactonic acid* (I, R=H), m. p. 171—173°, transformed by short treatment with warm, concentrated sulphuric



(I.)

acid into an isomeric *acid*, m. p. 150°; the second acid is obtained directly by the successive action of thionyl chloride and aluminium chloride and *p*-xylene on 3-methylbutanolide-1 : 2-dicarboxylic acid, m. p. 181—182°. Reduction of the two stereoisomeric acids by amalgamated zinc and concentrated hydrochloric acid affords ε-p-*xylylpentane*-βγ-*dicarboxylic acid*, m. p. 161—163°, whereas reduction of the acid, m. p. 150°, with amalgamated zinc and acetic acid yields ε-*keto*-ε-p-*xylylpentane*-βγ-*dicarboxylic acid*, m. p. 169—172°. The acid, m. p. 161—163°, is transformed by ring closure into a *substance*, m. p. 130°, which probably has the structure $\begin{matrix}C_6H_2Me_2-CO-\\ CH_2\text{———}CH\end{matrix}>CH\cdot CHMe\cdot CO_2H$. Treatment of the ketolactonic acid, m. p. 172°, with thionyl chloride followed by heating of the residue in a vacuum at 160—185° gives the *diketone*, $C_6H_2Me_2<\begin{matrix}CO\cdot CH\text{—}CHMe\\ CO\cdot CH\cdot O\cdot CO\end{matrix}$, m. p. 137—139°. Condensation of the anhydride, m. p. 162°, with methoxy-*p*-xylene in presence of aluminium chloride yields the *ketolactonic acid* (I, R=OMe), m. p. 207—208°, and an unidentified *product*, m. p. 156°. Reduction of the ketolactonic acid by Clemmensen's method yields ε-*methoxy*-p-*xylylpentane*-βγ-*dicarboxylic acid*, m. p. 131—132°, transformed by successive demethylation and ring closure into an unsaturated lactone, m. p. 250—252°, identical with the product of Clemo, Haworth, and Walton (A., 1930, 919). H. WREN.

Constituents of kawa root. X. Kawain and dihydrokawain. W. BORSCHE and W. PEITZSCH (Ber., 1930, **63**, [*B*], 2414—2417; cf. A., 1929, 442, 1453).—Technical kawa resin is dissolved in ether and the solution is extracted with 3% sodium hydroxide; after desiccation of the ethereal solution and removal of the ether the residue is subjected to prolonged fractional extraction with hot hexane. Slow evaporation of ethereal solutions of suitable solid extracts yields *kawain*, $CH<\begin{matrix}C(OMe)\cdot CH_2\\ CO\text{———}O\end{matrix}>CH\cdot CH{:}CHPh$, m. p. 105—106° after softening at 102°, $[\alpha]_D^{20}$ +105° in ethyl alcohol. It is isomerised by boiling 2*N*-sodium hydroxide to kawaic acid, m. p. 184—185°, and catalytically reduced to a mixture of much *dihydrokawain*, $CH<\begin{matrix}C(OMe)\cdot CH_2\\ CO\text{———}O\end{matrix}>CH\cdot CH_2\cdot CH_2Ph$, m. p. 56—58°, $[\alpha]_D^{18}$ +30° in ethyl alcohol, and little tetrahydrokawaic [β-methoxy-ζ-phenyl-Δ^{α}-heptenoic] acid. Dihydrokawain is transformed by 10% sodium hydroxide into *dihydrokawaic* [β-*methoxy*-ζ-*phenyl*-Δ^{α}-*heptadienoic*] *acid*, m. p. 139—140° (decomp.); the acid can be obtained by treatment of purified kawa resin dissolved in methyl alcohol with hydrogen in presence of palladium.

[With J. NIEMANN.] Dihydrokawain is isolated from the initial fractions of the extraction of kawa resin with hexane. H. WREN.

Constituents of kawa root. XI. Syntheses of methystic acid and kawaic acid. W. BORSCHE and B. R. BLOUNT (Ber., 1930, **63**, [*B*], 2418—2420).—*allo*Methysticin is converted by methyl orthosilicate in presence of methyl alcohol containing a trace of hydrogen chloride into methyl methystate, m. p. 162—164°, hydrolysed by sodium hydroxide to methystic acid, m. p. 187—188°. Methyl α-acetyl-γ-cinnamylideneacetoacetate is transformed by ammonia in presence of ether at the ordinary temperature into *allo*kawain [methyl γ-cinnamylideneacetoacetate], m. p. 93°, in nearly 80% yield; it is converted by methyl orthosilicate and subsequent hydrolysis into kawaic [β-methoxy-ζ-phenyl-$\Delta^{\alpha\gamma}$-heptadienoic] acid, m. p. 186° (decomp.). H. WREN.

Nitration of substituted benzaldehydes and stability of the aldehyde group. H. H. HODGSON and E. W. SMITH (J.S.C.I., 1930, **49**, 408—410T).—The introduction of a 5-nitro-group into *m*-nitrobenzaldehyde by direct nitration has so far proved to be impracticable on account of oxidation taking place under the severe conditions employed. To modify the deactivation of the nuclear carbon atoms, due to the combined symmetrical effect of the two

nitro-groups, two routes have been explored: (1) the use of substituted anils, which, however, could be nitrated only in the aniline portion of the molecule, and (2) the introduction of *op*-directing groups into the *m*-nitrobenzaldehyde nucleus. Of the various groups available, the amino-group was unsuitable because of its facile decomposition, although when protected, as in 3-nitro-4-acetamidobenzaldehyde, even acetyl nitrate failed to introduce a second nitro-group. When the hydroxyl group was present, as in 3-nitro-4-hydroxybenzaldehyde, dinitration readily occurred with formation of 3 : 5-dinitro-4-hydroxybenzaldehyde, although the hydroxyl group now resists methylation. Starting from 4-methoxy- or 4-ethoxy-benzaldehyde, the 3-nitro-group was introduced without difficulty, but attempts at further nitration resulted in the formation of 2 : 4-dinitro- and 2 : 4 : 6-trinitro-anisole. Attempts to dinitrate *o*-anisaldehyde produced 3 : 5-dinitro-2-methoxybenzoic acid. *p*-Chlorobenzaldehyde mononitrates and then oxidises only when the nitration conditions are made more stringent *p*-Bromobenzaldehyde gives both 4-bromo-3 : 5-dinitrobenzaldehyde and 4-bromo-3 : 5-dinitrobenzoic acid. The bromine atom in 4-bromo-3 : 5-dinitrobenzaldehyde is readily replaced by the amino- and methoxy-groups. 3 : 5-Dinitro-4-aminobenzaldehyde resists diazotisation and 3 : 5-dinitrotoluene resists oxidation.

Chloro-derivatives of vanillin and their reactions. L. C. Raiford and J. G. Lichty (J. Amer. Chem. Soc., 1930, **52**, 4576—4586).—*2-Chlorovanillin* (*2-chloro-4-hydroxy-3-methoxybenzaldehyde*), m. p. 128—129° (*oxime*, m. p. 157—158°; p-*bromophenylhydrazone*, m. p. 144—146°; *semicarbazone*, m. p. 220—221°), prepared by the usual method from 2-aminovanillin, condenses with benzidine forming *bis-2-chlorovanillylidenebenzidine*, m. p. 224—226°. Chlorination of vanillin with rather more than 1 mol. of chlorine in chloroform below 60° affords 5-chlorovanillin, m. p. 163° (lit. 165°) (*oxime*, m. p. 172°; p-*bromophenylhydrazone*, m. p. 161°; *semicarbazone*, m. p. 201°), converted by treatment with acetic anhydride and sodium acetate into the *acetyl* derivative, m. p. 201°, of *5-chloro-4-hydroxy-3-methoxycinnamic acid*, m. p. 235—236° after previous shrinking. *Bis-5-chlorovanillylidenebenzidine* has m. p. 252—254°. Chlorination of 4-acetoxy-3-methoxybenzylidene diacetate, m. p. 90—91° (lit. 88—89°), in acetic acid containing sodium acetate at about 40°, gives the *6-chloro*-derivative, m. p. 143—144°, hydrolysed by dilute potassium hydroxide solution to *6-chlorovanillin*, m. p. 167—168° (*oxime*, m. p. 178°; p-*bromophenylhydrazone*, m. p. 174°; *semicarbazone*, m. p. 241°); *bis-6-chlorovanillylidenebenzidine*, decomp. 263°, is also described. Bromination of 6-chlorovanillin in acetic acid containing sodium acetate furnishes *6-chloro-5-bromovanillin*, m. p. 214°, and chlorination of 6-bromovanillin in chloroform at about 40° yields *5-chloro-6-bromovanillin*, m. p. 202°.

Nitration of 6-chloro-4-acetoxy-3-methoxybenzylidene diacetate with fuming nitric acid at 20—30° affords the 2-*nitro*-derivative, m. p. 81—82°, hydrolysed to *6-chloro-2-nitrovanillin*, m. p. 155—157°. This is reduced by ferrous sulphate and ammonia to *6-chloro-2-aminovanillin*, m. p. 192—193° after softening at 190°, converted by the usual method into *2 : 6-dichlorovanillin*, m. p. 139—140° (*oxime*, m. p. 141°; *semicarbazone*, m. p. 213°); *bis-2 : 6-dichlorovanillylidenebenzidine* has m. p. 232°. The *acetyl* derivative, m. p. 67°, of 5-chlorovanillin yields with nitric acid (*d* 1·5) below 20° the *acetyl* derivative (+EtOH), m. p. 95—96°, m. p. (alcohol-free) 112°, of *5-chloro-2-nitrovanillin*, m. p. 137°. The last-named compound is reduced by ferrous hydroxide to *5-chloro-2-aminovanillin*, m. p. 136—137°, convertible into *2 : 5-dichlorovanillin*, m. p. 179° (*oxime*, m. p. 158°; p-*bromophenylhydrazone*, m. p. 158°; *semicarbazone*, m. p. 228°), also formed in small amount during the chlorination of vanillin. *Bis-2 : 5-dichlorovanillylidenebenzidine* has m. p. 254—255°. Chlorination of *5-chloro-4-acetoxy-3-methoxybenzylidene diacetate*, m. p. 115—116°, in acetic acid containing sodium acetate yields *5 : 6-dichloro-4-acetoxy-3-methoxybenzylidene diacetate*, m. p. 117—118°, hydrolysed by boiling with 10*N*-potassium hydroxide to *5 : 6-dichlorovanillin*, m. p. 192° [*oxime*, m. p. 203° (decomp.); p-*bromophenylhydrazone*, m. p. 163—164°; *semicarbazone* (+EtOH), m. p. (alcohol free) 237°], also obtained by direct chlorination of 6-chlorovanillin. *Bis-5 : 6-dichlorovanillylidenebenzidine*, decomp. 289°, is also described.

Treatment of a saturated solution of 2 : 6-dichlorovanillin in chloroform with sulphuryl chloride at the ordinary temperature furnishes *2 : 5 : 6-trichlorovanillin*, m. p. 154° (*oxime*, m. p. 173°; *semicarbazone*, m. p. 219°). *2 : 6-Dichloro-5-bromovanillin* has m. p. 167°.

One oxime only is obtained from each chlorovanillin examined and this (? *anti*) derivative could not be isomerised by hydrogen chloride (cf. Brady and Dunn, J.C.S., 1915, **107**, 1859; Raiford and Stoesser, A., 1928, 1246). H. Burton.

Chloroimines. III. Decomposition of aromatic aldchloroimines to form nitriles. Preparation of nitriles from aldehydes. C. R. Hauser and A. G. Gillaspie (J. Amer. Chem. Soc., 1930, **52**, 4517—4519).—Treatment of *o*- and *p*-chloro-, *o*- and *m*-nitro-, 2-chloro-5-nitro-benzylidene-, anisylidene-, and piperonylidene-*N*-chloroimines with cold alcoholic potassium hydroxide or sodium ethoxide solution affords the corresponding benzonitriles in 60—97% yield. H. Burton.

Isomerisation of hydroxyaldehydes. IV. Transformation of benzylbromoacetaldehyde and benzylglycollaldehyde. S. Danilov and E. Venus-Danilova (Ber., 1930, **63**, [*B*], 2765—2775; cf. A., 1929, 1448).—β-Phenylpropaldehyde in carbon disulphide at −5° is transformed by the gradual addition of bromine into the unstable *α-bromo-β-phenylpropaldehyde*, which readily becomes resinified and polymerised. It yields a crystalline *monohydrate*, m. p. 87·5—88°. With semicarbazide it yields *α-hydroxy-β-phenylpropaldehydesemicarbazone*, m. p. 136·5°. When heated with water and freshly precipitated barium carbonate the bromoaldehyde gives α-hydroxy-β-phenylpropaldehyde in moderate yield with 4% of β-phenylpropionic acid and halogenated condensation products. With silver oxide and hot

water, the products are 20% of α-hydroxy-β-phenylpropaldehyde, 9·4% of α-hydroxy-β-phenylpropionic acid, 5·6% of a condensation product of the bromoaldehyde, and 31% of β-phenylpropionic acid. Lead oxide and water afford mainly condensation products of the bromoaldehyde and 22·6% of β-phenylpropionic acid. *α-Hydroxy β-phenylpropaldehyde*, m. p. 51·5—52°, gives an *oxime*, m. p. 123°, semicarbazone, m. p. 136·5° (see above), *phenylosazone*, $C_{21}H_{20}N_4$, m. p. 137°, and *benzoate*, m. p. 70°. Oxidation of the aldehyde by permanganate in presence of pyridine gives phenylacetaldehyde and α-hydroxy-β-phenylpropionic acid; similar treatment of the benzoate and hydrolysis of the product affords α-hydroxy-β-phenylpropionic acid unaccompanied by neutral products. The hydroxyaldehyde is isomerised by sulphuric acid in the presence of alcohol at 130—135° to a mixture of α-phenylpropane-αβ-dione (*dioxime*, m. p. 238—239°) and acetylphenylcarbinolsemicarbazone, m. p. 194°, accompanied by a small amount of (?) *p*-diphenylbenzoquinone, m. p. 230°. The structure of the hydroxyketone is established by its conversion by magnesium phenyl bromide into methylhydrobenzoin, m. p. 103°, oxidised to benzoic acid and acetophenone.

H. WREN.

Mixed catalysts in the Friedel–Crafts reaction. Yield of benzophenone from benzoyl chloride and benzene using ferric chloride–aluminium chloride mixtures as catalysts. W. A. RIDDELL and C. R. NOLLER (J. Amer. Chem. Soc., 1930, **52**, 4365—4369; cf. Boswell and McLaughlin, A., 1930, 170).—Optimum yields (more than 90%) of benzophenone are obtained when 1·1 mols. of pure aluminium chloride are used per 1 mol. of benzoyl chloride in the Friedel–Crafts reaction. When mixtures (=1·1 mols.) of aluminium and ferric chlorides are used, the yields are approximately the mean of those obtained using the individual chlorides. Addition of ferric chloride to 1·1 mols. of aluminium chloride also causes a diminution in the yield. In all experiments with ferric chloride an iron-containing by-product is formed.

H. BURTON.

Forced reaction between anils and *p*-thiocresol. Reducing action of the thiol grouping. H. GILMAN and J. B. DICKEY (J. Amer. Chem. Soc., 1930, **52**, 4573—4576).—When benzophenoneanil is treated with *p*-thiocresol in boiling xylene with the exclusion of air, a mixture of di-*p*-tolyl disulphide and benzhydrylaniline is obtained; the last-named substance is isolated mainly as the additive *compound* (1 : 1), m. p. 83—84°, with benzophenoneanil. Benzylideneaniline and *p*-thiocresol afford similarly di-*p*-tolyl disulphide and benzylaniline; azobenzene is reduced to hydrazobenzene, which under the experimental conditions decomposes to aniline (and azobenzene). Nitrobenzene and benzophenone are not reduced by *p*-thiocresol.

Magnesium *p*-tolylthiol iodide (A., 1925, i, 810) does not react with benzophenoneanil or benzylideneaniline in ethereal toluene solution. H. BURTON.

ωω-Dihalides of aliphatic-aromatic ketones of the type Ar·CO·CHX$_2$, in particular ωω-chlorobromo-derivatives of the type Ar·CO·CHClBr. I. RABCEWICZ-ZUBKOWSKI (Rocz. Chem., 1930, **10**, 541—554).—The following substances have been prepared: *p-tolyl chlorobromo-* and *dichloro-methyl ketones*, m. p. 87° and 55·5—56°, respectively, o-4-*xylyl chlorobromo-* and *dichloro-methyl ketones*, m. p. 25·5—26° and b. p. 145—146°/10·5 mm., respectively, 4-*methoxy-*, 4-*bromo-*, and 4-*iodo-phenyl chlorobromomethyl ketones*, m. p. 88—89°, 82°, and 78·5—79°, respectively. The halogen of the side-chains is transferred to the nucleus on oxidation with dilute nitric acid; thus *p*-tolyl dibromomethyl ketone yields 3-bromo-4-methylbenzoic acid. R. TRUSZKOWSKI.

Ketonitriles and ketothiocyanates of the type Ar·CO·CH$_2$·CN and Ar·CO·CH$_2$·SCN. I. RABCEWICZ-ZUBKOWSKI and H. KAFLINSKA (Rocz. Chem., 1930, **10**, 555—569).—The following substances have been prepared by the action of potassium cyanide or thiocyanate on the appropriate chloro- or bromo-derivative: 4-*bromophenyl*, m. p. 162·4—163·4°, 4-*iodophenyl*, m. p. 187·4—188·4°, 3-*nitrophenyl*, m. p. 152—153°, p-*tolyl*, m. p. 104·6—105·2°, m-4-*xylyl*, m. p. 80·1—81°, and β-*naphthyl*, m. p. 127·6—128·2°, *cyanomethyl ketones*; *phenyl*, m. p. 74·1—74·6°, 4-*chloro-*, m. p. 138·6—139·2°, 4-*bromo-*, m. p. 148·8—149·2°, 4-*iodo-*, m. p. 154—155°, p-*tolyl*, m. p. 106·2—106·8°, p-*anisyl*, m. p. 124·2—124·8°, 3-*nitrophenyl*, m. p. 123·6—124·2°, m-4-*xylyl*, m. p. 80·8—81·0°, and β-*naphthyl*, m. p. 109·4—110°, *thiocyanomethyl ketones*. Bromination of cyanoacetophenone yields *benzoyldibromoacetamide*, m. p. 181·6—182·4°, whilst thiocyanoacetophenone gives an unstable *dibromide*, m. p. 132—134°, which loses hydrogen bromide on recrystallisation from alcohol, yielding a *substance*, $(C_9H_5ONS)_x$, m. p. 208—208·5°. R. TRUSZKOWSKI.

Reactivity of the positive hydrogen atom. V. Preparation of tetraphenyl*cyclo*pentadienone. W. DILTHEY and F. QUINT (J. pr. Chem., 1930, [ii], **128**, 139—149).—The condensation of benzil with dibenzyl ketone in cold alcoholic solution under the influence of alkali leads to 3-hydroxy-2 : 3 : 4 : 5-tetraphenyl-Δ^4-*cyclo*penten-1-one, previously obtained by use of aqueous alkali (J.C.S., 1901, 79, 1256), and probably identical with Lowenbein and Ulich's product from benzylidenediphenylmaleide and magnesium phenyl bromide (A., 1926, 171). It is converted by reduction with zinc and acetic acid into 2 : 3 : 4 : 5-*tetraphenyl*-Δ^4-cyclo*penten-1-one*, m. p. 162—163°, also obtained by replacing benzil by benzoin in the above condensation. At the b. p., 2 : 3 : 4 : 5-tetraphenyl-Δ$^{2:4}$-*cyclo*pentadien-1-one (Lowenbein and Ulich, *loc. cit.*) [*dibromide*, m. p. 169—170° (decomp. into the ketone and bromine: similarly decomposed by warming in a suitable solvent)] is formed by further elimination of water in the original condensation. It is also produced by the action of bromine in acetic acid at 100° on tetraphenyl*cyclo*penten-1-one, to which it is reduced by hydrogen and palladium, and also to some extent by zinc and acetic acid, being accompanied in the latter case by 2 : 3 : 4 : 5-*tetraphenyl*-Δ^{2,4}-cyclo*pentadien-1-ol* (+1AcOH), m. p. 139—140°, an unstable substance which is readily re-oxidised to the ketone. Unidentified substances of m. p. 163°, 220°, and 144°, obtained by catalytic hydrogenation of 3-hydroxy-2 : 3 : 4 : 5-tetraphenyl-Δ^4-*cyclo*penten-1-one, are described. H. A. PIGGOTT.

Tautomerism of α-diketones. H. MOUREU (Ann. Chim., 1930, [x], **14**, 283—405).—A detailed account of work previously reviewed (A., 1922, i, 843; 1923, i, 113; 1924, i, 405; 1925, i, 937; 1927, 246, 571, 884, 1173; 1928, 180, 419, 1334; 1929, 189, 448, 883, 929). H. BURTON.

4-Alkyl derivatives of 1-phenyl*cyclo*hexane-3 : 5-dione. I. H. EL-S. MATTAR, J. J. H. HASTINGS, and T. K. WALKER (J.C.S., 1930, 2455—2458).—The synthesis of derivatives of *cyclo*hexane-1 : 3-dione by addition of ethyl sodiomalonate to ketones of the type >C:CH·CO·CHR (R=H; cf. Vorländer, A., 1894, i, 527) is also applicable where R=alkyl. The following are prepared from the appropriate styryl alkyl ketones: *ethyl* 1-*phenyl*-4-*methyl*cyclo*hexane*-3:5-*dione*-2-*carboxylate* (+0·5H_2O), m. p. 121—123°; 1-*phenyl*-4-*methyl*cyclo*hexane*-3 : 5-*dione*, m. p. 212—213°; 1-*phenyl*-4-*ethyl*-, m. p. 200° (oxidises and resinifies in air); 1-*phenyl*-4-n-*propyl*-, m. p. 185°; 1-*phenyl*-4-n-*amyl*-cyclo*hexane*-3 : 5-*dione*, m. p. 191°; *ethyl* 1-*phenyl*-4-*benzyl*cyclo*hexane*-3 : 5-*dione*-2-*carboxylate*, m. p. 146°, and 1-*phenyl*-4-*benzyl*cyclo*hexane*-3 : 5-*dione*, m. p. 169—170°. Ethyl phenylacetate condenses with styryl ethyl ketone (but not styryl β-phenylethyl ketone) in presence of sodium ethoxide, and the product on decarboxylation gives 1 : 2-*diphenyl*-4-*methyl*cyclo*hexane*-3 : 5-*dione*, m. p. 167°. An improved preparation of styryl β-phenylethyl ketone (Harries and Gollnitz, A., 1904, i, 427) by alkaline hydrolysis of ethyl benzylacetoacetate, followed by decarboxylation of the product, is described. H. A. PIGGOTT.

Reduction of *p*-dimethylaminobenzil. S. S. JENKINS [with J. S. BUCK and L. A. BIGELOW] (J. Amer. Chem. Soc., 1930, **52**, 4495—4499).—Reduction of *p*-dimethylaminobenzil by the method previously described (A., 1929, 1072) affords either *p*-dimethylaminobenzoin (*p*-dimethylaminobenzoylphenylcarbinol) or p-*dimethylaminohydrobenzoin*, m. p. 112°, according to the amount of hydrogen consumed. The hydrobenzoin is dehydrated by heating with a 4 : 1 mixture of acetic and hydrochloric acids to α-p-*dimethylaminodeoxybenzoin* (*benzoyl*-p-*dimethylaminophenylmethane*), m. p. 128° (*oxime*, m. p. 139°), reduced catalytically (Adams) in alcohol at 60° to *α-phenyl*-β-p-*dimethylaminophenylethyl alcohol*, m. p. 78°. Reduction of *p*-dimethylaminobenzoin with tin and alcoholic hydrochloric acid containing a small amount of copper sulphate gives a mixture of α-(above) and β-p-*dimethylaminodeoxybenzoin* (p-*dimethylaminobenzoylphenylmethane*), m. p. 164° (*oxime*, m. p. 142°). The β-compound is reduced catalytically to β-phenyl-α-*p*-dimethylaminophenylethyl alcohol, m. p. 60° (Sachs and Sachs, A., 1905, i, 202). The last-named substance and its isomeride are dehydrated with acetic and hydrochloric acids to *p*-dimethylaminostilbene, which is reduced catalytically to *α-phenyl*-β-p-*dimethylaminophenylethane*, m. p. 63° [*methiodide*, m. p. 260—262° (all m. p. except this are corr.)]. H. BURTON.

Valency tautomerism in unsaturated systems. G. WITTIG and W. WIEMER (Annalen, 1930, **483**, 144—156).—The following dibenzoylnaphthalenes are prepared from magnesium phenyl bromide and the requisite dicyanonaphthalene: 1 : 5-dibenzoyl-, m. p. 185—186°; 1 : 6-dibenzoyl-, m. p. 175—176°; 2 : 6-*dibenzoyl*-, m. p. 184—186°, and 2 : 7-*dibenzoyl*-, m. p. 171—172°. The 1 : 5- and 2 : 6-derivatives react with magnesium phenyl bromide yielding 1 : 5-, m. p. 280° (decomp.), and 2 : 6-*di*(*hydroxydiphenylmethyl*)*naphthalene*, m. p. 279—281° (decomp.), respectively; crystalline compounds could not be obtained from the 1 : 6- and 2 : 7-compounds. Treatment of the above carbinols with hydrogen chloride in boiling dioxan solution furnishes 1 : 5-, m. p. 250—251°, and 2 : 6-*di*(*chlorodiphenylmethyl*)*naphthalene*, m. p. 250—253°, respectively. Treatment of these dichlorides with copper bronze (Naturkupfer C) in xylene in an atmosphere of nitrogen affords red solutions of 1 : 5- and 2 : 6-di(diphenylmethylene)napthalene, which are decolorised by oxygen only after many hours' treatment. The red solution of the 2 : 6-derivative when treated with phenyl iodochloride regenerates the corresponding dichloro-compound. The number of conjugated unsaturated linkings between the methylene carbon atoms is, in the above cases, four. In compounds of similar types containing five (Tschitschibabin, A., 1907, i, 503; Schlenk, A., 1915, i, 518) and six conjugated unsaturated linkings (see below), decolorisation by treatment with oxygen is rapid. This can be ascribed to the existence of the radical form of the hydrocarbon,

$CPh_2{:}R{:}CPh_2$ $\quad CPh_2{\cdot}R{\cdot}CPh_2$.

αβ-Di-*p*-benzoylphenylethane (A., 1928, 642) is treated with bromine in boiling nitrobenzene whereby hydrogen bromide is evolved and 4 : 4′-*dibenzoylstilbene*, m. p. 234—235°, is produced. This reacts with magnesium phenyl bromide forming 4 : 4′-*di*(*hydroxydiphenylmethyl*)*stilbene*, m. p. 208—212°, which with hydrogen chloride in benzene containing a little acetyl chloride gives 4 : 4′-*di*(*chlorodiphenylmethyl*)*stilbene*, m. p. 213—216° with darkening. Treatment of a suspension of this dichloride in chloroform with copper bronze in an atmosphere of nitrogen yields a blue solution of 4 : 4′-di(diphenylmethylene)-stilbene, which is decolorised by oxygen; the solid di-radical decomposes rapidly in air to a yellow substance. Treatment of the blue solution with phenyl iodochloride regenerates the above dichloride, which is readily hydrolysed to the dicarbinol. H. BURTON.

Syntheses of phenolic ketones according to Hoesch. IV. W. BORSCHE and K. DIACONT (Ber., 1930, **63**, [*B*], 2740—2743; cf. A., 1929, 1309).—Benzoylformic acid and resorcinol in presence of zinc chloride and ether are transformed by hydrogen chloride into 2 : 4 : 2′ : 4′-tetrahydroxytriphenylacetolactone, whereas phloroglucinol does not afford a crystalline product. Under similar conditions, acetyl cyanide and resorcinol give α-2 : 4-*dihydroxyphenylpropane*-αβ-*dione*, m. p. 159° (decomp.) [*disemicarbazone*, m. p. 243—245°; *bis*-2 : 4-*dinitrophenylhydrazone*, m. p. 249—250°]; the corresponding *monoketimine hydrochloride* is described. With phloroglucinol, acetyl cyanide appears to yield a *trihydroxyphenylpropanediol*. Resorcinol and propionyl cyanide give the *monoketimine hydrochloride* $C_{10}H_{12}O_3NCl$, hydrolysed to α-2 : 4-*dihydroxyphenyl*-

butane-αβ-dione, m. p. 150° (*disemicarbazone*, m. p. 205°; *bis*-2 : 4-*dinitrophenylhydrazone*, m. p. 245°).
H. WREN.

Reduction of substituted *p*-benzoquinones by sulphur dioxide alone and in presence of alkali. J. W. DODGSON (J.C.S., 1930, 2498—2502; cf. *ibid.*, 1914, **105**, 2435).—The sulphonation that accompanies reduction of a quinone by sulphur dioxide in aqueous solution increases as the proportion of alkali is increased to a maximum which corresponds approximately with the formation of alkali hydrogen sulphite, and then steadily decreases. In the case of monochlorobenzoquinone, chlorine is not liberated until the ratio of alkali to sulphur dioxide is greater than 1 : 1, some disulphonic acid being then produced. Displacement of chlorine from dichlorobenzoquinone, with consequent sulphonation, is more marked, and from tetrachlorobenzoquinone aqueous sulphur dioxide alone displaces a considerable proportion of chlorine, sulphonation occurring to a corresponding degree. *Barium toluquinolsulphonate*, p-*xyloquinolsulphonate*, *chloroquinolsulphonate*, 2 : 5-*dichloroquinolsulphonate*, and 2 : 3-*dichloroquinolsulphonate* are described, the last two being apparently contaminated by disulphonate.
H. A. PIGGOTT.

Anthraquinhydrone. O. BALLY (Ber., 1930, **63**, [*B*], 2938).—The green colour observed when anthraquinone is treated with potassium hydroxide is probably due to the formation of the potassium derivative of anthraquinhydrone (cf. Scholl and Bottger, A., 1930, 1438).
H. WREN.

Action of nitric oxide on caoutchouc. A. GORGAS (Ber., 1930, **63**, [*B*], 2700—2705).—Total caoutchouc prepared from "revertex" according to the method of Pummerer and Pahl (A., 1927, 1193), sol and gel caoutchoucs give iodine values corresponding with the absorption of 1 mol. of iodine per isoprene residue when treated by the author's modification of Hanus' process. With bromine iodide a somewhat low iodine value is observed. Differing thiocyanogen values are not observed for the differing varieties of caoutchouc.

Treatment of purified caoutchouc in carbon tetrachloride at 0° with nitrogen peroxide, prepared from formaldehyde and concentrated nitric acid, followed by the action of oxygen and repeated crystallisation and fractional distillation, does not lead to the formation of a homogeneous product. Addition of the peroxide is invariably accompanied by oxidation. In the material produced after 24 hrs.' action, about one third of the added nitrogen is evolved as ammonia by heating with concentrated alkali hydroxide, thus indicating the presence of an oximino-group and decomposition of the liberated hydroxylamine, $3NH_2{\cdot}OH{=}NH_3{+}3H_2O{+}N_2$. Addition of nitric oxide to caoutchouc proceeds more slowly than that of nitrogen peroxide and yields a heterogeneous product containing the oximino-group. Dilute nitric acid transforms caoutchouc into a nitrogenous product soluble in acetone and a non-nitrogenous material insoluble in this medium. Ammonia is evolved when the former substance is boiled with alkali hydroxide.

Carbamide is added to the nitric acid, the product of the change is a yellow, friable mass free from nitrogen.
H. WREN.

Isoprene and caoutchouc. XXII. *iso*Caoutchouc nitron. H. STAUDINGER and H. JOSEPH (Ber., 1930, **63**, [*B*], 2888—2899; cf. Pummerer and Gündel, B., 1928, 793).—A review of the literature shows that almost invariably the primary action of reagents on caoutchouc consists in fission of the labile macro-molecules into smaller fragments of hemicolloidal character which then react further with the reagent with rupture of the double linking. Treatment of purified caoutchouc in 0·2*M*-solution with nitrosobenzene in amount varying from 0·01 to 3 mols. and with nitrogen peroxide or benzoyl peroxide causes diminution in the viscosity of the solutions which is more marked with nitrogen peroxide than with nitrosobenzene and least obvious with benzoyl peroxide. Since with 0·01—0·02 mol. of nitrosobenzene the viscosity is but little diminished, the change cannot be due to initial oxidative degradation to hemicolloidal products and reaction of the latter with nitrosobenzene, but oxidative fission and nitron formation must occur simultaneously. Analyses of *iso*caoutchouc nitron disclose a deficiency of 1·5—2·0% of carbon and, assuming the determination of mol. wt. by Pummerer and Gündel (*loc. cit.*) to be correct, agree with an octameric nitron which has acquired by oxidation 2 atoms of oxygen or 1 mol. of hydrogen peroxide. The mol. wt. of the product in benzene is approximately twice as great as in nitrobenzene; the values in the latter medium vary considerably, but, on the average, are only slightly higher than those recorded by Pummerer and Gündel. The action of oxides of nitrogen on caoutchouc is accompanied by marked degradation of the hydrocarbon molecule, and the nitrosate is richer in oxygen than a caoutchouc nitrosite. *iso*Caoutchouc nitron is a polymeric-homologous mixture, since it can be separated by cold benzene into more and less freely soluble portions which differ in viscosity when dissolved in chloroform; the composition of the fractions is approximately the same. The oxidative degradation of the long caoutchouc molecule to hemicolloidal products of relatively similar order of magnitude instead of to those of widely varying length is attributed to the incomparably less stable condition of the longer molecules. The formation of a relatively simple, hemicolloidal *iso*caoutchouc nitron is thus not incompatible with the view that caoutchouc has a very high mol. wt.
H. WREN.

Isoprene and caoutchouc. XXIII. Cryoscopic measurements with caoutchouc solutions. H. STAUDINGER and H. F. BONDY (Ber., 1930, **63**, [*B*], 2900—2905).—The viscosity of solutions of caoutchouc in benzene is much greater with the fresh material than with that which has been dissolved in molten camphor. Treatment of caoutchouc with the last-named substance involves a profound degradation of the caoutchouc molecule and renders camphor an unsuitable medium for the determination of mol. wt. The observations of Pummerer and others (A., 1929, 1455) on the behaviour of caoutchouc and benzene are readily explicable, since they used gel solutions; the molecules are freely mobile only in much less

concentrated solution than those employed. The statement of Pummerer and Gündel (B., 1928, 793) that the authors' product is contaminated by nitrogen is not supported by experiment. Their values for the mol. wt. of sol caoutchouc in menthol do not appear to be established firmly, since considerably higher data are given by the method of isothermal distillation. The mol. wts. recorded by Pummerer for intact caoutchouc cannot be accepted, since they are identical with those observed for degraded products which have properties differing widely from those of caoutchouc. H. WREN.

Sclareol and its derivatives. M. M. JANOT (Compt. rend., 1930, **191**, 847—849).—Sclareol has *M* 250—265 in benzene, acetic acid, and camphor, $[\alpha]_D$ $-3{\cdot}3°$ in chloroform (rotations in other solvents are given). It is probably a tertiary alcohol, $C_{17}H_{30}O_2$ (cf. Volmar and Jermstad, A., 1928, 524). Sclareol distils at 188—189°/3 mm. or 218—220°/19 mm. to give a crystalline product, m. p. 104—105°, is not hydrolysed by alcoholic potassium hydroxide, may be acetylated and benzoylated only with difficulty and incompletely, and suffers a loss in weight of 45% when heated for 72 hrs. at its m. p. When heated with phenylcarbimide at 150° it gives carbon dioxide and diphenylcarbamide.

Bromination in carbon disulphide in presence of silver carbonate affords a *bromide* (Br 35·33%), m. p. 122—124°, and two other *substances*, m. p. 140—143°, and m. p. 134—135°, $[\alpha]_D$ $+12{\cdot}4°$ in pyridine. Sclareol is hydrogenated in alcohol, with palladium-black as catalyst, to a crystalline *derivative*, m. p. 114—115°, *M* 270 in camphor, $[\alpha]_D$ $-10{\cdot}1°$, Silver sclareolate (*loc. cit.*) melts at 152—154°. Sclareol possesses no marked ultra-violet absorption. T. H. MORTON.

Resin acid of the *iso*sylvic acid group. O. ASCHAN (Annalen, 1930, **483**, 124—132).—The preparation of an *iso*sylvic acid (cf. A., 1924, i, 533) is described and suggestions are made regarding its structure and that of pinabietic acid.

[With O. M. GADD.] Pinabietic acid dihydrobromide, m. p. 192—194° (Virtanen, A., 1921, i, 669), is converted by potassium hydroxide in 90% alcohol into *pinisosylvic acid*, $C_{20}H_{30}O_2$, m. p. 82° (*silver* salt; *tetrabromide*, m. p. 87°). Reduction of the dihydrobromide with zinc dust and acetic acid affords *dihydropinisosylvic acid*, m. p. 92° (impure *dibromide*, m. p. about 92°), which with hydrogen bromide in presence of ether and acetic acid gives a *hydrobromide*, m. p. 163—165°. When pinabietic acid dihydrobromide is boiled with acetone, hydrogen bromide is eliminated and a *monohydrobromide*, m. p. 186°, is formed. Pinabietic acid hydrochlorides could not be prepared. H. BURTON.

Reactions of *g*-strophanthin (ouabain) and *k*-strophanthin. L. EKKERT (Pharm. Zentr., 1930, **71**, 724—725).—To about 0·005 g. of substance is added a drop of a 1% alcoholic solution of furfuraldehyde, followed by a drop of sulphuric acid; ouabain shows under these conditions only a pale greenish- to greyish-brown colour, whilst strophanthin gives a deep indigo blue. If more (5 drops) of sulphuric acid be employed, the respective colorations are red to brown, and dark green (cf. Helbing, A., 1887, 1001; Richaud, 1921, ii, 601). R. CHILD.

Menthone series. VII. Condensation of menthylamines with *d*- and *l*-oxymethylenecamphor. J. READ and (MISS) C. S. STEELE (J.C.S., 1930, 2430—2434).—*d*-*neo*Menthylamine condenses with *d*- and *l*-oxymethylenecamphor to yield, respectively, *d*-neo*menthylamino*-d-, m. p. 105°, $[\alpha]_D$ $+317{\cdot}8°$ (all rotations in alcohol unless otherwise stated), and -l-, m. p. 94°, $[\alpha]_D$ $-129{\cdot}8°$, *-methylenecamphor*. *dl*-*neo*Menthylamine condenses similarly with *d*-oxymethylenecamphor, and the crude product, m. p. 92°, is separated into *d*-*neo*menthylamino-*d*-methylenecamphor (insoluble) and l-neo*menthylamino*-d-*methylenecamphor*, m. p. 92°, $[\alpha]_D$ $+130°$, which are converted by bromine in alcohol into d-, not melting below 220°, $[\alpha]_D$ $+18{\cdot}6°$ in water, and l-, $[\alpha]_D$ $-18{\cdot}5°$ in water, -neo*menthylamine hydrobromide*, respectively. Similarly, from the active components are obtained: d-iso*menthylamino*-d-, m. p. 110°, $[\alpha]_D$ $+281{\cdot}3$—$257{\cdot}5°$ (constant) in 48 hrs., and -l-, m. p. 99—100°, $[\alpha]_D$ $-212{\cdot}9°$ to $-160{\cdot}8°$ in 48 hrs., *-methylenecamphor*; l-*menthylamino*-d-, m. p. 90°, $[\alpha]_D$ $+196{\cdot}7$—$125{\cdot}0°$ in 16 hrs., and -l-, $[\alpha]_D$ $-170{\cdot}2°$, *-methylenecamphor*. In both these cases, however, the condensation product of the *dl*-base with *d*-oxymethylenecamphor, $[\alpha]_D$ $+162{\cdot}2$—$155{\cdot}2°$ in 48 hrs., and $[\alpha]_D$ $+140{\cdot}2$—$145{\cdot}6°$ in 16 hrs., respectively, is too soluble to effect resolution by fractional crystallisation, nor could any optical activity be detected in the unchanged base arising from a possible difference in the reaction velocity of the *d*- and *l*-forms. *l*- and *d*-*iso*Menthylamino-*d*-methylenecamphor appear to form a partial racemate which retains its stability when dissolved in alcohol, since the observed value, $[\alpha]_D$ $+162{\cdot}2°$, for the *dl*-condensation product differs considerably from the mean of the values of the individual components ($+247{\cdot}1°$). J. W. BAKER.

Autoxidation of piperitone in alkaline solution. W. TREIBS (Ber., 1930, **63**, [*B*], 2423—2428). —In alcoholic, alkaline solution, oxygen is absorbed most rapidly by the unsaturated ketones, carvone, piperitone, and carvenone, less rapidly by pulegone, *cyclo*hexenone, and verbenone, and not by dihydrocarvone. Benzylideneacetone reacts energetically, methylheptenone and mesityl oxide only very slowly. With 0·1 mol. of ketone in 40—60 c.c. of solvent, the amount of oxygen absorbed increases to a maximum of 1 mol. per mol. of ketone when the mol. ratio of alkali hydroxide to ketone is 1 : 1. In more dilute solution up to 2 mols. of oxygen are absorbed with formation of lower fatty acids derived from the alcohol by autoxidation. In acetone solution oxidation occurs only if alcohol is added; the presence of the latter in mol. ratio 1 : 1 suffices to complete the change in the same manner as in alcoholic solution. With aliphatic alcohols the rate of reaction appears to increase with increasing length of the hydrocarbon chain, but the total absorption is substantially independent of the nature of the alcohol. In the concentration 0·1 mol. in 40—60 c.c. and in presence of not more than 0·1 mol. of alkali hydroxide, *p*-benzoquinone, phenanthraquinone, β-naphthaquinone, and orcinol absorb 1 mol. of oxygen per mol., pyro-

catechol and quinol 2 mols., benzylideneacetone and resorcinol about 0·5 mol. Gold chloride greatly accelerates the absorption of oxygen by pulegone, but retards that by resorcinol. Salts of platinum and palladium are without action.

Piperitone dissolved in methyl-alcoholic potassium hydroxide is subjected to autoxidation and then distilled with steam whereby a small amount of phenolic material, probably containing thymol, is obtained. After acidification, the residual solution is again distilled with steam, thus leading to the isolation of an unsaturated *acid*, $C_{10}H_{16}O_2$, m. p. 57—59° (*calcium* salt), and a *lactone*, $C_{10}H_{16}O_2$, b. p. 246—248°/atm. pressure, 118—120°/13 mm., d_{15}^{20} 1·010, transformed slowly by 20% potassium hydroxide into the *hydroxy-acid* $C_{10}H_{18}O_3$, m. p. 113—114° (*sodium* and *potassium* salts). Reduction of the lactone by sodium in methyl or ethyl alcohol affords a *glycol*, $C_{10}H_{20}O_2$, b. p. 150—152°/13 mm. Digestion of the hydroxy-acid with 25% sulphuric acid yields mainly lactone with some unsaturated acid, $C_{10}H_{16}O_2$. Treatment of the lactone with methyl- or ethyl-alcoholic hydrogen chloride or sulphuric acid gives the *methyl* ester, b. p. 94—95°/15 mm., d_{15} 0·9450, and *ethyl* ester, b. p. 102—105°/14 mm., d_{15}^{20} 0·9467, of the unsaturated acid.

The residue from the distillation with steam is a brown resin; its solubility in alkali hydroxide increases with the amount of alkali used in its preparation. The soluble and insoluble portions have the same composition. H. WREN.

Photopolymerisation of piperitone. W. TREIBS (Ber., 1930, **63**, [*B*], 2738—2740).—Irradiation of piperitone dissolved in glacial acetic acid or alcohol and water by the mercury-vapour lamp yields three *dimerides*: (1) needles, m. p. 162°, which do not yield a semicarbazone, (2) needles, m. p. 142—144°, giving a *semicarbazone*, needles or cubes, m. p. 228—235° (decomp.) according to the rate of heating, and (3) rhombic leaflets, m. p. 157—159°, which do not give a semicarbazone. Insolation appears to yield only the first-named of the dimerides. H. WREN.

Hydratation of nopinene. V. Hydratation by nascent acids. G. AUSTERWEIL (Bull. Soc. chim., 1930, [iv], **47**, 1157—1159).—When a mixture of *l*-nopinene and alcohol is added to a solution of phthalic anhydride in xylene at 135—140° and the bornyl ethyl phthalate obtained is hydrolysed with sodium hydroxide in presence of sodium sulphoricinoleate, about 41% of *l*-borneol, m. p. 211°, is obtained (or 64% if the xylene is replaced by pinene), the remaining unhydrated nopinene being converted mainly (75%) into pinene, the residual 25% giving limonene, [α] —80°, dipentene, and terpinene but not terpinolene; a little *d*-fenchyl alcohol is also formed (cf. A., 1926, 619; 1927, 156, 1082; 1928, 69). R. BRIGHTMAN.

Sulphur compounds of terpenes. I. Action of sulphur on *d*-limonene and α-pinene. A. NAKATSUCHI (J. Soc. Chem. Ind. Japan, 1930, **33**, 409B).—*d*-Limonene was heated with sulphur (~5%) at 160° for 28 hrs., and the product was distilled under reduced pressure. *p*-Cymene (cf. Ruzicka, B., 1922, 482A) was obtained, together with a *sulphide*, $C_{10}H_{16}S$, m. p. —26·79°, b. p. 104·5—105·5°/16·8 mm., $[\alpha]_D^{25\cdot1}$ —12·31°, $n_D^{25\cdot8}$ 1·51534, $d_4^{27\cdot6}$ 0·9948 (*chloroaurate*, $C_{10}H_{16}SAuCl_3$). Probably sulphur is attached at the position of the double linking in the side-chain. Similar treatment of α-pinene yielded a polymerised product and a very small amount of a sulphide which was isolated as the methiodide (cf. Budnikov and Schilov, A., 1923, i, 118), and may or may not be identical with that described above. E. LEWKOWITSCH.

Condensation products of pernitrosocamphor with amines. P. SACCARDI (Annali Chim. Appl., 1930, **20**, 489—494).—Condensation of pernitrosocamphor with anæsthesin, *m*-anisidine, and *p*-aminobenzoic acid respectively yields 2-*camphoranæsthesin*,
$\begin{matrix}CH_2\\C_8H_{14}\end{matrix}\!>\!C{:}N{\cdot}C_6H_4{\cdot}CO_2Et$, m. p. 85°; 2-*camphor*-m-*anisidine*, b. p. 246—249°/35 cm., n^{18} 1·401, and 2-*camphor*-p-*aminobenzoic acid*, m. p. 238—239° (decomp.). Anthranilic acid condenses with pernitrosocamphor only as sodium salt, the resulting salt being unstable; *lead* 2-*camphor*-o-*aminobenzoate* is, however, stable and was analysed (cf. Saccardi and Romagnoli, A., 1927, 1196; Romagnoli, A., 1929, 72). T. H. POPE.

Spatial structure of *apo*cyclene and of other more simple tricyclic hydrocarbons. V. Stereochemistry of alicyclic compounds. S. S. NAMETKIN and L. G. BOGATSCHEVA (J. Russ. Phys. Chem. Soc., 1930, **62**, 1335—1342).—*apo*Cyclene prepared from *l*-fenchene is optically inactive; this result is explicable on the basis of the space formula given. R. TRUSZKOWSKI.

Oxidation of acetylenic glycols. The *o*-diketones of the tetrahydrofuran series. T. I. TENUIKOVA and P. A. TICHOMOLOV (J. Russ. Phys. Chem. Soc., 1930, **62**, 1217—1222).—Oxidation of tetratolylbutinenediol, m. p. 156°, with chromic acid gave 2 : 2′ : 5 : 5′-*tetratolyl*-3 : 4-*diketotetrahydrofuran*, deep purple, m. p. 182°, which on further oxidation yielded ditolyl ketone, m. p. 93°; a *phenylhydrazone*, m. p. 184—186°, *oxime*, m. p. 226°, and *quinoxaline*, m. p. 220—221°, were also obtained. M. ZVEGINTZOV.

Furan derivatives. I. J. RINKES (Rec. trav. chim., 1930, **49**, 1118—1125).—Nitration of 2-methylfuran (Reichstein, A., 1930, 783) with nitric acid (*d* 1·51) and acetic anhydride below —5° and treatment of the product with pyridine affords 5-*nitro*-2-*methylfuran*, m. p. 43·5°, b. p. 104°/12 mm., probably thus: $\begin{matrix}CH{:}CMe\\|\\CH{:}CH\end{matrix}\!>\!O$ —— $\begin{matrix}CH{:}CMe{\cdot}OH\\|\\CH{:}C(NO_2){\cdot}OAc\end{matrix}$ → $\begin{matrix}CH{:}CMe\\CH{:}C(NO_2)\end{matrix}\!>\!O$, together with a small yield of (?) the *monoacetate* of αγ-*dinitro*-$\Delta^{\alpha\gamma}$-*pentadiene*-αδ-*diol*, $OH{\cdot}CMe{:}C(NO_2){\cdot}CH{:}C(NO_2){\cdot}OAc$, m. p. 77—78°, a nitro-derivative of the assumed intermediate. Oxidation of 5-methylfurfuraldehyde (Fenton, J.C.S., 1901, 79, 807) with silver nitrate and sodium hydroxide affords 5-methylfuroic acid, converted by methyl-alcoholic hydrogen chloride into its *methyl* ester, b. p. 98°/15 mm. The latter is similarly nitrated in acetic anhydride to give a small yield of its 4-*nitro*-derivative,

m. p. 81°. Nitration of 5-methylfuroic acid itself affords mainly 5-nitro-2-methylfuran, identical with the product obtained above (replacement of the carboxyl by a nitro-group), together with a small yield of 4-*nitro-5-methylpyromucic acid*, m. p. 159—160°. Similar nitration of 4-methylpyromucic acid affords 2-nitro-3-methylfuran, m. p. 32·6°, and an *acid*, m. p. 195°, not obtained in sufficient quantity for analysis. J. W. BAKER.

Syntheses with ββ'-dichlorodiethyl ether. I. Derivatives of tetrahydropyran. C. S. GIBSON and J. D. A. JOHNSON (J.C.S., 1930, 2525—2530).—ββ'-Dichlorodiethyl ether, b. p. 66°/12 mm., m. p. —24·5°, is converted by prolonged boiling with 4 mols. of sodium iodide in acetone into -*di-iododiethyl ether*, b. p. 123·5—124°/10 mm. The dichloro-ether readily condenses with ethyl sodiomalonate to give ethyl tetrahydropyran-4 : 4-dicarboxylate (Kamm and Waldo, A., 1922, i, 105), b. p. 134—135°/12 mm., converted by hydrolysis and decarboxylation at 175—185° into tetrahydropyran-4-carboxylic acid, b. p. 146—147°/15 mm. (acid *chloride*, b. p. 85—86°/16 mm.; *methyl*, b. p. 80·5—81°/16 mm., and *ethyl*, b. p. 82·5°/12 mm., esters; *anilide*, m. p. 163°; *amide*, m. p. 179°). Similar condensation with ethyl sodiocyanoacetate affords *ethyl 4-cyanotetrahydropyran-4-carboxylate*, b. p. 122—125°/16 mm. This is hydrolysed by boiling aqueous-alcoholic potassium hydroxide to the 4 : 4-dicarboxylic acid, but hydrolysis with cold aqueous methyl-alcoholic potassium hydroxide affords 4-*cyanotetrahydropyran-4-carboxylic acid*, m. p. 160—162° (*amide*, m. p. 158°), decarboxylated at 180—200° to 4-*cyanotetrahydropyran*, b. p. 82—85°/10 mm. The dichloro-ether does not form a magnesium compound, whilst the di-iodo-ether gave no isolable product. Various unsuccessful experiments are recorded.

J. W. BAKER.

Diphenylene oxide series. II. N. M. CULLINANE (J.C.S., 1930, 2267—2269).—Nitration of diphenylene oxide with fuming nitric acid in sulphuric acid solution (cf. A., 1924, i, 534) gives 80% of the theoretical amount of the 2-nitro-derivative (cf. Mayer and Krieger, A., 1922, i, 746; Borsche and Schacke, A., 1924, i, 161). 2-*Chlorodiphenylene oxide*, m. p. 101°, prepared by the usual method from the 2-amino-derivative, is also formed when the diazonium sulphate from o-*chloro-2-aminodiphenyl ether*, m. p. 44°, is heated in 50% sulphuric acid solution.

The 3(?)-nitrodiphenylene oxide, m. p. 110°, of Borsche and Schacke (*loc. cit.*) is probably the 1-derivative, since the 3-nitro-compound has m. p. 141° (Ryan, Keane, and M'Gahon, A., 1928, 298). H. BURTON.

Tannins and related substances. XXIV. Catechins from kola nuts. K. FREUDENBERG and L. OEHLER (Annalen, 1930, 483, 140—143).—*d*-Catechin and *l*-epicatechin are the only catechins isolated from fresh kola nuts using the method previously described (A., 1924, i, 868). The names kolatin, kolatein (Goris, A., 1907, i, 631), and colacatechin (Casparis, A., 1930, 1223) should be deleted from the literature. Contrary to the statement of Casparis (*loc. cit.*), no catechin could be isolated from fresh or dry tormentilla root. H. BURTON.

Furfuraldehyde. Preparation of tetraethyldiaminodiphenylfurylmethyl chloride and diphenylfurylmethane. S. A. MAHOOD and H. F. ALDRICH (J. Amer. Chem. Soc., 1930, 52, 4477—4480).—Diethylaniline, furfuraldehyde, and zinc chloride at 100° (bath) give (yield, 31%) *tetraethyldiaminodiphenylfurylmethane*, m. p. 78° after previous sintering, converted by the usual method into the corresponding chloride, green. This dyes silk a yellower and less light-stable shade than does malachite-green.

Magnesium phenyl bromide converts ethyl pyromucate in boiling toluene into diphenylfurylcarbinol, m. p. 91° (corr.), reduced by zinc dust and acetic acid below 70° to *diphenylfurylmethane*, m. p. 51° (corr.), which, after a few days, becomes a gum.

H. BURTON.

Diflavone group. V. m-Methoxybenzaldehyde and diacetoresorcinol. E. M. RYAN and H. RYAN (Proc. Roy. Irish Acad., 1930, 39 B, 425—433).—4 : 6-Diacetoresorcinol reacts in hot alcoholic sodium hydroxide solution with *m*-methoxybenzaldehyde to form 4 : 6-*di*-m-*methoxybenzylideneacetoresorcinol*, m. p. 157°, which condenses, in alcoholic chloroform solution of hydrogen chloride, with benzaldehyde and piperonal yielding *dibenzylidene-*, m. p. 249—250°, and *dipiperonylidene-3' : 3''-dimethoxyflavanone*, m. p. 245°, respectively. Treatment of the dichalkone with sodium acetate and acetic anhydride affords the *diacetate*, m. p. 122°. This substance in chloroform solution reacts with bromine to yield a *bromide*, which in alcoholic potassium hydroxide solution undergoes cyclisation with the formation of 3' : 3''-*dimethoxydicoumarone*, m. p. 277—279° (decomp.) after softening at 275°. In a similar manner 4 : 6-diacetoresorcinol dimethyl ether condenses with *m*-methoxybenzaldehyde with the production of 1 : 3-*dimethoxy-4 : 6-di*-m-*benzylideneacetobenzene*, m. p. 157—158°. Bromine converts this substance into a *dibromide*, m. p. 213° (decomp.), a *tetrabromide*, decomp. 176°, and a *pentabromide*, m. p. 186° (decomp.).

T. H. MORTON.

Synthesis of substituted thioxanthhydrols. J. REILLY, P. J. DRUMM, and B. DALY (Proc. Roy. Irish Acad., 1930, 39 B, 515—522; cf. A., 1928, 63).—*p*-Tolyl sulphide condenses with phthalic anhydride in presence of carbon disulphide and aluminium chloride. Decomposition of an intermediate aluminium chloride *compound* by water at 0° affords 2-o-*carboxybenzoyldi*-p-*tolyl sulphide*, m. p. 207° (*oxime*, m. p. 129°; *silver* salt). The constitution is confirmed by a second synthesis from the potassium salts of thio-*p*-cresol and 2-chloro-5-methylbenzophenone-2'-carboxylic acid at 200—210° in presence of copper. Treatment of this substance with concentrated sulphuric acid at 100° for a few minutes, or successively with phosphorus pentachloride and aluminium chloride in benzene solution, results in the formation of 2 : 7-dimethylthiofluoran, m. p. 222°. The application of the Friedel–Crafts reaction, with carbon disulphide as the medium, to benzoyl chloride and *p*-tolyl sulphide affords 9-*phenyl*-2 : 7-*dimethylthioxanthhydrol*, m. p. 207°. This substance reacts with ethereal hydrogen chloride to form a *chloride-hydrochloride*, to which a quinonoid structure is assigned. Reduction with boiling alcoholic hydrogen

chloride, or with zinc and acetic acid converts the thioxanthhydrol into -*phenyl*-2 : 7-*dimethylthioxanthen*, m. p. 157°; treatment of the same substance with diethylaniline in boiling acetic acid produces 4'-*diethylamino*-9 : 9-*diphenyl*-2 : 7-*dimethylthioxanthen*, m. p. 211°.

p-Tolyl sulphide is conveniently prepared (cf. Otto, A., 1879, 926) by diazotising, at 5—10°, *p*-toluidine dissolved in dilute hydrochloric acid (2 mols.) with the theoretical quantity of sodium nitrite. This solution is added to a solution of thio-*p*-cresol (1 mol.) in dilute sodium hydroxide (1 mol.) at 60—70°. The disulphide, b. p. 186°/16 mm., may be obtained from the crude product by distillation under diminished pressure. The addition of bromine to an ethereal solution of thio-*p*-cresol affords di-*p*-tolyl disulphide (cf. Marcker, Annalen, 1865, **136**, 88). T. H. Morton.

Catalytic dehydrogenation of pyrrolidine. J. P. Wibaut, C. C. Molster, H. Kauffmann, and A. M. Lenssen (Rec. trav. chim., 1930, **49**, 1127—1130).—When pyrrolidine is passed over 30% platinised or palladised asbestos at 360°, slow and partial dehydrogenation to pyrrole occurs, the presence of the latter in the distillate being detected by the pine-splint and other tests. Unchanged pyrrolidine can also be isolated as its picrate. Some decomposition occurs, since, with the above catalysts, 8 and 5%, respectively, of hydrocarbons are mixed with the hydrogen evolved. These results together with those of Zelinski and Jurjev (A., 1929, 1461) indicate that the catalytic reduction of pyrrole is reversible.
J. W. Baker.

Catalytic synthesis of phenyl-substituted pyridines from aldehydes and ketones and ammonia. A. E. Tschitschibabin and D. I. Orotschko (J. Russ. Phys. Chem. Soc., 1930, **62**, 1201—1206).—The formation of phenyl-substituted pyridine derivatives by the condensation of aldehydes and ketones with ammonia in the presence of aluminium oxide or china clay as catalyst was investigated. Benzaldehyde and acetaldehyde at 305—310° condense with ammonia to give 4-phenylpyridine (picrate, m. p. 196—197°), together with some 2-phenylpyridine (picrate, m. p. 173—174·5°), the maximum yield being 25%. If acetone is used instead of acetaldehyde, 4-phenyl-2 : 6-dimethylpyridine, m. p. 62—63·5°, is obtained. Phenyl styryl ketone, acetone, and ammonia yield the same product. M. Zvegintzov.

2-Hydroxy-derivatives of quinoline bases. A. E. Tschitschibabin and A. I. Kursanova (J. Russ. Phys. Chem. Soc., 1930, **62**, 1211—1216).—The preparation of 2-hydroxy-derivatives from quinoline bases by heating them with anhydrous potassium hydroxide was investigated. The reaction proceeds smoothly at 250—260°, yields from 40% to 70% being obtained. 8-Methylquinoline gave 2-hydroxy-8-methylquinoline, m. p. 219—220°, and 6-methylquinoline the corresponding 6-compound. α- and β-Naphthoquinolines gave the corresponding hydroxy-derivatives, m. p. 285—286° and 252—253°, respectively, whilst *iso*quinoline yielded *iso*carbostyril, m. p. 209—210°.

The two 2-hydroxymethylquinolines when oxidised with potassium permanganate gave the corresponding methylisatins (m. p. 266° and 186°), together with some oxalylmethylanthranilic acid, m. p. 231°. Oxidation of α-naphthocarbostyril gave a deep red compound, m. p. 290°. M. Zvegintzov.

Synthesis of tryptophol. R. W. Jackson (J. Biol. Chem., 1930, **88**, 659—662).—Reduction of methyl indolyl-3-acetate (b. p. about 180°/2 mm.) according to the method of Marvel and Tanenbaum (A., 1923, i, 2) yields tryptophol, m. p. 57°, purification being effected through the picrate. A better yield (80—90%) is obtained by reduction of the ethyl ester (b. p. about 180°/2 mm.) by sodium and alcohol. W. O. Kermack.

Stereochemistry of phenylpyridine compounds. Preparation and investigation of 2-*o*-chlorophenylpyridine-3 : 6'-dicarboxylic acid and 6-phenyl-3-*o*-carboxyphenylpyridine-2 : 4-dicarboxylic acid. X. C. C. Steele and R. Adams (J. Amer. Chem. Soc., 1930, **52**, 4528—4535).—8-Chloro-α-naphthylamine, m. p. 95—96° (lit. 89—94°), prepared in 97% yield by reducing 8-chloro-1-nitronaphthalene with iron powder and water containing a little hydrochloric acid, is converted by the Skraup reaction into 10-*chloro-α-naphthoquinoline* (20% yield), m. p. 81·5—82°. This is oxidised by aqueous potassium permanganate at 100° to 2-o-*chlorophenylpyridine*-3 : 6'-*dicarboxylic acid*, m. p. 252—256° (decomp.) (*strychnine*, m. p. 171—173°; *brucine*, m. p. 168—170°; *morphine*, m. p. 200—204°; *cinchonine hydrogen*, m. p. 154—156°; *cinchonine*, m. p. 194—196°, and *quinine hydrogen*, m. p. 152—155°, salts). 2-Phenyl-β-naphthoquinoline-3-carboxylic acid (Dobner and Kuntze, A., 1889, 411) is oxidised by Immerheiser's method (A., 1889, 527) to 6-*phenyl*-3-o-*carboxyphenylpyridine*-2 : 4-*dicarboxylic acid*, m. p. 202° (74% yield) [*strychnine hydrogen*, m. p. about 238° (decomp.); *brucine hydrogen*, melts partly at 204° (decomp.), and *cinchonine dihydrogen* salts, m. p. 174—176°, resolidifying with m. p. 200—204° (decomp.); *trichloride*, m. p. 127—130°; n-*butyl* ester; *menthyl* ester, $[\alpha]_D$ —38° in acetone]. Neither of the above acids could be resolved. The various possibilities of optical isomerism in the phenylpyridine series are discussed. H. Burton.

Stereoisomerism in substituted 1 : 2 : 3 : 4-tetrahydroquinolines. II. S. G. P. Plant and R. J. Rosser (J.C.S., 1930, 2444—2455).—Reduction of 3 : 4-dimethylquinoline, m. p. 73—74° (Knorr, A., 1888, 1111, gives m. p. 65°) [picrate, m. p. 215—217° (lit. m. p. 205°); hydrochloride, m. p. 290° (decomp.)] (best prepared by the action of phosphorus oxychloride on 2-keto-3 : 4-dimethyl-1 : 2-dihydroquinoline and reduction of the 2-chloro-3 : 4-dimethylquinoline so formed with red phosphorus and hydriodic acid, *d* 1·7, in a sealed tube at 175—180°), with tin or zinc and alcoholic hydrochloric acid, sodium and boiling alcohol, or electrolytically, occurs slowly and affords only one stereoisomeric form of 3 : 4-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, an oil (*picrate*, m. p. 143—145°), isolated as its *phenylcarbamyl* derivative, m. p. 107—108°. Reduction of 2-keto-3 : 4-dimethyl-1 : 2-dihydroquinoline with sodium amalgam and boiling alcohol, however, affords a mixture (6 : 1)

of the two stereoisomeric *forms*, *A*, m. p. 127—128° (least soluble), and *B*, m. p. 117°, of 2-*keto*-3 : 4-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, separated by fractional crystallisation from the reaction product. The form A is converted by phosphorus oxychloride into 2-chloro-3 : 4-dimethylquinoline. Further reduction of the mixture of stereoisomerides with sodium and boiling alcohol gives only the previously described form of 3 : 4-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoline, together with a little 3 : 4-dimethylquinoline. The presence of the latter product suggests that the mechanism of the reaction is :

$$C_6H_4{<}\begin{matrix}CHMe{\cdot}CHMe\\NH—CO\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}CMe{:}CMe\\NH{-}CH{\cdot}OH\end{matrix} \longrightarrow$$

$$C_6H_4{<}\begin{matrix}CMe{:}CMe\\N{=\!=}CH\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}CHMe{\cdot}CHMe\\NH—CH_2\end{matrix}$$, a similar mechanism applying equally to the reaction of Blount, Perkin, and Plant (A., 1929, 1312). Reduction of 2 : 4-dimethylquinoline with sodium and boiling alcohol affords a mixture (2 : 3) of two inactive stereoisomeric *forms*, *A* (*hydrochloride*, m. p. 228°; 1-*acetyl* derivative, m. p. 50—51°; *picrate*, m. p 139—141°; 1-*phenylcarbamyl*, m. p. 121—122°, and 1-*benzoyl*, m. p. 115°, derivatives), and *B* (*hydrochloride*, m. p. 178—179°; *picrate*, m. p. 188—191°; 1-*phenylcarbamyl* derivative, m. p. 112—113°), isolated from the mother-liquor as its 1-*acetyl* derivative, m. p. 97—98°, of 2 : 4-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoline. The form A is probably the racemate of the *d*- and *l*-forms obtained by Thomas (J.C.S., 1912, **101**, 725). Reduction of 2 : 4-dimethylquinoline with tin and alcoholic hydrochloric acid, electrolytically, and with zinc and alcoholic hydrochloric acid affords a mixture of A and B forms in the ratios 9 : 1, —, and 5 : 1, respectively. A steric explanation of the failure of 3 : 4-dimethylquinoline to yield stereoisomerides is given on the assumption that 3 : 4-dimethyl-1 : 4-dihydroquinoline is an intermediate product. J. W. BAKER.

Friedel–Crafts reaction with 8-hydroxyquinoline. K. MATSUMURA (J. Amer. Chem. Soc., 1930, **52**, 4433—4436).—Acetyl chloride and 8-hydroxyquinoline react in presence of nitrobenzene and aluminium chloride, forming 8-*hydroxy*-5-*acetylquinoline*, m. p. 112—112·5° [*hydrochloride* (+3H_2O), m. p. 284—285° (decomp.); *hydrogen sulphate*, m. p. 248° (decomp.); *picrate* (+H_2O), m. p. 188—189°; *chloroplatinate*, m. p. 275° (decomp.); *methiodide* (+H_2O), m. p. 210° (decomp.)], the *oxime*, m. p. 193°, of which undergoes the Beckmann rearrangement, yielding 5-*acetamido*-8-*hydroxyquinoline*, m. p. 217—218° [*hydrogen sulphate*, m. p. 263° (decomp.)]. Chloroacetyl chloride reacts as above at 90—95° furnishing 8-*hydroxy*-5-*chloroacetylquinoline*, m. p. 158—159° [*hydrochloride*, m. p. 287° (decomp.); *hydrogen sulphate*, m. p. 263° (decomp.); *picrate*, m. p. 179°; *chloroplatinate*, m. p. 275° (decomp.)], reduced by iron powder and 80% alcohol containing a little hydrochloric acid to 8-hydroxy-5-acetylquinoline. 8-*Hydroxy*-5-*benzoylquinoline*, m. p. 118—119° [*hydrochloride*, m. p. 252—260°; *hydrogen sulphate*, m. p. 219—220°; *picrate*, m. p. 143—145°; *methiodide*, m. p. 199·5° (decomp.)], is prepared similarly from benzoyl chloride at 110—120°; its *oxime*, m. p. 147—148°, undergoes the Beckmann transformation yielding 5-*benzamido*-8-*hydroxyquinoline*, m. p. 237—238° [*hydrogen sulphate*, m. p. 221—222° (decomp.)]. Benzoylation of 8-hydroxyquinoline in pyridine in the cold gives 8-benzoyloxyquinoline, m. p. 122—122·5° (lit. 118—120°) (*hydrochloride*, m. p. 124°). H. BURTON.

***Py*-Alkylquinolines. Generalisation of the Skraup reaction applied to α-alkylglycerols.** R. DELABY and J. HIRON (Compt. rend., 1930, **191**, 845—847).—The application of a modification (A., 1930, 616) of the Skraup reaction to α-alkylglycerols and aniline leads to a mixture of 2- and (less) 4-alkylquinolines. The intermediate formation of the aldehyde, CHR:CH·CHO, is postulated. In this manner were prepared: 2-ethylquinoline, b. p. 128—131°/13 mm., d_4^{17} 1·050, n_D^{22} 1·5979 [*picrate*, m. p. 148°; *chloroplatinate*, m. p. 188°; *chloromercurate*, m. p. 118°; *iodomercurate*, m. p. 135°; *iodobismuthate*, m. p. 205° (decomp.)]; 2-propylquinoline, b. p. 142—145°/13 mm., d_4^{17} 1·038, n_D^{21} 1·5886 (*picrate*, m. p. 159; *chloroplatinate*; *chloromercurate*, m. p. 112°; *iodomercurate*, m. p. 112°; *iodobismuthate*, m. p. 186°), and 2-butylquinoline, b. p. 150—155°/13 mm., d_4^{18} 1·020, n_D^{22} 1·5799 (*picrate*, m. p. 143°; *chloroplatinate*, m. p. 163·5°; *chloromercurate*, m. p. 163·5°; *iodomercurate*, m. p. 163·5°; *iodobismuthate*, m. p. 163°). T. H. MORTON.

Quinoline and benzacridine derivatives yielding coloured adsorption compounds with iodine. W. O. KERMACK, R. H. SLATER, and W. T. SPRAGG (Proc. Roy. Soc. Edin., 1930, **50**, 243—261).—9-Methyl-3 : 4-benzacridine and 3 : 4 : 5 : 6-dibenzacridine in colloidal suspension give a red or blue coloration with solutions of iodine. Some closely-related benzacridine derivatives are inactive, but certain derivatives of 4-anilinoquinoline (Slater, A., 1930, 937) also develop a colour on treatment with iodine at concentrations of the order of 0·0001*N*. In the case of the active benzacridine compounds, the colour is still apparent at a concentration of 0·00001*N* or even less. The effect of variation of concentration of compound, iodine, and hydrogen ions has been investigated in certain instances. The action of certain inorganic salts has also been investigated, but in low concentrations these are without much effect. The methosulphates of the two active benzacridine bases also develop colours with iodine even with very low concentrations of the latter (less than 0·00001*N*). It is suggested that these methosulphates form micellar, colloidal solutions. The following new compounds have been prepared: 9 : 10-*Dihydro*-9-(3′ : 4′-*methylenedioxyphenyl*)-3 : 4 : 5 : 6-*dibenzacridine*, m. p. 305°, from piperonal, β-naphthylamine, and β-naphthol at 200—230°; 9-(3′ : 4′-*methylenedioxyphenyl*-)-3 : 4 : 5 : 6-*dibenzacridine*, m. p. 282°, by oxidation of the previous compound in acetic acid solution with an equimolecular quantity of bromine; 9-*methyl*-3 : 4-*benzacridine methosulphate*, m. p. 205°, and 3 : 4 : 5 : 6-*dibenzacridine methosulphate*, unmelted at 300°. W. O. KERMACK.

Action of aniline and derivatives on benzaldehyde and pyruvic acid. H. T. BUCHERER and R. RUSSISCHWILI (J. pr. Chem., 1930, [ii], **128**, 89—138).—A further investigation of Dobner's synthesis

of 2-phenylquinoline-4-carboxylic acid (cf. A., 1888, 300). The failure to increase the average yield of 50—55% is correlated with the observed absence of hydrogen among the reaction products. The interaction of benzylideneaniline with pyruvic acid in cold acetic acid gives 4 : 5-diketo-1 : 2-diphenylpyrrolidine (I; cf. A., 1898, i, 489; the previously reported instability is not confirmed) as main product, the proportions of 4-anilo-5-keto-1 : 2-diphenylpyrrolidine and 2-phenylquinoline-4-carboxylic acid (cf Döbner, *loc. cit.*; Borsche, A., 1909, i, 52) simultaneously formed being favoured by ether or alcohol as solvent at higher temperatures. The condensation of *o*-nitroaniline and 2-nitro-*p*-toluidine with benzaldehyde and pyruvic acid leads to *4 : 5-diketo-2-phenyl-1-*o*-nitrophenylpyrrolidine*, m. p. 154°, and *4 : 5-diketo-2-phenyl-1-2'-nitro-*p*-tolylpyrrolidine*, m. p. 213—214°, respectively (cf. Borsche, *loc. cit.*), the presence of the nitro-group tending to favour pyrrolidine formation. The aniline salt of the solid form of cinnamoylformic acid (A., 1903, i, 608) is converted quantitatively into I by heating alone or in alcoholic solution, thus confirming the *trans*-configuration previously assigned to this acid. Attempts at conversion of I into 2-phenylquinoline-4-carboxylic acid failed. It does not condense with aniline and cannot be regenerated from its 4-anil. Hydrolysis with 80% sulphuric acid gives (probably) *γ-anilino-γ-phenyl-α-keto-*n*-butyric acid*, decomp. 75—85° (*calcium* and other salts described). By heating with phenylhydrazine in presence of a little acetic acid, a *substance*, $C_{16}H_{14}O_2N_2$, m. p. 153·5° (unstable silver and magnesium salts), is formed, the solubility of which in alkali and ready conversion into a *p-nitrobenzeneazo*-derivative, decomp. about 115°, points to its constitution as 1-anilino-4 : 5-diketo-2-phenylpyrrolidine, or, possibly, 4 : 5-diketo-2 : 3-diphenylpyridazine. Use of excess of phenylhydrazine gives, in addition, a *substance*, $C_{16}H_{14}ON_2$(?), decomp. 124—125°, also obtained from the 4-anilo-compound and phenylhydrazine.

The preparation of the following derivatives of *m*-tolylenediamine, and their conversion by condensation with benzaldehyde and pyruvic acid in alcoholic solution into derivatives of 2-phenylquinoline-4-carboxylic acid, accompanied by a little of the corresponding diketopyrrolidine, are described: *4-nitro-*p'*-toluenesulphon-*o*-toluidide*, m. p. 157°; *4-amino-*p'*-toluenesulphon-*o*-toluidide*, m. p. 176°, by reduction of the preceding, or hydrolysis of the *p-toluenesulphonyl* derivative, m. p. 182—183°, of 2-aminoaceto-*p*-toluidide; *2-nitro-*p'*-toluenesulphon-*p*-toluidide*, m. p. 162—163°; *2-amino-*p'*-toluenesulphon-*p*-toluidide*, m. p. 164—165°, by reduction of the preceding: *7-amino-*, decomp. indefinitely, 250—270° (*hydrochloride*), *7-acetamido-*, decomp. 300—302°, by acetylation of the preceding, or from 4-aminoaceto-*o*-toluidide, and *7-*p*-toluenesulphonamido-2-phenyl-6-methylquinoline-4-carboxylic acid*, decomp. 273—274° (*methyl* ester, m. p. 224°; *ethyl* ester, m. p. 186—187°), from the appropriate acyl-*m*-tolylenediamine. *5-*p*-Toluenesulphonamido-2-phenyl-8-methylquinoline-4-carboxylic acid*, decomp. 98—103°, is prepared similarly. The condensation of resacetophenone and isatin in presence of 33% sodium hydroxide gives *2' : 4'-dihydroxy-2-phenylquinoline-4-carboxylic acid*, decomp. 305° (*methyl* ester, m. p. 211—212°; *ethyl* ester, m. p. 195—196°).

H. A. Piggott.

Diazotisation in the pyrazole series. J. Reilly and D. MacSweeney (Proc. Roy. Irish Acad., 1930, **39B**, 497—504).—Reduction of 4-nitroso-1-phenyl-3 : 5-dimethylpyrazole with tin and hydrochloric acid at 100° affords *4-amino-1-phenyl-3 : 5-dimethylpyrazole dihydrochloride*, from which the free *base* (*benzoyl* derivative, m. p. 153—154°; *chloroplatinate*) may be obtained. The base condenses with benzaldehyde (1 mol.) in presence of a trace of piperidine to give the corresponding *4-benzylideneamino*-derivative, m. p. 90—91°. Diazotisation with ethyl nitrite and hydrochloric acid yields *1-phenyl-3 : 5-dimethylpyrazole-4-diazonium chloride*, which may be obtained crystalline by evaporation under diminished pressure. This diazonium salt is exceedingly stable, losing only 20% of its diazo-nitrogen in aqueous solution during 6 hrs. at 100°. The diazonium salts, *chloroplatinate*, and *dichromate hydrochloride*, $(C_{11}H_{11}N_4)_2Cr_2O_7,HCl$, are described. It is suggested that these diazonium compounds can be represented only by a cyclic structure similar to that proposed by Forster and Muller (J.C.S., 1909, **95**, 2072) for triazole derivatives. The diazonium chloride couples readily with phenols and aromatic amines. With dimethylaniline, diethylaniline, *p*-toluidine, and α-naphthylamine it gives coloured *azo*-derivatives; with β-naphthol a red *azo*-compound, m. p. 189—190°, and with β-naphthylamine an orange *azo*-derivative, m. p. 195—196°. With α-naphthol-3 : 6-disulphonic acid and β-naphthol-6 : 8-disulphonic acid it yields soluble red *dyes*, and with 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid a purple soluble *dye*. With *m*-phenylenediamine a red azo-*dye* of the chrysoidine group is obtained. An aqueous solution of the diazonium chloride reacts with ethyl acetoacetate and acetylacetone, dissolved in alcohol, to produce *1-phenyl-3 : 5-dimethylpyrazole-4-azo-ethyl acetoacetate*, m. p. 84—85°, and *-4-azo-acetylacetone*, m. p. 115—116°, respectively.

T. H. Morton.

Reaction of antipyrine and pyramidone. Detection of antipyrine in pyramidone. M. Ribère (J. Pharm. Chim., 1930, [viii], **12**, 444—447).—A white precipitate, soluble in excess, is given by antipyrine, but not by pyramidone, with trichloroacetic acid or perchloric acid. Hot ammoniacal silver nitrate is reduced by pyramidone, but not by antipyrine. A 10% solution of mercury in nitric acid from which nitrous fumes have been almost completely removed gives with antipyrine a white precipitate, soluble at the b. p. and reprecipitated on cooling with a brick-red colour, and with pyramidone a violet coloration. A mixture of this reagent with an equal amount of 20% trichloroacetic acid enables the presence and approximate proportion of antipyrine in pyramidone to be determined. Samples of pyramidone containing (*a*) 25%, (*b*) 10%, and (*c*) 1—0·1% of antipyrine give in 1% aqueous solution: (*a*) the same reaction as with pure antipyrine, (*b*) a white precipitate and a red coloration at the b. p., (*c*) (by superposition) a violet ring and a white cloud extending into the upper layer.

H. E. F. Notton.

Pyrimidines. CXVII. Synthesis of nucleosides. G. E. HILBERT and T. B. JOHNSON (J. Amer. Chem. Soc., 1930, 52, 4489—4494).—Treatment of 2 : 6-dimethoxypyrimidine with acetobromoglucose at 50° affords *2-keto-6-methoxy-3-tetra-acetylglucosidopyrimidine*, m. p. 220—221°, together with 2-keto-6-methoxy-3-methylpyrimidine (cf. A., 1930, 928). Hydrolysis of the former compound with alcoholic hydrogen chloride gives *3-glucosidouracil* ($+0\cdot5H_2O$), m. p. 195—203° according to the rate of heating, m. p. (anhydrous) 207—209°, $[\alpha]_D^{25}$ +21·4° in water [*tetra-acetyl* derivative, m. p. 154—155°; *5-bromo*-derivative, m. p. 224° (decomp.), $[\alpha]_D^{25}$ +10·3° in water], which is similar in all its reactions to uridine (Levene and La Forge, A., 1913, i, 211). Catalytic reduction (Adams) of 3-glucosidouracil in 80% alcohol furnishes the 4 : 5-*dihydro*-derivative, decomp. 238° after darkening at 220°, $[\alpha]_D^{25}$ +9·3° in water, hydrolysed by 3% sulphuric acid to 4 : 5-dihydrouracil (cf. *loc. cit.*).

H. BURTON.

Pyrimidines. CXVIII. Molecular rearrangements in the thymine series. W. SCHMIDT-NICKELS and T. B. JOHNSON (J. Amer. Chem. Soc., 1930, 52, 4511—4516).—2 : 6-Dichloro-5-methylpyrimidine and methyl-alcoholic sodium methoxide give *2 : 6-dimethoxy-5-methylpyrimidine*, m. p. 61°, passing at 200° into 1 : 3-dimethylthymine. Treatment of the dimethoxy-derivative with methyl iodide affords *2-keto-6-methoxy-3 : 5-dimethylpyrimidine*, m. p. 144°, hydrolysed by hydrochloric acid to 3-methylthymine, m. p. 291° (lit. 280—282°). *2 : 6-Diethoxy-5-methylpyrimidine*, m. p. 36°, reacts with methyl and ethyl iodides forming *2-keto-6-ethoxy-3 : 5-dimethyl-*, m. p. 111°, and *2-keto-6-ethoxy-5-methyl-3-ethyl-pyrimidines*, m. p. 78°, respectively. The last-named compound is hydrolysed by hydrochloric acid to *2 : 6-diketo-5-methyl-3-ethylpyrimidine* (*3-ethylthymine*), m. p. 223°.

Acetobromoglucose and 2 : 6-dimethoxy-5-methylpyrimidine at 60° afford mainly 3-methylthymine, probably owing to the methyl bromide formed; acetochloroglucose does not react. A small amount of a substance, m. p. 316°, is obtained by similar treatment of 2 : 6-diethoxy-5-methylpyrimidine.

H. BURTON.

Action of sodamide on 2 : 5-dimethylpyrazine. A. E. TSCHITSCHIBABIN and M. N. SCHTSCHUKINA (J. Russ. Phys. Chem. Soc., 1930, 62, 1189—1199).—The reaction between sodamide and 2 : 5-dimethylpyrazine, b. p. 152—153°, in solution does not proceed readily, but in the pure state the two react, giving *2 : 2′ : 5 : 5′-tetramethyldipyrazine*, m. p. 68°, and *2 : 5 : 3′-trimethyldipyrazylmethane*, m. p. 135°. The structure of both was deduced from their oxidation products. On being oxidised with potassium permanganate, the former gave 2 : 5 : 3′-trimethyldipyrazinecarboxylic acid, m. p. 173° (decomp.), and 2 : 5-dimethylpyrazinecarboxylic acid, m. p. 117°. Under similar conditions, the 2 : 5 : 3′-trimethyldipyrazylmethane gave 2 : 5-pyrazinedicarboxylic acid, m. p. 256°, and a dibasic keto-acid, giving a hydrazone, m. p. 173°.

M. ZVEGINTZOV.

"Bis-5-phenyl-2-pyrroleindigo" [5 : 5′-diphenyl-Δ$^{2:2}$-bispyrrol-3-one]. W. MADELUNG and L. UBERMANN (Ber., 1930, 63, [B], 2870—2876).—Potassium phenylglycidate and potassium aminoacetate in aqueous solution afford *potassium β-carboxymethylamino-α-hydroxy-β-phenylpropionate trihydrate*, m. p. 96°, and *tetrahydrate*, m. p. 86°, from which the *lead* and *calcium* salts and the free *acid*, $CO_2H\cdot CH_2\cdot NH\cdot CHPh\cdot CH(OH)\cdot CO_2H$, m. p. 235°, are derived. The potassium salt is transformed by boiling acetic anhydride into *1-acetyl-3-hydroxy-5-phenylpyrrole-2-carboxylic acid*, m. p. 150°, converted by boiling water into *1-acetyl-3-hydroxy-5-phenylpyrrole*, m. p. 88°, from which *1-acetyl-3-acetoxy-5-phenylpyrrole*, m. p. 181°, is derived. Oxidation of crude 1-acetyl-3-hydroxy-5-phenylpyrrole with ferric chloride and hydrochloric acid gives *5 : 5′-diphenyl-Δ$^{2:2'}$-bispyrrol-3-one*,  m. p. above 300° (decomp.), which, contrary to Posner's theory (A., 1926, 1155), closely resembles indigotin in absorption spectrum, yields complex compounds with zinc chloride and titanium chloride in benzene, and silver and copper compounds with the metallic acetates in pyridine. The hyposulphite vat has only slight affinity for cotton. The corresponding *acetyl* derivative, m. p. 220°, is described.

H. WREN.

Formation and analysis of some 1 : 3 : 4-triazoles. H. MACUREVITSCH (Bull. Soc. chim., 1930, [iv], 47, 1160—1183, and J. Russ. Phys. Chem. Soc., 1930, 62, 1137—1163).—Further investigation of the reaction between *o*-toluidine and phenyl-*s*-di(thiocarbamyl)hydrazine has shown that the crystalline substance of m. p. 219—220° (A., 1927, 777) is 3-tolyliminothiourazole (*silver* salt; *acetyl* derivative, $C_9H_9N_4SAc$, m. p. 184—185°) and the substance, m. p. 300°, obtained as a secondary product is identical with Arndt's iminothiourazole, decomp. 303° (A., 1921, i, 813), the product m. p. 370° (*silver* salt) being a further condensation product which does not give the azo-reaction of Arndt (*loc cit.*) when oxidised with potassium ferricyanide. Aniline and *s*-di(thiocarbamyl)-hydrazine yield 3-imino-5-thio-4-phenylurazole, m. p. 263—264·5° (*silver* salt; *acetyl* derivative, m. p. 185—186°; *dibenzyl* derivative, m. p. 189—190°), identical with the 3-amino-5-thiol-4-phenyl-1 : 2 : 4-triazole obtained by Fromm (A., 1924, i, 882) and Arndt (A., 1922, i, 375). *m*-Toluidine similarly affords *3-imino-5-thiol-4-m-tolylurazole*, decomp. 309—310° (*silver* salt; *diacetyl* derivative, m. p. 189—190°); *o*-toluidine and *p*-toluidine yield, respectively, 3-imino-5-thiol-4-*o*-tolylurazole, m. p. 229—230° (*silver* salt; acetyl derivative, m. p. 190—191°; dibenzyl derivative, *3-benzylimino-5-benzylthiol-4-o-tolylurazole*, an oil), and 3-imino-5-thiol-4-*p*-tolylurazole, decomp. 297—298° (*silver* salt; *dibenzyl* derivative, m. p. 237—238·5°). *m*-Toluidine and phenyl-*s*-di(thiocarbamyl)hydrazine yield a substance, $C_9H_{10}N_4S$, m. p. 247—249° (decomp.), together with 3-imino-5-thiol-4-*m*-tolylurazole; *p*-toluidine similarly yields *3-p-toluidino-5-thio-1 : 2 : 4-triazole*, m. p. 263—264° (decomp.) [*silver* salt; *acetyl* derivative, m. p. 191—192° (sinters at 172°)], and a *substance*, decomp. 258—286°, and *m*-2-xylidine gives *3-m-2-xylylimino-5-thiourazole*, m. p. 203—204° (sinters at 196°), and a substance, m. p. above 370°. *o-Tolyl-s-di(thiocarbamyl)hydrazine*, decomp. 168—170°, obtained by condensing *o*-tolylthiocarbimide and thiosemicarbazide in aqueous alcohol, when

heated with aniline yields the substance, m. p. 259—260°, obtained from aniline and *s*-di(thiocarbamyl)-hydrazine or phenyl-*s*-di(thiocarbamyl)hydrazine, and 2-anilino-5-thiol-1-phenyl-1 : 3 : 4-triazole, together with a substance, m. p. above 370°.

These triazoles are amphoteric and the monometallic silver salts tend to form complex salts. True chloroplatinates are probably not formed, but unstable complex salts. All theso combinations give Arndt's azo-reaction with potassium ferricyanide, but a yellowish coloration is first produced.

R. BRIGHTMAN.

γ-Triazines. XVIII. Syntheses of *m*- and *p*-tolyl- and benzyl-diaminotriazines. A. OSTROGOVICH and G. GHEORGHIU (Gazzetta, 1930, **60**, 648—664).—Condensation of *m*- or *p*-toluonitrile or phenylacetonitrile with cyanoguanidine proceeds similarly to that of acetonitrile (A., 1911, i, 507), but *o*-toluonitrile remains unchanged, the cyanoguanidine being converted into a mixture of ammeline and melamine. m-*Tolyldiamino-γ-triazine*, $N{<}{\begin{matrix}C(C_6H_4Me){:}N\\C(NH_2){-}N\end{matrix}}{>}C{\cdot}NH_2$, m. p. 239—240°, forms a *hydrochloride*, m. p. 265°; a *sulphate* (+$2H_2O$), m. p. 260°; a *picrate*, m. p. 267—268°; a *diacetate*, m. p. 230—232°; a *monoacetyl* derivative, m. p. 248°, and a *diacetyl* derivative, m. p. 232—233°. p-*Tolyldiamino-γ-triazine*, m. p. 240°, forms a *hydrochloride*, m. p. 285°; a *sulphate* (+$3H_2O$), m. p. 298°; a *picrate*, m. p. 269°; a *diacetate*, m. p. 230—232°; a *monoacetyl* derivative, m. p. 273—274°, and a *diacetyl* derivative, m. p. 264°. Benzyldiamino-γ-triazine, m. p. 238—239° (slight decomp.) (Elzanowski, Diss., Fribourg, 1898, gave m. p. 233°), forms a *hydrochloride*, m. p. 215°; a *sulphate*, m. p. 193—203°; a *monosulphate* (+$2H_2O$), m. p. 178—183°; a *picrate*, 235° (blackening); a *diacetate*, m. p. 230°; a *monoacetyl* derivative, m. p. 239—240°, and a *diacetyl* derivative, m. p. 145°.

T. H. POPE.

Catalyst for the autoxidation of uric acid. FRÈREJACQUE (Compt. rend., 1930, **191**, 949—951).—The autoxidation of uric acid in potassium hydroxide solution (cf. Piaux, A., 1925, i, 592) is accelerated to a very marked extent by active charcoal; allantoin and potassium oxonate are formed at the ordinary temperature, but at 0°, oxonamide is produced. The oxidation of 1- and 7-methyl-, 1 : 3-dimethyl-, and hydroxymethylene-uric acids is catalysed by active charcoal, but xanthine, hypoxanthine, caffeine, and theobromine are not oxidised.

H. BURTON.

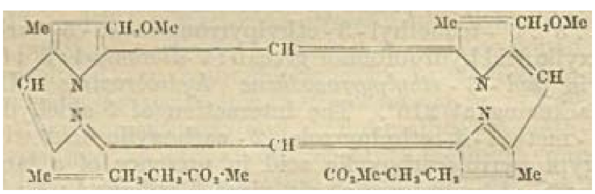
Preparation of 1 : 3 : 9- and 3 : 7 : 9-trimethyluric acid. H. BILTZ and H. PARDON (Ber., 1930, **63**, [*B*], 2876—2880).—8-Chlorotheobromine is converted by methyl-alcoholic sodium methoxide into 8-*methoxytheobromine*, m. p. 282°, which becomes isomerised at 290° to 3 : 7 : 9-trimethyluric acid, m. p. 373—375° (decomp.). Treatment of the last-named acid with methyl sulphate and sodium hydroxide yields tetramethyluric acid, m. p. 228°. 1 : 3-Dimethyluric acid is transformed into the *potassium* salt, which is treated with methyl *p*-toluenesulphonate in *o*-dichlorobenzene at 150°, whereby 1 : 3 : 9-trimethyluric acid mixed with some 1 : 3-dimethyluric acid results. The trimethyluric acid, decomp. 340°, is obtained by dissolving the product in ammonia solution and boiling or by dissolution in potassium hydroxide solution followed by treatment with carbon dioxide; in either case the more strongly acidic 1 : 3-dimethyluric acid remains in the solution. 8-*Chlorotheophylline*, m. p. indef. 304° (decomp.), obtained by treating theophylline with hydrochloric acid and potassium chlorate, cannot be converted smoothly into the corresponding methoxy-compound.

H. WREN.

Porphyrin synthesis. XXXI. Further pyrroporphyrins. H. FISCHER and H. BERG. **XXXII. Introduction of hydroxymethyl, methylmalonic and propionic acid residues into porphyrins.** H. FISCHER and H.-J. RIEDL. **XXXIII. Synthesis of pyrroætioporphyrins I, II, III, IV, VI, and VIII, and a dimethyldiethylporphin.** H. FISCHER and A. SCHORMÜLLER (Annalen, 1930, **482**, 189—213, 214—225, 232—251).—XXXI. Pyrroporphyrins 12, 2, and 3 are synthesised and shown to be different from pyrroporphyrin 15 by mixed-m. p. determinations of their methyl esters. 4-Bromo-5-aldehydo-3-methylpyrrole-2-carboxylic acid when condensed with cryptopyrrole, and the product treated with hydrobromic acid, gives 3-*bromo*-5-*carboxy*-4 : 3′ : 5′-*trimethyl*-4′-*ethylpyrromethene hydrobromide*, decomp. 130°, converted by bromine in formic acid into 3 : 5-*dibromo*-4 : 3′ : 5′-*trimethyl*-4′-*ethylpyrromethene hydrobromide*, (I), m. p. 175° (decomp.). This condenses with 5′-bromo-3 : 5 : 3′-trimethyl-4-ethylpyrromethene-4′-propionic acid in presence of methylsuccinic acid at 130° to give *pyrroporphyrin* 12 [*hæmin*; *methyl* ester, m. p. 242° (*hæmin*, m. p. 260°)] and *bromopyrroporphyrin* 12 [*copper* salt; *methyl* ester, m. p. 304° (*copper* salt, m. p. 259°)]. Bromination of 4′-bromo-4 : 3′ : 5′-trimethyl-3-ethylpyrromethene-5-carboxylic acid hydrobromide gives 5 : 4′-*dibromo*-4 : 3′ : 5′-*trimethyl*-3-*ethylpyrromethene hydrobromide* (II), darkening at 215°. The interaction of 5-aldehydo-3-methyl-4-ethylpyrrole-2-carboxylic acid with cryptopyrrolecarboxylic acid in presence of a large excess of hydrobromic acid gives 5-*carboxy*-4 : 3′ : 5′-*trimethyl*-3-*ethylpyrromethene*-4′-*propionic acid hydrobromide*, decomp. 170°, which on bromination in formic or acetic acid is converted into 5-*bromo*-4 : 3′ : 5′-*trimethyl*-3-*ethylpyrromethene*-4′-*propionic acid hydrobromide* (III), decomp. 216°. The hydrobromides II and III, when heated at 130° with methylsuccinic acid, condense to *pyrroporphyrin* 2 [*hæmin*; *methyl* ester, m. p. 229° (*hæmin*, m. p. 265°)] and *bromopyrroporphyrin* 2 [*copper* salt; *methyl* ester, m. p. 291° (*copper* salt, m. p. 235°)]. When similarly treated, I and III give *pyrroporphyrin* 3 [*hæmin*; *methyl* ester, m. p. 219° (*hæmin*, m. p. 274°)] and *bromopyrroporphyrin* 3 [*copper* salt; *methyl* ester, m. p. 254° (*copper* salt, m. p. 230°)]. An attractive alternative synthesis of pyrroporphyrin 3 is by heating 5-*carboxy*-4 : 3′ : 5′-*trimethylpyrromethene*-3-*propionic acid hydrobromide* (IV), decomp. 168°, with 5-bromo-4 : 3′-dimethyl-3 : 4′-diethyl-5′-bromomethylpyrromethene hydrobromide and succinic acid at 210° for 10 min. It is unnecessary to brominate IV, which is prepared by condensation of 2 : 4-dimethylpyrrole with 5-aldehydo-2-carboxy-3-methylpyrrole-4-propionic acid; consequently the sole by-product is the ætioporphyrin.

Deuteroætioporphyrin II (*hæmin*) and its *mono-bromo*-derivative (*copper* salt) occur as by-products in the above porphyrin syntheses, mixed, in the case of pyrroporphyrins 12 and 3, with the dibromo-derivative, in the case of pyrroporphyrin 12 with mesoporphyrin V, and in that of pyrroporphyrin 2 with mesoporphyrin II. The isolation of the first two from the combined residues from the preparation of pyrroporphyrins 12 and 3, and from that of porphyrin 2 is described. Mesoporphyrin II is readily formed by self-condensation of III in presence of methylsuccinic acid; and may also be synthesised as follows: hæmopyrrole-aldehydecarboxylic acid condenses with opsopyrrole to 4 : 5 : 3′-*trimethyl*-4′-*ethylpyrromethene*-3-*propionic acid hydrobromide*, decomp. 178°, converted by bromine in acetic acid into the 5-*bromo*-derivative, decomp. 204°, which is then fused with methylsuccinic acid. The action of 6% potassium methoxide on 3 : 5 : 3′-trimethyl-4-ethylpyrromethene-4′-propionic acid hydrobromide gives coproporphyrin, identified by its tetramethyl ester, in excellent yield. Spectroscopic observations gave identical results for isomeric pyrroporphyrins.

XXXII. Synthesis of hydroxymethylporphyrins from appropriate pyrromethenes is difficult and unsatisfactory, but the hydroxymethyl group can be introduced into deuterohæmin by the action of a large excess of chloromethyl ether and stannic chloride at 0°, the *O*-methyl groups being removed in the process. The product isolated by crystallisation from acetic acid is the *iron* salt of O-*monoacetyl*-1 : 3 : 5 : 8-*tetramethyl*-2 : 4-*di*(*hydroxymethyl*)*porphin*-6 : 7-*dipropionic acid*, m. p. above 270°. The *ether-ester*,



m. p. 215°, prepared according to Kuster (A., 1913, i, 1004) gives 2 : 3 : 4-trimethylpyrrole with hydriodic acid, and with hydrogen bromide in acetic acid the dibromomethyl derivative (*hydrobromide*). With ethyl potassiomalonate this gives (after esterification) *hexamethyl*-1 : 3 : 5 : 8-*tetramethylporphin*-2 : 4-*di*-(*methylmalonate*)-6 : 7-*dipropionate*, m. p. 202° [*iron* salt, m. p. 200° (sinters at 165°); *hexa-ethyl* ester, m. p. 161° (sinters at 122°)], hydrolysed by 1% hydrochloric acid at 180° to (after re-esterification) the tetramethyl ester of coproporphyrin III, identical in all respects with the synthetic material.

XXXIII. The syntheses of a number of ætioporphyrins and of 1 : ɔ-dimethyl-2 : 6-diethylporphin by fusion of the corresponding pyrromethenes with an equal mixture of succinic and methylsuccinic acids are described. The following new *pyrromethene hydrobromides* are described: 4 : 5 : 4′ : 5′-*tetramethyl*-3′-*ethyl*- (*A*), m. p. 230° (decomp.), from 2 : 3-dimethylpyrrole-5-aldehyde and hæmopyrrole; 4 : 5 : 3′ : 5′-*tetramethyl*-4′-*ethyl*- (*B*), m. p. 233° (decomp.); from the above aldehyde and cryptopyrrole; 3 : 5-*dimethyl*-4-*ethyl*-, m. p. 193° (decomp.) [*dibromo*-compound (*C*), m. p. above 300°], from pyrrole-2-aldehyde and cryptopyrrole; 4 : ɔ-*dimethyl*-3-*ethyl*-, m. p. 197° [*dibromo*-compound (*D*), m. p. 145°], from pyrrole-2-aldehyde and hæmopyrrole: 3 : 5-*dicarbethoxy*-4 : 3′ : 5′ *trimethyl*-4′-*ethyl*-, m. p. 160—162° (free *base*, m. p. 107°), from ethyl 5-aldehydo-3-methylpyrrole-2 : 4-dicarboxylate (*F*) and cryptopyrrole; and 3 : 5-*dicarbethoxy*-4 : 5 : 3′-*trimethylpyrromethene*-4′-*propionic acid hydrobromide*, m. p. 137—138° (decomp.), from *F* and cryptopyrrolecarboxylic acid; and the *methene hydrobromides*, m. p. 157° (decomp.) and 133°, from cryptopyrrole with furfuraldehyde and thiophen-2-aldehyde, respectively. The last did not form a porphyrin by the usual methods.

The condensation of 3-bromo-5-carboxy-4 : 3′ : 5′-trimethyl-4′-ethyl- and 5′-bromo-3 : 4′-dimethyl-4 : 3′-diethyl-5-bromomethyl-pyrromethene hydrobromides at 145—150° as described above gives *pyrroætioporphyrin I*, m. p. 335°, with some *bromopyrroætioporphyrin I*; *bromoætioporphyrin III* [*copper* salt, m. p. 323° (decomp.)] is similarly prepared from the brominated methene from hæmopyrrole and 4 : 5′-dibromo-3 : 5 : 3′-trimethyl-4′-ethylpyrromethene hydrobromide (A., 1930, 931). The brominated porphins may be debrominated by hydrazine and palladised calcium carbonate in presence of 10% alcoholic potassium hydroxide (*pyrroætioporphyrin III*, m. p. 330°). The following are prepared at 195—210°: *pyrroætioporphyrin II*, m. p. 330—332° (*copper* salt, m. p. 263°), from *A* and 5 : 5′-dibromo-4 : 4′-dimethyl-3 : 3′-diethylpyrromethene hydrobromide (*E*); *pyrroætioporphyrin IV*, m. p. 327° (*iron* salt, decomp. about 330°; *copper* salt, m. p. 333°), from *E* and 3 : 5 : 4′ : 5′-tetramethyl-3′ ethylpyrromethene hydrobromide; *pyrroætioporphyrin VIII*, m. p. 284° (*iron* salt, decomp. about 250°; *copper* salt, m. p. 245°), from *A* and 5 : 5′-dibromo-3 : 3′-dimethyl-4 : 4′-diethylpyrromethene hydrobromide; *pyrroætioporphyrin VI*, m. p. 309° (*iron* salt, m. p. about 325°; *copper* salt, m. p. 260°), from *B* and *E*; and 1 : ɔ-*dimethyl*-2 : 6-*diethylporphin*, m. p. 310° (*iron* salt; *copper* salt, m. p. 312°; *sulphonic acid*), from *C* or *D* alone (accompanied by a small quantity of a chlorin-like substance). The interaction of *F* with malonic acid in presence of aniline gives 2 : 4-*dicarbethoxy*-3-*methylpyrrole*-ɔ-*acrylic acid*, m. p. 244°, converted by reduction with sodium amalgam into the corresponding -*propionic acid*, m. p. 209°.

H. A. Piggott.

Conversion of phæophorbide *a* into phylloerythrin. H. Fischer and O. Sus (Annalen, 1930, 482, 225—232).—Phæoporphyrin a_6 (A., 1930, 932), on fractionation by the ether–hydrochloric acid method and crystallisation from pyridine and ether, gives a substance which analyses as phæoporphyrin a_5, and the homogeneity of a_6 must provisionally be regarded as doubtful. By heating with hydrogen bromide in acetic acid at 50—55° for 24 hrs., phæophorbide a_6 (purified as above), a-, and a_4 are all converted into phylloerythrin, identified by its methyl ester and its additive compound with chloroform. This affords a very convenient method of preparing phylloerythrin from chlorophyll.

H. A. Piggott.

***iso*Oxazoline oxides. X. Reduction.** E. P. Kohler and A. R. Davis (J. Amer. Chem. Soc., 1930,

52, 4520—4528).—Bromination of γ-nitro-α-anisoyl-βγ-diphenylpropane (I) (A., 1928, 523) in chloroform affords an *α-bromo*-derivative, m. p. 165°, converted by alcoholic pyridine into *5-anisoyl-3 : 4-diphenyl*iso*oxazoline oxide*, m. p. 158°. This is isomerised by treatment with potassium acetate and acetic acid in methyl alcohol to *5-hydroxy-5-anisoyl-3 : 4-diphenyl*iso*oxazoline*, m. p. 177° (*benzoate*, m. p. 173°), and converted by treatment with alkali into *α-oximino-γδ-diketo-δ-anisyl-αβ-diphenylbutane* (+Et_2O), m. p. 110° (decomp.). When a methyl-alcoholic solution of this oximino-derivative is heated with potassium acetate and acetic acid, *3-keto-4 : 5-diphenyl-2-anisylpyrrolenine oxide*, m. p. 182° (decomp.), is produced. The above bromo-compound, the *iso*oxazoline oxide, the hydroxy*iso*oxazoline, and the oximino-derivative are all converted by weak alkali into *5-anisoyl-3 : 4-diphenyl*iso*oxazole*, m. p. 156°, which is reduced by zinc dust and acetic acid to *3 : 4-diphenyl-5-α-hydroxy-*p*-methoxybenzyl*iso*oxazole*, m. p. 146°. Oxidation of this with sodium dichromate and acetic acid regenerates the anisoyldiphenyl*iso*oxazole.

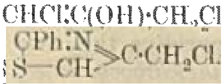
Catalytic reduction (Adams, Willstätter) of 5-anisoyl-3 : 4-diphenyl*iso*oxazoline oxide in methyl alcohol furnishes a mixture of I (small amount) and two stereoisomeric *3 : 4-diphenyl-5-α-hydroxy-*p*-methoxybenzyl*iso*oxazoline oxides*, m. p. 160° and 170°. Further reduction of these oxides affords *α-amino-γδ-dihydroxy-αβ-diphenyl-δ-anisylbutane*, m. p. 208°, whilst treatment with alcoholic potassium hydroxide solution gives anisaldehyde and *3 : 4-diphenyl*iso*oxazole*, m. p. 91°. This *iso*oxazole is also obtained by the action of 5% alcoholic potassium hydroxide on 5-anisoyl-3 : 4-diphenyl*iso*oxazole. 3 : 4-Diphenyl*iso*oxazole is degraded further by alkaline treatment to benzonitrile and phenylacetic acid, whilst hydrolysis of the product formed by the action of ozone with sodium hydroxide solution yields β-benzilmonoxime.

H. Burton.

Dioximes. LXVII. M. Milone (Gazzetta, 1930, **60**, 632—643).—Crystallographic measurements have been made of the glyoxime peroxides already described (A., 1928, 888; 1929, 334, 1072, 1316; 1930, 226) and of certain peroxides existing in two isomeric forms, for purposes of comparison with the furazans, which differ from the peroxides by only one atom of oxygen. The results show that the two peroxides obtained by dehydrogenation of the asymmetric glyoximes, OH·N:CAr·CMe:N·OH, crystallise in different systems. As far as the available data indicate, only one of the two peroxides, viz., that to which a furoxan (furazan oxide) structure is attributable, is isomorphous with the corresponding furazan (monoclinic); the analogy of crystalline form is hence due to the presence in each molecule of the penta-atomic ring, C_2N_2O, characteristic of the furazans. The other peroxide crystallises in the triclinic system, although it exhibits a habit similar to that of the corresponding furoxan and furazan. The furazans and furoxans crystallise in systems of higher degrees of symmetry than the corresponding dioxadiazines.

Phenylmethylfuroxan, m. p. 96°, forms rhombic crystals, $a : b : c$—0·59179 : 1 : 0·79354; 5-phenyl-4-methyl-1 : 2 : 3 : 6-dioxadiazine, m. p. 62°, monoclinic, $a : b : c$=1·36827 : 1 : 0·506001, β 103° 6′; *p*-anisylmethylfurazan, m. p. 66°, monocline, $a : b : c$=1·6524 : 1 : 1·15384, β 71° 35′; *p*-anisylmethylfuroxan, m. p. 99°, monoclinic, $a : b : c$=1·76427 : 1 : 1·52736, β 72° 33′; 5-*p*-anisyl-4-methyldioxadiazine, m. p. 80—81°, triclinic, $a : b : c$=1·299 : 1 : 0·9539, α 71° 18′ 48″, β 61° 59′ 10″, γ 76° 17′ 40″; diphenylfurazan, rhombic, $a : b : c$ = 0·81644 : 1 : 0·27766; 4 : 5-diphenyl-1 : 2 : 3 : 6-dioxadiazine, monoclinic, $a : b : c$—2·4803 : 1 : 1·0698, β 86° 16′; phenyloximinoacetonitrile peroxide (α-peroxide), triclinic, $a : b : c$ =1·7463 : 1 : 0·66613, α 84° 23′ 42″, β 63° 4′ 38″, γ 73° 9′ 22″, and 5-phenyl-1 : 2 : 3 : 6-dioxadiazine (β-peroxide), triclinic, $a : b : c$=1·5918 : 1 : 1·0314, α 86° 40′ 30″, β 60° 20′ 40″, γ 73° 37′ 20″.

T. H. Pope.

Use of *s*-dichloroacetone for the preparation of thiazoles. III. C. M. Suter and T. B. Johnson (Rec. trav. chim., 1930, **49**, 1066—1068).—*s*-Dichloroacetone reacts readily, in a suitable solvent, with thioamides to yield thiazoles in accordance with the scheme CHCl:C(OH)·CH_2Cl+SH·CPh:NH ⟶  The following compounds have been prepared in the above manner: 2-*phenyl-4-chloromethyl-*, b. p. 155—156°/4 mm., m. p. 51°; 2-p-*anisyl-4-chloromethyl-*, m. p. 55—56°; 2-*piperonyl-4-chloromethyl-*, m. p. 106—107°, *-thiazole*. The chemical behaviour and reactivity of the chlorine is comparable with that in benzyl chloride, and hence by the action of suitable reagents on the above are obtained: 2-*phenylthiazole-4-acetonitrile*, b. p. 180—185°/4 mm., and *-4-acetic acid*, m. p. 90° (*hydrochloride*, m. p. 206—207°), and 2-p-*anisylthiazole-4-acetonitrile*, b. p. 220°/5 mm., m. p. 73°. By the action of potassium phthalimide on the appropriate chloromethylthiazole are obtained: 4-*phthalimidomethyl-2-phenyl-*, m. p. 151—152°, and -2-p-*anisyl-*, m. p. 186—187°, *-thiazole*, hydrolysed to 2-*phenylthiazole-* (*dihydrochloride*, m. p. 217—219°; *monohydrochloride*, m. p. 188—189°), 2-p-*anisylthiazole-* (*dihydrochloride*, m. p. 224—225°), and 2-p-*hydroxyphenylthiazole-*, m. p. 205—206°, *-4-methylamine*. The phenylthiazolemethylamine is also obtained together with *di-(2-phenylthiazole-4-methyl)amine* (*dihydrochloride*, m. p. 190°) by the action of ammonia on the chloromethyl derivative.

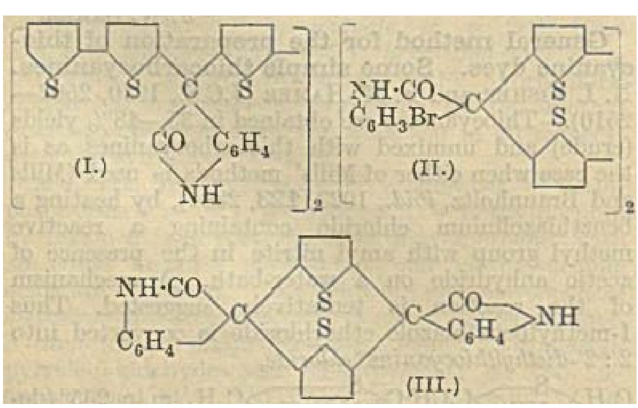
J. W. Baker.

General method for the preparation of thiocyanine dyes. Some simple thiocarbocyanines. N. I. Fisher and F. M. Hamer (J.C.S., 1930, 2502—2510).—Thiocyanines are obtained in 35—48% yields (crude) and unmixed with thiocarbocyanines as is the case when either of Mills' methods is used (Mills and Braunholtz, *ibid.*, 1923, **123**, 2804), by heating a benzthiazolinium chloride containing a reactive methyl group with amyl nitrite in the presence of acetic anhydride on a water-bath. A mechanism of the reaction is tentatively suggested. Thus 1-methylbenzthiazole ethochloride is converted into 2 : 2′-*diethylthiocyanine chloride*,

 m. p. 255° (decomp.), converted by sodium bromide and potassium iodide, respectively, into the corresponding *bromide*, m. p. 298° (decomp.), and iodide. The last-named is

identical with a specimen obtained by Mills' method. Similarly, the corresponding methochloride affords 2 : 2′-dimethylthiocyanine chloride, *bromide*, m. p. 287° (decomp.), and iodide, m. p. 290—292° (decomp.) (λ 4500 Å.) (Mills gives m. p. 279—280°). From 1-methyl-α-naphthathiazole ethochloride and methochloride are obtained, respectively, 2 : 2′-*diethyl*-5 : 6 : 5′ : 6′-*dibenzthiocyanine chloride*, m. p. 264° (decomp.) (λ 4800 Å.), *bromide*, m. p. 286° (decomp.), and *iodide*, m. p. 297° (decomp.), and 2 : 2′-*dimethyl*-5 : 6 : 5′ : 6′-*dibenzthiocyanine chloride*, m. p. 275° (decomp.), *bromide*, m. p. 309° (decomp.) (λ 4750 Å.), and *iodide*, m. p. 314° (decomp.). Only negative results were obtained with 2-methyl-β-naphthathiazole etho- and metho-chlorides. In all these derivatives the solubility decreases and the m. p. rises in the series chloride, bromide, and iodide. All are sensitisers for silver chloride emulsions, the position of the maximum being given in parentheses after the compounds concerned. Thiocyanines could not be prepared from 2 : 4-dimethylthiazole methiodide, m. p. 260° (decomp.) (lit. slow decomp. above 225°), and *ethiodide*, but by the action of ethyl orthoformate and pyridine they are converted into the corresponding *thiocarbocyanines*, m. p. 255° (decomp.) (λ 5900 Å.), and m. p. 271—294° according to the rate of heating (λ 5900 Å.), respectively, of the type $\begin{matrix}CH\text{—}S\\CMe\cdot NR\end{matrix}\!>\!C{:}CH\cdot CH{:}C\!<\!\begin{matrix}S\text{——}CH\\N(RX)\cdot CMe\end{matrix}$ but in abnormally low yields. The absorption band of these thiocarbocyanines relative to that of the corresponding derivatives from 1-methylbenzthiazole is shifted much less towards the blue than would be expected. J. W. BAKER.

Thiophen series. XXI. Indophenine. W. STEINKOPF and J. ROCH (Annalen, 1930, **482**, 251—264).—The condensation of dithienyl with isatin under the influence either of sulphuric acid or zinc chloride gives, not indophenine, as might be expected from Schlenk and Blum's formula (A., 1923, i, 1235), but an olive-green substance that from its ultimate analysis and mol. wt. appears to be *tris-α-dithienylbisindoxyl* (I). The presence of two isatin residues is confirmed by the formation of *di*-p-*nitro*- and *di*-p-*bromo-benzoyl* derivatives. Bromoisatin gives the corresponding *bromo*-derivative when zinc chloride is



used as dehydrating agent, but with sulphuric acid a blue compound is formed, which gives analytical results agreeing with cyclo*bis-α-dithienylbisindoxyl* (II). Unlike I, it can be reduced to a soluble leuco-compound. The structure of indophenine is provisionally represented by (III), and explanations of its intense colour independent of a quinonoid structure are given. The quinonoid structure postulated by Schlenk and Blum, if established, would be the sole example of this structure in the thiophen series. Indophenine may be prepared by use of zinc chloride in place of sulphuric acid as condensing agent, and consequently oxidation is not likely to be a necessary stage in the process. The crude product, made by either method, contains 40—50% of an olive-green *substance*, which remains undissolved on reduction with hyposulphite. Its mode of isolation and approximate composition ($C_{28}H_{18}O_2N_2S_3$) point to a structure of type I. Bromoindophenine contains a small amount of a similar substance.

2 : 2′-Dithienyl can be prepared in a yield of 44% by interaction of anhydrous cupric chloride and magnesium thienyl bromide in ether (Krizewski and Turner, J.C.S., 1919, **115**, 559). 5 : 5′-Dibromo- and 5 : 5′-*dimethyl*-2 : 2′-*dithienyl*, m. p. 67°, are similarly prepared. H. A. PIGGOTT.

Preparation and properties of dihydro-*m*-codeinone. C. SCHÖPF and H. PERREY (Annalen, 1930, **483**, 169—175).—Bromination of dihydro-*m*-thebainone (thebainol) (A., 1927, 1209) in methyl-alcoholic solution at the ordinary temperature and treatment of the product formed with an excess of alkali hydroxide gives 1-*bromodihydro*-m-*codeinone*, m. p. 241—246°, reduced by hydrogen in presence of palladous chloride, gum arabic solution, and dilute acetic acid to *dihydro*-m-*codeinone*, m. p. 196—201°. Oximation of this at the ordinary temperature gives the corresponding *oxime*, m. p. 176—180°, but at 50° a mixture of this and *m*-thebainoneoxime is produced. Dihydro-*m*-codeinone is readily isomerised to *m*-thebainone by treatment with hydrochloric acid at 100° or by boiling with 2*N*-sodium hydroxide solution, whilst reduction with sodium amalgam and alcohol gives dihydro-*m*-thebainone. H. BURTON.

Partial syntheses in the morphine series. I. Passage from the dihydrothebainone to the dihydrocodeinone series. C. SCHÖPF and T. PFEIFER (Annalen, 1930, **483**, 157—169).—Dihydrothebainone is converted by 1 mol. of bromine in acetic acid solution at about 15° into 1-*bromodihydrothebainone* (+0·5AcOEt), froths at 127° and becomes clear at 167°, m. p. (solvent-free) 167° [*hydriodide*, m. p. 215° (decomp.) after sintering and darkening at 198—200°; *hydrobromide*, m. p. 210—215° (decomp.); *oxime*, m. p. 178—180° (decomp.) after sintering from 168°]. Bromination with 2 mols. of bromine or further bromination of the above hydrobromide with methyl-alcoholic bromine at 35° affords a product (not isolated), which when treated with cold 7*N*-alkali hydroxide, passes into 1-*bromodihydrocodeinone*, m. p. 205—207° (*hydrobromide*, m. p. 217—218° after sintering at 215°), also obtained by direct bromination of dihydrocodeinone in acetic acid. Reduction of 1-bromodihydrocodeinone with zinc dust and aqueous-alcoholic ammonium chloride solution also gives 1-bromodihydrothebainone, owing to opening of the oxide ring. Similarly, 1-bromohydroxydihydro-

thebainone can be converted into 1-bromohydroxydihydrocodeinone, m. p. 181—184° (lit. 182°). Bromination of sinomenine with 2 mols. of bromine in acetic acid at 15—36°, evaporation of the solution below 40°/vac., and alkali treatment of the product formed yields 1-bromosinomeneine, decomp. 213° (cf. Goto and Nambo, A., 1930, 1049); an oxide ring is formed as in the above cases.

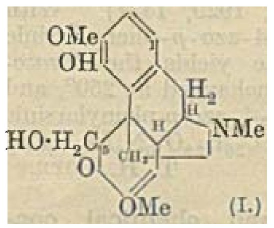
In these cases of ring (oxide) formation only one compound is produced. A strainless model can be constructed for compounds of the morphine series which shows that the hydrogen atom on C_5 which is in spatial proximity to the phenolic hydroxyl group attached to C_4 is that which is in the *trans*-position to the side-chain C_{15}–C_{16}–NMe. H. BURTON.

Sulphonation of alkaloids. Z. KITASATO and K. GOTO (Ber., 1930, 63, [*B*], 2696—2700).—Alkaloids which contain a hydroxyl or methoxyl group in an aromatic nucleus with free *p*-position are readily sulphonated below 10° by concentrated but not by fuming sulphuric acid. The alkaloidal sulphonic acids are generally well-crystallised substances in which the sulphonyl group is united to the basic nitrogen atom to form an internal salt. *Papaverinesulphonic acid*, $C_{20}H_{21}O_7NS$, m. p. 301° (decomp.), apo*morphinesulphonic acid*, $C_{17}H_{17}O_5NS,3H_2O$, m. p. above 300°, and *sinomeninesulphonic acid*, $C_{19}H_{23}O_7NS$, m. p. 265—267°, are described. Sinomenine hydrate affords *sinomeninonesulphonic acid*, $C_{18}H_{21}O_7NS,0{\cdot}5H_2O$, m. p. 275—280° (*dioxime*, m. p. above 300°, also obtained by sulphonation of sinomenine hydrate dioxime). It is probable that the sulphonic group occupies the *p*-position to the phenolic hydroxyl, since the acids do not give the diazo-reaction. Strychnine which does not contain a hydroxyl group and brucine in which the *p*-position to the methoxyl group is not free are not sulphonated under these conditions. Derivatives of sinomenine and thebainone in which the *p*-position to the phenolic hydroxyl is not free according to the evidence of the diazo-reaction (bromosinomenine, disinomenine, dithebainone) do not afford sulphonic acids.

Although thebainone dissolves to a dark red solution in concentrated sulphuric acid it can be recovered therefrom quantitatively and unchanged by successive addition of ice and an excess of sodium carbonate. H. WREN.

Sinomenine and disinomenine. XX. Benzeneazosinomenine. K. GOTO and H. SHISHIDO (Bull. Chem. Soc. Japan, 1930, 5, 311—314; cf. A., 1930, 1600).—The diazo-coupling reaction of phenolic alkaloids of the phenanthrene group produces a red colour visible at a dilution of 1 in 2×10^6 when the alkaloid tested has the *p*-position to the hydroxyl group unsubstituted. The following benzeneazo-compounds formed in certain cases have been isolated: *benzeneazo-sinomenine*, decomp. 253°; *-dihydrosinomenine*, m. p. 231° (decomp.); *-thebainone*, m. p. 152°. Reduction of the first-named by means of sodium hyposulphite affords 1-*aminodihydrosinomenine*, isolated as the *dihydrochloride* ($+CHCl_3+H_2O$), m. p. above 300°. R. CHILD.

Sinomenine and disinomenine. XXI. Reaction between sinomenine and formaldehyde. K. GOTO, H. SHISHIDO, and R. INABA (Bull. Chem. Soc. Japan, 1930, 5, 315—320).—Interaction of sinomenine and boiling aqueous formaldehyde (40%) affords 5-*hydroxymethylsinomenine* (I), m. p. 260° (decomp.), $[\alpha]_D^{29}$ −40·71° [*oxime*, (decomp. 240—245°; *methiodide*, m. p. 223° (decomp.)], and 1 : 5-*di*(*hydroxymethyl*)-*sinomenine* (II), m. p. 242° (252°), $[\alpha]_D^{30}$ −74·39° (*oxime*, decomp. 200—215°; *methiodide*, m. p. 210°, decomp. 280—285°). I on acetolysis gives methylethylamine (cf. sinomenine itself, Goto, A., 1926, 1160) and a nitrogen-free *substance*, $C_{23}H_{22}O_8$, m. p. 192—193°, probably diacetyl-5-acetoxymethylsinomenol (4 : 6 - diacetoxy - 3 : 7 - dimethoxy - 5 - acetoxymethylphenanthrene). Catalytic reduction of I yields *dihydro-5-hydroxymethylsinomenine* (III), m. p. 244°,



(I.)

$[\alpha]_D^{29}$ +73·03° [*oxime*, decomp. 215—225°; *methiodide*, m. p. 205—220° (decomp.)] (not obtained from dihydrosinomenine and formaldehyde). I and III give diazo-reactions visible at dilutions up to 1 in 2×10^6; II is less sensitive (1 in 2×10^4), indicating substitution of the 1-position, *para* to a hydroxyl group. R. CHILD.

Action of hydrobromic acid on certain arsinic acids. M. A. PHILLIPS (J.C.S., 1930, 2400—2401).—Boiling hydrobromic acid (*d* 1·445) reacts with 3-nitro-4-amino-, 4-nitro-3-amino-, 3-nitro-4-methylamino-, 4-*nitro*-3-*methylamino*- (by the action of methylamine hydrochloride on 3-chloro-4-nitrophenylarsinic acid at 150—160°), and 3 : 5-dinitro-4-aminophenylarsinic acid, to give good yields of 4-, and 5-bromo-2-nitroaniline, 4- and 5-bromo-2-nitromethylaniline, and 4-bromo-2 : 6-dinitroaniline, respectively. Hydriodic acid similarly converts 3-nitro-4-aminophenylarsinic acid into 4-iodo-2-nitroaniline. J. W. BAKER.

Arsenic derivatives of cysteine. J. M. JOHNSON and C. VOEGTLIN (J. Biol. Chem., 1930, 89, 27—31).—The hydrochlorides of cysteine and of 3-amino-4-hydroxyphenylarsenious oxide, when heated together in alcoholic solution, yielded an insoluble hydrochloride from which, by treatment with sodium hydroxide, was obtained 3-*amino*-4-*hydroxyphenyl*-*di*-SS-*cysteinylarsine*, $OH{\cdot}C_6H_3(NH_2){\cdot}As[S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H]_2$, m. p. 225—227° (decomp.); arsenious chloride and cysteine · hydrochloride yielded similarly, but at the ordinary temperature, SSS-*tricysteinylarsine*, $As[S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H]_3$, m. p. 260° (decomp.). The ready formation of these compounds is in accord with the authors' theory (A., 1925, i, 861) of the mode of protection of animals against the toxic effects of arsenious oxide derivatives by means of thiol compounds. C. R. HARINGTON.

Arsenical azo-derivatives. IV. S. BERLINGOZZI and M. LIGUORI (Annali Chim. Appl., 1930, 20, 494—500; cf. A., 1927, 675; 1928, 434, 1146; 1929, 1471).—Condensation of diazotised *p*-aminophenylarsinic acid with resorcinol yields 1 : 3-*dihydroxybenzene*-6-*azo*-p-*phenylarsinic acid* (cf. Schmitz, A., 1914, i, 342), which remains unchanged at 250° and on further coupling with diazotised *p*-aminophenylarsinic acid gives 1 : 3-*dihydroxybenzene*-4 : 6-*bisazo*-

p-*phenylarsinic acid*, $O:As(OH)_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_2(OH)_2 \cdot N_2 \cdot C_6H_4 \cdot AsO(OH)_2$, this also remaining solid at 250°. 1 : 3-*Dihydroxybenzene-6-α-naphthaleneazo-4-azo-*p-*phenylarsinic acid*, obtained from α-diazonaphthalene and 1 : 3-dihydroxybenzene-6-azo-*p*-phenylarsinic acid, does not melt at 250°. 1 : 3-*Dihydroxybenzene*-2 : 4 : 6-*trisazo*-p-*phenylarsinic acid*, unchanged at 250°, is obtained either from diazophenylarsinic acid and 1 : 3-dihydroxybenzene-4 : 6-bisazo-*p*-phenylarsinic acid or from diazophenylarsinic acid (3 mols.) and resorcinol (1 mol.). 1-*Amino*-3-*hydroxybenzene*-6-α-*phenylquinoline*-β-*azo*-4-*azo*-p-*phenylarsinic acid*, decomp. at about 180°, is formed from diazotised 3-amino-2-phenylquinoline and 1-amino-3-hydroxybenzene-4-azophenylarsinic acid (cf. A., 1929, 1471). With 1-amino-3-hydroxybenzene-4-azo-*p*-phenylarsinic acid, tetrazodiphenyl chloride yields the *tetrazo*-compound, $C_{36}H_{30}O_8N_{10}As_2$, unchanged at 250°, and with 1 : 3-dihydroxybenzene-4-azo-*p*-phenylarsinic acid, the *tetrazo*-compound, $C_{36}H_{28}O_{10}N_8As_2$, also unchanged at 250°. T. H. POPE.

Trypanocidal activity and chemical constitution. II. New sulphur derivatives of aromatic arsenicals (*cont.*). Derivatives of 2-thiolbenziminazole-5-arsinic acid. J. G. EVERETT (J.C.S., 1930, 2402—2408).—Oxidation of 2-thiolbenziminazole-5-arsinic acid (A., 1929, 709) with iodine in dilute aqueous solution affords *benziminazole-5-arsinic acid 2-disulphide* as its *monohydriodide*. The disulphide is readily converted by thiolacetamide into the *thiolacetamide*, m. p. 245° (decomp.), of the parent substance. 2-Thiolbenziminazole-5-arsinic acid reacts with chloroacetic acid and chloroacetamide in alkaline solution to give, respectively, 2-*carboxy*- and 2-*carbamyl-methylthiolbenziminazole-5-arsinic acid*, reduced by sodium hyposulphite to 5 : 5′-*arseno*-(2-*carboxymethylthiolbenziminazole*) and -(2-*carbamylthiolbenziminazole*), respectively. Oxidation of 2-thiolbenziminazole-5-arsinic acid with boiling alkaline potassium permanganate converts it into 2-*sulphobenziminazole-5-arsinic acid*, similarly reduced to 5 : 5′-*arseno*(*benziminazole-2-sulphonic acid*). The non-arsenated analogue *benziminazole 2-disulphide*, m. p. 198° (*monohydrochloride*, decomp. 210°), is obtained by oxidation of 2-thiolbenziminazole with iodine at 50°, whilst oxidation with alkaline potassium permanganate affords the corresponding *benziminazole-2-sulphonic acid*, m. p. 365° and $+0 \cdot 5H_2O$. Both the last-named and its arsenated analogue are very resistant to acid and alkaline hydrolysis. The trypanocidal activity of these derivatives against an experimental infection of *T. equiperdum* in mice has been investigated both by oral and intravenous injections. The therapeutic activity of the parent 2-thiolbenziminazole-5-arsinic acid is approached only by benziminazole-5-arsinic acid 2-disulphide, and this, owing to its ready hydrolysis, is probably present in the blood-stream and tissues as the free thiol. In the other cases replacement of the hydrogen of the thiol group causes adverse modification of the therapeutic activity in both the arsinic acid and arseno-derivatives. All these derivatives are inactive against *B. tuberculosis*. J. W. BAKER.

Comparative action of iron halides on magnesium and zinc organo-compounds. G. CHAMPETIER (Bull. Soc. chim., 1930, [iv], 47, 1131—1137).—Ferric chloride and ethereal magnesium phenyl bromide give diphenyl and a black precipitate of active iron (Job and Reich, A., 1922, i, 645; 1923, i, 873). The reaction ceases when 1 mol. of ferric chloride is present for 3 mols. of magnesium phenyl bromide. When a solution of the latter is added to an ethereal solution of ferric chloride, diphenyl ferrous chloride and magnesium chloride and bromide are formed until 1 mol. of magnesium phenyl bromide has been added. On further addition the latter reacts with ferrous chloride, yielding diphenyl and metallic iron until 3 mols. have been added per mol. of ferric chloride originally present, the second stage being much closer in consequence of deposition of metallic iron on the ferrous chloride. Although no evidence of the formation of an intermediate iron organo-compound was obtained, the fact that at −40° a mixture of ferric chloride (1 mol.) and magnesium phenyl bromide (3 mols.) does not give an immediate precipitate of metallic iron is regarded as indicating its existence. These results agree with those of Bennett and Turner (A., 1921, i, 472). Ferrous chloride and iodide similarly yield only diphenyl and metallic iron with magnesium phenyl bromide, but with zinc phenyl chloride in ether in an atmosphere of nitrogen ferrous iodide yields ferrous phenyl iodide, FePhI, which on hydrolysis gives benzene. R. BRIGHTMAN.

Mercuration of β-resorcylic [2 : 4-dihydroxybenzoic] acid. R. B. SANDIN and J. M. ZEAVIN (J. Amer. Chem. Soc., 1930, 52, 4369—4372).—β-Resorcylic acid (1 mol.) and mercuric acetate (0·5 mol.) react in hot acetic acid, forming *anhydro-5-hydroxymercuri-β-resorcylic acid*. With 2 mols. of the acetate in alcoholic acetic acid, *anhydro-3-hydroxymercuri-5-acetoxymercuri-β-resorcylic acid* is produced. Mercuration in alkaline solution (cf. Fox and Whitmore, A., 1929, 1091) affords *anhydro*-3 : 5-*dihydroxymercuri-β-resorcylic acid*. Quinonoid structures are suggested for these (coloured) mercurated derivatives. H. BURTON.

Formation of hetero-rings containing mercury atoms. W. STEINKOPF (Ber., 1930, 63, [*B*], 2937; cf. Vecchiotti, A., 1930, 1458).—The formation of rings of this type has been observed previously by Hilpert and Grüttner (A., 1914, i, 261, 262) and by Steinkopf and others (A., 1923, i, 125). H. WREN.

Constitution of double sulphonium mercuric iodides. Optically active mercuri-tri- and -tetra-iodides and cadmium tetra- and -penta-iodides derived from *l*-phenacylmethylethylsulphonium iodide. M. P. BALFE, J. KENYON, and H. PHILLIPS (J.C.S., 1930, 2554—2572).—The preparation of optically active sulphonium mercuri- and cadmi-iodides, and the inter-relations of the triethyl- and phenyldiethyl-sulphonium mercuri-iodides are described. l-*Phenacylmethylethylsulphonium mercuritri-iodide* [$XHgI_3$: $X = Ph \cdot CO \cdot CH_2 \cdot (Me)(Et)S^-$], m. p. 81—82°, $[\alpha]_{5461}$ −10·7° in acetone, is obtained from mercuric iodide and aqueous potassium iodide on the *l*-sulphonium *d*-camphorsulphonate. It is converted by excess of potassium iodide or by hydro-

gen sulphide into the l-*mercuritetraiodide* (X_2HgI_4), m. p. 122—123°, $[\alpha]_{5461}$ −9·3° in acetone, which may be reconverted into the tri-iodide by mercuric iodide in acetone. An explanation of the racemisation of these compounds based on the reversibility of sulphonium iodide formation, $[R_3\overset{+}{S}]+\overset{-}{I}\rightleftharpoons R_2S+RI$, is advanced. Both are rapidly racemised in presence of iodide ions. The tri-iodide, which gives the stable $[HgI_3]'$ ion, is optically stable in solution, but the tetraiodide, which ionises, $X_2HgI_4\rightleftharpoons 2X+HgI_3+I$, undergoes racemisation and profound decomposition when its solution is kept and also causes racemisation of the tri-iodide. Racemisation of the tetra- but not of the tri-iodide is accelerated by methyl iodide. The failure of Pope and Neville (J.C.S., 1902, **81**, 1552) to isolate these compounds in optically active forms appears to be due to prolonged contact with ionisable halides. The "*dl*-phenacylmethylethylsulphonium tri-iodide" of these authors (*loc. cit.*; cf. Rây and Adhikary, A., 1930, 1020) appears to be the dl-*tetraiodide*, m. p. 134°; dl-*phenacylmethylethylsulphonium tri-iodide*, m. p. 82—83°, is, however, readily prepared by allowing it to react with mercuric iodide. Attempts to prepare Pope and Neville's "mercuritrichloride" led instead to dl-*phenacylmethylethylsulphonium dimercuriheptachloride* ($X_3Hg_2Cl_7$), m. p. 153° (decomp.); the l-*compound* has m. p. 153°, $[\alpha]_{5461}$ −11·3° in methyl alcohol.

dl-, m. p. 126°, and l-*Phenacylmethylethylsulphonium cadmitetraiodide* (X_2CdI_4), m. p. 132—133°, $[\alpha]_{5461}$ −10·2° in acetone, are obtained by use of cadmium and potassium iodides in proportions corresponding with $KCdI_3$ and K_2CdI_4. By cadmium iodide in acetone they are converted into the dl-, m. p. 134—136°, and l-*cadmipentaiodide* (X_3CdI_5), m. p. 128°, $[\alpha]_{5461}$ −9·0° in acetone. Both the tetra- and penta-iodides have unstable ions, and rapidly lose their optical activity in solution.

l-Phenacylmethylethylsulphonium *d*-camphorsulphonate, $[\alpha]_{5461}$ +59·0°, and picrate, $[\alpha]_{5461}$ −13·5° in acetone, slowly lose their activity in solution.

Triethylsulphonium mercuritri-iodide (I) (Smiles and Hilditch, J.C.S., 1907, **92**, 1394) is obtained from equimolecular proportions of the sulphonium iodide or its components and mercuric iodide, or from triethylsulphonium mercuritetraiodide (II) (Hofmann and Rabe, A., 1897, i, 310) by heating or the action of mercuric iodide. It is stable at 165°, but is converted into II by reagents capable of removing mercuric iodide, *e.g.*, hydrogen sulphide, potassium iodide, or triethylsulphonium iodide. Triethylsulphonium dimercuripentaiodide (III) (Smiles and Hilditch, *loc. cit.*) is obtained from 1 mol. of sulphonium iodide and 2 mols. of mercuric iodide, or from I and mercuric iodide; it is converted into I by the sulphonium iodide, and into II by a large excess of this or by 1·5 mols. of potassium iodide. *Phenyldiethylsulphonium mercuritri-iodide* (IV), m. p. 56—57°, is prepared from equimolecular proportions of phenyl ethyl sulphide, ethyl iodide, and mercuric iodide, and gives when heated, or when treated with excess of mercuric iodide, the *trimercurioctaiodide*, $[(PhSEt_2)_2Hg_3I_8]$ (V), m. p. 65—66°. The reverse change is effected by heating V with potassium mercuritri-iodide. *Phenyldiethylsulphonium mercuritetraiodide*, m. p. 114—115°, is obtained from IV or V and potassium iodide or hydrogen sulphide, and is reconverted into IV by mercuric iodide, potassium mercuritri-iodide, or by heating, with evolution of phenyl ethyl sulphide and ethyl iodide in the last case. H. A. PIGGOTT.

Mol. wt. of cocosin. B. SJOGREN and R. SPYCHALSKI (J. Amer. Chem. Soc., 1930, **52**, 4400—4404).—Solutions of cocosin (coconut globulin) show an absorption maximum at 280 mμ and a minimum at 255 mμ at p_H 6·7; the specific volume is 0·746 at 20·2°. Determinations of the mol. wt. of the protein by the methods of sedimentation velocity and equilibrium at p_H 6·7—11·8 in phosphate buffers indicate the presence of two substances with mol. wt. of 104,000 and 208,000. The amount of the former increases with rise in p_H, probably owing to fission of the true cocosin molecule. H. BURTON.

Mol. wt. of coconut globulin. R. SPYCHALSKI (Rocz. Chem., 1930, **10**, 630—651).—Coconut globulin undergoes partial decomposition during preparation. The ultracentrifuge method indicates that two molecular species are present, of mol. wt. 208,000 (75%) and 104,000 (25%). R. TRUSZKOWSKI.

Pregl's method for the determination of carbon and hydrogen. F. HERNLER (Mikrochem., 1930, Emich Festschr., 148—151).—Details of the method are discussed. The humidity of the atmosphere in which the weighings are conducted is of importance for micro-combustion work, inaccurate results being obtained if the humidity is greater or less than 60—70%. The mean error of 16 determinations made at a humidity of 60—70% was for carbon 0·06%, and for hydrogen 0·02%. The best sequence of drying agents is soda-lime, calcium chloride, soda-asbestos, and calcium chloride. H. F. GILLBE.

Volumetric determination of methoxyl and ethoxyl groups. F. VIEBOCK and A. SCHWAPPACH (Ber., 1930, **63**, [*B*], 2818—2823).—The substance (20—50 mg.) is heated at 140° with 5 c.c. of hydriodic acid and 0·2 g. of coarse red phosphorus and the vapours, after passage through a suspension of fine red phosphorus in water, are absorbed in 10 c.c. of a solution of potassium acetate (20 g.) in glacial or 96% acetic acid (200 c.c.) containing 6—7 drops of bromine. The process is complete after 1 hr. The contents of the absorption vessel are rinsed into an Erlenmeyer flask containing 1—1·5 g. of dissolved sodium acetate, care being exercised that solid salt does not remain attached to the sides of the flask. Formic acid is cautiously added until the colour of the bromine disappears and a drop of methyl-red remains unchanged. After addition of 0·5—1 g. of potassium iodide and sulphuric acid, the liberated iodine is titrated with 0·1*N*-sodium thiosulphate. The insensitiveness of the absorbing liquid to phosphine and hydrogen sulphide renders the purification of phosphorus unnecessary and makes the process directly applicable to materials containing sulphur. H. WREN.

Determination of picric acid. M. FRANÇOIS and L. SEGUIN (Ann. Falsif., 1930, **23**, 481—485).—The picric acid is precipitated as cuprammonium picrate, $[C_6H_2(NO_2)_3{\cdot}OH]_2,CuO,2NH_3$, by means of

cuprammonium sulphate, the precipitate being dried and weighed. Phenol interferes with the precipitation and is removed by extraction with chloroform, the picric acid being first converted into its sodium salt by treatment with sodium carbonate to prevent its extraction by the solvent. Cuprammonium picrate is decomposed by hot water into ammonium picrate and copper oxide. B. W. Town.

Determination of cystine and cysteine. H. D. Baernstein (J. Biol. Chem., 1930, **89**, 124—131).—The solution of cysteine (or of cystine after preliminary reduction with Devarda's alloy) in dilute hydrochloric acid is treated with excess of iodine in potassium iodide, and the excess of iodine is determined by measurement of the nitrogen evolved when it is brought into reaction with hydrazine in the apparatus of Van Slyke and Neill (A., 1924, ii, 872). The error of the method is $\pm 4\%$. C. R. Harington.

Detection of tyrosine. J. A. Sánchez (Semana Méd., 1930, I, 1579—1981).—When tyrosine is treated with sodium nitrite, the nitroso-compound being then reduced with zinc and again treated with sodium nitrite, the diazo-compound gives an intense red colour with resorcinol in alkaline solution. A dilute solution of nitrosotyrosine gives a yellow colour with ammonia. Tyrosine gives with nitric acid a yellow, with sulphonylbenzenediazonium chloride a red, and with nitrobenzenediazonium chloride a violet colour; bromine gives a precipitate. After treatment with sodium hypochlorite reactions are obtained with phenylhydrazine, Fehling's solution, and Nessler's reagent. Chemical Abstracts.

Biochemistry.

Factors influencing the respiration of erythrocytes. I. Primitive avian erythrocytes. II. Mammalian reticulocytes. G. P. Wright (J. Gen. Physiol., 1930, **14**, 179—199, 201—213).—I. "Primitive red cells" from fowl's blood in phenylhydrazine anæmia have an oxygen consumption 20—25 times as great as that of normal red cells. The oxygen consumption of anæmic red cells is (*a*) independent of concentrations of sodium chloride between 0·6 and 1·10%, (*b*) affected by the reaction of the medium, being at a maximum at p_H 7·75, (*c*) increased by 15% by 0·6% of dextrose, (*d*) unaffected by low concentrations of glycine, alanine, histidine, and *l*-aspartic acid, and (*e*) reduced by a glycine content above 5 mg. of amino-nitrogen per 100 c.c.

II. Although a greatly increased respiration is observed in reticulocytes of an anæmic rabbit, the oxygen consumption per billion reticulocytes is not appreciably changed during regeneration. Respiration attains a maximum at p_H about 7·75 (intracellular) and is practically independent of the tonicity of the medium. Respiration is unaffected by glycine or alanine, but a slight depression is observed in the presence of dextrose. On the basis of equal cell volume, the respiration of "primitive" avian erythrocytes is twice that of rabbit reticulocytes, which is six times as great as that of the normal avian erythrocyte. A. Cohen.

Catalytic action of methylene-blue in living cells. O. Warburg, F. Kubowitz, and W. Christian (Biochem. Z., 1930, **227**, 245—271).—The consumption, in the presence of methylene-blue, of oxygen and dextrose by the red blood-cells of the rabbit has been quantitatively investigated and the results of Harrop and Barron (A., 1929, 1324) have been, in the main, confirmed. Pyruvic acid formed during the process of oxidation has been isolated as phenylhydrazone and determined by a micro-method. As regards the extent of their retarding effect on the rate of the oxidation stimulated by methylene-blue, ethyl-, propyl-, amyl-, and phenyl-urethanes, in this order, formed an ascending series. The inhibition of the action of methylene-blue by carbon monoxide was appreciable only when the concentration of the dye was low and direct inhibition by hydrogen cyanide was not proved. From these results and from others previously obtained (cf. Warburg and Kubowitz, A., 1930, 1053), as well as from consideration of the probable mechanism of the process, it is concluded that the action of methylene-blue involves a heavy metal (iron) catalysis similar to that which normally occurs in living matter. W. McCartney.

Glycolysis and phosphoric acid exchange in the blood-corpuscles of different animals. W. A. Engelhardt and M. Ljubimova (Biochem. Z., 1930, **227**, 6—15).—Continuous hydrolysis of phosphoric esters normally takes place in erythrocytes and a synthesis of these esters accompanies glycolysis. The following series indicates the order of intensity of hydrolysis with cells of different animals: ox<goat<horse<dog, pig<man, guinea-pig<rabbit. This series corresponds with the organic phosphorus content for the different animals except in the case of the pig. The glycolytic power of the corpuscles is in the following order: ox<goat<dog<horse<guinea-pig, man<rabbit. This series corresponds closely with the above, the pig again forming the exception, since the corpuscles in this case have no glycolytic power. The quotient mol. of bound phosphoric acid per mol. of sugar disappeared amounts to 0·2—0·3 for goat, ox, and horse and to 0·5—1·0 for dog, man, guinea-pig, and rabbit.

P. W. Clutterbuck.

Ortho- and pyro-phosphate in aerobic and anaerobic metabolism of blood-corpuscles. W. A. Engelhardt (Biochem. Z., 1930, **227**, 16—38).—Non-nucleated erythrocytes become able, in presence of methylene-blue, to utilise oxygen energetically. If the resting glycolysis is inhibited by addition of fluoride, a greater amount of phosphoric acid becomes fixed organically in presence of methylene-blue. Inhibition of respiration of nucleated erythrocytes causes a rapid increase of inorganic phosphate due, not to an increased decomposition of phosphoric ester, but to the inhibition of resynthesis which usually accompanies respiration. Aerobic

resynthesis from pyrophosphate after anaerobic hydrolysis is confirmed. P. W. CLUTTERBUCK.

Hydrolysis and esterification of phosphoric acid, and glycolysis of erythrocytes in various animals. M. N. LJUBIMOVA (Zhur. exp. Biol. Med., 1929, **12**, 405—415).—The ability of erythrocytes to eliminate phosphoric acid increases in the series ox, goat, or horse, dog, pig, guinea-pig, man, rabbit. Pig erythrocytes do not glycolyse; otherwise the glycolytic power rises in the same order. These two functions are also related, except for the pig, to the organic phosphoric acid content of the cells.

CHEMICAL ABSTRACTS.

Micro-determination of velocity of sedimentation of erythrocytes. G. C. E. BURGER (Arch. Néerland. Physiol., 1930, **15**, 565—584).—A pipette in which blood is diluted, citrated, and the sedimentation velocity of the erythrocytes measured, is described and by its use the effect of dilution on the velocity investigated. F. O. HOWITT.

Electrokinetic phenomena. III. "Isoelectric point" of normal and sensitised mammalian erythrocytes. H. A. ABRAMSON (J. Gen. Physiol., 1930, **14**, 163—177; cf. A., 1929, 1094).—The electrophoretic mobilities of intact human and sheep cells in 0·85% sodium chloride solution show no change of sign of charge with variation of p_H between 7·4 and 3·6. Reversal of sign is observed after sufficient time has elapsed and in the presence of normal and anti-sheep rabbit sera. It is claimed that the attainment of an isoelectric state is associated with adsorption of hæmolysis products. Sensitisation to hæmolysis by sera does not primarily affect the mobility of cells, and it is suggested that small changes of cell surface suffice to induce hæmolysis by complement.

A. COHEN.

Effect of administration of hydrochloric acid on the leucocyte count. J. GWORKÓWNA and B. SZABUNIEWICZ (Med. Doswiad., 1930, **11**, 183—188).—0·4% Hydrochloric acid introduced into the stomach of dogs either by a stomach tube or through a gastric fistula provokes a feeble leucopænia.

R. TRUSZKOWSKI.

Changes in exchange between blood and tissues following venesection. W. ITO (Tohoku J. Exp. Med., 1930, **14**, 236—253).—Of the total volume of blood rapidly removed from a normal rabbit 20% is replaced within 0·5 hr. by a fluid containing 0·1 as much protein, but about as much sodium chloride, as plasma, the exact composition depending on the amount of blood removed. The effect of poisoning by cantharidin or uranium is recorded.

CHEMICAL ABSTRACTS.

Hæmoglobins. Prosthetic group of hæmoglobin of *Chironomus*. A. KIRRMANN (Bull. Soc. Chim. biol., 1930, **12**, 1146—1150).—Blood from the larvæ of *Chironomus* yielded hæmin which was converted into mesoporphyrin by the method of Fischer and Koegl (A., 1924, i, 1130) and then into the methyl ester. The m. p. of this ester and also that of its complex with copper established the identity of the parent substance with the mesoporphyrin obtained by Fischer and Stangler (A., 1928, 76) from mammalian blood. O. HOWITT.

Regulation of the mineral content of body-fluids. I. *Maja squinada*, L. K. BIAŁASZEWICZ (Acta Biol. Exp., Warsaw, 1930, **5**, 57—84).—The order of velocity of disappearance from the hæmolymph of the above crab of various injected salts is: $KCl > CaCl_2 > MgCl_2 > MgSO_4$. These salts are eliminated from the hæmolymph to a small extent by the antennary glands, but chiefly by sorption by the tissues. R. TRUSZKOWSKI.

***Spirographis*-hæmin.** O. WARBURG, E. NEGELEIN, and E. HAAS (Biochem. Z., 1930, **227**, 171—183).—The absorption spectrum of the blood of *Spirographis* (cf. A., 1926, 313) is more closely related to that of the respiratory enzyme than to that of hæmoglobin. A method for the isolation of *Spirographis*-hæmin is described. The empirical formula $C_{32}H_{32}O_5N_4FeCl(\pm 1C, \pm 1H)$ closely resembles that for the hæmin of hæmoglobin and contains one atom of oxygen more than the latter. *Spirographis*-hæmin is a dibasic acid and, in the reduced condition, absorbs 1 mol. of carbon monoxide per atom of iron in the same way as ordinary hæmin. It differs, however, from the latter in that it contains either no or at most only one double linking reducible by means of palladium and hydrogen. The absorption spectra of the carbon monoxide compounds of *Spirographis*-hæmin and of chlorocruorin were investigated. Chlorocruorin absorbs more strongly than the hæmin, the maximum absorption being for the hæmin at 410 mμ. and for chlorocruorin at 440 mμ.

P. W. CLUTTERBUCK.

Catalytic action of the hæmins of blood and chlorophyll. O. WARBURG and F. KUBOWITZ (Biochem. Z., 1930, **227**, 184—199).—The effect of a number of hæmins on the respiration of non-nucleated red blood-cells is investigated. The ordinary hæmin of blood, *Spirographis*-hæmin, and coprohæmin have little or no effect, pyrrohæmin is more active, whilst the hæmin of phæophorbide-*a* (A., 1912, i, 287) increases the respiration by twenty times and produces an oxidation velocity which exceeds by far that of the normal nucleated red blood-cells of birds. The oxygen utilisation which arises under the action of the hæmin is due to the oxidation of sugar or to its degradation products (lactic acid). The catalysis by phæophorbide-*a*-hæmin is a surface reaction, since it is inhibited by narcotics, the inhibition being greater the greater is the adsorption of narcotic. The catalysis is also inhibited by carbon monoxide. P. W. CLUTTERBUCK.

Increased oxidation [of methylene-blue by hydrogen peroxide] produced by blood-pigments. K. BINGOLD (Biochem. Z., 1930, **227**, 457—461).—Although solutions of methylene-blue are not decolorised by hydrogen peroxide alone, decolorisation takes place when human blood which has previously been heated to 90° is added. Hæmatin and pigeon's blood act in the same way. When these substances which stimulate the oxidation are decolorised by treatment with hydrogen peroxide they lose their power to assist the decolorisation of methylene-blue by the peroxide.

W. MCCARTNEY.

Tryptophan and histidine as hæmatogenic amino-acids. G. FONTES and L. THIVOLLE (Compt.

rend., 1930, **191**, 1088—1090).—Subcutaneous injection of tryptophan and histidine (100 and 200 mg. per day, respectively) into dogs or rabbits fed on a normal full diet causes a marked increase in the hæmoglobin and red corpuscles of the blood, an even greater increase being caused by simultaneous daily injections of both amino-acids in the above proportion, which is that required for the synthesis of hæmatin. Since other amino-acids such as leucine, lysine, or phenylalanine have no similar action, it is concluded that the specific metabolic function of these amino-acids is the formation of blood-pigment, and the term "hæmatogenic amino-acids" is suggested for these two proteins. This view is confirmed by a decrease in hæmoglobin when rats are fed on a diet deficient in tryptophan and histidine. J. W. BAKER.

Blood-sugar. II. P. RONA and W. FABISCH (Biochem. Z., 1930, **227**, 205—220).—The agreement in results previously obtained (A., 1930, 360) in determinations of the normal human blood-sugar by the Hagedorn–Jensen and by the *B. coli* methods is confirmed. The same agreement in results is obtained with the blood of rabbits rendered hyperglycæmic with adrenaline. The determination by the two methods with the blood of diabetics showed differences which were often greater than the experimental error, but the results were not consistently larger or smaller by any one method. The blood-sugar values obtained in hypoglycæmic convulsions in rabbits by the Hagedorn–Jensen method are always greater than by the *B. coli* method. P. W. CLUTTERBUCK.

Course of blood-sugar curve after intravenous administration of sugar. O. JUTTEMANN (Arch. exp. Path. Pharm., 1930, **156**, 253—264).—In fed rabbits the amount of dextrose which is taken up by the tissues from the blood during the first hour after intravenous administration of dextrose (10 c.c. of 20—40% solutions) is about 2·4 g., whilst in fasting animals the corresponding quantity is only about 1·1 g. In starving animals treated with ergotamine or previously submitted to thyroidectomy, the uptake of sugar by the tissues is greater than with normal animals and approaches the figure obtained with normal fed animals. Atropine has a slight effect on starved animals in the same sense.

W. O. KERMACK.

Carbohydrate complex of serum-proteins and the clinical determination of "bound sugar" in the blood. C. RIMINGTON (Nature, 1930, **126**, 882—883).—The complex obtained from the proteins of horse-serum appears to be a tri- and not a disaccharide (cf. A., 1929, 837). Each molecule of glucosamine is associated with two of mannose, giving a substance of the empirical formula $C_{18}H_{33}O_{15}N$. A similar and apparently identical trisaccharide complex has also been isolated from the mixed serum-proteins of ox blood. The preparations are optically inactive. These complexes afford a satisfactory explanation of some of the contradictory observations on the "bound sugar" of the blood.

L. S. THEOBALD.

Relation between blood-sugar and -coagulation time. F. ŠVEC (Pflüger's Archiv, 1930, **224**, 62—64; Chem. Zentr., 1930, i, 3804).—Injection of insulin diminishes the coagulability of the blood. The coagulability increases regularly with increase in the blood-sugar. A. A. ELDRIDGE.

Diffusible non-protein constituents of blood and their distribution between plasma and corpuscles. O. FOLIN and A. SVEDBERG (J. Biol. Chem., 1930, **88**, 715—728).—In normal subjects the concentration of sugar in the corpuscles is 50—60% of that in the plasma, whilst in diabetics a higher percentage is found, but in no case does it reach 80%, *i.e.*, the percentage of free water in the corpuscles (cf. Ege and Roche, Skand. Arch. Physiol., 1930, **59**, 75). The concentration of urea and creatinine in the corpuscles is approximately 80% of that in the plasma. The average concentration of uric acid in the corpuscles is about 22% of that in the plasma, whilst the amino-acid-nitrogen concentration of the corpuscles is also usually less than half of that of the plasma. When extracts of unlaked normal blood are used, the total non-protein-nitrogen of the blood is practically equal to the sum of the urea-, uric acid-, creatinine-, and amino-acid-nitrogen, so that the residual nitrogen found when extracts of laked blood are employed has disappeared. For clinical purposes it is advantageous to carry out analysis on extracts of unlaked blood. W. O. KERMACK.

Distribution of amino-acids [in blood]. V. A. MESSING (Zhur. exp. Biol. Med., 1929, **12**, 393—400). —The distribution of various amino-acids, when added to dog's blood *in vitro*, between the plasma and cells is practically constant. If the amino-acid content is not much greater than the physiological concentration the erythrocytes maintain their normal content. CHEMICAL ABSTRACTS.

Amide-nitrogen of blood. V. Theory of ammonia metabolism. S. BLISS (J. Pharm. Exp. Ther., 1930, **40**, 171—193).—Oral administration of acid to normal dogs results in an increase in the protein-amide-nitrogen of the blood, and this is associated with a high ammonia excretion by the kidneys, whilst the administration of alkali results in a decrease in the protein-amide-nitrogen associated with a decrease in the urinary ammonia. During phloridzin acidosis the amide-nitrogen of the blood increases, whilst the urinary ammonia increases. After injection of lactic acid into the femoral artery, blood from the femoral vein shows an increase of protein-amide-nitrogen, indicating that the amide synthesis proceeds partly at least in the muscles. The synthesis of amide-nitrogen is probably of importance in the metabolism of ammonia and the mechanism of the acid–base equilibrium. The theory is advanced that ammonia plays a part in the neutralisation of acid in muscle, but that for the purpose of transport in the blood to the kidneys it is detoxicated by being converted into an amide, the ammonia being regenerated in the kidneys and appearing in the urine in combination with acid as ammonium salts. W. O. KERMACK.

Determination of bilirubin in serum. S. C. LI (Z. ges. exp. Med., 1930, **70**, 452—458; Chem. Zentr., 1930, i, 3705).—Despite the use of a third series of tubes, Glass' method is not sufficiently accurate for clinical purposes. A. A. ELDRIDGE.

Determination of inorganic sulphate in serum. R. S. Hubbard (J. Biol. Chem., 1930, **88**, 663—668).—The serum-proteins are coagulated with trichloroacetic acid and removed, the sulphate is precipitated as benzidine sulphate, and the latter separated by centrifuging, dissolved in dilute hydrochloric acid, and treated with hydrogen peroxide in presence of ferric chloride. The colour developed is compared with that produced by known amounts of benzidine under similar conditions. W. O. Kermack.

Determination of phosphorus in small amounts of serum. K. Koch (Biochem. Z., 1930, **227**, 334—339).—The phosphorus content of 2—5 c.c. of serum can be determined by a slight modification of the method of Embden (A., 1921, ii, 462). W. McCartney.

Determination of the catalase content of blood. E. Bach (Biochem. Z., 1930, **227**, 221—229).—Blood immediately after removal and dilution is treated at 18° with hydrogen peroxide–buffer mixture and the undecomposed peroxide is subsequently titrated with permanganate. The catalase activity of freshly removed and diluted blood quickly decreases. Blood diluted 2500 times loses 10—20% of its activity after keeping for 20 min. and 50—60% in a few hours. Undiluted and defibrinated bloods retain unchanged the catalase content for a considerable time. During the reaction not only peroxide but also catalase is decomposed, and the velocity of decomposition increases with increasing concentration of peroxide. The decomposition of peroxide and catalase is the greater the higher is the temperature. By use of a buffer, the errors due to the acidity of the peroxide are avoided. Under the author's conditions, the unimolecular constants for different time points gave comparable results. P. W. Clutterbuck.

Action of light on blood components. A. Furniss (Brit. J. Actinother., 1930, **5**, 187—188).—A review of work on the effect of visible, ultra-violet, and infra-red rays on various constituents of blood. W. O. Kermack.

Prothrombase. Preparation and properties. J. Mellanby (Proc. Roy. Soc., 1930, B, **107**, 271—285; cf. A., 1909, ii, 158).—Experimental details are given for the preparation of prothrombase (yield of 40 mg. per 100 c.c. of plasma) by globulin-complex precipitation at p_H 5·3 from diluted oxalated mammalian blood, and reprecipitation from a calcium hydrogen carbonate extract of the complex. On activation, 1 mg. of the preparation coagulates 100 c.c. of plasma in 20 sec. Prothrombase is a non-dialysable (collodion) acid meta-protein, destroyed in suspension at 100°; in solution it is not destroyed in 5 min. at 100°, but its subsequent conversion into thrombase is retarded. The activation of prothrombase by thrombokinase is greatly accelerated by traces of calcium and strontium, and, to a far smaller extent, by barium and magnesium. A. Cohen.

Significance of the benzene nucleus in the specificity of azoproteins. M. Adant (Compt. rend. Soc. Biol., 1930, **103**, 539—540; Chem. Zentr., 1930, i, 3323).—Substitution of the aniline molecule by benzidine or α-naphthylamine causes no change in the specificity of the antibody. The diazotised antigens behave in presence of their own antibodies exactly as in that of antibodies of antigens with a different aromatic nucleus. A. A. Eldridge.

Azoprotein gelatin-aniline. M. Adant (Compt. rend. Soc. Biol., 1930, **103**, 541—543; Chem. Zentr., 1930, i, 3323; cf. preceding abstract).—Serum of rabbits treated with gelatin and diazotised aniline precipitates both gelatin and its own antigen. A. A. Eldridge.

Purinolytic enzymes of human embryos. H. Beck and R. Truszkowski (Med. Doświad., 1930, **11**, 36—44).—Xanthine-oxidase, but not uricase, was found in twenty fœtuses from the eighth to the fortieth week of pregnancy. R. Truszkowski.

Purine content and nuclear-plasmic ratio of various organs. A. Rowińska (Med. Doświad., 1930, **11**, 310—317).—The ratio of purine- to non-purine-nitrogen is a fairly constant quantity for the same organs of different species (calf, ox, horse), varying from 0·0218 for the brain to 0·1636 for the thymus gland. The mean purine contents in mg. per 100 g. are as follows: muscle 88·8 (calf), 76·5 (ox), white and red chicken muscle 98·2 and 76·6, respectively, horse brain 37·2, lung 89·4, intestine 78·0; thyroid and suprarenal glands, 126 and 116·5, respectively, pancreas 283, spleen 215·3, kidney 112·5, calf thymus 415. R. Truszkowski.

Iodine content of the thyroid gland of the sheep and ox. A. Torino and G. Ruff (Compt. rend. Soc. Biol., 1929, **102**, 871—872; Chem. Zentr., 1930, i, 3453).—Similar values were obtained; regular variations with the season were not observed. Fellenberg's method indicated only 50% of the iodine; the glands were heated with sodium carbonate, ferrous sulphate and sulphuric acid were added, and the iodine was distilled into potassium iodide solution. A. A. Eldridge.

Traces of metals in animal tissues. A. C. Chapman (Nature, 1930, **126**, 761).—Vanadium, arsenic, and antimony are added to the list of metals occurring in animal tissues. L. S. Theobald.

Elements present in animal tissues. H. M. Fox and H. Ramage (Nature, 1930, **126**, 883).—The occurrence in animal tissues of elements other than those previously mentioned (A., 1930, 1609) is pointed out from the work of previous investigators. L. S. Theobald.

Pig-stomach fat. J. S. Hepburn and W. L. Trexler (Amer. J. Pharm., 1930, **102**, 569).—The fat extracted by light petroleum from desiccated pig stomach has iodine value (Hanus) 29·9, saponification value 184·3, Hehner value 90·5, $n^{27.5}$ 1·4663, soluble acids 0·06%. H. E. F. Notton.

Phosphatides. I. Liver-phosphatide of rabbits. W. R. Witanowski (Acta Biol. Exp., Warsaw, 1930, **5**, 207—215).—The alcohol–ether extract of rabbit liver contains, per 100 g. of fresh tissue, 57·3 mg. of total choline, 4·5 mg. of free choline, 21·7 mg. of total colamine, 177 mg. of organically combined phosphorus, and 24·8 mg. of lecithin-, cephalin-, and sphingomyelin-phosphorus. The choline content of rabbit brain is 97·7 mg., of skeletal muscle 30 mg.,

and of heart muscle 8 mg. per 100 g. Choline and colamine are present in approximately equimolecular quantities in the liver. R. TRUSZKOWSKI.

Phosphatides. I. Fatty acids of the cephalin fraction of brain. E. KLENK (Z. physiol. Chem., 1930, **192**, 217—232).—The cephalin fraction was separated into saturated and unsaturated acids. The saturated acid fraction yielded stearic and possibly palmitic acids; the unsaturated fraction after hydrogenation gave stearic and behenic acids. The unsaturated C_{22} acid contains at least four, possibly five, double linkings, and may thus be isomeric with clupanodonic acid. The proportions of the C_{18} and of the C_{22} groups in the total fatty acids are 73 and 25%, respectively. J. H. BIRKINSHAW.

Depressor substance in brain tissue. R. H. MAJOR and C. J. WEBER (J. Pharm. Exp. Ther., 1930, **40**, 247—252).—The depressor substance previously detected in extracts of brain (A., 1930, 104) has been obtained in protein-free solution giving a positive Sakaguchi and negative Pauly reaction. It is not identical with histamine, choline, or acetylcholine. W. O. KERMACK.

Relation of the mitochondria–Golgi complex to secretion. V. Further identification of neutral-red-stained material. VI. Method for demonstrating the mitochondria–Golgi complex and other cytoplasmic inclusions. W. C. MA (Chinese J. Physiol., 1930, **4**, 381—386, 387—389).—V. The material in the acinar cells of the pancreas, stained by neutral-red, is lipoidal in nature and is similar to the osmophilic Golgi substance.

VI. Histological technique is described for fixing and staining sections so as to demonstrate simultaneously mitochondria and Golgi material. W. O. KERMACK.

Refractive index of the cerebrospinal fluid as a check on the chemical analysis. W. J. PENFOLD and D. H. IRVING (Med. J. Austral., 1930, **1**, 772—779).—The average refractive index of normal samples was 1·335093. Calculated values based on this and on the chemical analysis agreed with observed values in more than 50% of the cases examined. Excess of urea leads to marked discrepancies. CHEMICAL ABSTRACTS.

Inhibitive action of the cœlomic fluid of the sea-urchin on membrane-formation and segmentation. M. BOGUCKI (Acta Biol. Exp., Warsaw, 1930, **5**, 47—55).—The fluid is without influence on the formation of fertilisation membranes and on segmentation of fertilised eggs, except in those cases in which it contains digestive ferments. These are inactive in alkaline media such as sea-water, washing with which, therefore, entirely removes the apparent inhibitive influence of the cœlomic fluid. R. TRUSZKOWSKI.

Elimination of foreign protein (egg-white) in human milk. H. H. DONNALLY (J. Immunol., 1930, **19**, 15—40).—Traces of egg-white were detected in the milk of three of eight fasting women after ingestion of raw egg. CHEMICAL ABSTRACTS.

Changes in the alkali reserve and sugar content of the bile by the action of various physiological excitants. II. Effect of acids, alkalis, and gastric juice. W. M. KARATYGIN and A. I. HEFTER (Z. ges. exp. Med., 1930, **70**, 666—682; Chem. Zentr., 1930, i, 3573).—Introduction of 100 c.c. of 0·1% hydrochloric acid into the intestinal canal of dogs diminishes the alkali reserve and increases the bile-sugar; 5% sodium carbonate solution introduced into the duodenum has the same effect. Ingestion of meat, bread, and milk raises the alkali reserve and diminishes the bile-sugar owing to excretion of gastric juice and increasing alkalescence. A. A. ELDRIDGE.

Salivary lipase. M. KATZENSTEIN (Z. ges. exp. Med., 1929, **69**, 179—192; Chem. Zentr., 1930, i, 3798).—The lipase content of human saliva is high in pathological conditions with diminished salivation and low in those with increased salivation. The parotic secretion is generally richer in lipase than the total saliva. Dog's saliva also contains lipase, but the parotic secretion contains none. A. A. ELDRIDGE.

Inhibitive action of intestinal biodialysates on the gastric secretion. J. WALAWSKI (Med. Doswiad., 1930, **11**, 348—372).—Injection into man or dogs of biodialysates into Ringer–Locke's fluid of the appendix and large intestine inhibits the secretion of gastric juice taking place under the action of histamine or secretin; this effect persists during 8 hrs. The effect is not obtained by injection of acid dialysates. The active factor is thermostable, but disappears on keeping. R. TRUSZKOWSKI.

Conditions and significance of biological methylation processes. F. A. HOPPE-SEYLER (Z. Biol., 1930, **90**, 433—466).—Trimethylamine oxide is present in the blood and urine of *Selachii* and in the former in sufficiently large quantities to be the chief constituent, apart from urea, responsible for the osmotic pressure. Small quantities of trimethylamine are also found in the urine. In fresh-water *Teleostii* neither trimethylamine oxide nor trimethylamine is found in the urine or other secretions, but in salt-water *Teleostii* both are present in the urine. W. O. KERMACK.

Formation of urine in the frog's kidney. XIX. R. HOBER (Pfluger's Archiv, 1930, **224**, 422—440; Chem. Zentr., 1930, i, 3457).—The urea content of the frog's kidney may be higher than that of the blood and urine. Experiments relating to the permeability for, and storage of, urea are described. A. A. ELDRIDGE.

Creatinuria. I. Acidosis and creatinuria. O. RIESSER and C. BRENTANO. **II. Relation between creatinuria and muscle-glycogen.** C. BRENTANO (Arch. exp. Path. Pharm., 1930, **155**, 1—20, 21—45). —I. Acidosis induced in rabbits by subcutaneous administration of ammonium chloride or ammonium phosphate does not necessarily lead to creatinuria nor to an excess of muscle-creatine, and in those cases when creatinuria follows acidosis, no proportionality exists between the degree of acidosis on the one hand and the degree of creatinuria or of the increase in muscle-creatine on the other. Alkalosis brought about by administration of sodium hydrogen carbonate subcutaneously may lead to creatinuria. Creatin-

uria is therefore not the direct result of acidosis. Under the influence of narcotics (urethane or morphine) marked creatinuria regularly occurs.

II. The creatinuria occurring after administration to rabbits of narcotics or during acidosis is accompanied by a fall in skeletal muscle-glycogen. When there is no creatinuria, as in certain cases of acidosis, there is no fall in muscle-glycogen. Creatinuria also occurs in other conditions when there is a fall of muscle-glycogen, as after administration of adrenaline, phloridzin, or of carbon monoxide and also during convulsions following camphor-poisoning.

W. O. KERMACK.

Uric acid in the urine of infants. R. DEBRÉ, R. GOIFFON, and S. YOSHIMATSU (Compt. rend. Soc. Biol., 1930, **102**, 994—997; Chem. Zentr., 1930, i, 3323).—When the uric acid : urea quotient is plotted against the urea concentration a hyperbolic curve is obtained. In the infant the uric acid is 1·2 g., and in the adult 0·55 g. per litre. A. A. ELDRIDGE.

Detection and determination of ammonia and amino-acids in urine. A. AGRESTINI and M. STANGANELLI (Annali Chim. Appl., 1930, **20**, 482—488).—The detection of ammonia in organic liquids by treatment with magnesium oxide or carbonate, sodium or calcium carbonate, alkali hydrogen carbonate, etc. at temperatures not above 50° is disturbed by the presence of carbamide or various amino-acids. Addition to 5—10 c.c. of the liquid of 5—10 drops of 10% potassium iodide solution, followed by a few drops of alkali hypochlorite, gives an immediate black coloration in presence of ammonium salt corresponding with 1 part of ammonia in 50,000 parts of solution. This reagent is less sensitive than Nessler's reagent, but is not affected by sulphides, mercaptans, amino-acids, carbamide, uric acid, alloxan, alloxantin, creatinine, etc., and is applicable to coloured liquids like urine. For the determination of ammonia, the Schiff–Sørensen method serves well in presence of carbamide, alloxan, etc., which do not react with formaldehyde, but not so well when amino-acids are present. The Folin method is disturbed appreciably by carbamide, alloxan, alloxantin, uric acid, and creatinine, and the use of permutit does not improve the results. The following procedure gives satisfactory results in presence of amino-acids such as alanine and glycine: 40 c.c. of the liquid are shaken with 20 c.c. of 7·5% disodium hydrogen phosphate solution for 3 min., the walls of the vessel being rubbed with a glass rod. After about 4 hrs., the liquid is filtered, 20 c.c. of the filtrate being neutralised and tested by Sørensen's method. T. H. POPE.

Iodometric determination of homogentisic acid in urine. E. METZ (Z. physiol. Chem., 1930, **193**, 46—48; cf. A., 1928, 195).—A defence of the author's method. Some of the modifications of Lieb and Lanyar (A., 1929, 593) are adopted.

J. H. BIRKINSHAW.

Anaerobic decomposition of volatile fatty acids in the human intestine. V. M. GUBIN and L. A. IVANOVA (Zhur. exp. Biol. Med., 1929, **12**, 360—364).—The fæces contain micro-organisms which produce anaerobic fermentation of the volatile fatty acids with evolution of gas. The hydrogen-ion concentration of intestinal contents depends on the anaerobic formation of volatile fatty acids and their decomposition to form methane and carbon dioxide.

CHEMICAL ABSTRACTS.

Putrefactive process and reduction of sterols in the suckling's intestine. G. BISCHOFF (Biochem. Z., 1930, **227**, 230—236).—On a milk diet considerable amounts of reduced sterols are formed in the fæces, the amount running parallel with the clinically observed intestinal putrefaction. Small amounts were also obtained in the non-putrefying stools during breast-feeding, but in this case the reduced sterol was dihydrocholesterol instead of coprosterol. In young children the coprosterol values were never so high on a pure milk as on a meat diet. Coprosterol is not resorbed in man. P. W. CLUTTERBUCK.

Artificially induced acidosis and alkalosis. G. MODRAKOWSKI and R. LENTZ (Med. Doświad., 1930, **11**, 274—287).—Acidosis produced by ingestion of ammonium chloride is accompanied in human subjects and in rabbits by acceleration of the rate of sedimentation of erythrocytes, and by concentration of the blood, expressed by increase in the concentration of plasma- and serum-proteins; at the same time the permeability of the capillaries is increased. Sodium hydrogen carbonate alkalosis provokes the opposite effects, with the exception of fibrinogen, the content of which is increased. From the point of view of respiration, this type of alkalosis is identical with acidosis, being accompanied by augmented elimination of carbon dioxide. R. TRUSZKOWSKI.

Acidosis and alkalosis. H. SIKORSKI and R. LENTZ (Med. Doświad., 1930, **11**, 318—329).—The action of the frog's heart is accelerated by reduction of the p_H of the liquid passed through it from 7·0 to 6·8. Reduction to 6·5 partly inhibits the heart-beat, as does also increase of p_H from 7·4 to 7·7.

R. TRUSZKOWSKI.

Reaction of the tissues and their buffering powers in local anæmia. N. OKUNEV (Biochem. Z., 1930, **227**, 319—325; cf. A., 1930, 942).—Experiments on the muscle of frogs suffering from experimental local anæmia showed that the anæmia causes local acidosis, which disappears, and is often succeeded by an alkaline reaction, when the normal circulation is restored or when the anæmia leads to necrosis. The buffering powers of the tissues affected by the anæmia differ from that of normal tissue, the difference apparently depending on the concentrations of hydrogen ions in the various regions. W. McCARTNEY.

Lipæmia in hæmorrhagic anæmia in rabbits. A. H. JOHANSEN (J. Biol. Chem., 1930, **88**, 669—673). —Repeated removal of blood from rabbits by venesection results in a fall of the hæmoglobin percentage to 30 and of the colloidal osmotic pressure to a little above 200 mm. of water, whilst the serum-lipins rise to about 1%. No œdema could be detected as a result of the lowered colloidal osmotic pressure.

W. O. KERMACK.

Liver enzymes in anaphylaxis. J. LASKOWSKI (Med. Doświad., 1930, **11**, 265—273).—The amylolytic and lipolytic powers of dog's liver are not affected

by anaphylactic shock due to injection of horse-serum, whilst the oxidase content is reduced by 20%.
R. TRUSZKOWSKI.

Hypertrophy and atrophy of muscular organs. III. Left ventricle after experimental aortic damage. H. WASSERMEYER and J. JACOBI (Arch. exp. Path. Pharm., 1930, **155**, 70—90).—The normal left ventricle of the rabbit's heart contains 1·08±0·17 mg. of ammonia and 0·48±0·05 g. of glycogen per 100 g. Between 21 and 37 days after experimentally damaging the aorta, so as to produce stenosis or insufficiency, a condition of fatigue of the muscle of the left ventricle sets in, indicated by a decrease in the glycogen and an increase in ammonia content, as well as by a loss in synthetic activity. This negative phase gradually disappears, to be ultimately replaced by a condition of muscular hypertrophy. By administration of digitonin after the operation, the intensity of the negative phase may be decreased.
W. O. KERMACK.

Action of certain amino-acids on the isoelectric point of human serum. F. VLES and A. DE COULON (Compt. rend., 1930, **191**, 1166—1168).—The administration of certain amino-acids to patients suffering from cancer results in a lowering of the isoelectric point of the serum.
W. O. KERMACK.

Oxygen content of blood from sarcoma. A. OSZACKI (Bull. Acad. Polonaise, 1930, B, 391—403).—The oxygen and carbon dioxide contents of venous blood from sarcomatous tissue were compared with those of venous blood from healthy tissue of the same organ or from the anatomically corresponding vein. In the former the oxygen content was definitely higher than in the latter.
F. O. HOWITT.

Phosphate and chloride excretion in cases of Frohlich's syndrome. S. M. LING, S. T. WOO, and H. CHANG (Nat. Med. J. China, 1930, **16**, 545—555).—In two cases the phosphate excretion was normal. Subcutaneous administration of "pituitrin" exerts only a transient effect in checking polyuria. Both chloride and phosphate concentrations of urine vary inversely as the volume. The pituitary does not control phosphate excretion.
P. G. MARSHALL.

Endemic goitre in Hungary in relation to the theory of lack of iodine. J. BODNÁR and J. STRAUB (Biochem. Z., 1930, **227**, 237—244).—The iodine content of the drinking-water of Bodahegyközség (Hungary), where goitre is particularly prevalent, is only 0—1 γ per litre. The iodine content of children's food (day) amounted to 15·8 γ. The daily urine of children affected with goitre contained 8 γ and of healthy children and adults 31—35 γ. Administration of iodine greatly benefited those affected.
P. W. CLUTTERBUCK.

Iodine in nutrition in North China. W. H. ADOLPH and S. C. CHEN (Chinese J. Physiol., 1930, **4**, 437—447).—Drinking-water and various foodstuffs from different localities were analysed in respect of their iodine contents. The average iodine intake per person in the non-goitrous areas is about 0·018 mg. per day, which is only slightly above the minimum iodine requirement (0·014 mg.), whilst in goitrous regions the average intake is probably considerably below this figure.
W. O. KERMACK.

Intensity of action of atophan and of salicylic acid on the excretion of uric acid in gout. (Rôle of kidney function in the occurrence of gout.) A. LUBLIN (Arch. exp. Path. Pharm., 1930, **155**, 331—353).—Salicylic acid surpassed atophan in promoting the excretion of uric acid by the kidneys in gout, but had not the favourable therapeutic effects of the latter on acute attacks of the disease.
W. O. KERMACK.

Experimental hyperparathyroidism in guinea-pigs leading to osteitis fibrosa. A. BODANSKY, J. E. BLAIR, and H. L. JAFFE (J. Biol. Chem., 1930, **88**, 629—647).—Single large doses of "parathormone" administered to young guinea-pigs cause a greater increase of blood-calcium and -phosphorus if the guinea-pigs have been fasting for 60 hrs. than when they are on their normal diet. The administration of single doses to adult fasting guinea-pigs has less effect on the blood-calcium than in the case of young fasting animals, but there is comparatively little difference between the adult fasting and the adult fed animals. After the administration of repeated small doses of "parathormone" the animals may be given progressively larger doses without any marked increase in blood-calcium. After such a series of doses, bone lesions develop resembling closely those characteristic of osteitis fibrosa in man. Similar lesions may also be produced by very large single doses.
W. O. KERMACK.

Serum-proteins in dogs with experimental hyper- and hypo-thyroidism. S. M. LING and H. C. CHANG (Chinese J. Physiol., 1930, **4**, 375—379).—The various fractions of the serum-proteins are not altered in quantity by thyroid feeding or by thyroidectomy.
W. O. KERMACK.

Precipitates of colloidal silver in inflamed tissues. H. KOLLER-AEBY (Kolloid-Z., 1930, **53**, 101—102).—When colloidal silver is injected intravenously it is precipitated in inflamed tissues in the form of microscopic particles. The amount of precipitation is proportional to the degree of inflammation, and the aggregation is not observed in healthy tissue.
E. S. HEDGES.

Liver function. III. Gaseous exchange in the destruction of liver function after administration of dextrose. M. TAKUWA (Japan. Med. World, 1930, **9**, 374—394).—After administration of dextrose to man the gaseous exchange, *R.Q.*, and free blood-sugar rise and return gradually to the normal value. In hepatic disease the gaseous exchange is unchanged or falls after administration of dextrose, and the *R.Q.* maximum is late. In normal rabbits the *R.Q.* rises; in rabbits the livers of which have been destroyed it falls.
CHEMICAL ABSTRACTS.

Urobilin substances. II. Excretion of urobilin substances in the urine and bile in various diseases. M. OSHIMA (Japan. J. Gastroenterol., 1930, **2**, 90—92).—The urobilin content of the urine is closely related to the liver function and is usually parallel to its concentration in the bile.
CHEMICAL ABSTRACTS.

Ammonia in nephrosis. A. MAGNUS-LEVY (Z. klin. Med., 1930, **112**, 257—274; Chem. Zentr., 1930, i, 3457).—The ammonia production of the nephrotic kidney, unlike that of the nephritic kidney, is usually considerably higher than normal; the values are, however, irregular. Ammonuria in nephrosis is primary, and in diabetes secondary. In rapidly increasing œdema the ammonia rises. Urease was not definitely detected in the urine.

A. A. ELDRIDGE.

Phosphatide-fat deposition in the spleen in Niemann-Pick disease compared with the lipin chemistry of Gaucher's and of Schüller-Christian's diseases. E. EPSTEIN and K. LORENZ (Z. physiol. Chem., 1930, **192**, 145—170; cf. A., 1930, 1208).—In each of the three chief types of general lipinosis the deposits consist of complex lipin-fat mixtures, but the diseases are characterised by definite chemical differences. The Niemann-Pick phosphatide lipinosis is distinguished by ether-soluble lecithin and probably by as yet undifferentiated ether-insoluble, alcohol-soluble phosphatides. The Gaucher cerebroside lipinosis is accompanied by the presence of kerasin and probably of a related cerebroside. The presence of cholesterol and its esters marks the Schuller-Christian type. J. H. BIRKINSHAW.

Œdema. II. Disease conditions with change of colloid osmotic pressure. H. HORSTERS (Arch. exp. Path. Pharm., 1930, **155**, 248—256).—In patients with normal circulation the average colloidal osmotic pressure was equal to 371 mm. of water, whilst the total osmotic pressure was the equivalent to that of a sodium chloride solution of 0·95—1·02%. The concentration of serum-proteins was about 8·5—9·0%, so that every 1 g. of serum-protein was equivalent to a pressure of 40—45 mm. of water. The colloidal osmotic pressure was low in cases of essential or renal hypertony, acute nephritis, cardio-renal insufficiency, amyloidosis, diabetic acidosis, and diabetic coma, but was normal in uncomplicated diabetes.

W. O. KERMACK.

Phosphatides. II. Choline derivatives in rabbits after extirpation of the suprarenals. W. R. WITANOWSKI (Acta Biol. Exp., Warsaw, 1930, **5**, 217—223).—The free choline content of the arterial plasma of rabbits rises from 0·4—0·75 mg. to 1·4—3·11 mg. per 100 c.c. 7 hrs. after extirpation of the suprarenals. Simultaneously the total choline content of the liver falls from 57·3 to 48·2 mg. per 100 g. R. TRUSZKOWSKI.

Chemical processes during cell division. L. RAPKINE (Compt. rend., 1930, **191**, 871—874).—On fertilisation the ova of *Paracentrotus lividus*, Lk., have a content of thiol groups of 0·035%, which in 30 min. falls to 0·010%, and then rises abruptly 10—15 min. before the first division to 0·046%. Immersion of the ova in a 0·00002*M*-mercuric chloride in sea-water for 5 min. is sufficient to prevent further division on transference back to the normal media. If, however, they are transferred to 0·001*M*-cysteine or -thioglycollic acid in sea-water 70—90% of the ova divide in the normal manner. Similar solutions of alanine or cystine do not show this effect. The reduction of cystine to cysteine in the ova is due to a hydrogen donator, similar to the thermostable residue of Hopkins, which may be destroyed by treatment with mercuric chloride. The donator, as measured by the reduction of methylene-blue, is most active 20—30 min. before the division of the cell; at the same time the lactic acid content of the ova is at a maximum. An increase of the lactic acid content is observed on placing the ova in nitrogen or 0·0005*M*-potassium cyanide. Ova which have been treated with sea-water containing mercuric chloride contain very little lactic acid, but on transference to the cysteine solution the lactic acid content becomes normal. It is concluded that cell division may be controlled by variation of the thiol content.

T. H. MORTON.

Biology of the meal worm (*Tenebrio molitor*). I. F. N. SCHULZ (Biochem. Z., 1930, **227**, 340—353).—Meal worms can live and, at some stages of development, can grow to maturity under conditions of great desiccation and can also exist for months in a state of suspended animation. Worms in such conditions consume greatly reduced amounts of food, but they can make use of water formed in respiration and they also insulate themselves very securely against loss of water by production of an enveloping wax-like covering. W. MCCARTNEY.

Catalase content of the Colorado potato beetle during metamorphosis. D. E. FINK (J. Agric. Res., 1930, **41**, 691—696).—On the first and second days of the prepupal stage there is a marked inhibition of catalase activity, which again rises to a maximum on the day of formation of the pupa, and thereafter again falls rapidly. P. G. MARSHALL.

Behaviour of κ-benzenesulphonylmethylaminoundecoic acid in the animal body. T. HOSODA (Z. physiol. Chem., 1930, **192**, 264—267).—κ-Benzenesulphonylmethylaminoundecoic acid when injected subcutaneously into a dog was oxidised to β-benzenesulphonylmethylaminopropionic acid. No evidence of γ- or δ-oxidation was found.

J. H. BIRKINSHAW.

Degradation of β-hydroxybutyric acid in the [animal] organism. Its connexion with carbohydrate metabolism. F. ROSENTHAL (Biochem. Z., 1930, **227**, 472—481).—In the mouse the degradation of β-hydroxybutyric acid takes place without an accompanying decrease in the total carbohydrate content of the animal, and such degradation also occurs even when this content is extremely low. Injection of excessive amounts of β-hydroxybutyric acid leads to a decrease in the glycogen content of the animal, but this decrease is a toxic effect and differs from the effects produced by anæsthetics such as ether and chloroform, which cause no decrease in the carbohydrate content of animals in which this is already low. No evidence of possible production of carbohydrates from fatty acids could be obtained.

W. MCCARTNEY.

Metabolism of sugars injected intravenously at a constant rate. W. WIERZUCHOWSKI [with M. ŁANIEWSKI, E. OWSIANY, and W. PIESKOW] (Acta Biol. Exp., Warsaw, 1930, **5**, 87—205).—Dextrose, galactose, and lævulose were injected intravenously into dogs at a rate of 2 g. per kg. per hr. The non-

protein *R.Q.* during 3 hrs. of injection was for dextrose 1·01, for lævulose 1·02, and for galactose 0·82; with the simultaneous administration of insulin the corresponding values were 1·05, 1·05, and 0·94. The maximum possible oxidation of sugars at the given rate of introduction was 0·5 g. per kg. per hr. Over the whole experiment 34% of total injected dextrose underwent oxidation, 41% of lævulose, and 56% of galactose; with simultaneous injection of insulin the above values are respectively 15, 24, and 87% higher. The specific dynamic actions of these sugars are respectively 9·7, 13·8, and 17·3%. The greatest raising of heat-production is observed during the second and third hours of injection, and amounts respectively to 51, 63, and 32%. Experiments in which the influence of insulin was studied are divided into a hyperglycæmic period during which sugar and insulin were injected simultaneously, and a hypoglycæmic period during which injection was discontinued; during the former period insulin augments heat-production due to introduction of dextrose by 20·6%, of lævulose by 37·8%, and of galactose by 23·4%, the maximal increment of heat-production amounting respectively during the third hour to 57, 85, and 32%. During the hypoglycæmic period, heat-production was still increased by 30·9%. During the 4-hr. hyperglycæmic period, approximately 50% of the increase in heat-production is due to specific dynamic action, whilst for the whole 8 hrs. of the experiment the appropriate value is 36·7%. The quotient of assimilation to oxidised sugar amounts for the whole experiment for dextrose to 3·04, for lævulose to 2·48, and for galactose to 1·82; for the first 4 hrs. to 4·73 for dextrose and 3·83 for lævulose (with insulin 4·43 and 2·94, respectively). The number of calories due to the specific dynamic action of 1 mol. of dextrose, lævulose, and galactose are respectively 214, 242, and 249 g.-cal.; injection of physiological fluid under analogous conditions leads to a specific increment of only 1·87 g.-cal. The heat-production and the value of the *R.Q.* are at the height of assimilation (third hour) inversely proportional, and the value of the specific increment in heat-production is directly proportional to the concentration of the given sugar in the blood. The carbon dioxide-combining power of the blood falls by 7·3—10·5% as a result of extra production of lactic acid; with elimination of this, the alkali reserve returns to normal. The blood-lactic acid curve does not coincide with the oxygen intake curve. On the whole it appears that the specific dynamic action and the intensity of oxidation of sugar are directly proportional to the production of lactic acid. R. TRUSZKOWSKI.

Effect of acid and alkaline buffer mixtures on carbohydrate metabolism and body temperature: experimental fever. F. FISCHLER and R. SCHMID (Arch. exp. Path. Pharm., 1930, **155**, 91—113).—When an isotonic alkaline buffer mixture (carbonate or phosphate) is administered to rabbits a decrease of the reducing power of the blood is observed together with a rise of body temperature up to about 3°. In rabbits with exhausted carbohydrate reserve only a very small rise in body temperature occurs, and the reducing power remains almost constant. When isotonic acid buffer mixtures are injected a similar but smaller rise of temperature occurs together with a marked increase in the reducing power of the blood. When adrenaline or ephedrine is administered as well as the alkaline buffer mixture, a more intense and more prolonged rise of temperature is observed. When dextrose or lævulose is administered after the alkaline buffer, the temperature tends to return to normal. W. O. KERMACK.

Metabolism of the frog's isolated heart. A. J. CLARK, C. P. STEWART, and R. GADDIE (Proc. Roy. Soc. Edin., 1930, **50**, 297—303).—The carbohydrate consumption of the heart perfused with Ringer's solution containing dextrose with and without frog's serum and insulin represents only a small part of its total metabolism and its *R.Q.* is usually lower than 0·9. During the perfusion some nitrogen is excreted into the perfusing fluid, and if assumed to be a product of protein breakdown is sufficient to account for about one half of the total metabolism. No evidence could be obtained that fat is consumed by the heart. Determinations of glycogen and of the *R.Q.* of the empty heart provide no evidence that the heart builds up glycogen from protein. During the first few hours of perfusion, the heart loses more than two thirds of its glycogen. Excess of dextrose and insulin fails to bring about glycogen storage or to increase carbohydrate consumption. W. O. KERMACK.

Effect of administration of sodium hydrogen carbonate on the excretion of ketonic substances by dogs deprived of carbohydrate. F. MAIGNON and E. KNITHAKIS (Compt. rend. Soc. Biol., 1929, **101**, 870—872; Chem. Zentr., 1929, i, 3807).—Dogs with transitory acetone-substance retention exhibit increased diuresis and ketonuria on administration of sodium hydrogen carbonate. In dogs exhibiting no such retention and not having become accustomed to deprivation of carbohydrate, sodium hydrogen carbonate does not cause diminution of the production of ketonic substances. A. A. ELDRIDGE.

Metabolic activity of muscle poisoned with fluoride. F. LIPMANN (Biochem. Z., 1930, **227**, 110—115).—Frog's muscles poisoned with fluoride are able to perform work without formation of lactic acid. The rate of decomposition of phosphagen is increased and considerable esterification of hexose with phosphate and decomposition of adenylpyrophosphoric acid occur. After contraction, the muscle passes into rigor. The results correspond with those obtained by poisoning the muscle with iodoacetic acid. P. W. CLUTTERBUCK.

Activity metabolism of the muscle, poor in carbohydrate, of cold-blooded animals. S. OCHOA (Biochem. Z., 1930, **227**, 116—134).—The carbohydrate metabolism of frog's muscle, the carbohydrate content of which had been depleted by the action of insulin, is compared with the development of tension both in oxygen and nitrogen. The K_{mo_2} value for semimembranosi is about 480. The results indicate that with muscle, rendered almost carbohydrate-free, the oxidation of carbohydrate is not sufficient to account completely for the development

of tension. Under anaerobic conditions the lactic acid formed corresponds with the carbohydrate present, but the K_{mL} value is considerably too large. It is not certain that the energy difference is derived from the hydrolysis of phosphagen. P. W. CLUTTERBUCK.

Is lactacidogen (hexosephosphoric acid) decomposed in muscular contraction? K. LOHMANN (Biochem. Z., 1930, **227**, 39—50).—Since there is no known method for fixing a muscle at the height of the single muscle twitch, it is difficult to decide whether any decomposition of lactacidogen occurs during contraction, but none is detectable. Lactacidogen may be a lactic acid former, but it seems doubtful that it is the immediate precursor. On the other hand, Embden's hypothesis that placing a muscle in liquid air at the height of contraction causes hydrolysis of lactacidogen is invalid. The difference in the hexosephosphoric acid contents of muscle killed before and after tetanic stimulation depends on a synthesis of ester in the stimulated muscle, the amount of difference being dependent on the duration and strength of the stimulus. P. W. CLUTTERBUCK.

Muscular contraction without formation of lactic acid. E. LUNDSGAARD (Biochem. Z., 1930, **227**, 51—83).—The non-formation of lactic acid during the work of a muscle poisoned with iodoacetic acid is confirmed and the ratio of the breakdown of phosphagen to the work done in the single muscle twitch and in tetanus (K_{mp} and K_{zP}, respectively) is determined. Curarisation did not change these values for muscle poisoned with iodoacetic acid. Poisoning the muscle in this way did not affect the chronaxie, and simultaneous curarisation increased the chronaxie to the same extent as with curarisation alone. Anaerobic resynthesis of phosphagen did not occur after poisoning with iodoacetic acid. The course of esterification and the type of ester formed are investigated. Hydrolysis of pyrophosphate during performance of work and in rigor is detected.
P. W. CLUTTERBUCK.

Effect of halogenoacetic acid poisoning on the solubility of the muscle-proteins. G. EMBDEN and E. METZ (Z. physiol. Chem., 1930, **192**, 233—244).—Poisoning of frogs with bromoacetic and iodoacetic acids produces a lowering of the solubility of the proteins of the gastrocnemius. Electrically-produced fatigue in isolated muscle poisoned with bromoacetic acid represents a further stage in the change of colloidal state. J. H. BIRKINSHAW.

Reaction changes of active muscle. F. LIPMANN and O. MEYERHOF (Biochem. Z., 1930, **227**, 84—109).—Muscle, under anaërobic conditions, changes its reaction chiefly by hydrolysis of creatinephosphoric acid and by formation of lactic acid and to a smaller extent by formation of ammonia, by esterification, etc. These changes result, in the first phases of anaerobic fatigue, in a gradual alkalisation which later passes over to an acidification. Only the alkalisation process occurs in muscle poisoned with iodoacetic acid. Both in normal and in poisoned muscle, the changes of acid–base equilibrium, as determined chemically, agree closely with those calculated from changes of tension of carbon dioxide.
P. W. CLUTTERBUCK.

Effect of enteral administration of biocatalysts from yeast on the course of chemical reactions in muscle and liver of exercising animals. J. A. COLLAZO, G. LISS, and C. PI-SUÑER BAYO (Biochem. Z., 1930, **227**, 326—333).—Administration of concentrated yeast extracts to rats which were kept well exercised produced increase of glycogen and of phosphorus and decrease of lactic acid, glutathione, and lactacidogen in the muscles. In the livers of such rats the glycogen, glutathione, and lactic acid contents are increased, whilst the phosphorus and lactacidogen contents are decreased. Examination of the livers and muscles of resting rats which received no yeast extract yielded results in harmony with the conclusions reached from observations on the exercising animals. W. MCCARTNEY.

Heat of rigor of mammalian muscle. E. C. SMITH (Proc. Roy. Soc., 1930, **B**, **107**, 214—222).—Measurements of the *post-mortem* rise in temperature and lactic acid content of the leg muscles of normal rabbits showed that the heat production during *rigor mortis* could be entirely accounted for by the breakdown of glycogen to lactic acid and the subsequent neutralisation of the latter. The muscle of a rabbit previously injected with iodoacetic acid showed no *post-mortem* production of heat or lactic acid. On the other hand, the muscles of rabbits starved for 24—48 hrs. showed a large excess heat production which could not be accounted for by the lactic acid produced. The *post-mortem* stiffening of normal rabbit's muscle as measured by a sclerometer was parallel to the production of heat. G. F. MARRIAN.

Variations in permeability of muscle-cell membranes and their biological effects. W. HOŁOBUT (Med. Doswiad., 1930, **11**, 189—197).—The immersion of muscle in isotonic calcium, magnesium, or hydrogen chloride solutions leads to the suppression of its excitability, which can, however, be restored by passing a constant current through the solution, using the muscle as the cathode; with the muscle as anode, the paralysing effect of the above salts is enhanced. Lithium and potassium chlorides and sodium hydroxide act in the inverse sense; in these excitability is restored by making the muscle the anode, and depressed by making it the cathode.
R. TRUSZKOWSKI.

Permeability. III. Cholesterol and lecithin in water and acid–base exchanges. J. DAHMLOS and A. SOLÉ (Biochem. Z., 1930, **227**, 401—428; cf. Spranger, A., 1930, 1054).—From examination of the blood and urine of rabbits to which lecithin, cholesterol, or ergosterol and also, in some cases, ammonium chloride or sodium hydrogen carbonate had been administered deductions are made concerning the permeability of tissues in the living organism and comparisons are made with results obtained *in vitro*.
W. MCCARTNEY.

Nitrogen content of normal and fasting white rats. S. DI FRISCO (Arch. Int. Physiol., 1930, **32**, 48—54; Chem. Zentr., 1930, i, 3324).—When the fat content is taken into account the nitrogen content per kg. of normal rats is surprisingly constant (3·6—4%); in hunger the values are 10% higher.
A. A. ELDRIDGE.

Nitrogen metabolism. I. Can ammonium salts replace proteins in the diet of white rats ? II. Relation between the nitrogen excreted and the nitrogen loss of fasting rats. U. LOMBROSO and S. DI FRISCO (Arch. Int. Physiol., 1930, **32**, 22—39, 40—47; Chem. Zentr., 1930, i, 3324).—I. Part of the nitrogen ingested as ammonium citrate is retained.

II. The nitrogen loss is much greater than that indicated by analysis of the urine and fæces.

A. A. ELDRIDGE.

Amino-acids of blood and tissues after injection of glycine. P. M. RE (Rev. Soc. Argentina biol., 1929, **5**, 498).—After injection of glycine (0·2 g. per kg.) a rise in blood-amino-acid is followed by a fall and a secondary rise. Hyper- is followed by hypo-glycæmia. Part of the glycine injected is eliminated in the urine. Normally the amino-acid-nitrogen of the liver is greater than that of kidney or muscle. The most marked increase was observed in the kidney. CHEMICAL ABSTRACTS.

Biological value of the proteins of mung bean, peanut, and bean curd. J. H. C. PIAN (Chinese J. Physiol., 1930, **4**, 431—436).—The biological values, determined on rats, of the proteins of mung bean (*Phaseolus aureus*), Chinese peanut (*Arachis hypogœa*), and curd made from soya bean are 58, 59, and 65%, respectively, and the coefficients of digestibility (nitrogen absorbed/nitrogen intake) 86, 95, and 96%, respectively. W. O. KERMACK.

Cereals and mineral metabolism. M. S. FINE (Cereal Chem., 1930, **7**, 456—465).—The occurrence or non-occurrence of rickets in rats fed on 60% whole wheat or 60% oats may be controlled by adjustment of the Ca : P ratio. Better growth and food consumption were observed with wheat than with oats.

E. B. HUGHES.

Mineral metabolism of dogs during inanition. S. SAKS (Acta Biol. Exp., Warsaw, 1930, **5**, 225—255).—The mineral excretion in the urine and fæces of dogs of about the same weight is fairly uniform during hunger for different animals, and amounts per kg. per diem over a 10-day period to 27·8 mg. P, 23 mg. S, 9·24 mg. Cl, 13·6 mg. Na, 48·3 mg. K, 7·38 mg. Ca, and 2·86 mg. Mg, with an excretion of 380 mg. N. Excretion of sodium and chlorine falls relatively with duration of inanition, whilst that of calcium rises. On the whole the rate of excretion of potassium is parallel to that of nitrogen, whilst that of magnesium is the most constant. The ratio of inorganic to organic phosphorus is the same during inanition as normally. Univalent cations are eliminated chiefly by the kidneys, as are also phosphorus and sulphur, whilst bivalent cations are chiefly excreted by the intestine. The ratio of calcium to phosphorus in the excreta during inanition is half that of the skeleton. The bases present in the excreta are not equivalent to the acids, the excretion of which rises during hunger. R. TRUSZKOWSKI.

Calcium metabolism. Citrates and urinary excretion of calcium. R. PROVERMAN and L. BRULL (Bull. Soc. Chim. biol., 1930, **12**, 1151—1157).—Oral or subcutaneous administration of sodium citrate lowers the serum-calcium, the urinary excretion of calcium being increased. These facts suggest that citrates play a part in the urinary elimination of calcium. F. O. HOWITT.

Phosphate metabolism. I. B. BLEYER and F. FISCHLER (Tierernahrung, 1930, **1**, 88—103; Chem. Zentr., 1930, i, 2118—2119).—The importance of the phosphoric acid esters with carbohydrates in animal and vegetable systems is discussed.

L. S. THEOBALD.

Pharmacological action of sea-water. III—V. A. RABBENO (Arch. Sci. biol., 1929, **14**, 26—40, 41—57, 58—75; Chem. Zentr., 1930, i, 3575).—Intravenous injection of sea-water increases the excretion of chloride, the curve being S-shaped. Sea-water, but not sodium chloride solution, mitigates glycosuria by increasing the production of urine. Injection of sodium chloride solution increases the excretion of water and greatly increases that of chloride. In general, sea-water is more toxic than sodium chloride solution. The difference is attributed to a high magnesium content associated with a low calcium content. A. A. ELDRIDGE.

Effect of the cations of Ringer's solution on the dimensions of the vessels of the frog. M. KOCHMANN (Biochem. Z., 1930, **227**, 488—491; cf. Misske, A., 1930, 809).—The combined action of the sodium, potassium, and calcium ions of Ringer's solution produces, in general, a contraction of the vessels of the frog, but if the proportions of the ions are altered (within isotonic limits) a relatively small series of mixtures which produce dilation can be prepared. The series of mixtures which can maintain the vessels at a constant dilation for periods of several hours is also relatively small. Very small alterations in the proportions of the different cations may produce large changes in the effect on the vessels and may even suffice, in some cases, to reverse it. A solution containing 0·5612% NaCl, 0·0234% KCl, and 0·0575% $CaCl_2$ is particularly suitable for use in the investigation of pharmacological action. W. MCCARTNEY.

Metabolic reactions to acidosis produced by ammonium chloride. N. MORRIS and O. MACRAE (Arch. Dis. Childhood, 1930, **5**, 207—227).—Administration of ammonium chloride, not associated with the appearance of acidosis, was accompanied by an increase in the blood-chlorine, -calcium, and -non-protein-nitrogen and in the urinary and fæcal calcium and phosphorus, whilst the blood-carbon dioxide and -phosphorus were diminished.

CHEMICAL ABSTRACTS.

Early diagnosis of lead poisoning. I. FLECKEL and I. TSCHERNOV (Zentr. Gewerbehyg. Unfallverhut., 1930, **17**, 65—74; Chem. Zentr., 1930, i, 3327).—The increased reticulocyte content of the blood is an early symptom. A. A. ELDRIDGE.

Lead poisoning; changes in the bone marrow. J. SPERANSKY and R. SKLIANSKAJA (Folia Hæmat., 1928, **36**, 289—315; Chem. Zentr., 1930, i, 3327—3328).—Experiments with guinea-pigs are described.

A. A. ELDRIDGE.

Mobilisation of lead under the influence of potassium iodide and sodium hydrogen carbonate. S. SCHACHNOVSKAJA (Z. ges. exp. Med., 1930, **70**, 513—526; Chem. Zentr., 1930, i, 3693).—

Administration of potassium iodide or sodium hydrogen carbonate to rabbits 7 months after poisoning by lead salts caused excretion of lead; the latter reagent caused a renewal of toxic symptoms.

A. A. ELDRIDGE.

Investigation into the distribution of lead in the organism on basis of a photographic (radiochemical) method. S. LOMHOLT (J. Pharm. Exp. Ther., 1930, **40**, 235—245).—A solution of lead chloride containing a very small quantity of the isotopic radium-*D* is injected subcutaneously into a suitable animal (*e.g.*, a young mouse or rat). The tissues of the animal after death are fixed in alcohol and sectioned. A section of a particular organ is allowed to remain in contact with a photographic plate with a thin gelatin coating for 1—20 days and the latter then developed. The degree of blackening of the plate gives a measure of the radium-*D* and therefore of the lead present in the section. The lead is deposited largely in the bones, to some extent in the liver and in the kidney cortex, but very little in the medulla. Only a very small amount is found in the brain.

W. O. KERMACK.

Pharmacology and pharmaco-dynamics of ointments. VI. Ung. hydr. praec. alb. Ph.G. [ointment containing NH_2·Hg·Cl]. C. MONCORPS (Arch. exp. Path. Pharm., 1930, **155**, 51—69).—Only slight absorption through the skin occurs, chiefly by way of the hair follicles. The nature of the base of the ointment has little effect on the rapidity of absorption of the mercury.

W. O. KERMACK.

Toxic action of baking-powders containing alum. A. CERIOTTI (Rev. fac. cienc. quim. La Plata, 1930, **6**, 51—53).—The aluminium chloride formed in the gastric juice is not precipitated by the alkaline pancreatic juice; the absorption of aluminium may lead to displacement of iron in organs such as the pancreas.

CHEMICAL ABSTRACTS.

Decomposition of amino-acids in the animal body in phosphorus poisoning. J. ARAI (Acta Schol. Med. Kyoto, 1930, **12**, 445—448).—Increased excretion of nitrogen indicates increased breakdown of protein. A slight decrease in the carbon dioxide output may indicate that the fatty acids produced by deamination of the amino-acids are not oxidised, but stored as fat.

CHEMICAL ABSTRACTS.

Iron content and resistance of the organism to hydrogen cyanide and hydrogen sulphide. F. KEESER (Arch. exp. Path. Pharm., 1930, **156**, 340—345).—Three groups of rabbits were fed on rice, greens, and greens together with ferrous chloride, respectively. The hæmoglobin content of the blood, and the iron content of the tissues of the animals in the last group were increased as compared with the first. The third group showed the smaller susceptibility to the toxic effects of sodium cyanide administered orally and of sodium sulphide subcutaneously, whilst the animals of group II were more resistant than those of group I.

W. O. KERMACK.

Salicylates. XIX. Question of acidosis following the administration of salicylates. C. C. JOHNSON (J. Amer. Med. Assoc., 1930, **94**, 784—789).—Sodium or ammonium salicylate or acetylsalicylic acid, administered gastrically or hypodermically to dogs and cats, caused respiratory stimulation with depletion of the alkali reserve of the blood; the p_H was unchanged, and acetone was not found in the urine.

CHEMICAL ABSTRACTS.

Influence of oxidation and tissue respiration on the toxicity of quinol on the frog's musculature. F. HINTEREGGER (Arch. exp. Path. Pharm., 1930, **155**, 354—380).—The toxic action of quinol on the frog's musculature is apparently due to the formation of quinone, and conditions such as further oxidation or strong alkali which inactivate the latter reduce the toxicity of quinol. Manganous sulphate increases the toxicity independently of p_H, presumably through its catalytic action in accelerating formation of quinone. The toxicity of quinol is not related to cell respiration. The muscles of animals treated with thyroxine, which has no action on the respiratory rate of intact frog's muscle, are abnormally sensitive to quinol, probably as the result of increased permeability of the cells. Lactic, pyruvic, and succinic acids reduce the toxicity of quinol, whilst sucrose has the opposite effect. Moderate stimulation of the muscle does not result in change of its sensitiveness to quinol, but complete exhaustion much increases it. The amount of quinol which disappears during perfusion of a limb is not affected by substances increasing cell permeability.

W. O. KERMACK.

Toxic properties of ethyl phthalate. P. BLICKENSDORFER and L. TEMPLETON (J. Amer. Pharm. Assoc., 1930, **19**, 1179—1181).—Ethyl phthalate, when injected intravenously into animals in doses of 0·25 c.c. per kg., may cause death by paralysis of the respiratory centre, but administration to rabbits, by means of a stomach-tube, in doses of 3 c.c. per kg. for eight successive days caused no abnormal after-effects. It is rapidly excreted by the kidney. Doses that are insufficient to cause paralysis may cause convulsions.

E. H. SHARPLES.

Effect of phloridzin intoxication on the sugar content of the aqueous humour. W. TYCHOWSKI (Med. Doswiad., 1930, **11**, 331—343).—The sugar content of the aqueous humour of dogs rises during the first 20—50 min. of phloridzin intoxication and then falls.

R. TRUSZKOWSKI.

Action on the frog's heart of new glucosides isolated from *Digitalis lanata*. K. W. MERZ (Arch. exp. Path. Pharm., 1930, **156**, 277—289).—The pharmacological actions of *lanata* glucoside I (*lanadigin*), II, III, and IV and the genins I, III, and IV have been investigated. The following data are given: lanadigin, $C_{41}H_{66}O_{17},4H_2O$, m.p. 245°, $[\alpha]_D^{20}$ +33·3°; glucoside III, $C_{36}H_{56}O_{14}$, m. p. 228—229°; glucoside IV, $C_{42}H_{66}O_{16}$, m. p. 195°, subsequently begins to melt at 225° after resolidifying, $[\alpha]_D^{20}$ about +5·5° in methyl alcohol.

W. O. KERMACK.

Pharmacological assay of strophanthin solutions. H. FASCHING (Arch. exp. Path. Pharm., 1930, **156**, 211—225).—A method for the assay of strophanthin employing the isolated *R. temporaria* heart is described.

W. O. KERMACK.

Action of rotenone on mammals. D. E. BUCKINGHAM (Ind. Eng. Chem., 1930, **22**, 1133—1134).—Rotenone administered by mouth in doses of 4 grains to sheep or pigs produced no visible effect. Dogs were not affected by doses up to 1 grain per lb. body-weight. *Derris* extract when administered by mouth was likewise without effect. B. W. TOWN.

Blood-calcium and -sugar, and opium preparations. H. ZAHLER (Deut. med Woch., 1930, **56**, 522—523; Chem. Zentr., 1930, i, 3455).—Opium, "pantopon," morphine, and "dilaudide" in therapeutic doses cause a rise in blood-sugar, which afterwards falls to a subnormal value. With equal daily doses the effect on the blood-sugar begins to vanish. The calcium metabolism appears to be more closely associated with the sedative action of the opiate. A. A. ELDRIDGE.

Effect of chronic injections of morphine on the nitrogen balance of dogs. N. P. PYATNITZKI and P. N. FEDOROV (Zhur. exp. Biol. Med., 1929, **11**, 54—57).—The nitrogen balance of dogs is unaffected by chronic injections of 0·01—0·02 g. of morphine. Tolerance is rapidly developed. Subsequent omission of the injection produces a negative nitrogen balance. CHEMICAL ABSTRACTS.

Poisoning by the seeds of the thorn apple (*Datura stramonium*). A. SARTORI (Chem.-Ztg., 1930, **54**, 890).—A fatal case of poisoning is recorded. Tests revealed the presence of atropine in the stomach and intestines. A. R. POWELL.

Pharmacological assay of aconitine solutions. W. BRANDT (Arch. exp. Path. Pharm., 1930, **156**, 203—210).—The characteristic action exerted in the frog's heart by aconitine in concentration of 1/750,000—1/1000,000 is used for the assay of aconite preparations. W. O. KERMACK.

Elimination of the chlorides and citrates of bismuth and quinine. H. F. LENORMAND (J. Pharm. Chim., 1930, **12**, [viii], 159—168).—Insoluble salts of bismuth, as the double chloride of bismuth and quinine, and the basic carbonate, in suspension in oil, injected intramuscularly into the dog are found in the urine for a longer period than in the case of the more soluble double citrate. The iodobismuthate, although it is similar to the double chloride in insolubility and dissociation by water, behaves similarly to the double citrate as regards elimination. Of the bismuth introduced only 46—54% was recovered in the urine over a period of 30 days. In the case of quinine the period of elimination is much shorter, but slower for the double chloride than for the double citrate. Of the quinine introduced 32—44% was recovered in the urine. W. J. BOYD.

[Pharmacology of] "sympatol." G. KUSCHINSKY (Arch. exp. Path. Pharm., 1930, **156**, 290—308).—The pharmacological action of "sympatol" (methyl-β-*p*-hydroxyphenyl-β-hydroxyethylamine) has been investigated. Compared to adrenaline the action of "sympatol" is more marked on the heart relative to its action on the blood-vessels, whilst the *m*-isomeride has a more marked action on the blood-vessels. W. O. KERMACK.

Physiological action of 3 : 4-dihydroxyphenylaminomethylcarbinol. RAYMOND-HAMET (Compt. rend., 1930, **191**, 869—871).—The conclusion of Barger and Dale (A., 1910, ii, 984) that 3 : 4-dihydroxyphenylaminomethylcarbinol (arterenol) is somewhat more active than adrenaline as a hypertensive agent is confirmed. As in the case of adrenaline, this action is sensitised by cocaine, but, whilst the action of adrenaline is neutralised by yohimbine, the action of "arterenol," in this respect resembling ephedrine, is unaffected. Unlike ephedrine in large doses, however, "arterenol," even when administered in lethal quantities, does not show a hypotensive action. T. H. MORTON.

Alloxan as an oxidising agent for thiol groups, as a capillary poison, and as a convulsive poison. R. LABES and H. FREISBURGER (Arch. exp. Path. Pharm., 1930, **156**, 226—252).—The toxic action of alloxan on the organism is correlated with (1) the tendency to form the strongly acidic alloxanic acid so that the p_H of the cells becomes unduly low, and (2) the ease with which alloxan is reduced by thiol groups (*e.g.*, cysteine). The formation of murexide in the tissues of mice injected with alloxan has been demonstrated. W. O. KERMACK.

[Toxicity of] iodised and arsenated pyridine derivatives. IV. A. BINZ, C. RATH, and K. JUNKMANN (Biochem. Z., 1930, **227**, 200—204).—The toxicities of the relatively poisonous substances, pyridine and 2-pyridone, and their less poisonous iodinated and arsenated derivatives are compared by intravenous injection into rats (cf. A., 1930, 1213). The toxicity of pyridine and 2-pyridone is of the same order. Substitution of an arsinic acid residue in position 5 or attachment of an acetic acid residue to the nitrogen atom considerably decreases the toxicity. Substitution of iodine in position 5 renders the 2-pyridone nucleus more toxic, but attachment also of an acetic acid residue to the nitrogen atom gives a much less toxic derivative. The toxicity of the same amount of iodine in "uroselectan" (sodium salt of 5-iodo-2-pyridone-*N*-acetic acid), sodium iodide, "selectan" (5-iodo-2-pyridone), "yatren," and "alival" is as 1 : 3·6 : 6·4 : 46·7 : 88. P. W. CLUTTERBUCK.

Sources of error in forensic determination of alcohol. L. KOHBERG (Deut. Z. ges. gerichtl. Med., 1930, **15**, 75—87; Chem. Zentr., 1930, i, 3470).—In diabetes the blood-alcohol is not appreciably above the normal value. Acetone must be tested for, and determined if necessary. In uræmia the blood-alcohol value is usually below the normal. Chloral, arising from chloral hydrate, affects the value; carbon monoxide does not give rise to significant error. The post-mortal action of alcohol-oxidase can, in the absence of bacterial decomposition, be neglected. The effect of non-alcoholic beverages and various fruits on the blood-alcohol cannot be ignored. A. A. ELDRIDGE.

Detoxication in the animal organism. I. Detoxication of "avertin." H. WAELSCH. **II. Glutathione content of blood and toxicity.** H. WAELSCH and E. WEINBERGER (Arch. exp. Path. Pharm., 1930, **156**, 356—369, 370—376).—In white mice anæsthetised by "avertin" (tribromoethyl alcohol), thiosulphate, colldoial sulphur, cysteine, and

"detoxin" (a commercial preparation of protein nature), but not sulphite or cystine, exert a protective action against the toxic effects of the anæsthetic.

II. During "avertin" anæsthesia, the glutathione content of the blood of man and of the rabbit is decreased. The glutathione content of human blood is lowered by oral administration of sodium phenylacetate (4 g.). This may be the result of the coupling of the phenylacetic acid with glutamic acid prior to excretion. W. O. KERMACK.

Adsorption and narcotic action. H. H. KING, J. L. HALL, A. C. ANDREWS, and H. L. COLE (J. Pharm. Exp. Ther., 1930, **40**, 275—289).—The surface tension of aqueous solutions of trional, tetronal, butylchloral hydrate, sulphonal, bromal hydrate, triacetin, diacetin, chloral hydrate, ethylurethane, monoacetin, methylurethane, and ethyl methyl carbamate have been measured (1) at a water–air interface, (2) at a water–paraffin interface, and (3) at a water–paraffin solution of lecithin interface. No general relationship was found between the adsorption at the water–air interface and narcotic action of the compound measured by its liminal value except in homologous series. The adsorption curves referring to the water–paraffin solution of lecithin surface are with certain narcotics somewhat irregular, which may be the result of chemical reaction in the surface layer between the narcotic and the adsorbed lecithin. With a few exceptions capable of explanation, there is a strong relationship between the narcotic action and the adsorption at the pure paraffin–water interface, the magnitude of adsorption increasing as the liminal value decreases. A similar though not quite so definite relationship is found between narcotic action and adsorption at a water–paraffin solution of lecithin interface. W. O. KERMACK.

Toxicology of local anæsthetics. G. TAUBMANN and G. JUNG (Arch. exp. Path. Pharm., 1930, **156**, 18—25).—The toxicity of a 1% novocaine solution is approximately doubled by the addition of 2·5 mg. of adrenaline per 100 c.c. The use of freshly prepared novocaine solutions containing 0·4% of potassium sulphate and 0·0005% of adrenaline is recommended. W. O. KERMACK.

Physiology of pyrimidines. III. Intermediary metabolism of uracil. L. R. CERECEDO (J. Biol. Chem., 1930, **88**, 695—700).—Administration of *iso*barbituric acid and of *iso*dialuric acid to dogs by mouth causes an increase in the amount of urea excreted and a decrease in the inorganic sulphates. It is concluded that these compounds are partly oxidised to urea and some unknown carbon compound and partly excreted as ethereal sulphates. It is suggested that they form intermediate steps in the oxidation of uracil in the body. W. O. KERMACK.

Reduction of osmotic pressure in serum by narcotics and hypnotics. M. R. BONSMANN and B. BRUNELLI (Arch. exp. Path. Pharm., 1930, **156**, 125—130).—The colloidal osmotic pressure of the blood-serum of the dog is reduced by 78—184 mm. of water by the administration of various narcotics, *e.g.*, "luminal," ether, chloral hydrate, and "pantopon," without any corresponding fall in the concentration of serum-protein. The lowered osmotic pressure coincides with a reduced urinary flow.
W. O. KERMACK.

Chloroform content in various tissues during anæsthesia and its relationship to theories of narcosis. J. L. McCOLLUM (J. Pharm. Exp. Ther., 1930, **40**, 305—325).—The solubility of chloroform in water at 37·5° is 1 g. per 100 c.c. The partition coefficient of chloroform between olive oil and water at 37·5° is 110. The chloroform content of the tissues of dogs submitted for various periods to chloroform anæsthesia has been determined as well as the lipin and water content of various tissues. Corpuscles contain more chloroform than does plasma, the excess being more than can be accounted for by their greater lipoidal content. Anæsthesia is produced when the brain cells contain about half the amount of chloroform that they can contain without the death of the animal. The passage of chloroform into the brain cells is progressive. The results do not support the Meyer–Overton theory of anæsthesia.
W. O. KERMACK.

Reduction of oxidation during ether narcosis. H. FUSS and E. DERRA (Arch. exp. Path. Pharm., 1930, **156**, 64—84).—In dogs anæsthetised by the ether drop method, the oxygen content of the arterial blood is considerably below normal and the lactic acid content is increased. When the ether–air method is used the oxygen content is slightly below the normal and the lactic acid content is slightly raised. With the ether–oxygen method the oxygen content is increased and the lactic acid content is not above normal. In all cases the hæmoglobin content is increased. The increase of lactic acid in the blood during ether narcosis appears to be related to the degree of oxygen unsaturation. W. O. KERMACK.

Effect of ether anæsthesia and shock on blood-calcium. W. C. EMERSON (J. Lab. Clin. Med., 1928, **14**, 195—200).—Ether anæsthesia and asphyxia are followed by an increase (18 or 20%, respectively) in the serum-calcium; following anæsthesia with hyperventilation the serum-calcium decreases slightly. Shock has no effect on the serum-calcium.
CHEMICAL ABSTRACTS.

Diuretin hyperglycæmia in cats. I. FUJI (Tohoku J. Exp. Med., 1930, **15**, 285—323).—Diuretin administered subcutaneously to cats (0·35—0·5 g. per kg.) caused immediate hyperglycæmia with two maxima; during this period food caused marked alimentary hyperglycæmia. Section of the splanchnic nerves and semilunar ganglia prevented the primary hyperglycæmia. Glycosuria appears during the second phase. The urine contains salicylic acid.
CHEMICAL ABSTRACTS.

Sensitiveness of white mice to poisons after treatment with "caseosan," "sufrogel," and alcohol. H. VOLLMER (Arch. exp. Path. Pharm., 1930, **155**, 160—184).—White mice are less sensitive to the action of alcohol if "caseosan" has been administered 2—7 days previously. They are not protected against morphine, colchicine, or quinol. "Sufrogel" does not protect against alcohol. Repeated daily administration of alcohol usually results in a decrease in sensitiveness only on the fourth and

fifth days, after which the sensitiveness is greater than normal. W. O. KERMACK.

Sensitiveness of white mice to poisons after treatment with substances increasing oxidation. H. VOLLMER and C. BUCHHOLZ (Arch. exp. Path. Pharm., 1930, **155**, 185—218).—Previous administration to white mice of various compounds likely to increase the rate of oxidation in the organism (thyroxine, sodium lactate, dextrose, and methylene-blue) reduces their sensitiveness to the narcotic effects of alcohol, but increases it to the toxic effects of quinol and colchicine. Their sensitiveness to morphine is not influenced by administration of thyroxine nor did sodium succinate have any action in this respect. W. O. KERMACK.

Increase of oxidation and alteration of sensitiveness to poisons of white mice by irradiation. H. VOLLMER and J. BEHR (Arch. exp. Path. Pharm., 1930, **155**, 219—247).—When white mice are irradiated with an Osram-vitalux or with a quartz-mercury lamp their sensitiveness is decreased to the toxic effects of alcohol but increased to quinol and colchichine. Their sensitiveness to morphine is unaltered. Application of the method of Lipschitz to the tissues of irradiated rats indicates an increase of the oxido-reductive mechanism.

W. O. KERMACK.

Influence of irradiation on the sensitiveness of white mice to poisons. O. RIESSER and A. HADROSSEK (Arch. exp. Path. Pharm., 1930, **155**, 139—159).—By irradiation of white mice or rats with an Osram-vitalux lamp, they are protected against narcotic doses of ethyl alcohol, the ultra-violet rays being those responsible for the action. The animals could not be protected against the narcotic action of chloral hydrate or paraldehyde by irradiation sufficient to protect against ethyl alcohol, nor could they be protected against the lethal action of acetonitrile, morphine, hydrogen sulphide, or tetanus toxin.

W. O. KERMACK.

Differential action of *X*-rays on tissue, growth, and vitality. I. II. Biological reaction in relation to "antagonism." III. Biological reaction in relation to area. IV. Biological reaction in relation to time. W. MOPPETT (Proc. Roy. Soc., 1929, **B**, **105**, 402—421; 1930, **B**, **107**, 293—301, 302—307, 308—312).—I. Histological observations of the reaction of the allantoic membrane of the embryo chick to *X*-rays are described. Atrophy and hypertrophy of a particular tissue are associated with definite wave-length bands. The maximum destruction is observed at 0·5 Å. in 1·25 hrs., whilst growth is stimulated by exposure for 0·5 hr. to the same radiation. Neutralisation of biological action ("antagonism") occurs with mixed radiation. It is suggested, in view of the magnitude of effective wave-lengths, that biological changes are due to atomic ionisation.

II. Further experimental confirmation of "antagonism." Atrophy by normally effective diffracted *X*-rays is also prevented by prior exposure to direct radiation.

III. The threshold dose of *X*-radiation for a reaction varies as the area of tissue irradiated. This is explained by summation of stimuli from adjacent parts so that the threshold dose is inversely proportional to the square of the area when the area is small.

IV. The inverse relationship between threshold dose and time of exposure is modified by atomic changes and biological repair. Mouse skin is more resistant to *X*-rays than is the allantoic membrane.

A. COHEN.

Effect of diathermy on serum-protein concentration and fractions of human serum. H. HIRSCH (Arch. exp. Path. Pharm., 1930, **156**, 346—355).—Application of diathermy of short duration results in a decrease of the concentration of serum-protein with an increase in the globulin–albumin ratio and a decrease in the viscosity.

W. O. KERMACK.

A new enzymic oxidation (metaoxidase). I. BOAS (Biochem. Z., 1930, **227**, 135—139).—Plant juices contain an extremely thermolabile substance which gives with an alcoholic solution of benzidine and guaiacum a rose-red and a deep blue colour, respectively, the pigments being extractable with amyl alcohol, ether, and chloroform. This substance is designated *metaoxidase*, but it is not decided whether it is a new enzyme or one of the group of phenolases. It is present exclusively in plant foods and is entirely absent from animal foods (flesh, fish, milk, eggs). Market vegetables are poor, but fruits, especially stone fruits, and mushrooms are very rich in metaoxidase. Market vegetables, on the other hand, are rich in peroxidase. Whereas treatment of plant juice with 3% hydrogen peroxide for 24 hrs. does not decrease the peroxidase and oxidase action of the juice, the metaoxidase is completely destroyed. Metaoxidase is not identical with tyrosinase and is rapidly destroyed by the action of gastric juice.

P. W. CLUTTERBUCK.

Action of adenosinemonophosphoric acids and adenosinetriphosphoric acid on dehydrogenation processes induced by plant and animal enzymes. H. J. DEUTICKE (Z. physiol. Chem., 1930, **192**, 193—216).—The dehydrogenase prepared from the seeds of *Corchorus capsularis* was studied by means of the Thunberg technique. The hexosediphosphoric acid from muscle and that from yeast behaved similarly in accelerating methylene-blue reduction. The reduction in presence of boiled muscle extract is principally due to adenosinetriphosphoric acid. Muscle-adenylic acid, which is inactive alone, in low concentration accelerates reduction after addition of hexosediphosphate and especially of monophosphate, but does not affect the rate of decolorisation produced by adenosinetriphosphate. In higher concentrations it has an inhibiting effect. Inhibition is produced by yeast-adenylic acid at all concentrations. Dehydrogenase preparations from muscle are also stimulated by adenosinetriphosphoric acid and to a smaller degree by hexosediphosphoric acid. Muscle-adenylic acid alone (but not yeast-adenylic acid), inosic acid, and its corresponding pentosephosphoric acid stimulate the muscle enzyme. J. H. BIRKINSHAW.

Dehydrogenating power of cereal seeds in presence of plant acids and purines as hydrogen donators. A. FODOR and L. FRANKENTHAL (Bio-

chem. Z., 1930, **225**, 417—425).—The dehydrogenating actions of wheat, barley, and oats were compared. Extracts of the flour showed only self-dehydrogenation and dehydrogenation of added donators in presence of boiled yeast juice. Boiled pea juice at high concentrations has an activating effect on wheat and barley extracts. With wheat, strong self-dehydrogenation occurs. Potassium malate, which hastens dehydrogenation in presence of boiled yeast juice, here acts as an inhibitor. With wheat, in presence of yeast juice, formate, malate, and purines are most active in stimulating dehydrogenation; with barley, citrate, pyruvate, malate, purines, and especially oxalate; with oats, pyruvate, oxalate, and especially malate. Phosphate inhibits the action of wheat, but favours that of barley and oat extracts.

J. H. Birkinshaw.

Active group of liver-catalase. K. Zeile and H. Hellstrom (Z. physiol. Chem., 1930, **192**, 171—192).—Purified extracts of horse's liver showing high catalase activity contained a porphyrin–iron complex, characterised by its specific absorption bands, 629, 540, and 500 mμ. The enzymic activity was directly proportional to the amount of iron–porphyrin present in the preparation. The complex yields dissociable hydrocyanic acid and hydrogen sulphide compounds; the inhibition of the catalase action by these poisons is thus explained. The dissociation constant of the hydrocyanic acid compound, about 8×10^{-7}, confirms the value of the dissociation constant for catalase–hydrocyanic acid obtained from the kinetics of the reaction.

J. H. Birkinshaw.

Mechanism of enzyme reactions. I. Influence of hydrogen-ion concentration on the action of liver-esterase. H. G. K. Westenbrink and H. M. Romijn. **II. Hydrolysis of a mixture of two esters by liver-esterase.** H. G. K. Westenbrink (Arch. Néerland. Physiol., 1930, **15**, 529—537, 538—544).—I. The action of liver-esterase on the monoethyl esters of the homologous series of dibasic aliphatic acids (oxalic to sebacic) at various p_H values of the reaction mixture was investigated. The optimum p_H progressively increases from 5·6 to 7·3 as the series is ascended. No relation exists between the p_H–activity and p_H–ionisation curves for any of the acids; hence the p_H–activity curves for these substrates are determined merely by their structure.

II. In the action of liver-esterase on a mixture of the monoethyl esters of sebacic and azelaic acids the enzyme is divided between the substrates and consequently the reaction velocity lies between those observed for the separate reactions. The results are contrasted with those obtained by Northrop (A., 1922, i, 693) on the hydrolysis of proteins by trypsin.

F. O. Howitt.

Susceptibility of various sugars to fermentation by rat's liver: its dependence on the state of nourishment of the animal and on the time of year. O. Rosenthal (Biochem. Z., 1930, **227**, 354—384).—The fermentation of lævulose, glyceraldehyde, and dihydroxyacetone, but not that of glycogen, sucrose, maltose, lactose, galactose, mannose, dextrose, and hexosediphosphoric esters, is greatly accelerated by the presence of liver tissue from rats which have been sufficiently fed. The liver tissue from fasting rats has only a slight accelerating effect, and even amongst tissues from the other rats wide differences in accelerating power occur according to the compound concerned and to the time of year at which the rats are used. The differences in the behaviour of the various tissues are attributed to variations in their content of a fermentation activator. The rate of dismutation of methylglyoxal by the tissues is about four times as great as the maximum rate of fermentation of lævulose or of glyceraldehyde and is almost independent of the state of nourishment of the rats and of the time of year at which they are used. It is supposed that the amount of activator in the tissue is always sufficient to accelerate this dismutation, but only sometimes sufficient for acceleration of the other fermentations.

W. McCartney.

Intestinal nucleotidase. P. A. Levene and R. T. Dillon (J. Biol. Chem., 1930, 88, 753—769).—The action of intestinal nucleotidase on the following compounds has been studied at p_H 8·6—8·7: glyceryl phosphate, hexosemonophosphate from α- and from β-di*iso*propylidenefructose, Neuberg's monophosphate, hexosediphosphate and its methylglucoside, hexosemonophosphate from mono- and from di-*iso*propylideneglucose, adenylic acid, inosic acid, uridinephosphoric acid, yeast-nucleic acid, and thymus-nucleic acid. The nucleotides are hydrolysed almost as rapidly as are the sugar esters, but the nucleic acids are acted on much more slowly. Uridinephosphoric acid is more rapidly hydrolysed than is adenylic acid and the latter more rapidly than inosic acid. Thymus-nucleic acid is sometimes more resistant than yeast-nucleic acid. The rates of hydrolysis of hexosediphosphate and its methylglucoside are exactly the same. Different samples of enzyme prepared by precipitation from a solution with acetone usually hydrolysed a standard glycerophosphate solution at approximately the same rates and showed a constant parallelism in their capacity for hydrolysing both nucleotide and thymus-nucleic acid, but one sample behaved exceptionally. The use of magnesium to remove phosphate ions formed in the reaction was not advantageous.

W. O. Kermack.

Destruction, in the seed of *Soja hispida*, of one enzyme without suppression of activity of two others. R. Fosse, A. Brunel, P. de Graeve, P. E. Thomas, and J. Sarazin (Compt. rend., 1930, **191**, 1025—1028).—By heating an aqueous extract of ground soya beans for 30 min. at 78°, keeping this for 24 hrs. at 0°, and centrifuging, the activity of uricase is completely destroyed, whilst that of urease and allantoinase is unimpaired. The same result is obtained by drying the beans themselves in a vacuum over calcium chloride (the water content falling from 13·1% to 6·9%), and keeping them in sealed tubes at 82° for 50 hrs.

C. W. Shoppee.

Basic processes of the Abderhalden reaction. E. Abderhalden and S. Buadze (Fermentforsch., 1930, **12**, 129—179).—A general exposition and confirmation.

J. H. Birkinshaw.

Appearance of the Abderhalden reaction after parenteral administration of the pituitary preparation "praehormone," and of the ovarian

hormone "folliculin." E. ABDERHALDEN and S. BUADZE (Fermentforsch., 1930, **12**, 262—272).—After injection of praehormone or folliculin castrated animals gave the Abderhalden reaction with ovarian tissue. J. H. BIRKINSHAW.

Activation of cathepsin and papain. E. WALDSCHMIDT-LEITZ and A. PURR (Naturwiss., 1930, **18**, 952—953).—The action of papain on gelatin, purified by a process including treatment with potassium cyanide, in presence of citrate buffer incubated at 30°, with and without the addition of hydrocyanic acid or of a thiol compound (*e.g.* glutathione), was investigated. The presence of the activator resulted in an increased amino-nitrogen production in both cases. Hence the authors conclude that the question of whether catheptic activation (Willstatter and Bamann, A., 1929, 354) depends on a reaction of activator with enzyme or on a complex formation with inhibitory metals (Krebs, A., 1930, 957) is still unsettled. F. O. HOWITT.

Determination of peptic activity: the Gates method of proteolytic titration. A. GILMAN and G. R. COWGILL (J. Biol. Chem., 1930, **88**, 743—752).—The pepsin solution adjusted to a determined p_H value is allowed to act at 25° on the gelatin film of a photographic plate containing reduced silver and so arranged that as the gelatin is digested, the liberated silver particles fall to the bottom of the fluid and so do not interfere with the continuation of the reaction. After a suitable interval the opacity of the remaining gelatin film is measured in a colorimeter, comparison being made with a suspension of silver obtained by dissolving away the gelatin of a reduced film. The loss in opacity of the film is a measure of the activity of the pepsin. The method is very satisfactory and requires only small quantities (0·5 c.c.) of pepsin solution. W. O. KERMACK.

[**Concentration of pepsin and chemistry of its action.**] B. LUSTIG (Biochem. Z., 1930, **227**, 385).—The differences between individual results calculated according to the method of Smorodincev and Adova (A., 1930, 1475) do not correspond with the differences in the activities of the samples of pepsin used. It is the changes which the amino- and carboxyl groups undergo and not their amount or ratio which are important for the action of pepsin. W. McCARTNEY.

Capability of dilute alkali hydroxide, erepsin, and trypsin-kinase for hydrolysing the CO·NH linking in polypeptides and related compounds in which the amino- and carboxyl groups are variously substituted. E. ABDERHALDEN and E. RIESZ (Fermentforsch., 1930, **12**, 180—222).—A number of widely varying substrates were prepared, usually by condensing the requisite chloride with the amino-acid: p-*cresoldisulphonyl*-dl-*leucylglycine*, m. p. 140°; m-*cresoldi*(*sulphonyl*-dl-*leucine*)*mono*(*sulphonyl*-dl-*leucylglycine*), m. p. 117—120°, from *m*-cresoltrisulphonyl chloride and *dl*-leucylglycine methyl ester; m-*cresoltrisulphonyl*-dl-*leucine ethyl ester*, m. p. about 60°, yielding with *N*-sodium hydroxide m-*cresol trisulphonyl*-dl-*leucine*, m. p. (indef.) 80—120°; o-*cresoldisulphonylglycine*, m. p. 128°; m-*carboxybenzenesulphonylglycine*, m. p. 178°; m-*carboxybenzenesulphonyl*-dl-*leucine*, m. p. 187°; m-*carboxybenzenesulphonyl*-dl-*leucylglycine*, m. p. 190°; *di*(*ethanesulphonyl*-dl-*leucyl*)*diketopiperazine*, m. p. 140°, from ethanesulphonyl chloride and *dl*-leucylglycine; a *compound*, $C_{11}H_{20}O_5N_2S$, m. p. 117°, from β-bromoethanesulphonyl chloride and leucylglycine methyl ester; *benzoylglycylaspartic acid*, m. p. 191°; o-*nitrophenylthiolglycine ethyl ester*, m. p. 83°; o-*nitrophenylthiol*-dl-*leucine ethyl ester*, m. p. 90°; o-*nitro*-p-*chlorophenylthiol*-dl-*leucine ethyl ester*, m. p. 99°; o-*nitro*-p-*chlorophenylthiol*-dl-*leucylglycine*, m. p. 128—130° (*methyl* ester, m. p. 97—100°); *dichlorodinitrophenylthiol oxide*, sinters at 115°, decomp. at high temp.; o-*nitro*-p-*chlorophenylthiol*-dl-*leucine*, m. p. 126°; *phenyl*-dl-*leucylglycine*, m. p. 139°; *dinitrophenyl*-dl-*leucylglycine*, m. p. 150—152°; 2 : 4-*dinitrophenylcystine*, m. p. 156°, from 1-chloro-2 : 4-dinitrobenzene and cysteine hydrochloride; p-*aminobenzoyl*-dl-*leucylglycine*, m. p. above 250°, from *p*-aminobenzoyl chloride, m. p. 31°, which readily forms p-*aminobenzoyl*-p-*aminobenzoic acid*, m. p. above 300° (decomp.); p-*aminobenzoyl*-dl-*leucylglycine methyl ester*, m. p. 60°; o-*chlorobenzoyl*-dl-*leucylglycine*, m. p. 208—210°; o-*nitrobenzoyl*-dl-*leucylglycine*, m. p. 231°; o-*nitrobenzoyl*-dl-*leucine*, m. p. 145°, yielding on reduction o-*aminobenzoyl*-dl-*leucine anhydride*, m. p. 255°; o-*nitrobenzoylglycine*, m. p. 190°, yielding on reduction o-*aminobenzoylglycine anhydride*, m. p. 320° (decomp.); dl-α-*bromoisohexoyl*-o-*aminobenzoic acid*, m. p. 110°, yielding on ammation *leucyl*-o-*aminobenzoic anhydride*, m. p. 185° (*hydrochloride*, decomp. 215—220°), which on methylation gives a *monomethylimide*, m. p. 105°; α-*hydroxyisohexoyl*-o-*aminobenzoic acid*, m. p. 146°; *chloroacetyl*-dl-*leucyl*-o-*aminobenzoic acid*, m. p. 176°; *chloroacetyl*-o-*aminobenzoic acid*, m. p. 185°; *glycyl*-o-*aminobenzoic acid*, m. p. 215—220° (decomp.); dl-α-*bromoisohexoyl*-p-*aminobenzoic acid*, m. p. 173°; dl-*leucyl*-p-*aminobenzoic acid*, m. p. 220° (by-product, α-*hydroxyisohexoyl*-p-*aminobenzoic acid*, m. p. 193—195°); *chloroacetyl*-dl-*leucyl*-p-*aminobenzoic acid*, m. p. 217°; *toluenesulphonchloroacetamide*, m. p. 88—89°; N-*glycyltoluenesulphonamide*, m. p. 207°; N-α-*bromoisohexoylglycyl*-p-*toluenesulphonamide*, m. p. 137°; m-*carboxybenzenesulphonchloroacetamide*, m. p. 212° (decomp.), giving N-dl-α-*bromoisohexoylglycyl*-m-*carboxybenzenesulphonamide*, m. p. 174°; dichlorodiacetimide; diglycineimide; N-*chloroacetylbenzamide*, m. p. 157°; chloroacetylcarbamide; dl-*leucyltaurine*, m. p. 285°.

Various factors such as valency, position of entry of the substituent, strength of the acidity or basicity of the substituent, and polysubstitution exert an effect on the ease of hydrolysis of the CO·NH linking by dilute alkali hydroxide. J. H. BIRKINSHAW.

Removal of halogen by dilute alkali from stereoisomeric halogenoacylamino-acids and their behaviour towards erepsin and trypsin-kinase. E. ABDERHALDEN and F. SCHWEITZER (Fermentforsch., 1930, **12**, 231—243).—*dl*-Norvaline was separated into optically active components by formylation and crystallisation of the brucine salt. l-*Norvaline*, m. p. 300° (uncorr.), $[\alpha]^{22}$ −5·08°, with bromoacetyl bromide furnished *bromoacetyl*-l-*nor*-

valine, m. p. 92°, $[\alpha]_D^{20}$ $+9{\cdot}20°$. Likewise there were prepared *bromoacetyl*-d-*norvaline*, m. p. 95°, $[\alpha]^{20}$ $-8{\cdot}6°$; l-α-*bromopropionyl*-l-*norvaline*, m. p. 110°, $[\alpha]_D^{19}$ $-9{\cdot}0°$; l-α-*bromopropionyl*-d-*norvaline*, m. p. 105°, $[\alpha]^{20}$ $-18°$; d-α-*bromopropionyl*-d-*norvaline*, $[\alpha]_D$ $+8{\cdot}5°$; d-α-*bromopropionyl*-l-*norvaline*, $[\alpha]^{22}$ $+15°$; *racemate A* of *dl*-α-bromopropionyl-*dl*-leucine, m. p. 149—150° (corr.); *racemate B*, m. p. 118—119°; *racemate A* of dl-α-*bromoisohexoyl*-dl-*valine*, m. p. 173—174° (uncorr., decomp.); *racemate B*, m. p. 125—126°. Dilute alkali hydroxide removes bromine much more rapidly from *d*-α-bromopropionyl-*d*-norvaline and from *l*-α-bromopropionyl-*l*-norvaline than from the *l*-*d*- and *d*-*l*-compounds. Racemate A (cf. A., 1930, 816) behaves like the first pair and racemate B like the second pair of compounds. Of the racemates from *dl*-α-bromopropionyl-*dl*-leucine, A is hydrolysed more slowly than B. Trypsin-kinase hydrolyses A more rapidly than B. Of the racemates from α-bromo*iso*hexoylvaline the halogen is removed more rapidly from A than from B. Trypsin-kinase did not attack either racemate. Erepsin hydrolysed none of the substrates. J. H. Birkinshaw.

Homogeneity of erepsin. E. Abderhalden and E. von Ehrenwall (Fermentforsch., 1930, **12**, 223—230).—Erepsin completely free from trypsin hydrolyses chloroacetyl-*d*-alanine and chloroacetyl-*dl*-leucine, but not chloroacetyl-*l*-tyrosine. Trypsin-kinase hydrolyses chloroacetyl-*l*-tyrosine and chloroacetyl-*dl*-leucine, but not *chloroacetyl*-d-*alanine*. Trypsin-kinase solutions which originally did not hydrolyse leucylglycine gain this power on keeping. J. H. Birkinshaw.

Oxidation–reduction. Brewers' yeast. R. Fabre and H. Simonnet (Compt. rend., 1930, **191**, 1075—1077).—The conclusion previously reached (A., 1930, 949) that reducing sulphur compounds are extracted from rabbits' liver by Ringer's solution only after the tissue has been killed is confirmed by a similar investigation with brewers' yeast. A centrifuged aqueous extract of fresh yeast gives no reaction with ammoniacal nitroprusside, but a strong positive reaction is obtained when the extraction is carried out in an atmosphere of chloroform. Desiccation of the yeast over phosphoric oxide in a vacuum causes a progressive increase in the amount of reducing sulphur compounds extracted by water. The aqueous extract of desiccated yeast reduces cystine. J. W. Baker.

Porphyrin of component *c* of cytochrome: relationship to other porphyrins. R. Hill and D. Keilin (Proc. Roy. Soc., 1930, **B**, **107**, 286—292).—Methods of preparing two different porphyrins from the *c* component of cytochrome from bakers' yeast are described. Treatment of the *c* component with hydrogen bromide and acetic acid yields hæmatoporphyrin identical in solubility and absorption spectrum with ordinary hæmatoporphyrin. Both are convertible into protoporphyrin, and the facts support the view that cytochrome is derived from protohæmatin in yeast cells. Under the action of hydrogen chloride and sulphur dioxide, the *c* component yields "*porphyrin*-c," insoluble in ether, acetic acid, or chloroform. This shows absorption bands at 6230, 5975, 5675, 5354, and 5000 Å. in pyridine, whilst the bands for a solution in *N*-hydrochloric acid are at 5970 and 5520 Å. Its copper compound in pyridine shows absorption at 5648 and 5298 Å., and the pyridine-hæmochromogen prepared from it is indistinguishable in absorption spectra from the *c* component in aqueous pyridine, exhibiting bands at 5498 and 5212 Å. A. Cohen.

Arbitrarily influenced asymmetric cleavage of *dl*-borneolphosphoric acid by yeast- and taka-phosphatase. M. Kuroya (Biochem. Z., 1930, **225**, 452—463).—The borneol eliminated from *dl*-borneolphosphoric acid by yeast- or taka-phosphatase was lævorotatory for a 50% fission and dextrorotatory for a higher degree of hydrolysis. Addition of strychnine in the taka-phosphatase hydrolysis lowered the activity of the borneol produced and only lævorotation was observed. With yeast-phosphatase the alkaloid also lowered the rotation of the borneol obtained, and in the case of advanced hydrolysis reversed the rotation as compared with the alkaloid-free substrate. J. H. Birkinshaw.

Detection and intensity of mitogenetic radiation. I. H. Schreiber and W. Friedrich (Biochem. Z., 1930, **227**, 386—400).—Attempts to detect mitogenetic radiation from germinating yeast cultures (*Saccharomyces ellipsoideus*) by a modification of the method of Elster and Geitel (Physikal. Z., 1916, **17**, 268) were unsuccessful. Since the sensitivity of the apparatus used was known, some conclusions could be reached as to the behaviour which the radiation, if it occurs at all, must exhibit. W. McCartney.

Effect of ionised air on rate of respiration of fungi. S. R. van A. de Boer (Ann. Bot., 1930, **44**, 989—999).—No effect was observed with *Phycomyces Blakesleeanus* and *Polyporus destructor*. F. O. Howitt.

Resorption of ammoniacal and nitrate-nitrogen by *Aspergillus oryzæ*. T. Sakamura (Planta, [Z. wiss. Biol.], 1930, **11**, 765—813).—In culture solutions containing ammonium salts and nitrates *A. oryzæ* may assimilate either form of nitrogen preferentially or both simultaneously. When ammonia absorption predominates the c_H of the culture solution increases and the growth of the fungus is retarded, but when nitrate assimilation is high the reaction of the nutrient remains practically constant, growth is luxuriant, and the total nitrogen absorbed is high. The form of nitrogen chiefly utilised varies with cultural conditions and to a large extent with the nature of the carbohydrate present. The ease of nitrate absorption in the presence of sugars decreases in the order lævulose>sucrose>dextrose. In ammoniophilic cultures the addition of phosphates tends to limit acidification and causes improved growth. A. G. Pollard.

Variations in the fatty acids of *Aspergillus niger* as a function of the mineral composition of the culture medium. C. Pontillon (Compt. rend., 1930, **191**, 1148—1151).—*A. niger* has been grown on various liquid media differing in their mineral composition and p_H, and analysed at various periods of growth in respect of fatty acids. In slightly alkaline media, the quantity of fatty acids formed is approximately equal to that obtained in the neutral medium, but in acid medium it is decreased. The

mol. wt. of the fatty acids is approximately independent of the p_H and is minimal at the time of fructification. The iodine value of the fatty acids is about 30 in a neutral medium and is greater in an acid medium. It is still more raised in an alkaline medium and is minimum immediately before sporulation. In a medium kept approximately neutral it is somewhat high and relatively constant. W. O. KERMACK.

Acidoproteolytic bacteria in pasteurised milk. C. GORINI (Compt. rend., 1930, **191**, 885—886).—Thermophilic acidoproteolytic bacteria of the type *subtilis* are responsible for the premature coagulation of milk pasteurised for 30 min. at 53°. It is possible for spores of these organisms to survive pasteurisation at 80—85°. T. H. MORTON.

Cultural characteristics and metabolism of the organism producing red spots in English cheese. J. G. DAVIS and A. T. R. MATTICK (Zentr. Bakt. Par., 1930, 80, 30—33; Chem. Zentr., 1930, i, 2113).—The red spots are practically pure cultures of a bacterium, $0.85\times2\mu$, the characteristics of which are described. A living pigmented culture is quickly decolorised in air, but not after death caused by drying or by treatment with alcohol, whereby the pigment is fixed. The pigment is insoluble in water, ether, benzene, chloroform, glycerol, dilute acid, and alkali, Boiling with concentrated acid, but not alcoholic alkali, decomposes it; concentrated sulphuric acid gives a deep blue colour. The pigment appears to play no part in the metabolism of the organism.

L. S. THEOBALD.

Growth of anaerobic micro-organisms and the potential of the culture medium. H. PLOTZ and J. GELOSO (Ann. Inst. Pasteur, 1930, **45**, 613—640).—*P. D.* are measured by two electrical methods using the calomel electrode, anaerobiosis being best produced by evacuation of the apparatus. A colorimetric method is also employed. A definite potential is always finally established, corresponding with r_H 5.5 ± 0.5, irrespective of the nature of the organism employed. The curves obtained for bouillon containing platinum-black are similar to those obtained for bacterial cultures. Rapid growth takes place provided that the potential corresponds with a value of r_H 0—14. P. G. MARSHALL.

Specificity of the tuberculin type of sensitiveness produced with the different protein substances of egg-white. L. DIENES (J. Immunol., 1930, **18**, 279—283). CHEMICAL ABSTRACTS.

Antigenic substances of the tubercle bacillus. V. Antigenic substances of the synthetic culture medium. L. DIENES and E. W. SCHOENHEIT (J. Immunol., 1930, **18**, 285—314).—In filtrates of cultures grown on Long's synthetic medium two distinct antigenic substances, separable by acid precipitation, are present together with the carbohydrate-precipitable substance.

CHEMICAL ABSTRACTS.

Separation of antibodies from serum-proteins. M. FRANKEL and L. OLITZKI (Nature, 1930, **126**, 723—724).—Active antibodies free from proteins have been obtained from diphtheria antitoxin and antityphoid serum by Willstatter's method of adsorption on kaolin and specific elution with solutions of glycine containing 2% of sodium chloride.

L. S. THEOBALD.

Action of dyes on bacteria. M. KAWAI (Zentr. Bakt. Par., 1930, I, **115**, 241—271; Chem. Zentr., 1930, i, 3319).—There is a connexion between the chemical structure of dyes and their growth-inhibiting power. The inhibitive effect of basic dyes, particularly of triaminotriphenylmethane, is increased by alkyl groups. Dyes containing chlorine, and their double metallic salts, have a strong effect, whilst those containing sulpho-, nitro-, carboxyl, and hydroxyl groups have little effect. Dyes favour the development of abnormal bacterial forms.

A. A. ELDRIDGE.

Effect of small additions of acid for increasing the germicidal action of E.C. [electrolytic chlorogen] on bacterial spores. C. S. R. AYYAR (Agric. J. India, 1930, **25**, 213—219).—The addition of 0·035 g. of citric acid to a 0·2% solution of the disinfectant increases its efficiency to the point of destroying resistant spores after 30 min. contact (cf. A., 1930, 645). E. HOLMES.

Bacteriophage, a central biological problem. C. J. SCHNUURMANN (Kolloid-Z., 1930, **53**, 231—239).—A discussion. E. S. HEDGES.

Kinetics of bacterium–bacteriophage reaction. A. P. KRUEGER and J. H. NORTHROP (J. Gen. Physiol., 1930, **14**, 223—254).—An analytical study of a system containing antistaphylococcus bacteriophage (*P*) acting on *S. aureus* (*B*), using methods already described (cf. A., 1930, 960). It is shown that, following a short lag, during which rapid adsorption of *P* by *B* occurs, there is logarithmic increase of *B* and *P*, the latter proceeding more rapidly. Phage formation is dependent on bacterial growth, and lysis, which is also logarithmic, begins when $\log [P]/[B]=2.1$. Equations deduced to determine the commencement of lysis under standard conditions are experimentally confirmed. A. COHEN.

Fat metabolism of the liver. I. Effect of hormones on the fat content of the liver. II. Effect of biogenic amines. Z. OSHIMA (Z. ges. exp. Med., 1929, **64**, 694—706, 707—713; Chem. Zentr., 1930, i, 3801).—The increase in the fatty acid content of the liver of rabbits after subcutaneous injection rose in the order thyroxine, menoformone, pituitrin. The increase is due chiefly to saturated acids. Choline has little, and tyramine a marked, effect; histamine causes a small reduction in the fatty acid content.

A. A. ELDRIDGE.

Water content of various tissues of animals treated with powdered mammary gland. C. I. PARHON, M. CAHANE, and A. BLINOV (Bull. Acad. Sci. Roumaine, 1930, **13**, 165—167).—In guinea-pigs treated daily with mammary gland powder there is a very slight increase in the water content of the brain and of liver, whilst other organs suffer a diminution.

F. O. HOWITT.

The unitary versus the multiple hormone theory of posterior pituitary principles. J. J. ABEL (J. Pharm. Exp. Ther., 1930, **40**, 139—170).—New methods are described for the preparation of an active substance from fresh pituitary gland or from

commercial pituitary powders in the form of a colourless dry powder which in respect of its oxytocic, pressor, and melanophore-expanding activities is 50—60 times as powerful as the international standard preparation. Some preparations are even more active, but the ratios of the pressor, oxytocic, and melanophore-expanding activities remain approximately constant. After boiling with 0·25% acetic acid, however, the material may be separated into fractions in which one or other activity is particularly marked, whereas such fractionation appears to be impossible before boiling. It is therefore considered probable that the initial preparations contain a unitary principle, the molecules of which carry at least four groups respectively responsible for the four characteristic activities, and that treatment with hot dilute acid results in the separation from the unstable molecule of the groups exerting the specific activities. The crude unitary principle as isolated contains at least 50% of inactive protein and also a crystalline base of unknown composition, m. p. about 179°. It is probable that the commercial product pitressin, as primarily isolated, is the unitary product minus the oxytocic group, so that it has approximately equal activities in international units in respect of its pressor, melanophore-expanding, and anti-diuretic functions. A further scission into its individual components may take place during sterilisation.

W. O. Kermack.

Assay for the testicular hormone by the comb-growth reaction. T. F. Gallagher and F. C. Koch (J. Pharm. Exp. Ther., 1930, **40**, 327—339).—The variability in the responses of brown Leghorn capons to injections of testicular hormone is not specially related to age and weight of the bird nor to the initial size and shape of the combs. The best results are obtained by determining the minimal dose injected on five successive days causing a growth of 3—7 mm. in the height and length of the comb. A bird unit is defined as the amount of the hormone which when injected daily for 5 days yields an average of 5 mm. increase in length and height of the combs of at least five brown Leghorn capons.

W. O. Kermack.

Influence of nutrition on blood-sugar regulation. IV. Reversal of the effect of food by removal of the thyroid. E. Geiger (Arch. exp. Path. Pharm., 1930, **156**, 333—339).—In normal rabbits the fasting blood-sugar level is higher after feeding on green food than after oats, and the rise in blood-sugar after oral administration of dextrose, according to Staub's method, is also greater. After thyroidectomy the higher values are obtained with oat feeding. The effect of green feeding is therefore exerted through an action on the thyroid gland.

W. O. Kermack.

Calcium content of skeletal muscles after thyroparathyroidectomy and "parathormone" injection. F. Y. Hsu and C. Tsai (Chinese J. Physiol., 1930, **4**, 423—429).—The normal calcium content of the muscles of dogs varies from 6·4 to 12·2 mg. per 100 g. of fresh tissue, the average values for temporal, diaphragm, and gastrocnemius muscle being 9·5, 9·4, and 8·5 mg., respectively. After thyroparathyroidectomy the calcium content of the muscle is below normal, whilst the results obtained after administration of "parathormone" to normal animals were inconstant, but in no case was a decrease observed. The results do not support the view that muscle is the immediate source of the calcium mobilised by the parathyroid hormone.

W. O. Kermack.

Plasma-calcium-raising principle of bovine parathyroid glands. I. Preparation and properties of the product. W. R. Tweedy (J. Biol. Chem., 1930, **88**, 649—657).—Potent preparations of parathyroid hormone in dry form in quantities of 1—3 mg. per gland may be separated from hot hydrochloric acid extracts by removal of inert material with acetone, followed by trichloroacetic acid precipitation of the active fraction, and removal of inert lipoid material from this fraction by chloroform extraction. The product dissolved in dried phenol retains its activity when heated at 70° for 7 hrs., but is partly inactivated at 150° for 1 hr. and completely inactivated at 175° for ½ hr. in an atmosphere of nitrogen. Complete inactivation results when the active material is suspended in 0·5% hydrochloric acid in absolute alcohol and heated for 20 min. at 70°, or when it is suspended for 1 hr. in absolute alcohol saturated with gaseous hydrogen chloride at 10°.

W. O. Kermack.

Medullary substance of the adrenals in the biochemistry of the organism. S. A. Schtscherbakov, V. S. Simnitzki, and V. R. Dmitriev (Pfluger's Arch. Physiol., 1930, **224**, 328—336; Chem. Zentr., 1930, i, 3452).—Experiments on the electrical stimulation of the splanchnic nerve show that adrenaline is a true hormone, having an important effect on the carbohydrate economy of the cells.

A. A. Eldridge.

Influence of adrenaline on immediate variations of the alkaline reserve. Role of apnœa. Comparative action of formaldehyde and of acetylcholine. J. Gautrelet, D. Bennati, E. Herzfeld, and L. Vallagnoso (Bull. Soc. Chim. biol., 1930, **12**, 1100—1145).—The alkaline reserve and reaction of the blood immediately after injection of adrenaline were investigated in chloralosed dogs. There is a well-marked increase in alkaline reserve within three minutes of intravenous injection, the p_H undergoing a parallel rise. Vagotomy greatly reduces these effects and the apnœa is eliminated. Practically no change occurs in the alkaline reserve during the apnœa due to formaldehyde or acetylcholine, whilst administration of adrenaline in amounts insufficient to cause apnœa results in an increase in the alkaline reserve. The action of adrenaline during paralysis of the sympathetic system by atropine or of the parasympathetic by yohimbine and by ergotamine and the changes in the alkaline reserve following peripheral stimulation of the splanchnics were also studied.

F. O. Howitt.

Influence of adrenaline on the blood-sugar content in connexion with reticular-endothelial blockage. H. Gnoinski (Med. Doswiad., 1930, **11**, 117—123).—Intravenous injection of colloidal silver raises the blood-sugar level by 30%, at the expense of hepatic glycogen, whilst adrenaline causes

an increase of 70%; injected simultaneously, an increase of only 43% is observed, this time at the expense chiefly of muscle-glycogen. The inhibitive effect of colloidal silver on the action of adrenaline persists for at least 8 hrs. R. TRUSZKOWSKI.

Role of suprarenal glands in hyperglycæmia caused by injection of colloidal silver. P. DEMANT (Med. Doswiad., 1930, **11**, 81—87).—Injection of colloidal silver into suprarenalectomised dogs does not provoke the hyperglycæmia observed under such conditions in normal animals, nor are the calcium or sodium chloride contents of the blood affected by the injection. Colloidal silver acts by exciting the sympathetic through the reticular-endothelial system, thereby provoking the activity of the chromogenic substance of the suprarenal glands, which in turn leads to hyperglycæmia. R. TRUSZKOWSKI.

Action of insulin, adrenaline, and morphine on the distribution of sugar in the organism during digestion in angiostomised dogs. N. P. KOCHNEVA (Arkh. biol. nauk, 1930, **30**, 45—56).—In the first 2 hrs. after subcutaneous injection of adrenaline together with or after injection of carbohydrate alimentary hyperglycæmia is not observed, whilst after intravenous or subcutaneous injection of insulin the absorption from the alimentary tract continues and the blood-sugar does not reach high values only because of the retention of sugar by the kidneys. During the absorption of protein from the intestine, blood-sugar is equally distributed in different parts of the body; administration of insulin leads to renal retention of sugar. Subcutaneous injection of morphine as well as of adrenaline during digestion of carbohydrate arrests the absorption of carbohydrate from the intestine. The injection of morphine and adrenaline, as well as carbohydrate, into fasting animals leads to retention of sugar by the lungs.
CHEMICAL ABSTRACTS.

Metabolic-physiological action of insulin in phloridzin diabetes. W. MÖBIUS (Pflüger's Archiv, 1930, **224**, 511—526; Chem. Zentr., 1930, i, 3454).—Disappearance of ketonuria, retardation of fat infiltration of the liver, and diminution of glycosuria are outstanding indications. A. A. ELDRIDGE.

Influence of the blood on the activity of insulin. A. A. SCHMIDT and R. L. SAATCHIAN (Zhur. exp. Biol. Med., 1929, **11**, 37—40).—When added to defibrinated blood insulin loses little of its activity. The insulin remains entirely in the serum. The rapid disappearance of insulin when injected intravenously is due to its absorption by the tissues.
CHEMICAL ABSTRACTS.

Effect of some tissues of the animal organism on the activity of insulin. A. A. SCHMIDT and R. L. SAATCHIAN (Zhur. exp. Biol. Med., 1929, **11**, 42—53).—Rabbit's muscle tissue inactivates insulin very little; increasingly greater effect is exhibited by spleen, kidney, and liver tissue. The inactivation is probably due to the action of proteolytic enzymes.
CHEMICAL ABSTRACTS.

Difference of activity of technical insulin and of crystalline preparations in relation to primary insulin hyperglycæmia. M. BÜRGER and H. KRAMER (Arch. exp. Path. Pharm., 1930, **156**, 1—17).—The hyperglycæmic action of commercial insulin, exhibited within 20 min. of intravenous administration to rabbits and other animals, is possessed in varying degree by each of 14 different samples of insulin. It is not a property of crystalline insulin and is still possessed by an insulin solution after it has been heated so as to become inactive in respect of its hypoglycæmic activity. It is therefore due to the presence in commercial insulin preparations of some other product apparently originating in the pancreas. W. O. KERMACK.

Callicrein, a pancreatic hormone. H. KRAUT (Chem.-Ztg., 1930, **54**, 849—851).—A summary of work previously abstracted (A., 1926, 1168; 1928, 798, 1057; 1930, 1069, 1624). R. K. CALLOW.

Quantitative differentiation of vitamins-*A* and -*D*. II. H. C. SHERMAN and H. K. STIEBELING (J. Biol. Chem., 1930, **88**, 683—693; cf. A., 1927, 702).—The best conditions for the determination of vitamins-*A* and -*D* when rats are used as test animals are discussed. The vitamin-*A* content of a substance is best estimated by finding the amount required to produce limited growth (3—4 g. per week) on a diet otherwise adequate, whilst the vitamin-*D* content may best be assayed by finding the amount required to produce a degree of calcification midway between the maximum and minimum obtainable respectively with abundance and in the practically complete absence of vitamin-*D*. W. O. KERMACK.

Growth-promoting action of carotenoids. N. RYDBOM (Biochem. Z., 1930, **227**, 482—487).—Normal growth is promoted in rats by intramuscular injection, every second day, of 0·06 mg. of carotene.
W. MCCARTNEY.

Biochemical investigations on rubrene. M. JAVILLIER and L. EMERIQUE (Compt. rend., 1930, **191**, 882—884).—Administration of rubrene (2·4—5 mg. per kg. daily) is without effect on rats suffering from vitamin-*A* deficiency. Larger doses of rubrene are without toxic action; 75% is excreted unchanged, and of that absorbed none can be detected spectrometrically in any tissue. T. H. MORTON.

Composite nature of vitamin-*B*. M. SKARZYNSKA-GUTOWSKA (Med. Doswiad., 1930, **11**, 176—182).—Pigeons develop polyneuritis, with loss of weight, when fed on polished rice with the addition of either the colloidal or the crystalloidal constituents of vitamin-*B* extracts; the administration of both fractions together has a protective influence.
R. TRUSZKOWSKI.

[Derangement of the resorption due to lack of vitamin-*B*.] G. GAL (Biochem. Z., 1930, **227**, 492; cf. A., 1930, 1625).—Acknowledgment of prior work of Never (Pflüger's Archiv, 1930, 787) is made. W. MCCARTNEY.

Activator *Z* and its relation to the growth factor of yeast, bios, and to the vitamins-*B*. T. PHILIPSON (Z. physiol. Chem., 1930, **193**, 15—45).—Activator *Z* is not precipitated by the method of Kinnersley and Peters for the purification of the antineuritic factor, but the carbon treatment indicated that it could be separated into two components. The Lucas and Eastcott method gave a separation

of the growth factor (bios) from the activator Z. The activator is soluble to the extent of 3000 Z units per litre in 95% alcohol. Various methods of separation were compared; the best was Chick's mercury precipitation method.

The factor Z was separated into two components by treatment with basic lead acetate. The two fractions are separately less active than is the original mixture. The full activity of the filtrate is restored by the addition of the portion of activator present in the precipitate, or in many cases by the addition of inositol. The evidence is not sufficient to affirm that inositol is the active component of the precipitate.

J. H. Birkinshaw.

Influence of vitamin-*D* on growth and protein metabolism. F. Goebel (Med. Doświad., 1930, **11**, 124—151).—Non-irradiated ergosterol has little effect on animals maintained on a vitamin-*D*-deficient diet, and kept in the dark, an increase in weight of 28% being observed in 2 weeks. When the rats are kept in the light, they gain 50% under the same conditions, as compared with 65% for normal control rats. The gain in weight of thyroidectomised rats during 4 weeks is 68%, and on a diet containing "vitasterol" 82%, as compared with 150% for normal animals. The rate of growth after removal of the thymus is unaffected by the administration of "vitasterol." Nitrogen retention is augmented by 6—20% by administration of 0·05—10·0 mg. of "vitasterol" daily to young rabbits; no ill effects are observed as a result of such large doses. In the case of "vitasterol"-fed rats nitrogen retention is 24% higher than that of those receiving a normal diet; the nitrogen contents of the liver, spleen, kidneys, and muscles are respectively 20, 44, 33, and 39% higher than are those of control rats, whilst for rabbits the corresponding figures are 22, 11·7, 5·2, and 11·1%.

R. Truszkowski.

Antirachitic substances. X. Relation of the *iso*ergosterols to vitamin-*D*. W. M. Cox and C. E. Bills (J. Biol. Chem., 1930, **88**, 709—713).—When ergosterol is irradiated in alcoholic solution until the antirachitic activity has begun to decline a band at 248 mμ ($\varepsilon = 16{,}000$) begins to appear. This band closely resembles that characteristic of the various *iso*ergosterols, but the substance responsible for it differs from the known *iso*ergosterols in not being precipitable by digitonin.

W. O. Kermack.

Further observations on the toxic effects of irradiated ergosterol. J. C. Hoyle (J. Pharm. Exp Ther., 1930, **40**, 351—372).—When ergosterol dissolved in alcohol is irradiated two substances are formed which may produce toxic effects when administered in excess. One of these is vitamin-*D*; the second is an unknown substance which, less readily destroyed by over-irradiation than is vitamin-*D*, is chiefly responsible for the arterial lesions produced by over-dosage with ergosterol irradiated in alcohol. This substance is not readily formed when ergosterol is irradiated in oil. Excess of vitamin-*D* may result in the formation of urinary calculi and also retardation of growth. Bread and milk together protect animals against the arteriosclerosis following overdosage with ergosterol irradiated in alcohol, but bread or milk alone, or a synthetic diet modified to resemble bread and milk in composition or one poor in calcium and phosphorus, has no protective effect.

W. O. Kermack.

Action of irradiated ergosterol and the parathyroid hormone on tissue-phosphatases. W. Heymann (Biochem. Z., 1930, **227**, 1—5).—The influence of irradiated ergosterol, of irradiation by the sun, and of parathyroid hormone on the glycero- and hexosedi-phosphatase content of various organs of the rat is investigated *in vitro*. Whereas "vigantol" is without effect, irradiation with ultra-violet light in 6 of 15 experiments caused an inhibition of these enzymes. Both enzymes (of bone) are inhibited *in vitro* by parathyroid hormone. P. W. Clutterbuck.

A new nutrition factor. A. Bakke, V. AscheHoug, and C. Zbinden (Compt. rend., 1930, **191**, 1157—1159).—The addition of wheat germ to the diets of black rats causes their coats to turn silver-grey. A disease of the eye, resembling but not identical with xerophthalmia, and a derangement of the reproductive functions are also associated with the effect. The action is neutralised by whole wheat, which brings about a rapid return of the original black coat.

W. O. Kermack.

Accumulation of electrolytes in plant cells. Suggested mechanism. G. E. Briggs (Proc. Roy. Soc., 1930, **B**, **107**, 248—269).—The problem of the mechanism by which cations and anions accumulate in the interior of plant cells in greater concentration than that in which they are present in the surrounding medium is treated theoretically. The suggestion is made that alternating phases in which the cell membrane is permeable to cations and then to anions would explain this accumulation.

G. F. Marrian.

Accumulation of electrolytes. II. Nature of accumulation in *Valonia*. W. J. V. Osterhout. **III. Behaviour of sodium, potassium, and ammonium in *Valonia*.** A. G. Jacques and W. J. V. Osterhout (J. Gen. Physiol., 1930, **14**, 285—300, 301—314; cf. A., 1930, 1483).—II. The concentration of potassium chloride in cell sap of *V. macrophysa* is about forty times as great as that in sea-water. It is suggested that accumulation is due to entrance of potassium hydroxide (and sodium hydroxide to a smaller extent) by virtue of a higher external thermodynamic potential. A salt is formed with a weak acid produced by the cell, and potassium chloride is produced by hydrogen chloride entering from the sea-water. Electrolyte penetration is considered to be molecular.

III. The rise in concentration of sodium and fall in that of potassium in cells of *V. macrophysa* placed in sea-water containing ammonium chloride are explained by their diffusion in accordance with the gradients of their respective thermodynamic potentials. The accumulation of ammonium chloride in cell sap is explained in a manner similar to that for potassium chloride.

A. Cohen.

Kinetics of penetration. III. Equations for the exchange of ions. W. J. V. Osterhout (J. Gen. Physiol., 1930, **14**, 277—284).—Mathematical. Equations are given determining the rate of exchange

of ions of the same sign between the interior of a living cell and external solution under standard conditions. A. COHEN.

Kinetics of oxygen uptake and of carbon dioxide output of pea-meal. A. FODOR, L. FRANKENTHAL, and S. KUK (Biochem. Z., 1930, **225**, 409—416; cf. A., 1930, 964).—Addition of potassium formate to the meal as donator changes the oxygen uptake only slightly, but in presence of phosphate the carbon dioxide production by well-germinated peas sinks to about half the former value. With only slightly germinated material and in absence of phosphate, the effect on the carbon dioxide production is small. The carbon dioxide production is increased, but the oxygen uptake is unchanged in the presence of an acceptor (*e.g.*, acetaldehyde) with the donator. Potassium cyanide inhibits both processes. These effects are explained on the hypothesis that methylglyoxal (hydrate) is dehydrogenated and pyruvic acid is decarboxylated. J. H. BIRKINSHAW.

Seasonal change in the catalase content of conifer leaves. J. DOYLE and P. O'CONNOR (Ann. Bot., 1930, **44**, 907—915).—Suspensions formed by grinding the leaves with water and calcium carbonate were examined manometrically for catalase content at different seasons of the year. The results confirmed the earlier finding of Doyle and Clinch (A., 1928, 1408) that the catalase content rises in winter and remains unchanged during that season. The theory of Burge (A., 1926, 541) of a close relationship between catalase content and general metabolism was not confirmed. Abnormal temperature effect was also studied. F. O. HOWITT.

The role and significance of quinic acid in higher plants. A. KIESEL (Planta [Z. wiss. Biol.], 1930, **12**, 131—143).—Seasonal variations in the quinic acid contents of leaves of various trees are recorded. Quinic acid is probably an assimilation product, not directly derived from carbohydrates. A. G. POLLARD.

Iodine-phenol for histological detection of starch. J. KISSER (Mikrochem., Emich Festschr., 1930, 175—179).—The difficulty of detecting small quantities of starch in, *e.g.*, chloroplasts is noted. A mixture of 8 parts of iodine-phenol, 4 parts of iodine-alcohol, and 1 part of water is satisfactory, in that it does not readily form an emulsion with water, and if the alcohol is replaced by glycerol the mixture is still less disturbed by the presence of water, and the refractive index of the phenol is not reduced to too great an extent. H. F. GILLBE.

Transformation of carbohydrates in the banana. I. Formation of starch. H. BELVAL (Chinese J. Physiol., 1930, 4, 365—372).—The leaves and fruit of the banana have been analysed in respect of their water and carbohydrate contents. In the limb of the leaves sucrose predominates, but in the nerve and especially in the petiole its place is taken by reducing sugars, presumably due to its hydrolysis as it proceeds towards the fruit. In the base of the peduncle the reducing sugars predominate, but in the upper part these tend to disappear, whilst in the very young fruit they are practically absent, being presumably converted into insoluble carbohydrates. W. O. KERMACK.

Biochemical studies on the bamboo. III, V. Chemical development of shoots. D. KAMIJA and K. NISHIOKA. **IV. Chemical development of sheaths.** T. TASHIMA. **VII. Seasonal variation in the chemical composition of the Madake (*Phyllostachys quilioi*, F.M.).** T. NAGASAWA (Chikashige Anniv. Vol., 1930, 149—159, 161—165, 167—173, 183—193).—III, V. The nodes contain total reducing sugars (pentose+hexose), cellulose, lignin, and pentosan to the extent of 12·16, 18·6, 0·7, and 23·7%, respectively. The ash content varies as the water content, and the water-soluble ash is related to the content of reducing sugars. The internode gas contains nitrogen, oxygen, and carbon dioxide, the oxygen content varying inversely with that of carbon dioxide in every stage of life. The respiration curve of the culm is similar to that of the hexosan content (not the hexose content). In slabs of internode taken from the base of the shoots, the largest amount of non-protein-nitrogen and fatty acids is found in the inside slabs along with the least amount of carbohydrate. The different slabs of the youngest internodes do not vary greatly in composition.

IV. The sheaths of the youngest portions of the shoots are richer in total nitrogen and hexoses but poorer in protein and polysaccharides than the oldest portions. The total ash content varies from 0·72 in the youngest to 0·42% in the oldest portions. The ash is rich in silica, alumina, and iron, but poor in phosphorus.

VII. The seasonal variation of hexoses and polysaccharides runs parallel with that of ash and water. Total nitrogen decreases and fat increases with age. P. G. MARSHALL.

Function of the mannitol in olives. R. NUCCORINI [with M. ARONOVSKIS] (Annali Chim. Appl., 1930, **20**, 535—546).—The mannitol contained in olives is formed by reduction of lævulose and contributes to the formation of oleanolic acid, from which the fatty acids of the glycerides are derived. T. H. POPE.

Physiology of the nitrogen exchange in higher plants with special reference to nitrate accumulation. W. DITTRICH (Planta [Z. wiss. Biol.], 1930, **12**, 69—119).—Plants may be classified according to their capacity for accumulating nitrates in the tissues. The nitrate content of plants increases with age and varies daily with light intensity and transpiration. Leaves and roots exhibit a preferential reducing power for nitrates as compared with the stems. The sap of nitrate-accumulating plants has a lower reducing power than that of plants poor in nitrate. Nitrate-accumulating plants utilise the reserve nitrate if grown in nutrients containing carbohydrates only. The nitrate storage of sugar beet occurs in the central regions only. Optimum reducing power of the expressed plant sap is associated with p_H about 7·6. Nitrate-accumulating plants have more alkaline sap than others. The fate of nitrates in plant-tissues is largely controlled by the p_H value of the sap, and the reduction process is ascribed to enzymic activity. A. G. POLLARD.

Determination of seed quality from enzyme content. M. I. LISCHKEVITSCH (Fermentforsch., 1930, **12**, 244—261).—Barley and wheat from northerly regions had a higher catalase, amylase, and protease content than grain from lower latitudes. The difference in wheat was not so sharply defined, but the catalase content was much higher than that of barley. In peas and soya beans the geographical factor had no effect. Castor oil and hemp seeds from northern areas had a stronger lipolytic action than seeds from southern districts. J. H. BIRKINSHAW.

Oil and lipase-like enzyme in Para rubber seed. Y. IWAMOTO (J. Soc. Chem. Ind., Japan, 1930, **33**, 409—411B).—Malayan rubber seeds yielded ether-extracted oils having acid values from 7·2 to 110·9 according to the condition of the seed. An oil extracted by light petroleum from fresh seeds had d_4^{15} 0·9234, n^{20} 1·4757, acid value 7·12, iodine value 138·8, f. p. 2°, saponif. value 189·2, Reichert–Meissl value 2·28, acetyl value 2·41, unsaponif. matter 1·62, insoluble hexabromide (fatty acids) 15·48%, solid acids (lead salt–ether method) 17·81% (m. p. 62°), liquid acids 79·99%. Linolenic, linoleic, and oleic acids were present, and the solid acids appeared to consist of stearic (70%) and palmitic acid (30%). Cold-pressing yielded 28·5% of a pale yellow sweet oil (acid value 19·7) and a second hot-pressing a further 16·7% of a brown oil. The kernels contained a lipolytic enzyme. E. LEWKOWITSCH.

Soluble enzymes secreted by hymenomycetes. Anti-oxygenic function of quinones. L. LUTZ (Compt. rend., 1930, **191**, 880—882).—The oxidation of guaiacol and α-naphthol in cultures of *Corticium quercinum*, *Coriolus versicolor*, and *Pleurotus ostreatus*, which contain both oxidases and reductases, is prevented by the addition of benzoquinone, or less effectively by thymoquinone. In cultures of *C. quercinum* the reduction of methylene-blue is accelerated by the presence of benzoquinone. The mechanism suggested is the cyclic reduction and re-oxidation of the benzoquinone. T. H. MORTON.

Carboxylic tannins. L. REICHEL (Naturwiss., 1930, **18**, 952).—In order to extract carboxylic tannins in a non-polymerised form they must be isolated as salts. Vacuum-distillation of extracts at reactions equal to those of the original sources (investigated for leaves of *Quercus*, *Rosa canina*, and *Tilia*) resulted in residues which contained only small amounts of condensation products. Crystalline acetyl derivatives were obtained from oak- and lime-tannins; that from the oak had two carboxyl groups and the acetylation indicated 10—12 hydroxyl groups, corresponding with a formula of $C_{24}H_{28}O_{18}$ or for the tannin. Acid hydrolysis of the acetylation product resulted in the formation of ellagic acid and phlobaphen, but no sugar was detected. F. O. HOWITT.

Presence of tannins in flowers. S. IONESCO (Compt. rend., 1930, **191**, 867—868).—The presence of tannins has been demonstrated in the flowers of a large number of shrubs, trees, and herbaceous plants. The flowers, after decolorisation with 96% alcohol or acetone, show colour reactions typical of the tannins. The flowers may be divided into two groups according as they give, with iron salts, a green coloration due to catechu tannins, or a blue coloration due to tannins containing a digallic acid residue. To the first class belong the trees and shrubs, *Æsculus hippocastanum*, *Liriodendron tulipifera*, *Philadelphus coronarius*, *Pirus communis*, *Symphoricarpus racemosus*, and *Syringa vulgaris*; to the second the trees and shrubs, *Acer platanoides*, *Rhus cotinus*, and *Rosa canina*, and the herbaceous plants, *Fragaria vesca*, *Geum urbanum*, *Helianthemum glaucum*, *H. guttatum*, *H. lavandulifolium*, *Lysimachia nummularia*, *Pæonia romanica*, *Potentilla argentea*, and *P. recta*. T. H. MORTON.

Quercetin in *Magnoliaceæ* and its distribution in the plant kingdom. T. WEEVERS (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 778—785).—Quercetin may be isolated from the flowers of *Magnolia Yulan*, var. *Soulangiana*, but not from the leaves or stems; it is not present in the blooms of *M. stellata*. Quercetin is not the colouring matter responsible for the brown coloration observed in these flowers on freezing or on oxidation with hydrogen peroxide. During the development of *M. Yulan* from the bud to the flower, a period of marked anthocyanin production, the amount of quercetin present does not decrease, but rather shows a slight increase. T. H. MORTON.

Preparation and properties of franguloside (frangulin) from black alder bark. M. BRIDEL and C. CHARAUX (Compt. rend., 1930, **191**, 1151—1153).—Franguloside exists in the bark in a combined form, from which it may be set free by the action of an enzyme present in the bark. A yield of 2·5% may be obtained after hydrolysis by the enzyme, the small yields previously recorded representing only that portion of franguloside accidentally set free by the manipulations employed. Franguloside, $C_{21}H_{20}O_9,H_2O$, has m. p. 246° on rapid heating, m. p. 249° after changing colour at 197° on slow heating, $[\alpha]_D$ — 134·40° in 80% acetic acid. W. O. KERMACK.

Capsanthin. L. CHOLNOKY (Magyar Chem. Fol., 1930, **36**, 11—16, 17—25; Chem. Zentr., 1930, i, 3560).—The ground pericarp (2 kg.) is percolated with light petroleum (2 litres), the extract diluted with 1 litre of ether, and left over-night in contact with 30% methyl-alcoholic potash (200 c.c.). The crystals which separate are dissolved in 2 litres of ether, the solution being repeatedly washed with water and dried with sodium sulphate. After evaporation to 500 c.c., 1·5 litres of light petroleum are added, the yield of colouring matter precipitated being 3 9 g. The product is recrystallised from methyl alcohol. A. A. ELDRIDGE.

***Psyllium* seed.** J. S. HEPBURN and T. L. LAUGHLIN (Amer. J. Pharm., 1930, **102**, 565—568).—One sample contained moisture 8·5%, crude fat 6·4%, insoluble ash 2·9%, soluble ash 0·2%, crude protein 17·8%, crude fibre 11·5%, nitrogen-free extractives 52·6%, pentosans 9·8%, and galactans 0·3%. The blackish-brown, acid gum extracted by hot water contained pentosan 16·4% and galactan 0·02%. It is free from starch, does not reduce Fehling's solution, and is precipitated by lead acetate

or alcohol, but not by borax, ferric chloride, or copper sulphate. H. E. F. NOTTON.

Pigment of the water-melon. L. ZECHMEISTER and P. TUZSON (Ber., 1930, **63**, [*B*], 2881—2883).—The fruit of *Cucumis citrullus* contains extremely little lipoid material. Xanthophyll and esterified carotenoids are absent. The pigment consists of a mixture of lycopene and carotene, separated from one another by means of their differing solubilities in light petroleum. For South Hungarian material the ratio of lycopene to carotene varies between 8 : 1 and 10 : 1. H. WREN.

Presence in edible plants of allantoin, allantoic acid, allantoinase, and uricase. R. FOSSE, A. BRUNEL, P. DE GRAEVE, P. E. THOMAS, and J. SARAZIN (Compt. rend., 1930, **191**, 1153—1155).—Allantoin is present in a large number of edible plants, including many grains, legumes, and vegetables. Allantoic acid, allantoinase, and uricase are not so widely distributed, but are not infrequently also present.

W. O. KERMACK.

Paraffins of tobacco. M. E. KURILO (U.S.S.R. State Inst. Tobacco Ind., Bull. 69, 1930, 35—42).—After treatment with cold alcohol to remove resins, the product extracted from cigarette tobacco by hot ether, light petroleum, benzene, or alcohol consists of a mixture of saturated hydrocarbons of m. p. 58—70°. Fractionation of the mixture yielded heptacosane, m. p. 59—59·5°, and hentriacontane, m. p. 67·5—68°. The constituents of tobacco described by Kissling as waxes (" Handbuch der Tabakkunde ") are most probably mixtures of hydrocarbons. The paraffin contents of cigarette tobaccos of different types are very nearly constant.

T. H. POPE.

Nicotine metabolism in the tobacco plant. G. S. ILJIN (U.S.S.R. State Inst. Tobacco Ind., Bull. 69, 1930, 81—85).—When isolated tobacco seedlings are placed in toluene vapour, profound decomposition of the nitrogenous material takes place. The amino-acids and amides decreased markedly in amount and a larger amount of ammonia was formed, liberation of carbon dioxide continuing during the whole period of the experiment but diminishing in intensity towards the end. If sufficient oxygen is supplied, the nicotine completely disappears, this process occurring more slowly if the supply of oxygen is restricted. Under these conditions, nicotine is not formed as a result of initial hydrolysis of the protein material but requires profound decomposition of the nitrogenous substances to ammonia which, by condensation with non-nitrogenous carbon compounds, gives rise to the nicotine molecule. It is probable that nicotine is a reserve form of nitrogen and that it participates in the general cycle of biological processes of the organism, its physiological function being analogous to that of asparagine. T. H. POPE.

Microanalytical tobacco determinations. III. Determination of those constituents of the ash which influence smouldering. J. BODNAR and L. BARTA. **IV. Determination of nicotine.** J. BODNAR and V. L. NAGY (Biochem. Z., 1930, **227**, 429—451, 452—456; cf. B., 1928, 546; A., 1929, 729).—III. The capacity of tobacco to smoulder satisfactorily when being smoked depends to a large extent on the amount and composition of the ash which it yields. Micro-methods can be applied to the determination of potassium, calcium, chloride, phosphate, and sulphate in the ash from 0·5 g. of tobacco.

IV. The residue left when 10·0 c.c. of the supernatant ether–light petroleum solution is evaporated to dryness is dissolved in water (10·0 c.c.) and titrated with 0·01*N*-hydrochloric acid, methyl-red being used as indicator. W. MCCARTNEY.

Power of liberating iodine from iodides possessed by the *Phæophyceæ*. H. KYLIN (Z. physiol. Chem., 1930, **191**, 200—210).—No special iodine liberator was found in extracts of *Laminaria digitata*. When the fresh leaves were placed in contact with paper containing starch and slightly acidified with aqueous acetic acid an iodine reaction was detected. In the surface cells of *Laminaria* there appears to be an iodide-oxidase, but " iodine volatilisation " happens in nature only when, owing to some change in osmotic equilibrium, iodide diffuses to the outer wall of the surface cells.

J. H. BIRKINSHAW.

Liberation of iodine from the iodiferous parts of *Bonnemaisonia asparagoides* by ultra-violet irradiation. R. LAMI (Compt. rend., 1930, **191**, 863—865).—When the iodiferous parts of *B. asparagoides* are irradiated with ultra-violet light, iodine diffuses out into the surrounding water. It is suggested that this is due rather to direct liberation of loosely bound iodine than to its liberation by acid diffusing from the vacuoles, following necrosis caused by the irradiation. T. H. MORTON.

Influence of inorganic ions on the properties of seeds. I. Crystal-polyamphion theory of gels and the crystal-polyamphion-emulsoid theory of biological phenomena. V. KURBATOV. **II. Changes in p_H and p_{Cl} during the soaking of seeds in solutions of different ionic composition.** S. A. GLUCKMANN (Protoplasma, 1930, **9**, 34—65, 66—96).—I. A theoretical discussion.

II. Seeds soaked in aqueous solutions tend to bring the p_H value of the liquid to a definite point, viz., 7·0 in water, a lower value in solutions of univalent salts, and still lower with bivalent salts. The p_H value of solutions in contact with seeds changes sharply in a few hours and subsequently remains constant, being independent of temperature or the extent of swelling of the seeds. During soaking chloride ions are leached from seeds at a rate varying with the nature of the salts in solution, being greatest for salt solutions of univalent metals, followed in order by bi- and tervalent metals. The rates of swelling of the seeds in various solutions were in the order water>univalent>bivalent>tervalent salts. Effects of soaking are irreversible and may be directly continued in subsequent soakings. The increased rate of germination following soaking in water is retarded by the use of salt solutions to an amount increasing with the concentrations and with the valency of the metal. The yield of plants was not affected by the soaking of the seed. A. G. POLLARD.

Calcium oxalate crystals in the seed coat of *Fumaria officinalis*, L. J. Greger (Planta [Z. wiss. Biol.], 1930, **12**, 49—52).—Contrary to general opinion, monoclinic crystals of calcium oxalate are formed in the outer integument of the seed coat of *F. officinalis* in the early stages of development and are subsequently absorbed. A. G. Pollard.

Precipitation of calcium oxalate in plant cells. A. Niethammer (Planta [Z. wiss. Biol.], 1930, **12**, 53—59).—Calcium oxalate crystals are formed in fruit cells and are reabsorbed as the fruit ripens. The formation of calcium oxalate is not merely the deposition of unutilisable material, but represents a temporary storage of reserve material in excess of the metabolic requirements of the plant.

A. G. Pollard.

Biochemistry and histochemistry of fruits and seeds. II. A. Niethammer (Biochem. Z., 1930, **227**, 462—471; cf. A., 1930, 964).—In unripe fruits and seeds deposits of calcium oxalate, which in most cases disappear as ripening proceeds, are often found. The acetaldehyde content of most fruits increases with increasing ripeness, the increases in the case of dry seeds and fruits being maintained only until the germinating power has reached its maximum.

W. McCartney.

Determination of the acid-base balance in the ash of plants. D. E. Frear (J. Biol. Chem., 1930, **88**, 675—681).—The finely-powdered plant material (2 g.) is wetted with 10 c.c. of water and mixed with 25 c.c. of 25% magnesium nitrate solution. After drying the mixture is ignited first at 250° and then at 500°. The ash is mixed with 10 c.c. of water and 60 c.c. of *N*-nitric acid and kept for 3 hrs. just below the b. p. The excess of nitric acid is titrated with standard alkali. A blank test is made using 1 g. of sugar in the place of plant material.

W. O. Kermack.

Sugar content [of plants] and the action of potassium. J. Szolnoki (Wein u. Rebe, 1930, **11** 583—584; Chem. Zentr., 1930, i, 3449).—The effect of potassium on the formation and storage of sugar is regarded as being photo-electric in character.

A. A. Eldridge.

Mechanism of the separation of silica gels in plant cells. H. Pfeiffer (Protoplasma, 1930, **9**, 120—127; Chem. Zentr., 1930, i, 3447).—Dehydration of adsorbed hydrosols is indicated.

A. A. Eldridge.

Stempell's detection of mitogenetic radiation by means of Liesegang rings. G. van Iterson, jun., and W. H. van der Heide (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 702—706).—The claim of Stempell (Biol. Zentr., 1930, **50**, 248) that there exists a residual mitogenetic radiation (cf. Siebert, A., 1930, 966), proceeding from minced onion roots, capable of passing through quartz or uviol glass and of causing distortion in growing Liesegang rings, is not confirmed. T. H. Morton.

Parasitic behaviour of *Pseudomonas tabaci* (Wolf and Foster) causing "wildfire" in tobacco. K. Boning (Z. Parasitenk. [Z. wiss. Biol.], 1930, **2**, 645—755).—The sensitiveness of tobacco plants to "wildfire" is largely dependent on nutritional factors. The greatest sensitiveness results from insufficient supplies of potash and excessive nitrogen. Phosphate deficiency increases the sensitiveness to infection, but generous phosphatic manuring has no very marked beneficial effect. Liming did not affect the incidence of disease to any appreciable extent. A. G. Pollard.

Rust diseases of cereals. III. Copper adsorption of oat-smut spores (*Ustilago avenæ* [Pers.], Jens). A. Terényi (Z. physiol. Chem., 1930, **192**, 274—280; cf. A., 1930, 648).—Oat-smut spores adsorb up to 50% more copper from copper sulphate, acetate, and cuprammonium sulphate solutions than wheat-smut spores, but are less sensitive, since they require 3% of adsorbed copper to prevent germination as against 0·5% for the wheat fungus. Oat-smut spores treated for 15 min. with copper solution are again capable of germination on extraction with 0·5% hydrochloric acid; if the copper treatment is continued for 24 hrs. the hydrochloric acid does not restore the germinating power, since the copper has penetrated to the interior of the spores. Cuprammonium sulphate renders the spores of both species incapable of germination. J. H. Birkinshaw.

Resistance to poisons of desiccated plant tissues. W. W. Allen (Ann. Bot., 1930, **44**, 1001—1009).—Moss (*Mnium hornum*), when thoroughly desiccated by drying in air, can withstand several hours' immersion in absolute alcohol, acetone, ether, or xylene, being able to grow when transferred directly to water and then planted. Such treatment with chloroform or dilute alcohol, however, proved fatal. F. O. Howitt.

Fine structure of wood tracheids according to the examination of fossil woods. E. Opfermann and G. Rutz (Papier-Fabr., 1930, **28**, 780—786).—Lignite (fossil wood) is discussed with reference to its importance in the theory of coal formation. The fibrous constituents of lignite have been isolated and investigated microscopically. Tracheids of coniferous woods were present to the exclusion of deciduous woods. Many of the tracheids presented a similar appearance to that of swollen ramie fibre. Swelling by means of cuprammonium caused the tracheids to assume a spiral formation similar to that shown by cotton under the same conditions, the middle lamella of the wood acting similarly to the cuticle of cotton.

T. T. Potts.

Structure of lignite. F. Luft (Papier-Fabr., 1930, **28**, 787—791).—*X*-Ray spectrographic analysis of the fossil wood tracheids referred to in the preceding abstract shows that interference figures similar to those of native cellulose, and not of the ordinary woods, are obtained. The spiral structure of the middle lamella, shown to be an early condition of the tracheids, appears to be absent in the tracheids as examined. The lamella appears to consist primarily of a number of parallel layers, and a similar condition is shown to be naturally present in the spurs of *Opuntia papyracantha*. T. T. Potts.

Technique of microchemical reactions. G. C. van Walsem (Z. wiss. Mikros., 1930, **47**, 81—82; Chem. Zentr., 1930, i, 3703—3704).—The staining and microscopical examination of urinary sediments are described. A. A. Eldridge.

Staining of fat [for microscopical analysis]. W. GROSS (Z. wiss. Mikros., 1930, 47, 64—68; Chem. Zentr., 1930, i, 3704).

Determination of uric acid in urine by means of its absorption spectrum. J. EISENBRAND (Arch. Pharm., 1930, 268, 520—536).—In solutions of p_H 5—6, uric acid shows a very intense absorption band at 289 mμ (ε=11,800) and is responsible for more than half the total absorption of urine at this wavelength. An expression is given by which the concentration of uric acid solutions may be derived from absorption data, and no other substance absorbing in this region is precipitable from urine by ammonium chloride. Precipitation followed by optical determination offers, however, no advantage over the original method of Hopkins, since the chief faults of the latter lie in the difficulty of filtering the precipitate, which consists almost entirely of uric acid, and not, as has been supposed, of ammonium urate, and in the uncertainty as to the amount of uric acid remaining in the filtrate (cf. Jung, A., 1922, i, 1070). An improved method is based on the fact that the absorption spectrum of uric acid changes considerably with the p_H, the greatest change in intensity being observed at about 300 mμ. Two equal quantities of 2—5 c.c. of urine with 10 c.c. of 0·1*N*-hydrochloric acid and 0·1*N*-sodium hydroxide, respectively, are each diluted to 100 c.c. and the intensities of absorption (E_1 and E_2, respectively) for the line Hg_{303} are compared by means of Scheibe's spectrophotometer. The concentration of uric acid in mg. per 100 c.c. is given by $2{\cdot}58(E_2-E_1)$, the absorptions being calculated for 1 c.c. of undiluted urine. The differences between the results obtained by this method and by Hopkins' method (without correction for the filtrate) vary between 20·6 mg. and 3·1 mg. per 100 c.c. This apparent variation in solubility is not attributed to p_H variations, but to the formation in certain cases of colloidal solutions of uric acid, which may easily be obtained at p_H 4—5, even in the absence of organic protectives. The new determination can be completed in 30 min., or, using photo-electric apparatus, in 6 min.

H. E. F. NOTTON.

Determination of uric acid in urine. D. GANASSINI (Arch. Ist. Biochim. Ital., 1930, 2, 505—508).—To obviate a possible slight loss of uric acid and also the use of potassium iodide and silver nitrate, the Salkowski–Ludwig reagent employed in the author's method (A., 1914, ii, 823) may be replaced by zinc sulphate solution, followed by a slight excess of sodium carbonate, the uric acid being thus precipitated as basic zinc urate. This is dissolved in dilute hydrochloric acid and the zinc precipitated as phosphate by adding disodium hydrogen phosphate; the uric acid dissolves as neutral sodium urate and is determined in the filtrate by titration with 0·1*N*-iodine, indigo-carmine being used as indicator.

T. H. POPE.

Colorimetric determination of the p_H of urine. V. C. MYERS and E. MUNTWYLER (J. Lab. Clin. Med., 1930, 15, 752—755). CHEMICAL ABSTRACTS.

Glass light filter for Folin's new micro-determination of blood-sugar. H. TAUBER (J. Lab. Clin. Med., 1930, 15, 766—767).—A yellow glass filter is employed. CHEMICAL ABSTRACTS.

Tests for madar juice (*Calotropis gigantea*) and for snake venom. D. N. CHATTERJI (Analyst, 1930, 55, 683—684).—The crude chemical characteristics of extracts of the juice are described. Snake venom is detected by its toxicity to frogs.

D. G. HEWER.

Gravimetric methods in biochemistry. II. Determination of potassium, using the torsion balance. L. JENDRASSIK and P. PETRAS (Biochem. Z., 1930, 226, 381—386).—For the determination of potassium in urine and in liquids of similar potassium content the metal is precipitated as cobaltinitrite, which is weighed on a torsion balance. Ammonia must be removed from urine before precipitation and if much protein is present it should be removed first by precipitation with lead acetate. W. MCCARTNEY.

Determination of iron in biological material. R. HILL (Proc. Roy. Soc., 1930, B, 107, 205—214).—2 : 2′-Dipyridyl gives with ferrous salts, or with ferric salts in the presence of a reducing agent, a red colour over the p_H range 3·5—8·5. The presence of other metals, unless in great excess, does not influence the colour. The colour is adsorbed by insoluble proteins, but not by vegetable fibres. Adsorption by proteins, however, is small in the presence of sulphur dioxide and sodium acetate, or of 30% ethyl alcohol. Iron can be determined in biological material without preliminary ashing in the following way. 2 : 2′-Dipyridyl is added to a suspension of the substance in acetate buffer in the presence of sulphur dioxide and sodium hyposulphite. The mixture is filtered and the coloured filtrate is matched against a series of iron–2 : 2-dipyridyl standards. The iron in baker's yeast and egg-yolk was shown to be in the ferric state. 2 : 2′-Dipyridyl inhibits the catalytic action of iron but not of copper on the oxidation of cysteine.

G. F. MARRIAN.

Colorimetric determination of small amounts of arsenic in biological material. E. H. MAECHLING and F. B. FLINN (J. Lab. Clin. Med., 1930, 15, 779—782).—The solution containing arsenic is treated with an acidified solution of ammonium molybdate which has previously been reduced by means of hydrazine sulphate. CHEMICAL ABSTRACTS.

Determination of iodine in organic products. G. PFEIFFER (Biochem. Z., 1930, 228, 146—153).—Further details and modifications of the author's method are given, the combustion being now carried out in a heated quartz tube in presence of a platinum catalyst (cf. A., 1928, 928; 1929, 110, 1204).

P. W. CLUTTERBUCK.

Can the formula of Arrhenius be used in biology? J. BELEHRADEK (Protoplasma, 1928, 5, 310—318).—It is concluded that Arrhenius' law cannot be applied to heterogeneous systems. Changes in μ for biological reactions with changes in temperature are attributed to changes in the viscosity of the protoplasm. CHEMICAL ABSTRACTS.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

FEBRUARY, 1931.

General, Physical, and Inorganic Chemistry.

Isotope effect on band spectrum intensities. J. L. DUNHAM (Physical Rev., 1930, [ii], **36**, 1553—1559).—Theoretical. In order to discover whether the transition probability of a given line is different for two isotopic molecules, the effect of the nuclear mass on intensities is calculated on the basis of Hutchisson's expressions for the vibrational transition probability (cf A., 1930, 1331). It is shown that there is a change in the vibrational, but not in the electronic, part of the transition probability with nuclear mass. The effect of a change in nuclear mass on the population, regarded as a simple Boltzmann distribution, of the initial state is also found. Results are applied to find the magnitude of the isotope effect for certain bands which have been used to measure the abundance of the isotopes in oxygen (cf. Babcock, A., 1929, 971), nitric oxide (cf. Naudé, A., 1930, 1232), and chlorine (cf. Elliott, *ibid.*, 977). The effect is small, and generally less than 10%. N. M. BLIGH.

Change in electron coupling in rare gases. C. J. BAKKER (Naturwiss., 1930, **18**, 1100).—The extension to p^5s and d^9s configurations by Laporte and Inglis (A., 1930, 971) of the quantum-mechanical theory of Houston (A., 1929, 480) on the relation between the triplet interval ratio to the singlet–triplet interval for two-electron configurations in which one electron is in an s-state has been applied to the rare gases. Experimental results of Back (A., 1925, ii, 341) for the g values of the singlet and middle triplet levels of the $2p^53s$ configuration of the Ne I spectrum have been compared with calculated values. Experimental data on the Zeeman effect were used to derive g values of analogous levels of the configurations $3p^54s$ in the A I and $4p^55s$ in the Kr I spectra. In the spectrum of Xe I only the g values of the middle triplet level of the configuration $5p^56s$ could be measured. For the spectra of Ne I, A I, Kr I, good agreement was found between calculated and experimental g values; with Xe I the agreement is not so good. W. R. ANGUS.

Method of applying the slitless spectrograph to the measurement of the Doppler shift. N. DEISCH (J. Opt. Soc. Amer., 1930, **20**, 685—692).—Descriptive. W. GOOD.

Ultra-violet light theory of auroræ and magnetic storms. E. O. HULBURT (Physical Rev., 1930, [ii], **36**, 1560—1569).—Various difficulties and anomalies in the recently proposed theory (cf. *ibid.*, 1929, **33**, 412; **34**, 344) are removed by the application of further developments of the theory of the high atmosphere (cf. A., 1930, 392). N. M. BLIGH.

Paschen–Back effect in hyperfine structure. S. GOUDSMIT and R. F. BACKER (Z. Physik, 1930, **66**, 13—30).—The method developed by Heisenberg and Jordan and by Darwin for the Paschen–Back and Zeeman effects in ordinary multiplets is applied to the interaction of nuclear spin and resultant outer electronic angular momentum, to give the Paschen–Back and Zeeman separations and component line intensities. The theory is accurate only when the Paschen–Back effect is fully developed, and lines of small hyperfine separation should, therefore, be chosen for its verification. Two rules are deduced for transition from strong to weak fields, viz., (i) the projection, M_F, of the resultant of all angular momenta in the field direction remains unchanged; (ii) different levels with the same value of M_F do not cross over in energy value. The theoretical results are compared with Back's experimental results for bismuth (cf. this vol., 137). A. B. D. CASSIE.

Extended energy functions of the hydrogen molecule. P. M. DAVIDSON and W. C. PRICE (Proc. Roy. Soc., 1930, **A**, **130**, 105—111).—Mathematical. A formula is deduced for the potential energy of a diatomic molecule which holds for all values of the internuclear distance. Previous formulæ fail either at small distances, or at large distances, or both. The present formula appears as the sum of two series, the significance of which is discussed in terms of the forces between the components of the molecule. L. L. BIRCUMSHAW.

New bands in the secondary spectrum of hydrogen. III. D. B. DEODHAR (Phil. Mag., 1930, [vii], **10**, 1082—1095; cf. A., 1930, 263; Finkelnburg, A., 1929, 118).—The wave numbers, estimated intensities, term values, and quantum analysis of the recently discovered group of seven bands in the violet region are tabulated and discussed. N. M. BLIGH.

Effect of crossed electric and magnetic fields on the Balmer lines of hydrogen. W. STEUBING (Naturwiss., 1930, **18**, 1098—1099).—The effect of the simultaneous action of an electric and a magnetic field has been studied. A crossed field does not produce new components, but there results a kind of displacement of Stark effect components which follows identically the intensity changes of individual components. The results on the intensity differences of components in relation to the direction of the electric field are of importance in deciding whether experimental results on the intensity distribution of Stark effect components are in harmony with the theory of

Schrödinger. Weak magnetic fields do not exert a marked influence on the intensity distribution.

W. R. ANGUS.

Experimental arrangement of the H_2 band system into singlet and triplet systems. W. FINKELNBURG (Z. Physik, 1930, **66**, 345—349).—The distinct forms of the excitation function–exciting voltage curves for singlet and triplet terms were used to distinguish H_2 singlet and triplet bands; *A*-, *B*-bands belong to a singlet system, and α-, β- to a triplet system. The subsidiary maximum which appears only in the H_2 triplet excitation function–exciting voltage curve is in accord with Beutler and Eisenschimmel's hypothesis that during a collision process the resultant electron spin of the colliding entities must remain unchanged.

A. B. D. CASSIE.

Stark effect in some helium lines in the visible spectrum. K. SJÖGREN (Z. Physik, 1930, **66**, 377—388).—The Stark effect was determined quantitatively, by Stark's original method, for fields of 175—550 kilovolts per cm. The lines $2S-3P$, $2S-3D$, $2P-4S$, $2P-4D$, $2P-4F$, $2P-4P$, $2p-4s$, $2p-4d$, $2p-4f$, and $2p-4p$ were investigated.

A. B. D. CASSIE.

Change in electron coupling in the rare gases. C. J. BAKKER (Nature, 1930, **126**, 955).—From experimental data on the Zeeman effect of the rare gases, the experimental *g* values of the analogous levels of the configuration $3p^54s$ in A I and $4p^55s$ in Kr I are obtained. Agreement between observed and calculated *g* values is satisfactory in the case of Ne I, A I, and Kr I.

L. S. THEOBALD.

Nuclear moment of Li^6 and Li^7. H. SCHULER (Z. Physik, 1930, **66**, 431—435).—Hyperfine structure of the Li II 5485 Å. line was investigated by means of a Perot–Fabry etalon with a maximum plate separation of 3 mm. Results for Li^7 agree approximately with Güttinger's formulæ (cf. A., 1930, 1487) for nuclear spin of ½ and of 3/2 units, but do not give sufficient detail to decide between the two values. Li^6, 5485 Å., has no hyperfine structure of separation greater than one fifth that of Li^7.

A. B. D. CASSIE.

C IV lines in the visible and near ultra-violet. Term system for C IV. B. EDLEN and J. STENMAN (Z. Physik, 1930, **66**, 328—338).—The spectrum due to a carbon arc acting in a vacuum was examined. The spark lines C I, C II, C III, and C IV were distinguished by their separate variations in intensity with variation of the self-induction of the discharge circuit. New C II and C III lines, and the most intense C IV lines due to transitions between orbits of total quantum number 4 and 5, and 5 and 6, were observed. These lines were arranged into a term system, which includes more accurate values of terms of principal quantum number 6 than have hitherto been given. The doublet separations in 2^2P, 3^2P, and 4^2P fit Lande's formula.

A. B. D. CASSIE.

Nuclear spin of nitrogen. W. R. VAN WIJK (Arch. Néerland., 1930, [iiiA], **13**, 29—57).—The general theory of diatomic molecular spectrum structure is briefly surveyed. Measurements were made of the negative band spectrum of nitrogen due to the N_2^+ molecule, and of the second positive group due to the neutral molecule. The value 2 : 1 was found for the ratio of alternating intensities of the negative bands 3914, 3884, 4278, and 4237 Å., and for the positive bands 3371, 3805, and 3755 Å. From investigation on the 3914 band, the ratio was found to be independent of the pressure. The agreement of intensity measurements with other criteria for nuclear spin value was investigated from the 3776 Å. thallium line, which showed strong absorption and confirmed the value ½ for the nuclear spin.

N. M. BLIGH.

Bergmann series in the argon spectrum. E. RASMUSSEN (Naturwiss., 1930, **18**, 1112—1113).—Among the inert gases Bergmann series had been observed in the spectrum of xenon only. The corresponding series has been obtained in the argon spectrum, which was photographed on negative plates, using a plane grating spectrograph (dispersion 17 Å./mm.). A table of the observed series is given. The limiting terms $3d_6$, $3d_-$, $3d_3$, $3d^1{}_1$, $3d_4$ and the term series *mU* and *mV* have been determined. Certain new combinations of principal and subsidiary series have been found and are tabulated. From these combinations the terms $2s_2$, $2s_3$, $2s_4$, $2s_5$, and $3s''$ were evaluated. Wave-lengths greater than 1 μ have been provisionally measured by extrapolation.

W. R. ANGUS.

Structure of the iron spectrum. M. A. CATALAN (Anal. Fís. Quím., 1930, **28**, 1239—1385).—A comprehensive survey, with a bibliography, is given of previous work on the atomic structure of iron, with extensive tables of the wave-lengths and intensities of all the arc lines recorded, and of the Zeeman effect. More than 2350 lines of the Fe I spectrum are classified in 304 levels, and there are 8 series, 51 terms, and 275 multiplets. It is shown that the most intense lines originate by addition of a valency electron to the atomic residue in one or both of the spark configurations $3d^64s$ and $3d^7$.

H. F. GILLBE.

Intensity measurements of the multiplet z^5G-e^5F. W. A. M. DEKKERS and A. A. KRUITHOF (Z. Physik, 1930, **66**, 491—493).—Intensity relations in the z^5G-e^5F multiplet of nickel were determined from a carbon arc, one of the poles of which contained a nickel bead, or alternatively, 10% of nickel sulphate; the other pole was either of carbon or of a nickel–zinc alloy. Deviations from the summation rule always occurred.

A. B. D. CASSIE.

Intensity measurements of the copper arc lines. L. S. ORNSTEIN and D. VERMEULEN (Z. Physik, 1930, **66**, 490; cf. A., 1930, 1329).—Copper in a carbon arc gives the ratio of intensities of the 1^2S-2^2P copper doublets as 1 : 2, which agrees with the summation rule value.

A. B. D. CASSIE.

Series of the silver arc spectrum, Ag I. H. A. BLAIR (Physical Rev., 1930, [ii], **36**, 1531—1534; cf. A., 1930, 1227).—The high series members of Ag I were measured, using a Schüler tube source and helium standards. Data for the complete diffuse, sharp, and principal series are tabulated, including a few new lines, and correcting existing values. No terms of the quadruplet system nor of the d^9s^2 ^2D were found (cf. McLennan, A., 1928, 1167; Shenstone, *ibid.*,

450). Ritz formulæ for the series were deduced; the value of the lowest term $d^{10}5s^2S$ is 61104·4, giving an ionisation potential of 7·53 volts. N. M. BLIGH.

Band spectrum of silver hydride. E. BENGTSSON (Nature, 1931, **127**, 14).—The rotational structure of 14 bands belonging to $\longrightarrow {}^1\Sigma$ have been analysed and arranged in a vibrational scheme. The vibrational levels of the lower electronic state can be represented by the formula $F''(v)=1723·5v''-33·5v''^2-0·0094v''^3$; the excited electronic state shows certain irregularities which may originate from a perturbing level. The dissociation energies in both states are $D'\sim6300$ and $D''\sim19,000$ cm.$^{-1}$ approximately. L. S. THEOBALD.

Effect of gases on the optically excited cadmium I spectrum. P. BENDER (Physical Rev., 1930, [ii], **36**, 1535—1542).—An apparatus is described for producing intense optically-excited cadmium radiation for an investigation of the quenching effect of nitrogen, carbon monoxide, and hydrogen on the optically excited cadmium spectrum. Each gas decreases the intensity of each of the spectral lines. Nitrogen and carbon monoxide have a low quenching efficiency, the former being the less efficient, and are less effective in quenching the resonance line λ 3261 than the remainder of the spectrum. Kinetic energy collisions of molecules of these gases with excited cadmium atoms transfer them from the 2^3P_1 to the metastable 2^3P_0 state. Hydrogen has a high quenching efficiency, collisions with the 2^3P_1 cadmium atoms forming cadmium hydride molecules and atomic hydrogen (cf. Bates, A., 1929, 156). The effects are compared with similar phenomena for mercury (cf. Klumb, *ibid.*, 480). N. M. BLIGH.

Optical excitation of cadmium hydride and zinc hydride bands. P. BENDER (Physical Rev., 1930, [ii], **36**, 1543—1552; cf. preceding abstract).—Excitation of a cadmium–hydrogen gas mixture with light from a hydrogen–cadmium, but not from a helium–cadmium, discharge produces an intense true optical resonance of cadmium hydride bands; these are produced also through excitation of CdH molecules by collisions of the second kind between excited cadmium atoms and either normal CdH molecules or H_2 molecules. The mechanism of the resonance excitation is discussed. Zinc hydride bands were produced as true optical resonance radiation by hydrogen–zinc electric discharge. Mercury hydride bands were excited, using a water-cooled mercury arc, through collisions of the second kind (cf. Gaviola and Wood, A., 1929, 239) and the mechanism is discussed in relation to the foregoing results. N. M. BLIGH.

Photo-electric intensity measurements in the mercury spectrum. II. L. S. ORNSTEIN and J. F. CUSTERS (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 809—813).—Further measurements on the intensity of certain lines in the mercury spectrum have shown that the relations previously reported (A., 1930, 1080) hold not only for the pressure region investigated, but also at very low pressures, the measurements having been extended by the use of a more sensitive photo-electric cell. With falling pressure the peak of the curve connecting potential with current density is displaced in the direction of higher current density, but the peak potential falls at first and rises again later. The intensity, I, of the line 5461 Å. has been measured as a function of the current density i, and at all pressures the ratio I/i increases with decreasing current density.
E. S. HEDGES.

Fluorescence of excited mercury atoms. Z. ZAJAC (Compt. rend., 1930, **191**, 1304—1306; cf. Pienkovski, A., 1928, 813).—Mercury vapour was excited simultaneously by an oscillating electric discharge and a low-pressure mercury arc in an evacuated sealed tube connected with a mercury reservoir, both of which could be heated independently so as to vary either the vapour pressure ($t°$ const.) or the density (p const.). A bluish-green luminescence appeared at 0·05 mm. in the positive region and attained a maximum intensity at 140° and 0·3 mm. Above 1 mm. pressure a continuous spectrum was obtained, the intensity of the mercury arc lines (λ 5461, 4358, and 4047) being greater than that obtained by electrical excitation alone. Since the intensity of the fluorescence is proportional to that of the activating light, it is concluded that a single stage of absorption precedes emission, and that the oscillating discharge produces a non-uniform distribution of the atoms in the 2^3P_{012} state, followed by passage to the 2^3S_1 state consequent on absorption of certain incident radiations. The fluorescence results from the return to the normal state. J. GRANT.

Fluorescence of mercury vapour under atomic and molecular absorption. (LORD) RAYLEIGH (Nature, 1931, **127**, 10).—Mercury vapour gives the green fluorescence when excited by wave-lengths as long as 3450 Å. The discontinuous nature of the fluorescence excited by wave-lengths near the resonance line 2537 Å. is confirmed by the fact that the addition of hydrogen suppresses the fluorescence arising from atomic absorption, leaving the molecular effect practically unaltered. L. S. THEOBALD.

Zeeman effect in the hyperfine structure of the thallium line, 3775 A. E. BACK and J. WULFF (Z. Physik, 1930, **66**, 31—48).—The Zeeman effect of this particularly simple line was observed for magnetic fields of 17,050, 29,700, and 43,350 gauss with a 6·3-metre Rowland grating. The results are discussed in relation to Goudsmit and Backer's theory (see this vol., 135) of the position and intensity of the Zeeman components. The presence of ordinarily forbidden transitions predicted by this theory was verified. Generally, the experimental results are in good agreement with theory if a nuclear spin momentum of ½ unit is assumed. A. B. D. CASSIE.

Hyperfine structure of bismuth. P. ZEEMAN, E. BACK, and S. GOUDSMIT (Z. Physik, 1930, **66**, 1—12).—New experiments on the hyperfine structure of the bismuth arc lines, and their Zeeman effect, are described. The results complete earlier work, without changing the theoretical deductions. A scheme of term levels is given. The excited levels have not been sufficiently investigated to give more than their total and inner quantum numbers. The coefficient of proportionality in a Lande separation formula for interaction of nuclear spin, and resultant electronic

angular momentum of the outer shell, is given for the different levels. Intensity formulæ for the hyperfine structure are also given. The different arc lines, their hyperfine structure, and Zeeman components are discussed in detail. An appendix by BACK and J. WULFF shows photographs of the 10 hyperfine Zeeman components of bismuth, agreeing with the assigned nuclear spin of $4\frac{1}{2}$ units. A concave grating and a Hilger echelon were used to obtain the photographs. A. B. D. CASSIE.

Reflexion of long wave-length X-rays. J. THIBAUD (J. Phys. Radium, 1930, [vii], 1, 404).—A discussion of the results of Valouch (cf. A., 1930, 1229) in relation to the author's formulæ (cf. *ibid.*, 512). N. M. BLIGH.

Fine structure of certain X-ray emission lines. J. VALASEK (Physical Rev., 1930, [ii], **36**, 1523—1530).—The $K\alpha$ lines of iron, cobalt, nickel, copper, molybdenum, and silver were investigated, using two specially constructed single-crystal spectrometers. The fine structure reported by Davis and Purks (cf. A., 1928, 451, 819) was not confirmed. Photomicrographic curves from plates taken in the first and second order are reproduced, and widths of α_1 lines and the β_1 line of molybdenum are tabulated.
N. M. BLIGH.

Scattering power for X-rays of the atoms in magnesium oxide and sodium fluoride. R. W. G. WYCKOFF and A. H. ARMSTRONG (Z. Krist., 1930, **72**, 433—441; Chem. Zentr., 1930, ii, 353).—The intensities of the principal lines, using Mo$K\alpha$ radiation, have been measured. The results for sodium fluoride agree with those of Havighurst. A. A. ELDRIDGE.

Wave-length of X-rays. T. H. LABY and R. BINGHAM (Nature, 1930, **126**, 915—916).—Using Rowland's method of coincidence of lines, the K line of carbon has been photographed over a range of $n\lambda$ from 0 to 810 Å. By comparison with the $L\alpha$ and Ll lines of copper the wave-lengths 44·7 and 44·8 Å. have been obtained for the carbon line relative to 13·32 Å. for the copper $L\alpha$ line. The aluminium $K\alpha_1\alpha_2$ line is 8·315 Å. relative to copper $K\alpha_1\alpha_2$ 1·5392 Å. L. S. THEOBALD.

Satellites of the $K\beta_1$ line of elements from iron to zinc. S. KAWATA (Mem. Coll. Sci. Kyoto, 1930, **A**, **13**, 383—387).—The wave-lengths of two new satellites discovered on the short wave-length sides of $K\beta_1$ and $K\beta_2$ of each of the elements from iron to zinc have been determined. W. GOOD.

Absorption formula of X-rays. II. M. ISHINO and S. KAWATA (Mem. Coll. Sci. Kyoto, 1930, **A**, **13**, 375—381; cf. A., 1928, 212).—The results of experimental determination of the absorption coefficients of elements and aqueous salt solutions for various wave-lengths are given. It is shown that the true atomic absorption coefficient is not proportional to $\lambda^p Z^q$, where p and q are constants independent of the wave-length, λ, and the atomic number, Z. p and q are nearly equal to but less than 3 and 4, respectively. W. GOOD.

X-Ray absorption in gases. W. W. COLVERT (Physical Rev., 1930, [ii], **36**, 1619—1624).—Using double reflexion of X-ray spectral lines from a platinum-surfaced mirror and a calcite crystal in order to increase homogeneity of the beam, absorption measurements were made with neon, sulphur dioxide, chlorine, and argon, and mass absorption coefficients for the range of radiation wave-lengths 0·496—2·288 Å. are tabulated. N. M. BLIGH.

Glow discharge at the active electrode of an electrolytic rectifier. J. S. FORREST (Phil. Mag., 1930, [vii], **10**, 1003—1014).—The luminosity appearing on the surface of the active electrode of a rectifying cell was investigated, using cells with active electrodes of aluminium, tantalum, and tungsten, through observations on the $P.D.$-current curves, thickness, and pressure of the gas layer on the electrode surface, spectrum of the glow, influence of magnetic fields, and comparison with the cathode glow. Evidence suggests that the glow is produced by the ionisation of oxygen molecules by collision with electrons, and the subsequent recombination of the electrons with the ionised molecules.
N. M. BLIGH.

Photo-ionisation of cæsium vapour by absorption between the series lines. C. BOECKNER and F. L. MOHLER (Bur. Stand. J. Res., 1930, **5**, 831—842).—The photo-ionisation of cæsium produced by a small continuous absorption between the series lines has been measured by the space-charge method. The relative sensitivity, $I(\lambda)/I(3200$ Å.), increases with the square root of the pressure within the range 3750—3250 Å. The values are almost independent of the temperature on the red side of 3500 Å., but on the other side the effect is reduced to about half by a rise in temperature of 70°. These results indicate that absorption between the lines is of molecular origin and that the work of dissociation of Cs_2 is about 0·26 electron volt (cf. A., 1930, 1079).
A. R. POWELL.

Photo-electric processes. M. STOBBE (Ann. Physik, 1930, [v], **7**, 661—715).—A theoretical contribution to the quantum mechanics of photo-electric processes. W. GOOD.

Photo-electric effect of aluminium and aluminium amalgams. H. GERDING (Z. physikal. Chem., 1930, **B**, **11**, 1—37).—The photo-electric current from aluminium and its amalgams with 0·06, 0·26, and 0·38% Hg has been studied in relation to the wave-length of the incident light, the time of exposure, and the condition of the illuminated surface. The quotient c/I (electron emission/intensity of light) in a vacuum is increased by scraping the surface, especially for wave-lengths near the photo-electric threshold, which is itself displaced towards the red. A scraped surface becomes fatigued in a vacuum, and more rapidly after contact with air, the photo-electric threshold in this case being displaced towards the ultra-violet. The maximum values of c/I and of the photo-electric threshold obtained by continued scraping in a vacuum are least for pure aluminium, slightly higher for the 0·06%, and highest for the 0·26% and 0·38% amalgams. This result affords support to the view that passivity is primarily attributable to differences in the metal itself. The fatigue observed on keeping is due to adsorption of air, and is caused by the negative contact potential acquired

by the air film, acting as a retarding potential for the expelled electrons, increasing the work required for their expulsion. F. L. USHER.

Photo-electric emission from thin films of cæsium. L. R. KOLLER (Physical Rev., 1930, [ii], **36**, 1639—1647; cf. Campbell, A., 1928, 1297; Zworykin, A., 1929, 1262; Olpin, A., 1930, 1230).—The photo-electric properties and methods of preparing thin films of cæsium were investigated. In one type a thin film of cæsium is adsorbed on a thin layer of oxygen previously adsorbed on the silvered bulb of the photo-electric cell. In the other, a thin film of cæsium is adsorbed on a layer of suboxides of cæsium obtained by coating a cathode with metallic cæsium and admitting traces of oxygen; the photo-electric current was recorded simultaneously. Results show that the most sensitive surfaces are obtained when a suboxide, rather than the normal oxide Cs_2O, has been formed, and that their properties are due to the arrangement of molecules very near the surface. N. M. BLIGH.

Radio-frequency properties of ionised air. E. V. APPLETON and E. C. CHILDS (Phil. Mag., 1930, [vii], **10**, 969—994).—The measurement of the dielectric constant of a conducting ionised medium is examined mathematically and an investigation, suggested thereby, of the high-frequency behaviour of ionised gases by measuring the dielectric constant of air is described. As ionisation increased the dielectric constant reached a minimum value from which it increased to greater than unity. This divergence from theoretical prediction was found to be due to the formation of ionic sheaths round the electrodes, thus increasing the capacity of the condenser. The variation of the thickness of the sheaths with the potential across them was examined by a wireless method, and gave results in agreement with the theory of collectors due to Langmuir and Mott-Smith. The influence of an imposed magnetic field on the radio-frequency properties of ionised air was studied, and the existence of a predicted inverse Zeeman effect confirmed. Pronounced absorption occurs at a critical frequency corresponding with a particular value of the imposed field; the ratio of the two last-named confirms the electronic nature of the electric carriers, supporting Larmor's theory of the refractive deviation of wireless waves in the upper atmosphere by free electrons. N. M. BLIGH.

Internal conversion of nuclear energy. H. CASIMIR (Nature, 1930, **126**, 953—954).—An expression for the coefficient of internal photo-effect has been deduced using Dirac's equation, and a comparison of the calculated photo-effects with the internal conversions measured by Ellis and Aston for radium-*C* (A., 1930, 1339) shows that the number of ejected electrons is larger than would be expected from the internal photo-effect. This shows that for the hard γ-rays of radium-*C* the ejection of atomic electrons is due mainly to interaction in the nuclear region. L. S. THEOBALD.

Effective cross-section of krypton towards slow electrons. J. HOLTSMARK (Z. Physik, 1930, **66**, 49—59).—The data of Hartree for the atomic field of krypton, duly corrected for polarisation energy, have been used to compute the effective cross-section of krypton molecules towards electrons of energy from 0 to 7 volt$^{-\frac{1}{2}}$. The agreement between the resulting values and the experimental results of Ramsauer and Kollath is satisfactory. R. W. LUNT.

Liberation of electrons from a metal surface by positive ions. II. F. M. PENNING (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 841—857; cf. A., 1928, 681).—Measurements have been made of γ, the average number of electrons liberated from a metal surface by each positive ion, using positive ions of neon at different velocities. When extrapolated to zero velocity, the result $\gamma_0=0{\cdot}05$ is obtained, indicating that positive neon ions of zero velocity can liberate electrons. The experiments were conducted in such a way that metastable atoms, high-velocity neutral atoms, and light quanta could not strike the collecting electrodes. At higher velocities the value of γ depends on the material surface of the cathode and on the presence of impurities. E. S. HEDGES.

Characteristic velocities of electrons scattered from metallic surfaces. G. BERNARDINI (Atti R. Accad. Lincei, 1930, [vi], **11**, 1096—1099).—Electrons having velocities of 34—50 volts emitted from a tungsten–thorium filament were allowed to impinge on brass and zinc surfaces, and the magnetic spectra of the resulting scattered electrons were photographed. The lines in these spectra correspond with characteristic electron velocities, but it is not certain whether they are really characteristic of the metallic surface, or are due to adsorbed gas. O. J. WALKER.

Free electrons in metals and the role of reflexions according to Bragg. L. BRILLOUIN (J. Phys. Radium, 1930, [vii], **1**, 377—400).—Theoretical. An investigation made of the nature of electron waves in a metal, and the conditions for selective reflexion analogous to those of Bragg for *X*-rays, using the Schrödinger perturbation method, leads to data on the movement of free electrons in the crystal lattice in agreement with that of Bloch (cf. A., 1929, 247; Peierls, A., 1930, 281). The method is extended to the electronic moments, and leads to a series of surfaces, forming by their interlacing a lattice dividing the electron waves into zones, the separating planes corresponding with Bragg's conditions. Each zone corresponds with the waves obtained by the coupling of those of a certain quantum level of the ion; the condition for the numbering of the waves gives an expression for the wave-length, and agrees with the apparent numbering obtained by considering the ions as point charges. The formula for the electron energy is analogous to that of the free electrons of space, but involves an apparent mass which may become negative, and differs from the true mass. The problem is thus analogous to the numbering of the external orbits of complex atoms involving the true and the apparent quantum number of the Rydberg formula. Results deduced for a number of metals are tabulated. N. M. BLIGH.

Capture of electrons by ions. G. WATAGHIN (Atti R. Accad. Lincei, 1930, [vi], **11**, 993—997).—

The probability of the transition of an ion from its free state to the nth quantum state by the capture of electrons has been calculated from the principles of wave mechanics. The result affords an explanation of the experiments of Davis and Barnes (cf. A., 1929, 971). F. G. TRYHORN.

Energy losses of electrons in carbon monoxide and carbon dioxide. E. RUDBERG (Proc. Roy. Soc., 1930, **A**, **130**, 182—196).—An extension of previous work (this vol., 12). In the case of carbon monoxide, the pressures used ranged from 7 to 62×10^{-3} mm., and for carbon dioxide from 15 to 24×10^{-3} mm. The energy distribution of the electrons after passing through the gases showed a number of well-marked maxima which are characteristic of the energy levels of the molecules under investigation. The various maxima for carbon monoxide are correlated with transitions from the normal to excited states of the molecule, known from the analysis of the band spectra of the neutral or singly-ionised carbon monoxide molecules. In cases where a maximum is attributed to a single electronic level, an examination of the potential energy curves for the molecule shows that the position of the maximum in respect to the different possible vibrational levels is in excellent agreement with the Franck–Condon principle (A., 1927, 89). No evidence of the ionisation of soft X-ray levels has been found for either of the gases. L. L. BIRCUMSHAW.

Emission of electrons under the influence of chemical action at lower gas pressures. O. W. RICHARDSON and L. G. GRIMMETT (Proc. Roy. Soc., 1930, **A**, **130**, 217—238; cf. Brotherton, A., 1924, ii, 377; Richardson and Brotherton, A., 1927, 713).—Details are given of a method whereby controllable and measurable pressures of carbonyl chloride can be obtained down to 10^{-5} mm. of mercury. The emission of electrons from an alloy of sodium and potassium (NaK) in this gas has been examined down to measured pressures of 10^{-5} and to extrapolated pressures of 5×10^{-6} mm. under various conditions. The results show that the saturation current i_0 increases continuously with the partial pressure p of the gas from zero up to a critical value in the neighbourhood of $p=10^{-3}$ mm. This critical value depends on the rate of flow of the alloy, being smaller the slower are the drops. The maximum total charge which can be emitted by any one drop appears to be a fixed quantity, proportional to the size of the drop. Evidence is adduced to show that the experimentally determined velocity distribution function among the electrons approaches a limit as the pressure is reduced. L. L. BIRCUMSHAW.

Secondary electronic emissions from metal foils and animal tissues. W. V. MAYNEORD (Proc. Roy. Soc., 1930, **A**, **130**, 63—80).—The relative intensities of beams of X- and γ-radiation of different wave-lengths, when measured by the ionisation chamber method, depend on the material of the chamber. A mathematical theory is developed which shows that, neglecting certain secondary factors, small ionisation chambers artificially made sensitive by the insertion of foils of different elements show a maximum sensitivity in the region of medium wave-lengths, when compared with an air chamber. This is confirmed by experiment. An ionisation chamber for the measurement of the intensity of γ-rays is described; it was found that the relative intensities of primary and secondary scattered beams of rays had different values according to the materials composing the chamber. A region of maximum sensitivity was also observed with ionisation chambers containing animal tissues. The significance of these observations is discussed. L. L. BIRCUMSHAW.

Specific charge of the electron. F. KIRCHNER (Physikal. Z., 1930, **31**, 1073—1075).—The use of an oscillating circuit for determination of the specific charge of the electron (cf. *ibid.*, 1929, **30**, 773) has been considerably improved, and gives for e/m_0 the value $1{\cdot}7602\pm0{\cdot}0025$ e.m.u. This agrees with the spectroscopic value, but deviates unaccountably from the cathode ray value. A. B. D. CASSIE.

Application of electron interference to structure analysis. E. RUPP (Physikal. Z., 1930, **31**, 1076—1078).—Thomson's method for determination of the structure of a surface layer by reflexion of electrons of approximately 30 kilovolts (cf. A., 1930, 1082) is inapplicable to very thin layers. Electrons of 100 volts energy penetrate approximately 10 crystal planes, and may therefore be applied to thin layers. Reflexion from (100) planes of copper after various heat treatments was investigated by plotting intensity against electron velocity for a fixed angle of incidence. A. B. D. CASSIE.

Magnetic analysis of negative ions in mercury vapour. W. M. NIELSEN (Proc. Nat. Acad. Sci., 1930, **16**, 721—727).—Ions produced by a discharge in mercury vapour at a pressure of the order of 10^{-4} mm. have been analysed magnetically to determine the nature of the negative ions. The experimental method consisted in sweeping out of the path of a beam of electrons projected in the mercury vapour parallel to a magnetic field either positive or negative ions by means of a crossed electric field. The separated ions are further accelerated in a second electric field. Curves are given showing the ratio of ion to total electron current against m/e. Hg^-, CO^-, and C^- are identified. At m/e equal to 19 and 60 two peaks (not identifiable) are observed. All the peak maxima appear in the analysis of the positive ions. The apparatus did not give trustworthy results at higher pressures because of the formation of a positive space charge in the electron beam. W. GOOD.

Pressure and high-velocity vapour jets at cathods of a mercury vacuum arc. E. KOBEL (Physical Rev., 1930, [ii], **36**, 1636—1638).—Measurements on a mercury arc and fixed cathode spot gave the value $0{\cdot}017\times10^{-3}$ g. per amp. sec. for the amount of mercury vaporisation, and $16—43\times10^5$ cm. per sec. for the vapour velocity, in good agreement with the results of Tanberg (cf. A., 1930, 832) for the vaporisation of copper from the cathode of a copper arc. N. M. BLIGH.

Distribution of rays in molecular streams. P. CLAUSING (Z. Physik, 1930, **66**, 471—476).—Formulæ are deduced for the space distribution of molecules streaming through a short tube into a

vessel the radius of which equals its length, the length being is small compared with the molecular free path. If diffuse scattering by the walls of the entrance tube governs this space distribution, large departures from the cosine law should occur. This is in contradiction with Mayer's experimental results (*ibid.*, 1929, **58**, 373). A. B. D. CASSIE.

Relationship between electron diffraction maxima and the emission of soft X-rays. H. W. B. SKINNER (Naturwiss., 1930, **18**, 1097—1098).—An explanation of the experimental results of Rupp (A., 1930, 1493) is offered. W. R. ANGUS.

Introduction of exchange into the statistics of an electronic gas. L. GOLDSTEIN (Compt. rend., 1930, **191**, 1306—1308).—The application of the statistical method (Dirac) to the atom is based on the analogy between atomic electrons and a degenerate electronic gas. Fermi's formulæ must be revised to include the energy of electronic exchange, which, together with the kinetic and potential energies, makes up the total energy of a system of electrons. It is shown mathematically that the energy of agitation of an electronic gas is made up of the energy of kinetic agitation and the energy of exchange agitation. J. GRANT.

Equations of electron theory and Dirac wave mechanics. N. R. SEN (Z. Physik, 1930, **66**, 122—128).—Mathematical. A. B. D. CASSIE.

Dirac theory of protons and electrons. G. I. POKROVSKI (Z. Physik, 1930, **66**, 129—136).—Theoretical. Some apparent difficulties of Dirac's theory are explained, and an upper limit for the energy of one quantum is deduced. Another result of the theory is that all motion is quantised, so that two successive transitions must have a definite time interval between them. A. B. D. CASSIE.

Graphical calculation of the magnitudes involved in an electron in motion. G. FOURNIER (Compt. rend., 1930, **191**, 1302—1304).—It is shown that the relations between the lengths of the lines and angles involved in the construction of a trigonometrical circle correspond with the magnitudes of an electron in motion, *e.g.*, the ratio of electronic velocity to that of light, the Lorentz concentration and time-transformation factors and the factors required for the calculation of the emission potential and the Broglie wave-length, and the product of H and the radius of a circle described by an electron in a field of H gauss. J. GRANT.

Properties of nuclear electrons. J. KUDAR (Physikal. Z., 1931, **32**, 34—37).—Theoretical. A. J. MEE.

Measurement of cross-section of non-inert gas molecules for slow electrons. E. BRUCHE (Ann. Physik, 1930, [v], **7**, 579—587)—Polemical against Brose and Saayman (A., 1930, 1084). A. J. MEE.

Measurement of cross-section of non-inert gas molecules. H. L. BROSE and E. H. SAAYMAN (Ann. Physik, 1930, [v]. **7**, 588—595).—A reply to Bruche (see above). A. J. MEE.

Measurement of cross-section of non-inert gas molecules. E. BRUCHE (Ann. Physik, 1930, [v], **7**, 596—600).—A reply to Brose and Saayman (see above). A. J. MEE.

Measurement of magnetic susceptibilities of gases. H. BUCHNER (Ann. Physik, 1930, [v], **7**, 716—730).—A method (Gouy method with torsion balance) for the measurement of magnetic susceptibilities of gases is described; it gave for carbon dioxide a value, $(-8\cdot6\pm0\cdot4)\times10^{-10}$, in good agreement with existing data. Between 0 and 600 mm. pressure the volume susceptibility is found to be directly proportional to the pressure; similarly for mixtures of carbon dioxide and oxygen (0·125—0·430% O_2), the mixture law being confirmed. The Glaser pressure anomaly is apparently due to adsorption effects. Under certain conditions Glaser curves could be obtained in experiments with undried oxygen and with undried carbon dioxide. A critical review of existing researches in this field is made and it is concluded that the mass susceptibilities of carbon dioxide and mixtures of it with oxygen are independent of the pressure. W. GOOD.

Unit of at. wt. F. W. ASTON (Nature, 1930, **126**, 953).—Attention is directed to the need for a reconsideration of the scale of at. wts. arising from the complexity of oxygen. L. S. THEOBALD.

At. wt. of potassium from plant ash. H. H. LOWRY (J. Amer. Chem. Soc., 1930, **52**, 4332—4333).—Determinations of the potassium-chlorine ratio with potassium from cotton ash and wheat flour ash yield the at. wt. 39·111±0·013 and 39·091±0·016 (Cl=35·457), respectively, which are in good agreement with accepted values for potassium. This is evidence that plant cells do not absorb selectively the radioactive isotope of potassium from the normal mixture of isotopes (cf. Zwaardemaker, A., 1926, 554; Loring and Druce, Chem. News, 1930, **140**, 34). J. G. A. GRIFFITHS.

Revision of the at. wt. of thallium. Analysis of thallous bromide. O. HONIGSCHMID and H. STRIEBEL (Z. anorg. Chem., 1930, **194**, 293—298).—Analysis of thallous bromide by precipitation of silver bromide yields for the at. wt. of thallium 204·390±0·008, in agreement with that obtained previously by analysis of the chloride. The solubility of thallous bromide in water at 18°, 25·68°, and 68·5° is 423·3, 579, and 2520 mg. per litre, respectively. H. F. GILLBE.

Separation of the isotopes of bromine. At. wt. of bromine from the ratio Ag : AgBr. P. HARTECK and H. STRIEBEL (Z. anorg. Chem., 1930, **194**, 299—304).—The theory of the separation of isotopes by fractional sublimation is described. The most volatile fraction obtained by fractionally subliming bromine in a current of hydrogen at −18·5°, −25°, and −36° had an at. wt., determined from the ratio Ag : AgBr, of 79·916+0·001, which is identical with that of ordinary bromine. The failure to produce any separation is ascribed to the fact that in a mixture of isotopes the vibrational energies of the individual atoms and molecules are so inter-related that the difference of the vibrational energies of two isotopes is less for a mixture than for the separated isotopes, and the magnitude of the effect is therefore reduced to less than the experimental error. H. F. GILLBE.

Relation between the emission of long-range α-rays and γ-rays. (MME.) P. CURIE (Compt. rend., 1930, **191**, 1055—1058).—An extension and comparison with experimental results of Gamow's theory, from which it is concluded that in the cases of radium-*C'* and thorium-*C'* Gamow's formula gives approximate results. J. GRANT.

Formation of long-lived active molecules in hydrogen subjected to the action of α-particles from radon. E. C. TRUESDALE (J. Physical Chem., 1930, **34**, 2472—2478).—The work of Duane and Wendt (Physical Rev., 1917, **10**, 117) has been repeated using certain refinements. Hydrogen sulphide could be detected in small amounts only when sulphur was present in the reaction sphere surrounding the radon, and no evidence of the existence of long-lived active hydrogen or of triatomic hydrogen was obtained. L. S. THEOBALD.

Scattering of hard γ-rays. C. Y. CHAO (Physical Rev., 1930, [ii], **36**, 1519—1522; cf. A., 1930, 1086).—In order to investigate the deviation of the absorption coefficient for heavy elements from that predicted by the Klein–Nishina formula measurements were made on the scattering of γ-rays from thorium-*C* by aluminium and lead. For lead additional scattered rays were observed; these are considered to have a nuclear origin, since their wave-length and space distribution are inconsistent with an extra-nuclear scatterer. N. M. BLIGH.

Scattering of hard γ-rays. L. LANDAU (Naturwiss., 1930, **18**, 1112).—Polemical against Beck (A., 1930, 1496). W. R. ANGUS.

Artificial excitation of nuclear γ-rays. W. BOTHE and H. BECKER (Z. Physik, 1930, **66**, 289—306).—An apparatus for the efficient use of α-rays from a polonium source in exciting nuclear levels in non-radioactive substances is described. Nitrogen, carbon, oxygen, neon, calcium, and silver showed no secondary nuclear emission within the limits of experimental error; lithium, beryllium, boron, fluorine, magnesium, and aluminium showed emission, beryllium emission being much more intense than the others. Absorption measurements of this emission from boron and beryllium showed it to be of approximately the same wave-length as the hardest γ-radiation from radioactive substances, but the hard secondary radiation from lead (cf. A., 1922, ii, 13) could not be detected. A curve showing the approximate variation of intensity of the secondary radiation from beryllium with the energy of the exciting α-particles was obtained, but is not sufficiently accurate for theoretical interpretation. Possible theoretical interpretations of the results, on Gamow's model of the nucleus, are discussed. A. B. D. CASSIE.

A γ-radiation from polonium. W. BOTHE and H. BECKER (Z. Physik, 1930, **66**, 307—310).—Experiments described (cf. preceding abstract) showed that polonium emits a hitherto unobserved hard γ-radiation. One quantum of this radiation is emitted for every 10^5 atoms disintegrated, and it is therefore probably due to excitation of polonium nuclei by α-particles emitted by the disintegrating atoms. A. B. D. CASSIE.

Attempts to find a stable isotope of polonium. G. VON HEVESY and A. GUENTHER (Z. anorg. Chem., 1930, **194**, 162—178).—The electrochemical behaviour of polonium has been investigated and the best conditions for its electrolytic isolation have been determined. The p_H of the electrolyte is of importance; in presence of bismuth the acid concentration should be between *N* and 0·33*N*, as at higher concentrations polonium is redissolved and at lower concentrations bismuth separates as a result of hydrolysis. In presence of tellurium electrolysis with a current density of 10^{-3} amp. per cm.^{2} from a *N*-acid solution yields a deposit containing only traces of tellurium; gold considerably decreases the yield. The best yield and the purest product are obtained by electrolysis with a *P.D.* of 1 volt and a current density of $1—10\times10^{-4}$ amp. per cm.^{2}, using a rotating molybdenum cathode. Polonium, together with tellurium, may be separated from bismuth by precipitation with a reducing agent such as stannous chloride, and from tellurium by precipitation of the hydroxide. By application of these reactions large quantities of the minerals hessite, calaverite, nagyagite, bismuth telluride, and bismuth glance, and of metallic bismuth, have been worked up with addition and final re-separation of polonium as a radioactive indicator, in order to separate a stable isotope of polonium, but *X*-ray analysis of the final precipitate shows that any such substance cannot be present in the minerals to a greater extent than 10^{-11} g. per g. H. F. GILLBE.

Determination of radium by the emanation method. R. G. FULTON (J. Assoc. Off. Agric. Chem., 1930, **13**, 497—503).—The Boltwood method (A., 1904, ii, 666) as modified by Sale (J. Assoc. Off. Agric. Chem., 1925, **8**, 531) was used in the examination of a radioactive water sample, a water-soluble salt, and a refractory material. A few minor manipulative details were modified. The results were satisfactory and were checked against the methods of Schlundt and Moore (A., 1905, ii, 368) and of Barker (A., 1918, ii, 371). Cyrtolite ore also was examined by the procedure prescribed for a refractory substance with satisfactory results. H. J. DOWDEN.

Can lead be made radioactive? G. GUEBEN (Ann. Soc. Sci. Bruxelles, 1930, **50**, B, 117—121).—Experiments have been conducted with lead of 99·95% purity; one specimen was wrapped in black paper and shielded from penetrating radiation, a second specimen was exposed to sunlight for 7 months, a third was exposed to the radiation from a mercury-vapour lamp for 580 hrs., a fourth was subjected to *X*-rays for 185 hrs., and a fifth was submitted to radiations from radium emanation for 7 months. None of the lead specimens became radioactive after the treatment. It is concluded that the radioactivity observed in leaden roofs is due not to the absorption of radiation, but to the accumulation of a radioactive deposit from the atmosphere. E. S. HEDGES.

Mode of working of Geiger counting chambers. C. BOSCH and H. KLOMB (Naturwiss., 1930, **18**, 1098).—Geiger counters with copper, silver, gold, iron, and zinc electrodes in helium were used. The presence of electronegative impurities promoted the counts.

When counters were filled with highly purified helium and the electrodes completely degassed they did not exhibit counting properties. Immersion of a counter in liquid air inhibited its counting properties for the duration of the cooling. It is suggested that the occurrence of "counts" may be due to the presence of an adsorbed layer of gas, perhaps water vapour, on the electrode. W. R. ANGUS.

Origin of the penetrating corpuscular radiation of the atmosphere. B. ROSSI (Naturwiss., 1930, **18**, 1096—1097).—Experiments have been made to test the results of Bothe and Kolhorster (Z. Physik, 1929, **56**, 571; 1930, **59**, 1). The origin of atmospheric penetrating corpuscular radiation is discussed. W. R. ANGUS.

Evidence for a stellar origin of the cosmic ultra-penetrating radiation. V. F. HESS (Nature, 1931, **127**, 10—11).—It is concluded that the sun contributes about 0·5% to the total intensity of the cosmic ultra-radiation at 2·5 km. above sea-level, and that the penetrating power of the solar ultra-rays is at least equal to that of the total cosmic radiation. L. S. THEOBALD.

Thunderstorms and the penetrating radiation. B. F. J. SCHONLAND (Proc. Roy. Soc., 1930, **A**, **130**, 37—63).—An ionisation electroscope capable of measuring small and rapid changes in the intensity of the penetrating rays is described. A search for beams of downward-moving "runaway" electrons in the negative fields below thunder-clouds failed to yield positive results, and it is considered that such electrons are probably stopped by direct nuclear collisions before reaching the ground. Thunderstorms at distances greater than 10 km. caused no special changes in the ionisation, but overhead storms produced a reduction in the ionisation and thus succeeded in stopping some of the ionising particles. L. L. BIRCUMSHAW.

Quantum mechanics of dispersion and magneto-rotation on Dirac's theory of the electron. W. KROLL (Z. Physik, 1930, **66**, 69—108).—Mathematical. Electron spin and the relativity correction are taken into account in deducing the dispersion and magneto-rotation due to a single electron atom. A. B. D. CASSIE.

Atomic dimensions and quantum theory. K. C. MAZUMDER (Z. Physik, 1930, **66**, 119—121).—A mean value of the radii of the atomic valency electrons is deduced on the new quantum theory by assuming these electrons moving in the field due to an effective nuclear charge. A table of the effective nuclear charge and effective total quantum number for the atoms H to Ba is given. These atomic radii show a definite periodicity, with maxima at the alkali metals. A. B. D. CASSIE.

Deduction of Planck's radiation law from the viewpoint of adsorption. A. GANGULI (Z. Physik, 1930, **66**, 137—142).—Theoretical. A. B. D. CASSIE.

Values and inter-relationships of c, e, h, M_p, m_0, G, and R. W. N. BOND (Phil. Mag., 1930, [vii], **10**, 994—1003).—Theoretical. The values and significance of certain non-dimensional products of the universal constants are examined in the light of the latest available values of the latter. N. M. BLIGH.

Higher order approximations in the Born method of collision calculations. C. MØLLER (Z. Physik, 1930, **66**, 513—532).—Mathematical. Higher order approximations can be comparatively simply obtained by use of Dirac impulse co-ordinates instead of ordinary space co-ordinates. The second order approximations for scattering of α-particles and for elastic scattering of electrons are worked out. A. B. D. CASSIE.

Para-ortho separations and mean values of the *S*-terms of higher quantum numbers for helium. E. A. HYLLERAAS (Z. Physik, 1930, **66**, 453—470).—Mathematical. A. B. D. CASSIE.

New methods of quantitative chemical analysis by spectra. H. LUNDEGARDH (Z. Physik, 1930, **66**, 109—118).—The author's previous technique for obtaining the spectra of materials in an acetylene flame has been extended by the use of a photo-cell and galvanometer to measure the intensity of the light emitted. Approximately linear curves are obtained for the galvanometer deflexion as a function of the amount of material introduced into the flame in the case of potassium, calcium, and sodium salts, the spectral lines used being 4047·2, 4226·7, and 5890·2 Å., respectively.

It has been demonstrated that by a careful choice of conditions the intensity of the carbon line 2296·8 Å. is proportional to the concentration of carbon dioxide in a gas through which a condensed discharge is allowed to pass between gold or palladium electrodes. R. W. LUNT.

Deformation of electron shells. II. Absorption spectrum, molecular volume, and refraction of rare-earth salts. P. W. SELWOOD (J. Amer. Chem. Soc., 1930, **52**, 4308—4316; cf. A., 1930, 1235). —Observations have been extended to include neodymium nitrate and chloride at concentrations between 1*N* and 10*N*. Whilst the increase of concentration of the nitrate is associated with an increase of molecular refraction, the converse is true of the chloride solutions. For both salts, an increase of concentration leads to marked increases of molecular volume and pronounced shifts of the absorption bands towards the red. Crystals of the nitrate show a greater shift than does the concentrated solution.

A comparison of the absorption spectra of the nitrates of praseodymium, samarium, europium, gadolinium, holmium, and erbium in 0·2*N* and 10*N* aqueous solutions shows that increase of concentration leads to slight shifts of the bands towards the red in the case of the first three and definite shifts towards the blue in the case of the last two. The latter phenomenon suggests some radical difference in the atomic structure of these last rare-earth elements. Gadolinium exhibits no shift, and visible lines could not be detected (cf. Freed and Spedding, A., 1929, 1362). J. G. A. GRIFFITHS.

Validity of Beer's law for violet solutions of iodine. S. PAPP (Magyar Chem. Fol., 1929, **35**, 177—189; Chem. Zentr., 1930, i, 3405).—Beer's law is valid in the greater part of the visible spectrum for

0·5—0·0005M solutions of iodine in carbon tetrachloride, carbon disulphide, and hexane, but deviations were observed in the violet and the ultra-violet.
A. A. ELDRIDGE.

Absorption of ultra-violet light by some organic substances. (MLLE.) B. CHARLAMPOWICZÓWNA and L. MARCHLEWSKA (Bull. Acad. Polonaise, 1930, **A**, 376—398).—Using the same method as in the previous investigation (A., 1930, 10), measurements have been made of the absorption by alcoholic solutions of 1 : 6- and 2 : 6-dimethylnaphthalene, β- and α-naphthyl ethyl ether, indene, thionaphthene, 2 : 2′-diphenol, 2-hydroxydiphenyl, di*cyclo*pentadiene, *iso*quinoline, acridine, carbazole, diphenylene oxide, fluorene, phloridzin, salicin, and arbutin and by aqueous solutions of amygdalin, over the wave-length range 2100—3300 Å. The positions of the absorption maxima are given and the molecular extinction coefficients are tabulated.
J. W. SMITH.

Absorption spectra and constitution in the deoxybenzoin series. L. SZEGO and P. OSTINELLI (Gazzetta, 1930, **60**, 677—688).—The absorption spectra in the ultra-violet region of a number of isomeric substitution derivatives of deoxybenzoin have been measured in order to determine the effect on the absorption of the position of the carbonyl group relative to the substituent. The compounds examined were of the type $X\cdot C_6H_4\cdot CH_2\cdot CO\cdot C_6H_4\cdot Y$, in which X and Y were respectively OH, H; H, OH; Me, H; H, Me; Cl, H; H, Cl; Cl, Me; Me, Cl; OH, Me; Me, OH. The proximity of the carbonyl group to the substituent in the case of the monosubstituted derivatives, or to the group having the greater absorptive effect in the case of the disubstituted derivatives, causes enhanced absorption. This behaviour is contrary to that shown by compounds containing the azoxy-grouping. F. G. TRYHORN.

Absorption of light and constitution. I. Homopolar organic compounds. A. BURAWOY (Ber., 1930, **63**, [*B*], 3155—3172).—The absorption of light by organic homopolar compounds is referred to two types of chromophors : (1) radical-like chromophors such as the unsaturated atoms of free radicals and groups containing double linkings (*R* chromophors) and (2) conjugated systems (*K* chromophors). The bands caused by these two types of chromophor (*R* and *K* bands) are distinguished by their markedly different persistence; the maxima of the one band type are always approximately over, those of the other type under a layer of 50 mm. of a 0·000001N solution. The bathochromic action of hydrocarbon residues introduced into the *R* chromophors increases generally with their affinity demand, that is, saturating action; thus with aliphatic substituents it increases with the length of the carbon chain and the propinquity of the introduced methyls, whilst with the more effective aromatic substituents and other systems of double linkings increase occurs in the sequence $Ph<CH{:}CMe_2 <C_6H_4Ph<$α-naphthyl$<CPh_3$. Bathochromic effect is never produced by positive (auxochromic) groups on *R* bands; hypsochromic action is pronounced with direct substitution, feeble with union to aromatic substituents. A saturation of the *R* chromophor is always observed thereby. In contrast with *K* bands, *R* bands are always displaced towards the ultra-violet approximately in accordance with the dielectric constant of the solvent. The radical character of the *R* chromophor is of paramount importance for the *R* band absorption, but in the case of groups with double linkings the second atom has a varying influence, increasing the absorption with increasing degree of polarity, *i.e.*, in the sequence $C{:}NH<C{:}O< C{:}S$ or $N{:}N$, $N{:}O$. There is no parallel between degree of saturation and absorption of light. The absorption of conjugated systems of polar constitution increases with the length and with the degree of polarity.

The bathochromic action of positive (auxochromic) groups is attributable to their power of increasing the polarity of a chromophor group. Bathochromic action is observed only when they occur in conjunction with the conjugated system which causes the absorption of light, or complete such a system, that is, when they are the terminal groups of a chromophor system. In all other cases (when they are not terminal members of the chromophor groups causing the absorption bands), in substitution of *R* and *K* chromophors they have a powerful hypsochromic action in instances of direct substitution, whilst in union with aromatic substituents they have little effect. The cause of solvatochromism is found in the change of polarity of the *K* chromophor (of conjugated systems). The corresponding *K* bands are displaced towards the red approximately according to the dielectric constants (ionising power) of the solvents, the effect of the latter increasing with the degree of polarity of the *K* chromophor. An attempt is made to explain the hypsochromic action of positive groups by branchings in the chromophors and the ultra-violet displacement of the *R* bands by the action of the solvents.
H. WREN.

Residual luminescence in the infra-red of photo-luminescent crystals and micro-crystals. F. MARTIN (J. Phys. Radium, 1930, [vii], **1**, 401—403).—Using filtered infra-red light from a mercury-vapour and a tungsten lamp, the residual luminescence excited in crystals of a number of phosphorescent substances which had been kept in the dark for six months was examined with a photo-electric cell as detector connected with a differential triode amplifier. Observations were made as a function of the decrease in the persistence of the phosphorescence, the intensity of which varied widely for different substances, and the results reported show a relation between the disappearance of the residual and transient luminescence and the extinction effect. N. M. BLIGH.

Infra-red region of the spectrum. I. Introductory and experimental. II. Absorption spectrum of sulphur dioxide. C. R. BAILEY, A. B. D. CASSIE, and W. R. ANGUS (Proc. Roy. Soc., 1930, **A**, **130**, 133—141, 142—156).—I. Full details are given of a prism spectrometer (a Hilger D. 42 constant-deviation instrument fitted with quartz, fluorite, rock-salt, and sylvine prisms), by means of which a high order of accuracy may be obtained in infra-red measurements. The possibilities of experimental error due to uncertainty in (1) drum reading, (2) setting the prism at minimum deviation,

(3) value of the prism angle, and (4) temperature of the prism are discussed. The maximum possible error in any wave-length reading may be taken as that due to an error of 4 sec. of arc in the semi-minimum deviation.

II. By means of this apparatus, the infra-red absorption spectrum of sulphur dioxide has been investigated in the region 1—22 μ, and the results are compared with those obtained by Coblentz. Certain unexplained differences exist between the two sets of bands; thus, no trace has been found of Coblentz's bands at 3·18 and 10·37 μ, whilst in place of that at 5·68 μ there is one at 5·34 μ. The observed infra-red spectrum has been co-ordinated with the Raman spectrum of the liquid. The following values have been deduced for the molecular constants of sulphur dioxide: moments of inertia, 55, 50, and $4·7 \times 10^{-39}$ g.-cm.^{2}, respectively; lengths of side, S–O $4·8 \times 10^{-8}$ cm., O–O $2·0 \times 10^{-8}$ cm., whence the angle OSO=24°; fundamental vibration frequencies: a_1+b_1, 606 cm.$^{-1}$; a_2 1152 cm.$^{-1}$; b_2 0; a_3+b_3 1361 cm.$^{-1}$

L. L. Bircumshaw.

Infra-red absorption of formaldehyde vapour. I. E. O. Salant and W. West (Physical Rev., 1929, [ii], **33**, 640).—Ultra-violet absorption bands of the vapour of formaldehyde show rotational lines corresponding with quite a small moment of inertia of molecule (Henri and Schou, A., 1928, 935). Measurements extending from the visible to 3·6 μ have now been made. The strongest bands occur at [3·31, 3·38, 3·47], 218, [1·77, 1·84], 191, [144, 1·40], and 1·25 μ. The 1·4 and 1·8 μ bands appear as doublets and the 3·4 μ band as a triplet with evidence of rotational structure. The separations of the lines in the band at 3·4 μ appear much smaller than would be indicated by the moment of inertia derived from the ultra-violet lines.

L. S. Theobald.

Measurements of light emission by alkali halide phosphors. W. Bünger (Z. Physik, 1930, **66**, 311—327).—An apparatus which determines the number of quanta of monochromatic light absorbed for the emission of one quantum of fluorescent or phosphorescent light is described. A crystal consisting of the ions of one alkali halide transforms absorbed radiation into chemical energy, but a mixed crystal transforms part of the absorbed radiation into fluorescent or phosphorescent radiation. The quantum efficiency of 0·015, 0·183, 0·33, 0·367, and 1·83 mol.-% TlCl in potassium chloride crystals for the production of fluorescent and phosphorescent radiation was determined. Radiation absorbed at the longer wave-length band (300 mμ) of potassium chloride containing thallium chloride reappears as fluorescent, without phosphorescent, radiation with a quantum efficiency of 0·5—0·8; the shorter wave-length band (200 mμ) reappears as fluorescent radiation with a quantum efficiency of 0·22—0·4, and as phosphorescent radiation with a quantum efficiency of 0·02—0·04. The phosphorescent quantum efficiency varies with wave-length almost as the absorption coefficient.

A. B. D. Cassie.

Apparatus for investigating the Raman effect in organic compounds. S. Ziemecki (Bull. Acad. Polonaise, 1930, **A**, 309—317).—An apparatus suitable for investigation of the Raman effect at higher temperatures is described. The vessel to contain the substance under investigation is constructed of glass or quartz and is fitted with a plane window. It is immersed in paraffin in a metal thermostat with plane transparent windows on opposite sides.

J. W. Smith.

Raman spectrum of dioxan. D. S. Villars (J. Amer. Chem. Soc., 1930, **52**, 4612—4613).—The wave-numbers and intensities of the lines in the modified (Raman) radiation from dioxan in the light of the mercury arc are tabulated.

J. G. A. Griffiths.

Raman effect at the critical point. G. Placzek (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 832—840).—Measurements at the critical point of the system methyl alcohol–hexane indicate that the intensity of the Raman lines remains unaltered, but that of the continuous Raman spectrum increases. The continuous spectrum is discussed in relation to the vibrations of molecular complexes and the structure of liquids.

E. S. Hedges.

Raman spectra of pinene. G. B. Bonino and P. Cella (Nature, 1930, **126**, 915).—Eight weak lines which can be represented by the formula $\Delta\nu = B \times (4m+4)$ have been observed near the line ν=23,257 in the Raman spectra of *d*- and *l*-pinene. The distance between the atoms of hydrogen and carbon in the CH_2 group calculated from this is $1·16 \times 10^{-8}$ cm., in good agreement with Mecke's value of $1·13 \times 10^{-8}$ cm.

L. S. Theobald.

Raman lines of simple polyatomic molecules. G. B. B. M. Sutherland (Nature, 1930, **126**, 916—917).—The Raman spectrum of hydrazine shows three lines of approximately equal intensity at 3196, 3270, and 3344 cm.$^{-1}$ together with a doubtful one at 1720 cm.$^{-1}$ The three lines are due to N–H vibrations. Hydrazine hydrate gives the same three lines but of weaker intensity.

L. S. Theobald.

Raman spectra of some triatomic molecules. S. Bhagavantam (Nature, 1930, **126**, 995).—The spectrum of gaseous sulphur dioxide shows a line 1154 cm.$^{-1}$ Liquid hydrogen cyanide shows a triplet giving the shifts 2076, 2097·2, and 2122 cm.$^{-1}$, of which the middle component is the most intense. Krishnamurti's results for carbon disulphide (A., 1930, 1237) have been confirmed and, in addition, three new feeble bands at 4438, 4605, and 4680 Å. have been discovered in the spectrum of carbon disulphide excited by the mercury line 4358·3 Å. Assuming these to be due to Raman transitions, three new wave-numbers are given for carbon disulphide: 412, 1229, and 1577 cm.$^{-1}$

L. S. Theobald.

Raman spectrum of diamond. S. Bhagavantam (Indian J. Physics, 1930, **5**, 573—586; cf. A., 1930, 1345).—The Raman spectrum of a large clear diamond gave, on either side of the intense principal line 1332 cm.$^{-1}$, feebler lines of frequency shifts 1158, 1288, 1382, 1431, 1480, and 1585, the last being the most prominent; these values correspond closely with some of the very weak infra-red absorption maxima. The optical activity of the oscillation corresponding with the 1332 line and the absorption bands, and its variation in different specimens of diamond, are

discussed. Results are considered in relation to specific heat data, and are not in good agreement with the classical theories of Born and Debye. The anti-Stokes line corresponding with the principal line of frequency shift 1332 has been observed, and is shifted 1332 wave-numbers from the exciting line, in exact agreement with the shift of the Stokes line. An intensity of the principal Raman line six times that of the 992 benzene line is explained from density considerations. N. M. BLIGH.

Raman effect with cadmium arc excitation. P. KRISHNAMURTI (Indian J. Physics, 1930, **5**, 587—591).—A cadmium arc with a 50% Sn–Cd alloy has been used for the first time for exciting Raman lines. Ferrous and nickel sulphates showed no lines at about 10 μ, in agreement with previous results (cf. A., 1930, 1344). For sulphur crystals with 5086 Å. excitation all the frequencies previously reported were found (cf. *ibid.*, 1237), together with a very faint line (ν_6= 183 cm.$^{-1}$). The 4800 and 6439 Å. radiations excited the three strongest sulphur frequencies with moderate intensity. The use of the 6439 Å. line for orange- or red-coloured substances is considered.

N. M. BLIGH.

Polarisation of Raman lines: some hydrocarbons. S. BHAGAVANTAM (Indian J. Physics, 1930, **5**, 603—608; cf. A., 1930, 1236).—The polarisation of the Raman lines in benzene, *cyclo*hexane, and pentane was investigated; relative intensities and depolarisations are tabulated, and theoretical explanations of the observed degrees of polarisation are discussed. The different components of the characteristic hydrogen frequency appear with varying degrees of polarisation. Benzene gives lines showing no detectable polarisation. N. M. BLIGH.

Origin of the continuous spectra in Raman scattering. N. N. PAL and P. N. SENGUPTA (Indian J. Physics, 1930, **5**, 609—610).—Using the combined vacuum distillation system and Wood's tube, the previously proposed theory of the continuous spectrum (cf. A., 1930, 1237) was investigated for benzaldehyde. During circulation, no continuous spectrum was observed, but appeared after the circulation was stopped, and is attributed to the breaking down under the action of light of the yellow first product of photochemical action on the benzaldehyde. N. M. BLIGH.

Characteristic frequencies of radicals in different chemical combinations. N. N. PAL and P. N. SENGUPTA (Indian J. Physics, 1930, **5**, 611—614).—From a consideration of the frequencies attributed to the CN radical in a number of different types of compounds it is shown that the nature of the linking, rather than the mass of the substituent radical, mainly determines the frequency. N. M. BLIGH.

Forms of oscillation of the benzene ring in Raman effect. S. BHAGAVANTAM (Indian J. Physics, 1930, **5**, 615—631).—From the theory of vibrations of an elastic solid circular ring the geometrical characteristics of the vibrations of a hexagonal ring are deduced and applied to the interpretation of the observed Raman frequencies of benzene. The properties and persistence in benzene derivatives of the 992 frequency are adequately explained. Available data on the Raman spectrum and infra-red absorption of benzene are discussed. The existence of further oscillations and corresponding lines being indicated by theory, six new Raman lines of very low intensity were observed, using long exposures, at 4163·8, 4397·2, 4438·4, 4494·2, 4505·8, and 4513·0 Å. The origin and relation of these lines to infra-red absorption data are discussed. N. M. BLIGH.

Raman spectra of inorganic crystals. I. Substances containing XO_3 and XO_4 groups. II. Some hydroxides, cyanides, and thiocyanates. P. KRISHNAMURTI (Indian J. Physics, 1930, **5**, 633—650, 651—662; cf. A., 1930, 1237, 1344).—Using specially designed pyrex mercury arcs to obtain intense excitation, investigations were made by the powder method. All the observed frequencies of the chlorates are active, corresponding with infra-red maxima; the principal frequency (ν_3—930 cm.$^{-1}$) becomes smaller for bromates and iodates, and splits into two components in sodium bromate (770 strong; 842 weak), and into four components in potassium iodate (733, 751 strong; 784, 808 weak). The splitting is discussed in relation to group structure. Aqueous solutions gave Raman lines in the same positions as the crystals, the components of the principal frequency tending to disappear. Sodium and potassium perchlorates gave lines (ν_1=462; ν_2=633; ν_3= 933 cm.$^{-1}$) similar to those of sulphates; potassium periodate gave lines ν_3, 794 strong, 841 weak. The periodate frequencies show considerable changes in solution. Ammonium molybdate gave intense lines and a doubling of the principal frequency (932 strong; 880 medium) shown also in solution. Sodium tungstate gave only one line, 928, unaltered in solution. In all cases results are discussed in relation to infra-red data.

II. The following substances were examined and data are tabulated. Sodium, barium, and strontium hydroxides, sodium and mercuric cyanides; potassium ferrocyanide; a concentrated solution of potassium silver cyanide; potassium, ammonium, and barium thiocyanates. Sodium hydroxide gave a sharp line 3630 cm.$^{-1}$, due to the OH ion; strontium and barium hydroxide octahydrates gave faint lines 3484, 3417, due either to water of crystallisation or to the OH ions. Mercuric cyanide gave a strong line, 2192, due to the CN group, and a weaker line, 276, due to the Hg–CN oscillation. The CN frequency is shown to be raised by covalent linkings between the CN group and other atoms or groups. The influence of dissolution on cyanides is small. Potassium thiocyanate gave a strong line, 2050, and a weak line, 747, for the solid and in solution. The ion is shown to be S:C:N, the double linking explaining the lower frequency as compared with the C:N ion. N. M. BLIGH.

Intensities of lines in Raman spectra. S. C. SIRKAR (Indian J. Physics, 1930, **5**, 593—601; cf. A., 1930, 1344).—The ratio of the absolute intensities of the displaced to the corresponding undisplaced lines was determined for Raman lines of *cyclo*hexane having shifts of 2853 and 800, and of benzene having shifts of 3080 and 990. The intensities were found to be greater than is indicated by the fourth-power law,

relative to the visible lines, the deviation being greater as the frequency shifts increase. The deviations for the above lines are 216, 63, 267, and 51%, respectively.
N. M. BLIGH.

Relative intensities of different Raman lines due to different exciting frequencies. S. C. SIRKAR (Indian J. Physics, 1930, **5**, 663—668; cf. A., 1930, 1344, and preceding abstract).—In order to obtain further evidence on deviations from the Rayleigh fourth-power law, the ratios of the absolute intensities of the two Raman lines of nitrobenzene shifted by 1342 and 1582 wave-numbers were measured for excitation by mercury 5461 and 4358·6 Å., and gave the values 6·5, 2·74, and 15·9, 3·1, respectively. The probability of abnormally great intensity of the 1342 line excited by 4358·6 Å. is discussed.
N. M. BLIGH.

Modification of the fine structure of a spectral line by molecular diffusion. Influence of angle of diffusion. M. VACHER (Compt. rend., 1930, **191**, 1121—1123).—Investigations by the method previously described, but with additional precautions (cf. A., 1929, 489), of the modifications due to molecular diffusion in benzene at different angles of diffusion, θ, show that as this angle increases the broadening of the line increases, and its "centre of gravity" shifts towards the red, the edge towards shorter wave-lengths remaining unchanged. The results point to the diffused radiation consisting of two lines, one undisplaced, the other displaced towards the red (cf. following abstract). C. A. SILBERRAD.

Fine structure of a spectral line in molecular diffusion. J. CABANNES (Compt. rend., 1930, **191**, 1123—1125).—The theory (cf. Tamm, A., 1930, 397, and preceding abstract) that diffusion of light in a dense medium is dependent on the elastic waves produced by thermal agitation requires that the diffused radiation produced by radiation of wave-length λ should be replaced by two symmetrical lines of wave-lengths $\lambda \pm d\lambda$, where $d=\lambda(2un/c)\sin\theta/2$, where u is the velocity of sound, c/n that of light in the diffusing medium, and θ the angle of diffusion). The experimental results, although showing values of $d\lambda$ proportional to $\sin\theta/2$, do not indicate either disappearance of the original radiation or appearance of any radiation of shorter wave-length.
C. A. SILBERRAD.

Photo-electric behaviour of salts. H. ERBEL (Z. Physik, 1930, **66**, 59—68).—The experiments of Werner (A., 1929, 1217) on the photo-electric sensitivity of cadmium iodide, lead chloride, and potassium nitrate have been repeated on account of a lack of the necessary precautions in the technique employed. The results of Werner have been confirmed subject to minor differences. R. W. LUNT.

Comparison of molecular ionising potentials in an alternating electric wind. W. M. THORNTON (Phil. Mag., 1930, [vii], **10**, 1052—1063).—A new method of comparing ionisation in a gas in a strong electric field is described. The ions are caused to move as the field reverses, and the alternating molecular motion cools a hot wire enclosed in the gas and forming one electrode. The molecular ionisation is measured from the curves connecting the applied voltage and the galvanometer deflexions of a bridge, of which the hot wire is one arm. Results for helium, neon, and argon show that the cooling of the wire is inversely proportional to the ionising potentials. The method is extended to hydrogen, oxygen, nitrogen, air, the paraffin series, and several other gases; results are in good agreement with calculated values. The relations of oxygen and hydrogen to carbon and nitrogen are deduced and discussed. N. M. BLIGH.

Dielectric polarisation of elements. C. ZAKRZEWSKI and D. DOBORZYŃSKI (Bull. Acad. Polonaise, 1930, **A**, 300—308).—With the exception of the elements of group VII, all elements so far investigated show the same values for the dielectric polarisation in both liquid and gaseous states, and these values are independent of temperature. Hence the molecules of these elements possess no dipole moment. Chlorine, bromine, and iodine, however, are dipolar molecules, the values of the electric moment increasing with increasing at. wt. The actual values which have been deduced, however, for these dipole moments show considerable discrepancies. J. W. SMITH.

Dielectric constant of ammonia as a function of temperature and density. F. G. KEYES and J. G. KIRKWOOD (Physical Rev., 1930, [ii], **36**, 1570—1575).—Using an apparatus previously described (cf. A., 1930, 1347) the dielectric constant of ammonia was measured over a range of densities at 100°, 125°, 150°, and 175°. The Clausius-Mosotti function was found to increase with increasing density, and an expression for it at low densities is deduced. The permanent electric moment of the ammonia molecule was calculated as $1{\cdot}44\times10^{-18}$ e.s.u. For an interpretation of the experimental facts it is shown that the assumption that the function is valid and the mean molecular polarisability increases with the density is justified. Previous results for carbon dioxide are further discussed. N. M. BLIGH.

Dependence of molecular polarisation of propyl chloride and αβ-dichloroethane on temperature, especially with regard to free rotation. R. SANGER (Physikal. Z., 1931, **32**, 21—26).—The electric moment of propyl chloride has been redetermined. The value is $2{\cdot}04\pm0{\cdot}007\times10^{-18}$. The structure of propyl chloride is discussed, and it is shown that the experimental results support the assumption of completely free rotation of the end groups C·Me and C·Cl about the axis, but are not in agreement with the assumption of the existence of two forms of molecule of an approximately constant mixing ratio. The molecular polarisation of αβ-dichloroethane bears a linear relationship to the reciprocal of the temperature as required by the Debye theory. The molecule therefore possesses a constant moment, *i.e.*, a moment independent of temperature. The actual value of the moment is not known with accuracy, but it lies between 1·2 and $1{\cdot}4\times10^{-18}$. A constant electric moment is compatible only with completely free rotation or with complete rigidity. For completely free rotation, however, it has been calculated that the electric moment of the compound should be about $2{\cdot}4\times10^{-18}$, assuming no deformation of the carbon tetrahedron.

This would have to be considerable to reduce the moment to that found experimentally. A. J. MEE.

Change of the dielectric constant of nitrobenzene with temperature. J. MAZUR (Nature, 1930, **126**, 993).—The dielectric constant of nitrobenzene has been measured over the range $-75°$ to $30°$. The value of ε steadily increases with a fall in temperature from 35·4 at 30·01° to a maximum of 35·18 [38·18 ?] at 9·6°, and then decreases sharply to 11·82 at 7·713°; after this the decrease is slowly asymptotic to a limiting value of 9·709 at $-75°$. Irregularities in the rate of change of ε between 9·6° and 7·713° suggest possible complications in the region of the m. p. of nitrobenzene. L. S. THEOBALD.

Dielectric polarisation of some pure organic compounds in the dissolved, liquid, and solid states. S. O. MORGAN and H. H. LOWRY (J. Physical Chem., 1930, **34**, 2385—2432).—The dielectric constants, densities, and refractive indices of dilute solutions of methyl chloride, bromide, or iodide, and of methylene chloride in hexane or carbon tetra chloride or both, have been measured. For the methyl halides temperature and dielectric constant can be connected by the equation $\varepsilon=\alpha T^{-1}-\beta$, where α and β are constants, whilst density is a nearly linear function of temperature. For non-polar substances, the relation $\varepsilon=\varepsilon_{m.p.}-\delta(T-T_{m.p.})$, where δ is the rate of change of dielectric constant with temperature, holds, and for polar substances the results can be represented by the equation $\varepsilon=$ $+$ $T_{m.p.})^2$. Condensers have been designed for measuring the dielectric constants of liquids and solids and the use of these for direct capacity measurements is discussed.

L. S. THEOBALD.

Electromechanical properties of Rochelle salt crystals. W. G. CADY (Physical Rev., 1929, [ii], **33**, 278—279).—The piezo-electric strain constants, δ, of sodium potassium tartrate are known but not those of the moduli, ε. The values ε_{14} $1{\cdot}64\times10^6$, ε_{25} $-53{,}300$, and ε_{36} 43,400 have been computed from Pockel's values of the strain constants and Mandell's determinations of the elastic constants. The extent to which the dielectric constant is modified by the presence of piezo-electricity has also been calculated. The natural vibration frequencies of plates of the salt differently oriented with respect to the crystal axes have been measured. L. S. THEOBALD.

Dispersion [refraction] of the cyclic hydrocarbons. M. GODCHOT and (MLLE.) G. CAUQUIL (Compt. rend., 1930, **191**, 1326—1328).—The specific dispersion $\Delta n/d$ at 13·5°, where Δn is the difference between refractive indices determined for λ 0·589 μ (Na yellow) and 0·436 μ (Hg violet), and d the density at the same temperature (cf. Darmois, A., 1921, ii, 1), was determined for 11 hydrocarbons with one double linking, and 12 saturated hydrocarbons belonging to the *cyclo*-pentane, -hexane, -heptane, and -octane series. Δn increases regularly with increase in mol. wt., the unsaturated hydrocarbons giving a value 20 units higher than the corresponding saturated hydrocarbon produced by hydrogenation in the presence of a platinum oxide catalyst. $\Delta n/d$ is not strictly constant for all members of a given series and does not depend on the nature of the ring. Mean values of 124×10^{-4} and 151×10^{-3} were found for all the saturated and unsaturated hydrocarbons, respectively. In general, the conclusions of Darmois were confirmed, and the use of the additive properties of the ratio for the determination of benzene hydrocarbons ($\Delta n/d=250\times10^{-4}$) in petrol is indicated.

J. GRANT.

Molecular refractivity of methyl alcohol. M. VELASCO (Anal. Fís. Quím., 1930, **28**, 1228—1238).—The dielectric constant of benzene solutions of methyl alcohol has been measured at fractional molar concentrations from 0·0248 to 0·4981, and the molecular polarisation has been calculated. With increase of concentration $P_{1,2}$ rises to a maximum, indicating that the solute is polar and that it is composed of associated molecules, whilst P_2 is maximal at about 0·3 fractional molar concentration and falls again at higher concentrations; at infinite dilution P_2 is **55·3**. The molecular refractivity of methyl alcohol at 20°, calculated from measurements of the refractive index, is 8·23, and the electric moment μ is $1{\cdot}5\times10^{-18}$. The experimental results are shown to be in accordance with the Debye theory of solution.

H. F. GILLBE.

Anomalous dispersion of crystalline lead chloride in the region of its first ultra-violet proper frequency. K. HECHT (Z. Physik, 1930, **66**, 339—344).—The refractive index of lead chloride, vaporised and subsequently deposited on a quartz plate to give crystal layers of from 10 to 50×10^{-6} mm. thick, was determined from the shift of Young's interference fringes when the layer was inserted in the path of one of the interfering beams. The region investigated was that of the first ultra-violet natural frequency at 272 mμ, and the results complete the measurements of Bauer between 360 and 290 mμ.

A. B. D. CASSIE.

Magnetic rotatory power of hydrocarbons in the gaseous state. R. DE MALLEMANN and P. GABIANO (Compt. rend., 1930, **191**, 1319—1320).—The Verdet, molecular, and specific constants (reduced to 0° and 760 mm., and corrected for compressibility) of gaseous methane, ethane, propane, butane, *iso*pentane, and *iso*hexane, and of liquid butane, pentane, and hexane have been measured for λ 578 $\mu\mu$. In confirmation of calculated values, the ratios of the specific rotations obtained for the gaseous and liquid states are: butane 0·87, pentane 0·86, and hexane 0·85. Previous divergencies are attributed to foreign gases, such as hydrogen or ethylenic derivatives, in the materials which have now been eliminated. The dispersions for λ 546 and 436 $\mu\mu$ are approximately 1·125 and 1·184 for all the hydrocarbons. J. GRANT.

Rotatory magnetic polarisation of organic substances liquefied by fusion. C. SALCEANU (Compt. rend., 1930, **191**, 1316—1318).—Determinations with three mercury lines of the magnetic rotation of the plane of polarisation (λ 578 $m\mu$), of the ratio of this rotation to that of water at 20°, of Verdet's constant ρ (ρ for water at 20° 0·0136), and of the ratio of ρ to the density at 83·5—188° for naphthalene and at 34—174° for 2-methylnaphthalene gave values of the dispersion ratios at 83·5° and 49°,

respectively, of α_v/α_j 1·15 and α_i/α_j 2·16 in both cases. The variations of these ratios with temperature are negligible. Their values calculated from measurements of birefringence, on the assumption that the dispersions for the magnetic and Kerr birefringences are approximately equal (Cotton and Mouton), are α_v/α_j 1·13 and α_i/α_j 1·90 for 2-methylnaphthalene, the value 1·73 for the latter being hitherto considered the maximum for aromatic substances. The magnetic *P.D.* used was 36,000 gauss per cm. and the field 12,000 gauss. J. GRANT.

Mutarotation in pure and in mixed solvents. J. N. RAKSHIT (J. Physical Chem., 1930, **34**, 2539—2548).—The mutarotation of solutions of morphine, codeine, and narcotine hydrochlorides in mixtures of water and ethyl alcohol have been measured at 35°. The molecular rotations of morphine and codeine hydrochlorides increase with dilution, whilst that of narcotine hydrochloride increases with dilution in pure aqueous solutions and decreases with dilution in pure alcoholic solutions and in most water–alcohol mixtures. The results obtained support the view that mutarotation is due to a reaction between solute and solvent. L. S. THEOBALD.

Optical activity and salt effect. P. A. LEVENE and A. ROTHEN (J. Physical Chem., 1930, **34**, 2567—2581).—The optical rotation of aqueous solutions of mandelic acid has been measured at 25° and the calculated rotations for the undissociated acid and for the mandelate ion are $[M]_D^{25}=237{\cdot}2(6)°$ and $[M^-]^{25}=176{\cdot}7°\pm0{\cdot}05(5)°$, respectively. The dissociation "constant" calculated from observed rotations increases with concentration from 4·2 to 4·8×10. The temperature coefficients of the rotation of the acid and of the mandelate ion are large and are of the same order of magnitude between 20° and 30°. The curves representing the effect of strong bases on the rotation of the mandelate ion show that for lithium, sodium, calcium, and barium, the molecular rotation has the same value at zero concentration of base and that no break occurs when 1 equiv. of base has been added. The mandelates of these bases are completely dissociated at a concentration 0·05*N*. Neutral salts increase the rotation of the mandelate ion, the influence of the ions $Ca^{••}$, $Ba^{••}$, and $Sr^{••}$ being especially marked. The effect decreases with an increase in the size of the ion for both uni- and bi-valent ions and the effect of the cation predominates over that of the anion. With mandelic acid the salt effect is less pronounced. Ethyl nitrite and acetic acid act similarly to the cations and alcohol to the anions. The effect of neutral salts on the rotation of α-methylglucoside and of sucrose is much less than in the case of mandelic acid. L. S. THEOBALD.

Origins of stereochemistry. E. PATERNÒ (Gazzetta, 1930, **60**, 910—911).—Polemical. Objection is taken to the references made by Oddo in his recent "Treatise of Organic Chemistry" to the author's paper of 1869 in that they do not give a correct account of the theory of stereochemistry put forward at that date. O. J. WALKER.

Nature of per-acids and the "acid nucleus" theory. S. HAKOMORI (Bull. Chem. Soc. Japan, 1930, **5**, 333—344).—It is suggested that when a polar molecule is brought into the vicinity of an electrically neutral molecule combination may occur as a result of electrical induction. The magnitude of this "induction valency" will vary with the dielectric constant of the medium surrounding the molecules. It is supposed that in the ordinary oxy-acids the anhydride or "acid nucleus" is held together by co-valencies, but is united to water by induction valency. Similarly, the per-acids may be regarded as formed by the union of acid nuclei with hydrogen peroxide by induction valency. The intensity of the induction effect may be expected to influence the colour of the resulting compound. If the displacement due to induction is very small the acid will be colourless or yellow, and comparatively stable. The colour changes of indicators are ascribed to the inducing action of the hydrogen ion. R. CUTHILL.

Properties and applications of molecular forces. F. LONDON (Z. physikal. Chem., 1930, **B**, **11**, 222—251).—The theory of intermolecular attractive forces due to reciprocal perturbation of electronic orbits (A., 1930, 1239) is further developed. It is shown that these forces are equivalent to a general cohesive force comparable with that of gravity and are superposable, *i.e.*, the force between any two given molecules is practically unaffected by the presence of other molecules. The values of the forces can be deduced fairly accurately from optical dispersion data. The force between two unlike molecules in a binary mixture is in general less than the geometric mean of the forces in the two components in the pure state; the wider apart are the characteristic spectral regions of the two molecular species, the greater is this disparity. By means of the theory of the new attractive forces, the heat of sublimation of a molecular lattice may be calculated, and the values obtained for various face-centred cubic lattices are in such agreement with the experimental values as to indicate that the energy of such lattices is determined, at least as far as order of magnitude is concerned, by the attractive forces. The theory also yields the equation ϕ/T_c=constant, where ϕ is the heat of sublimation at 0° Abs. and T_c is the critical temperature. By applying the theory to an adsorbed gas, all the characteristics of adsorption free from such complications as the presence of chemical polar or homopolar linkings may be accounted for and the heat of adsorption, ϕ', calculated in a satisfactory manner. It is further deduced that $\phi'/T_c^{\frac{1}{2}}$=constant. The energies of dissociation of molecules in which the binding forces are of the van der Waals type, *e.g.*, the compounds of mercury with argon and krypton, are also calculated. The new theory does not permit the calculation of the attractive force between two molecules as close together as, for instance, the atoms in the hydrogen molecule. R. CUTHILL.

Parachor of aliphatic acids of high mol. wt. G. B. SEMERIA and G. RIBOTTI-LISSONE (Gazzetta, 1930, **60**, 862—866).—The parachor for the following acids has been determined. The values at 95° are: oleic 766·93, elaidic 764·93, βγ-oleic 763·70, stearic 778·87, erucic 938·91, brassidic 934·36, and behenic 951·36. The results indicate that oleic and erucic

acids have a *cis*-configuration, whereas elaidic, $\beta\gamma$-oleic, and brassidic acids have a *trans*-configuration.

O. J. WALKER.

Reflexion of X-rays at crystals. V. H. SEEMANN (Ann. Physik, 1930, [v], 7, 633—649).—The characteristic features of X-ray diagrams obtained by reflexion of a pencil of X-rays of wide divergence on crystals are interpreted theoretically. W. GOOD.

Fluorescence of quartz under the influence of cathode rays of low voltage. H. PETERS (Physical Rev., 1930, [ii], 36, 1631—1635).—The production of a red fluorescence by cathode rays in glass and quartz tubes was investigated. Contrary to the views of Wood (cf. A., 1930, 653), the presence of oxygen or other gases was not found to be essential. The fluorescence showed a continuous spectrum with two maxima in the red, one in the green, and one in the blue; no oxygen line was found. The disappearance of the fluorescence after bombardment for about 70 hrs. indicates that the SiO_2 group in the glass passes into an allotropic form. N. M. BLIGH.

Lattice constant of quartz. O. BERGQVIST (Z. Physik, 1930, 66, 494—498).—The lattice constant of quartz was determined by means of the Cu$K\alpha$ and Fe$K\alpha$ lines, to first and second approximations; *i.e.*, the lattice constant was first determined by neglecting the refractive index, and from this value the refractive index was calculated and used to determine the second approximation. A. B. D. CASSIE.

X-Ray investigations on rubber. E. OTT (J. Amer. Chem. Soc., 1930, 52, 4612; cf. B., 1926, 681). —Exposure of translucent rubber to X-rays results in the formation of an opaque spot defined by the diameter of the beam of X-rays. With increasing exposure, the spot becomes more opaque, due to progressive crystallisation, and the X-ray pattern becomes sharper, owing to increasing size of the particles. The opaque spot did not change during storage, but was removed by slight warming.

J. G. A. GRIFFITHS.

Method for growing large crystals of the alkali halides. J. STRONG (Physical Rev., 1930, [ii], 36, 1663—1666; cf. Ramsperger, A., 1928, 351).—In addition to the conditions specified by Stober (cf. Z. Krist., 1925, 61, 299) for growing large crystals from fused salts, two new conditions are postulated. The bottom and top of the still plastic crystal must be brought to the same temperature to avoid strains during cooling, and the crystal must be removed from the container before cooling begins, to eliminate strains due to the temperature contraction of the melting pot. Cylindrical alkali halide crystals can thus be prepared 4·5 in. long and 4·5 in. in diameter.

N. M. BLIGH.

Distribution of [crystal] structure types in the periodic system. H. PERLITZ (Festschr. Jub. Ver. Estn. Chem., 1929, 10—13; Chem. Zentr., 1930, ii, 685).

Possible orientation of cubic crystals deposited on a mica plate. L. ROYER (Compt. rend., 1930, 191, 1346—1348).—All the alkali halides of cubic symmetry give an oriented deposit on a cleavage plane of mica (epitaxy) when the parameter of the diagonal of the face of the cube is between certain limits. It is deduced that the cubic alkali phosphohexafluorides (RPF_6) prepared by Lange and Müller (A., 1930, 877), which give, although with difficulty, deposits oriented similarly to those of the halides, are analogous in structure to the halides, the parameters of the a' (111) faces being for each case K 5·49, Rb 5·64, NH_4 5·59, and Cs 5·80 Å. The great difficulty with which the cæsium compound is oriented and the impossibility of the orientation of cæsium chloride (parameter 6·08 Å.) are explained by the large differences between the parameter concerned and that of mica (5·12 Å.). The lower limit for orientation on mica is represented by potassium chloride (parameter 4·43 Å.). J. GRANT.

Crystal structure of para-hydrogen at liquid helium temperatures. W. H. KEESOM, J. DE SMEDT, and H. H. MOOY (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 814—819).—The X-ray spectral lines obtained from solid hydrogen at the temperature of liquid helium are in good agreement with those calculated for a hexagonal close-packed lattice having a 3·75 Å. and c/a 1·633. With 2 molecules in the elementary cell $d_{\text{calc.}}$ for 2° Abs. is 0·088. Solid hydrogen is said to be isotropic at the m. p., but the X-ray data do not agree with a cubic structure. It is suggested that there may be a transformation point between 4° and 14° Abs. E. S. HEDGES.

Lattice distance and reflecting power for X-rays of bismuth according to the plane of cleavage. E. ADINOLFI (Rend. Accad. Sci. Fis. Mat. Napoli, 1930, [iii], 36, 69—75).—A new arrangement for obtaining the lattice distances of crystals by Bragg's method is described, direct comparison being made with that of calcite along the face (100), which is taken as the basis for spectrometric measurements. In this way the lattice dimension for the (111) face of bismuth crystals is found to be 3·970 Å. Comparison of the structural factors of calcite and bismuth shows that, whereas that of calcite is constant, that of bismuth, in the same frequency field, increases as the wave-length of the radiations used diminishes, so that increase in the frequency is accompanied by increase in the number of the bismuth electrons taking part in the phenomenon of reflexion.

T. H. POPE.

Structure of hydrogen phosphide (PH_3) and of hydrogen arsenide (AsH_3). G. NATTA and E. CASAZZA (Gazzetta, 1930, 60, 851—859).—X-Ray examination of phosphine and arsine at −170° shows that these two substances are isomorphous and crystallise in the face-centred cubic system with a cell containing 4 mols. The data are: PH_3, a 6·31±0·01 Å., v 251×10^{-21} c.c., d_{calc} 0·896, and AsH_3, a 6·40±0·02 Å., v 262×10^{-21} c.c., 1·96. The space-group is probably T_h^2 or O_h^1. O. J. WALKER.

Determination of the crystal structure of hydrogen sulphide and selenide and nitrogen dioxide at the temperature of liquid air. L. VEGARD (Naturwiss., 1930, 18, 1098, and Nature, 1930, 126, 916; cf. Natta, A., 1930, 1350).—By means of methods previously described by the author (A., 1930, 19) the crystal structures of the solid compounds at liquid-air temperature have been determined. Hydrogen

sulphide and selenide are isomorphous, cubic, with 4 mols. in the unit cell. The sulphur and selenium atoms are arranged in a face-centred lattice. It is concluded that the molecule is linear. The most probable space configurations are T^4 for an asymmetrical and T_h^5 for a symmetrical molecule. Hydrogen sulphide has a 5·76 Å., ρ 1·17, and the selenide 6·10 Å. and 2·34, respectively.

Solid nitrogen dioxide has also a cubic structure, but it is more complex than hydrogen sulphide or selenide; a and ρ are 7·77 Å. and 1·93, respectively, indicating 6 mols. in the unit cell. The structure is made up of space-centred lattices. T^5, the only possible space distribution, gives one parameter for nitrogen and three parameters for the oxygen atoms. With certain assumptions parameter values are found which give excellent agreement between calculated and observed intensities. W. R. ANGUS.

Structure of silicon tetrafluoride. G. NATTA (Gazzetta, 1930, **60**, 911—922).—Examination of solid silicon tetrafluoride at $-170°$ by the powder method shows that it has a cubic-centred lattice with a cell containing 2 mols. of SiF_4: a 5·41±0·01 Å., v 158×10^{-24} c.c., $d_{calc.}$ 2·17. The tetrafluoride is a non-ionic compound and belongs to the space-group O-. The co-ordinates of the atoms are: Si (0, 0, 0) ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), F (u, u, u)(u, u, u)(u, u, u)(u, $\bar{u}$, u), ($\frac{1}{2}$+u)($\frac{1}{2}$+u)($\frac{1}{2}$+u), ($\frac{1}{2}$+u)($\frac{1}{2}$—u)($\frac{1}{2}$—u), ($\frac{1}{2}$—u)($\frac{1}{2}$+u)($\frac{1}{2}$—u), ($\frac{1}{2}$—u)($\frac{1}{2}$—u)($\frac{1}{2}$+u), where u=0·17. The radius of the neutral fluorine atom is 0·50 Å. O. J. WALKER.

Crystal structure of the compound Fe_2B. G. HAGG (Z. physikal. Chem., 1930, **B**, **11**, 152—162).—A modification of the crystal structure proposed for the above compound by Wever and Muller (A., 1930, 1372) is suggested. From a consideration of the volumes of the atoms involved it seems probable that the tetrahedra which constitute the iron lattice are all very nearly equal. The boron atoms occupy a fourfold point position and are situated in the largest gaps between the tetrahedra of the iron lattice, each boron atom having 8 iron atoms equidistant from it. The value of 0·97 Å. is deduced for the radius of the boron atom. R. CUTHILL.

Structure of compounds of the type MM'_2O_4. I. Cadmium and calcium indates. L. PASSERINI (Gazzetta, 1930, **60**, 754—761).—By calcining mixtures of the nitrates in the required proportion at about 900° the compounds CdO,In_2O_3 and CaO,In_2O_3 have been prepared. An X-ray examination by the powder method shows that these substances crystallise in the tetragonal system of the hausmannite type analogous to that of the spinels. The elementary cell contains 8 mols. of the compound. CdO,In_2O_3 has c/a 1·14, a 8·650±0·005, c 9·875±0·007 Å., v $739\cdot0\times10^{-24}$ c.c., $d_{calc.}$ 7·30; for CaO,In_2O_3 the corresponding values are 1·12, 8·770±0·005, 9·822±0·007, $755\cdot5\times10^{-24}$, and 5·87. O. J. WALKER.

Crystallisation of potassium alum and the action of certain impurities on its habit. H. E. BUCKLEY (Z. Krist., 1930, 73, 443—464; Chem. Zentr., 1930, ii, 366).

Crystal structure of $NiSnCl_6,6H_2O$. L. PAULING (Z. Krist., 1930, 72, 482—492; Chem. Zentr., 1930, ii, 353).—The unit cell, a 7·09 Å., α 96° 45′, contains one molecule; space-group probably C_{3i}^2. A. A. ELDRIDGE.

X-Ray diffraction. I. Structure of amorphous carbon. II. Some colloidal solutions and liquid mixtures. III. Some aromatic hydrocarbons in the solid and liquid states. P. KRISHNAMURTI (Indian J. Physics, 1930, 5, 473—488, 489—499, 543—558).—Using CuK radiation the diffraction patterns of various amorphous carbons showed strong scattering extending to about 7° with the primary beam. The patterns have two rings in addition to central scattering, the prominent first ring corresponding with the (002) reflexion of graphite, with spacing about 3·8 Å. compared with graphite 3·4 Å. The fainter and broader outer ring showed a spacing 2·12 Å. comparable with the (111) spacing of graphite 2·06 Å. The spacing of carbon obtained by the reaction of carbon tetrachloride and molten sodium showed it to be the most finely-divided form. Results agree with the clustering of the carbon atoms to form highly anisotropic units of about 60 atoms per unit, and are in accord with chemical evidence. Data for colloidal graphite are also reported.

II. Investigations previously reported (cf. A., 1929, 246, 751) were extended to aqueous solutions of starch, tannic acid, and gum arabic, which showed strong molecular scattering at small angles to the primary beam. The mol. wt., calculated from the extents of the coronas, were 6200, 3134, and 2810, respectively. A study of the effect of dilution on the inner ring for associated liquids like acetic acid showed disappearance of the ring even in very concentrated solutions, indicating a breaking up of association. The influence of dilution on liquids showing two prominent haloes was investigated in mesitylene–*cyclo*hexane and ethyl *o*-phthalate–benzene systems. These showed changes in the patterns ascribed to more random orientation of the solute molecules with increasing dilution.

III. A comparison was made of the powder and liquid X-ray diffraction patterns for seven representative aromatic hydrocarbons in addition to hexamethylbenzene previously reported (cf. A., 1930, 983). Naphthalene, phenanthrene, acenaphthene, and fluorene showed two rings in the liquid state, whilst diphenyl, dibenzyl, and stilbene show only one, this being due to the difference in arrangement of neighbouring molecules, or impedance to free rotation, or vibration introduced by *o*- and *m*-substitution in the aromatic nucleus. Stilbene shows also a faint inner ring probably due to association. The origin of the liquid patterns is discussed in relation to the dimensions of the molecules as derived from crystal structure data. N. M. BLIGH.

Crystallography of certain racemates and the corresponding optical antipodes of the asparagine group. G. CAROBBI (Rend. Accad. Sci. Fis. Mat. Napoli, 1930, [iii], **36**, 49—55).—*l*- and *d*-Chloroacetylasparagines, m. p. 150°, d 1·538, form monoclinic crystals, $a:b:c$=0·7876 : 1 : 0·4281, β 96° 22′; *r*-chloroacetylasparagine, m. p. 105°, d 1·560, triclinic crystals, $a:b:c$=0·9068 : 1 : 0·8617, α 63° 29′, β 113° 20′, γ 117° 15′; *l*- and *d*-benzenesulphonyl-

asparagines, m. p. 163°, *d* 1·434, monoclinic crystals, $a:b:c=0\cdot7557:1:0\cdot7105$, β 104° 42′; *r*-benzenesulphonylasparagine, m. p. 172°, *d* 1·559, monoclinic; *r*-benzoylasparagine, m. p. 184°, *d* 1·433, monoclinic crystals, $a:b:c=0\cdot8865:1:0\cdot5929$, β 92° 12′.

T. H. POPE.

Crystal structure of thiophen. G. BRUNI and G. NATTA (Atti R. Accad. Lincei, 1930, [vi], 11, 929—934).—The *X*-ray spectrum of thiophen has been determined by the powder method, using a spectrograph designed for low-temperature measurements. The unit cell of thiophen (4 mols.) is tetragonal with an axial ratio a/c 0·757; at −170° the cell constants are a 7·225, c 9·54±0·01 Å., volume 498×10^{-24} c.c., $d_{calc.}$ 1·11. Considerable advantage is gained in the examination of organic compounds by using a calcium anticathode owing to the great intensity of the Ca$K\alpha$ (3351·69) and $K\alpha'$ (3354·95) lines. F. G. TRYHORN.

Crystal structure of benzene and its relations with that of thiophen. II. G. BRUNI and G. NATTA (Atti R. Accad. Lincei, 1930, [viii], 11, 1058—1062; cf. A., 1929, 1223, and preceding abstract).—An *X*-ray examination has been made by the powder method of solid benzene at −170°. The rhombic bipyramidal elementary cell has a 7·34, b 9·52, c 6·74; $d_{calc.}$ 1·099. There is no true isomorphism between thiophen and benzene, but there are certain analogies in the dimensions of their unit cells, which have volumes of 471 and 498×10^{-24} c.c., respectively.

O. J. WALKER.

Crystal structure of quinonoid compounds and of a molecular compound similar to quinhydrone. E. HERTEL and G. H. RÖMER (Z. physikal. Chem., 1930, B, 11, 90—96).—The unit cell of the lattice of anthraquinone has a height of 3·95 Å. and contains 8 molecules which have the planes of their rings all parallel but are at different heights. 2 : 7-Dinitroanthraquinone, on the other hand, has a unit cell which is 38·4 Å. high and contains 4 molecules, arranged with the planes of their rings at right angles. The crystal structure of the compound of fluorene with 2 : 7-dinitroanthraquinone, $C_{13}H_{10},C_{14}H_6O_2(NO_2)_2$, is such as to exclude the possibility of three-dimensional alternation (cf. this vol., 153). R. CUTHILL.

***X*-Ray examination of E. Fischer's polypeptides.** F. V. LENEL (Naturwiss., 1931, 19, 19).—The *X*-ray interference rings of certain polypeptides (*dl*-leucyltetraglycylglycine, *l*-leucyloctaglycylglycine, *l*-leucyltriglycyl-*l*-leucyloctaglycylglycine, *l*-leucyltriglycyl-*l*-leucyltriglycyl-*l*-leucyloctaglycylglycine) show that the high-molecular polypeptides are crystalline.

F. O. HOWITT.

***X*-Ray study of mannitol, dulcitol, and mannose.** T. C. MARWICK (Nature, 1931, 127, 11—12). The following data have been obtained for mannitol, dulcitol, and mannose, respectively: space-group Q_4, C^5_{2h}, and Q_4; a 8·65, 8·61, and 7·62 Å.; b 16·90, 11·60, and 18·18 Å.; c 5·56, 9·05, and 5·67 Å.; d 1·497, 1·466, 1·501 g. per c.c.; mols. per unit cell, 4, 4, and 4; for dulcitol β is 113° 45′. The data suggest that in all cases the long dimension of the molecule corresponds with the a axis; in the alcohols the molecules appear to have the long-chain configuration, and in the carbohydrate, that of the mannopyranose ring with the longest dimension in the direction of the a axis. L. S. THEOBALD.

Structure of the crystal lattice of cellulose. W. T. ASTBURY and T. C. MARWICK (Nature, 1931, 127, 12—13).—From an examination of the available data for cellulose and the sugars it is concluded that the 6-atom sugar ring is associated in the crystalline state with certain linear dimensions which are approximately constant and that one dimension, at least, corresponds with one of the axial lengths of the unit cell. L. S. THEOBALD.

***X*-Ray diffraction in heated liquids and in solutions.** V. I. VAIDYANATHAN (Indian J. Physics, 1930, 5, 501—524; cf. A., 1929, 746).—The scattering of *X*-rays was examined at temperatures ranging from 25° to 235° for *cyclo*hexanone, terpineol, *cyclo*hexene, benzene, phenol, diphenylamine, propionic acid, acetonitrile, ethyl *o*-phthalate, *o*-nitrobenzaldehyde, tetranitromethane, octane, pentane (cf. Ramasubramanyam, A., 1928, 1312), and hexoic acid. Diffuseness and contraction of the haloes with rise of temperature was observed, and an increase in scattering at small angles, comparable, in the case of benzene, with that observed in the scattering of light. The ratio of the intensity of the *X*-ray scattering at small angles to that of the primary beam, for water and benzene, is in fair agreement with the value calculated from the Einstein–Smoluchowski formula. Of the two haloes present, the inner one did not appreciably diminish in intensity with rise of temperature in the case of associated liquids, indicating that their origin depends primarily on molecular form and polarity, and not on association. The ratio of the intensity of incident to scattered radiation was examined quantitatively for dilute aqueous solutions of dextrose and sucrose and the results are compared with theoretical calculations. N. M. BLIGH.

***X*-Ray interpretation of the structure and elastic properties of hair keratin.** W. T. ASTBURY and H. J. WOODS (Nature, 1930, 126, 913—914).—From a consideration of the stretching properties of hair keratin and the *X*-ray data a skeleton of the keratin complex which gives a quantitative interpretation of the fundamental points is advanced. The skeleton consists of a peptide chain folded into a series of hexagons, each of which is in effect a diketopiperazine ring. L. S. THEOBALD.

***X*-Ray studies on paraffin wax and vaseline.** S. TANAKA and A. TSUJI (Mem. Coll. Sci. Kyoto, 1930, A, 13, 369—374).—The influence of temperature and mechanical operations on the *X*-ray diffraction patterns given by paraffin wax and vaseline has been studied. Below the m. p. spectral lines characteristic of the crystalline powders are obtained, but these decrease in intensity with temperature rise and disappear on melting. The transformation occurs in a different manner for each substance. W. GOOD.

Diffraction of *X*-rays in liquids: effect of temperature. E. W. SKINNER (Physical Rev., 1930, [ii], 36, 1625—1630).—The effect of temperature on *X*-ray diffraction was examined for mesitylene, *m*-2- and *m*-4-xylenol, phenol, naphthalene, benzene, *cyclo*hexane, di-*n*-propylcarbinol, heptoic

acid, *tert.*-butyl alcohol, lauryl alcohol, octane, βη-dimethyloctane, and ββδ-trimethylpentane. The general results are in agreement with those of Vaidyanathan (cf. A., 1929, 746), and strongly support the cybotactic space-group condition in liquids. Space rearrangements within these groups with change of temperature are indicated. Anisotropic expansion within the space-groups in the liquids is indicated.

N. M. BLIGH.

Structure of organic molecular compounds. E. HERTEL and H. KLEU (Z. physikal. Chem., 1930, B, **11**, 59—75; cf. A., 1930, 668).—The crystal structure of the equimolecular compound of acenaphthene with 2 : 6-dinitro-*m*-xylene has been determined. A comparison of the dimensions of the unit cell of the compound with those of the constituents enables a diagram of the mode of combination to be constructed. The space-groups of the three substances, in the order named above, are $V_h^{?}$, $C_{2h}^{?}$, and C_{2h}. A simple relation subsists between the corresponding dimensions: thus $a_{AB}=\frac{1}{2}a_A+a_B$; $b_{AB}=b_A+b_B$; $c_{AB}=c_A-c_B$, where A denotes acenaphthene and B dinitroxylene. The structure of acenaphthene is discussed, and a criterion of a "molecular compound" is proposed.

F. L. USHER.

One- and two-dimensional alternation in crystal structure of organic molecular compounds. E. HERTEL and G. H. ROMER (Z. physikal. Chem., 1930, B, **11**, 77—89).—In the lattice of an organic molecular compound it may happen as a result of the mutual saturation of residual valencies that the molecules of one of the components form a chain or net-work. Hence instead of the molecules of the components alternating with each other along all three principal axes of the crystal (cf. preceding abstract) they alternate along only two ("two-dimensional alternation") if chains are present, and along only one ("one-dimensional alternation") if net-works are present. The lattice of the compound of fluorene and 1 : 3 : 5-trinitrobenzene, $3C_{13}H_{10},4C_6H_3(NO_2)_3$, for instance, is composed of alternating net-works of fluorene and trinitrobenzene molecules. In the compound of anthracene with 1 : 3 : 5-trinitrobenzene, $C_{14}H_{10},C_6H_3(NO_2)_3$, on the other hand, the lattice is a body-centred translational lattice of the Γm′ class with the space-grouping $C_s^{?}$, and the trinitrobenzene molecules are arranged in chains. 1 : 3 : 5-Trinitrobenzene itself has a simple rhombic translational lattice in which the molecules form groups of four with the characteristic symmetry C_s, or C_2. In the lattice of 2 : 4 : 6-trinitrotoluene the space-grouping is and here also the molecules are grouped in fours.

R. CUTHILL.

Use of the rule of ferromagnetic anisotropy in calculating the properties peculiar to polycrystalline iron. N. S. AKULOV (Z. Physik, 1930, **66**, 533—542).—A formula is deduced by means of which it is possible to calculate, from measurements on single crystals, the magnetisation, the magnetostriction, and the change in resistance of pure polycrystalline ferromagnetics. This formula is strict at saturation.

J. FARQUHARSON.

Magnetic properties of rhenium. W. H. ALBRECHT and E. WEDEKIND (Naturwiss., 1931, **19**, 20—21).—The magnetic susceptibilities of potassium perrhenate and metallic rhenium were found to be $-0{\cdot}13(\pm0{\cdot}05)\times10^{-6}$ and $+0{\cdot}046(\pm0{\cdot}02)\times10^{-6}$, respectively. The value for rhenium does not lie between those of its neighbouring elements, osmium and tungsten.

F. O. HOWITT.

Doubling of the Curie points of nickel. R. FORRER and A. HOFFMANN (Compt. rend., 1930, **191**, 1049—1049).—The difference between the paramagnetic Curie point determined from Weiss' law (θ_p) and the ferromagnetic point corresponding with disappearance of permanent magnetisation (θ_f) is of the order of 20°. The dependence on the previous thermal and mechanical treatments of nickel of the difference between θ_f and the Curie point (θ_h) of the coercive field has been investigated. It is large (14·5°) for nickel which has been bent and then straightened, 1·5° for nickel ruptured by stretching, and 5—14·5° for nickel annealed under various conditions. Annealed nickel always shows a displacement of the Curie point, whilst variations with temperature of the mechanical constants of mechanically-treated nickels are linear, and give relatively unambiguous values. The results indicate the presence of two ferromagnetic nickels having different Curie points, which must be segregated, since solid solutions have only one Curie point. The first ferromagnetic Curio point is at 361° and is independent of the method of treatment; $(\theta_{f_2}-\theta_{f_1})$ is of the order of 6° and is characteristic of the annealed nickel (cf. Lapp, A., 1928, 577). The difference $(\theta_{h_2}-\theta_{f_2})$ is of the same order as $(\theta_{h_1}-\theta_{f_1})$, *i.e.*, 5—14·5°. The ratio of the magnetisations of the two types of nickel equally removed from θ_f is unity.

J. GRANT.

Magnetisation of a ferromagnetic substance under the influence of an alternating field. S. PROCOPIU (J. Phys. Radium, 1930, [vii], **1**, 365—372).—The magnetisation of iron and steel wires was studied, using a constant magnetising field, on which were superimposed in turn longitudinal and circular alternating or oscillating fields. Curves are plotted, and it was found that the magnetisation increases to a maximum when the alternating or oscillating field reaches the coercive value for the substance, after which it decreases. The variation of magnetisation is least at high frequencies of the order 2×10^6 periods per sec.

N. M. BLIGH.

Influence of internal transverse magnetism in determinations of electrical resistance of wires of iron, nickel, and of their alloys. M. MEDICI (Rend. Accad. Sci. fis. mat., 1930, **35**, 248—255).—The transverse magnetism produced in a wire by the passage of an electric current affects the resistance of the wire, but the effect tends to disappear after a certain time. With iron there is an increase of resistance due to the transverse magnetic field, which decreases gradually with time and approaches that of the unmagnetised metal. Iron previously heated shows the opposite behaviour. With nickel and iron–nickel alloys, both before and after heating, the transverse magnetism produces a decrease in the resistance. Alloys containing 44% and 49% Ni lose their magnetisation in a short time; with the 36% alloy the effect of the transverse magnetic field is

the most protracted, whereas the 22% alloy, which has practically no ferromagnetism, returns rapidly to its original state. For all the alloys the variation of the resistance is proportional to the intensity of the current used to produce the transverse magnetism.

O. J. Walker.

Direction of magnetisation of single ferromagnetic crystals. F. C. Powell (Proc. Roy. Soc., 1930, A, **130**, 167—181).—Theoretical. It is shown that Mahajani's theory of ferromagnetism (cf. A., 1929, 495) fails in the case of cubic crystals. The observed deviation between the directions of magnetisation and the applied field in both cubic and non-cubic crystals can be satisfactorily accounted for by taking into consideration the magnetic interaction between the effective electrons (*i.e.*, those of which the magnetic moments contribute to the magnetisation of the crystal) and the atoms to which they belong. It is supposed that this interaction can be represented by a field b fixed in the crystal, the " crystalline field." The theory has been worked out only for cases when the applied field is great enough to produce saturation and when thermal effects can be neglected. The required magnitude of G is in agreement with that deduced from spectroscopic data, and is estimated to be 5·6, 8·2, and $4{\cdot}5\times10^5$ gauss for nickel, iron, and cobalt, respectively.

L. L. Bircumshaw.

Anomalous diamagnetism and crystal structure. V. I. Vaidyanathan (Indian J. Physics, 1930. **5**, 559—572).—Colloids of graphite, bismuth, and antimony investigated magnetically showed a decrease of diamagnetism on colloidalisation, the effect being most marked in graphite. The anisotropy of single crystals of graphite was approximately 1 : 6·7 for the c axis perpendicular and parallel to the field, respectively. In the compounds of bismuth and antimony the ionic values are smaller than in the crystal state, and vary as deduced from different compounds.

N. M. Bligh.

Molecular field and atomic order in ferromagnetic crystals and in hydrogenised iron. L. W. McKeehan (Nature, 1930, **126**, 952—953).—A discussion.

L. S. Theobald.

Magnetic isotropy of a paramagnetic alum. C. G. Montgomery (Physical Rev., 1930, [ii], **36**, 1661—1662; cf. A., 1930, 1354).—In order further to test, using a paramagnetic material, Forrest's theory (cf. A., 1927, 299) of variation in magnetic susceptibility with direction of the applied field for certain crystals, measurements were made on potassium chromium alum. The crystals were found to be magnetically isotropic, in opposition to Forrest's deductions.

N. M. Bligh.

Effect of internal stress on the magnetic susceptibility of metals. K. Honda and Y. Shimizu (Nature, 1930, **126**, 990—991).—Cold-working markedly decreases the diamagnetic susceptibility of a metal belonging to the cubic system; in the case of copper, severe cold-working changes the susceptibility of copper from diamagnetic to paramagnetic. Data for silver are also given.

L. S. Theobald.

Magnetic forces in a crystal of the rock-salt type. J. Bouman (Arch. Neerland., 1930, [iiiA], **13**, 1—28).—Mathematical. The magnetic fields due to the lattices of elementary magnets are calculated, and the partition of the magnets in the crystal is investigated, having regard to crystal symmetry, absence of magnetisation, and the equilibrium of the magnets under the mutual influence of their magnetic fields.

N. M. Bligh.

Magnetic properties of certain platinum- and palladium-cobalt alloys. F. W. Constant (Physical Rev., 1930, [ii], **36**, 1654—1660).—In order to obtain evidence on ferromagnetism, an investigation was made, using the above alloys, of the magnetic properties of ferromagnetic atoms in a state of isolation from one another intermediate between that of the pure metal and that of Gerlach and Stern's experiments. A lowering of the Curie point and a decrease in the remanent magnetisation and coercive force with decrease in the percentage of cobalt were found, in agreement with theory, in relation to which is discussed the observed increase in the magnetisation per cobalt atom.

N. M. Bligh.

High-pressure gas charging of metals. H. Jellinek (Z. Physik, 1930, **66**, 543—557).—Iron, palladium, and silver absorb hydrogen and nitrogen at high pressures after activation. The activation and purification process consisted of heating a wire of 2 mm. diameter by means of a current of 38 amp. for about 1 hr. The heating process was repeated until the electrical resistance of the metal became fixed. The absorption of gas was then measured by means of variation in electrical resistance. The resistance of iron in hydrogen showed an 8·9% increase between 0 and 35 atm. pressure, in nitrogen a decrease of 4·5% between 0 and 15 atm., and an increase of 13·3% between 15 and 20 atm. The resistance of palladium in hydrogen increased by 4·4%, and in nitrogen by 3·8%, between 0 and 20 atm. Silver in hydrogen increased its resistance by 13·1% between 0 and 35 atm.

A. B. D. Cassie.

Variable resistances and their hydrodynamic analogy. R. Auerbach (Z. Physik, 1930, **66**, 499—512).—The analogy existing between the behaviour of electrical resistances which do not obey Ohm's law and have large temperature coefficients, and the hydrodynamic behaviour of solutions of solvated colloid solutions, is noted and discussed.

A. B. D. Cassie.

Electrical conductivity of amorphous quartz. W. Gnann (Z. Physik, 1930, **66**, 436—452).—The dependence of the electric current passing along a quartz cylinder, 1·2 cm. long and 1 cm. diameter, on the moisture of the surrounding atmosphere, and on the applied voltage, and its time of application, were studied. Immediately after applying the *P.D.* a comparatively large current passes, owing to the absence of an opposing potential. This initial current reaches a constant smaller value after a few hours. Both the final constant current and the opposing current are largely dependent on the moisture content of the surrounding atmosphere, and the surface currents are greater than the volume currents even at medium moisture content. The volume resistance of quartz is more than 6×10^{19} ohm per cm. The final constant current obeys approxi-

mately Ohm's law. Bakelite C also shows equally large hygroscopic effects. A. B. D. CASSIE.

Unipolarity of pressed lead sulphide. F. TREY (Naturwiss., 1930, **18**, 1099).—The effect of pressure and heat treatment on the unipolarity of lead sulphide crystal detectors is discussed. The detector properties are bound up with the normal crystal structure of the sulphide. Unipolar properties are connected with the resistance of the lead sulphide. Only good-conducting lead sulphide crystals of normal crystal structure can exhibit unipolar properties. At strong pressures significant properties of lead sulphide as a detector are good conductivity and unipolarity. W. R. ANGUS.

Polymorphous organic selenium compounds. O. BEHAGHEL (Z. wiss. Phot., 1930, **29**, 230—233).—No relation could be found in the appearance of polymorphous forms in sulphur and selenium compounds of similar constitution. *p*-Phenylenebis-selenoglycollic acid, *p*-phenyleneselenothiodiacetic acid, and other selenoglycollic acid derivatives and certain mono- and di-selenides do not exhibit the polymorphism shown by the corresponding sulphur compounds; diselenodiglycollic acid may be obtained in three modifications, but the corresponding sulphur compound does not exhibit polymorphism (cf. A., 1930, 100). J. W. GLASSETT.

Determination of the mol. wt. of hæmocyanin by the centrifugal method. T. SVEDBERG and E. CHIRNOAGA (Bul. Chim. pura appl., Bukarest, 1929, **31**, 23—52; Chem. Zentr., 1930, ii, 248—249).—The determination of hæmocyanin from *Helix Pomatia* in isoelectric solution of p_H 4·7 is described. The diffusion constants depend on the concentration when this exceeds a limiting value, presumably owing to the operation of intramolecular forces. The value 5×10^6 ($\pm5\%$) was obtained; the hæmocyanin is regarded as a chemical individual. At p_H 7 the "molecules" are spheres of radius $12{\cdot}1\times10^{-7}$ cm.; each molecule contains 300 atoms of copper. The preparation of the hæmocyanin is described. The specific volume of hæmocyanin in solutions of p_H 8—3·8 is 0·730—0·755. In agreement with Dhere and Burdel, absorption bands were found at 610—530, 360—310, and 290—260 μμ. On the acid side of the isoelectric point the absorption is markedly less and is displaced towards the red. A. A. ELDRIDGE.

Magnetic susceptibility of gases. II. Temperature dependence. F. BITTER (Physical Rev., 1930, [ii], **36**, 1648—1653; cf. A., 1930, 1102).—The molecular susceptibilities $\times10^6$ for carbon dioxide, nitrogen, and hydrogen at 25° gave the values −24·2, −14·8, and −5·8, and at −185°, −14·2 and −3·3 for the two last-named gases, respectively. Results of previous investigators are tabulated for comparison, and are in fair agreement. The low-temperature result for nitrogen indicates that if a permanent moment is present it is less than 0·04 of a Bohr magneton. The anomaly of the difference in the values for hydrogen at the two temperatures is discussed. N. M. BLIGH.

Heat of vaporisation of liquids. J. HYBL (Z. Eis- Kalte-Ind., 1930, **37**, 85—86; Chem. Zentr., 1930, ii, 208).—Kamerlingh Onnes' formula $r=a(T_{crit}-T)-b(T_{crit}-T)^2+c(T_{crit}-T)^3$ gives results in best accord with observations on water and ammonia. Values of a, b, c, and $T_{crit.}$ for 12 organic and inorganic liquids are tabulated; the heat of vaporisation between −40° and 40° has been calculated and expressed graphically. The curves are similar; hence the heat of vaporisation for equal values of $T_{crit.}-T$ can be obtained by multiplication of the value for water by a constant factor. A. A. ELDRIDGE.

Latent heats of evaporation of nitromethane and benzonitrile. J. C. PHILIP and S. C. WATERTON (J.C.S., 1930, 2783—2784).—Redeterminations of the latent heats of evaporation of nitromethane and benzonitrile by Brown's method (J.C.S., 1903, **83**, 987) give values of 135·4 and 106·5 g.-cal./g., respectively. These values are higher than those recorded in the literature. The theoretical values of the b. p. elevation constants are calculated from these values to be 2·05° and 4·01°, respectively; these are only slightly higher than the experimental values (cf. Landolt and Bornstein), which are now determined as 1·86° and 3·87°, respectively. H. BURTON.

Emissive laws of nickel. W. DEL REGNO (Atti R. Accad. Lincei, 1930, [vi], **11**, 989—993; cf. A., 1929, 1353).—The method previously used for bismuth has been applied in the determination of the exponent in the Stefan–Boltzmann equation for the total emissivity of nickel. The value 4·586 was obtained from measurements over the range 60—360°. F. G. TRYHORN.

Influence of the elastic deformation of drawing on the specific heat of metals. M. GAUDINO (Rend. Accad. Sci. fis. mat., 1930, **35**, 204—207).—Permanent deformation produced in nickel, brass, and lead wires by drawing them almost to the breaking point bring about a slight increase in the specific heat of the metal. O. J. WALKER.

Necessity for adopting a standard substance for ebullioscopic and tonometric measurements. W. SWIENTOSLAWSKI (J. Chim. phys., 1930, **27**, 496—502).—Attention is directed to the errors in temperature and vapour-pressure measurements and to the lack of concordance in the published data, which cannot be attributed entirely to the presence of impurities in the liquids investigated. Agreement can be reached only by the universal adoption of a comparative method of measurement, and water is suggested as a suitable standard. It is further recommended that (1) when determining the b. p. or vapour pressure of a liquid at a given temperature the b. p. and vapour pressure of the standard under the same conditions should be noted, (2) when the b. p. of the liquid differs considerably (30° or 40°) from that of the standard under the same pressure, comparison should be made with an auxiliary liquid, the b. p. of which is as near as possible to that of the liquid investigated, and is known in relation to the standard, (3) the coefficients dp/dt should be determined in such a way that the corresponding coefficients of the standard can be defined under the same conditions, (4) the b. p. of the liquid and of the

standard should be determined at various pressures so that the relation $t_{subs.} = f(t_{H_2O})$ may be established.
E. S. HEDGES.

Comparative ebullioscopic and tonometric researches with eight standard organic substances. A. ZMACZYNSKI (J. Chim. phys., 1930, **27**, 503—517).—The variation of b. p. with pressure over the range 380—2000 mm. has been determined for 8 organic liquids and for water. An empirical equation for the relation between the b. p. of the substances studied and that of water at the same pressure has been established in the form $t_{subs.} = A \quad + C(t_{H_2O})^2$ and tables of the values of the coefficients A, B, and C are given. A table of the ratio $(dt/dp)_{subs.} : (dt/dp)_{H_2O}$ is given and the coefficients dt/dp have been calculated for 760 mm. The following values of b. p./760 mm. have been determined from the data and are compared with those in the literature: ethyl bromide, 38·386°; carbon disulphide, 46·262°; acetone, 56·131°; chloroform, 61·152°; benzene, 80·122°; toluene, 110·606°; chlorobenzene, 131·687°; bromobenzene, 155·908°.
E. S. HEDGES.

Thermal conductivity of liquids. J. F. D. SMITH (Ind. Eng. Chem., 1930, **22**, 1246—1251).—The following results were obtained in c.g.s. units for thermal conductivities at the temperatures stated: ethyl alcohol 99·8%, 30°, 0·000435; 95%, 30°, 0·000460; water 30°, 0·00144; 75°, 0·00148; toluene 30°, 0·000357; 75°, 0·000338; *iso*amyl alcohol 30°, 0·000362; 75°, 0·000358; data are given for the following hydrocarbon oils: Rabbeth spindle oil, Velocite B, red oil, light heat-transfer oil. The empirical equation $kZ^{0\cdot12}/\rho C^{0\cdot4} = 8\cdot1 \times 10^{-4}(\rho C M^{1\ 6})^{1\cdot15}$ gives the thermal conductivities of all non-metallic liquids at 30° and atmospheric pressure, where k is thermal conductivity in c.g.s. units, ρ is d_{liquid}/d_{water} at 30°, Z viscosity in centipoises, C sp. heat, and M mol. wt.
H. INGLESON.

Specific heat charts for gases [at high temperatures]. A. C. HALFERDAHL (Chem. & Met. Eng., 1930, **37**, 686—687).—The mean specific heats of hydrogen, nitrogen, oxygen, carbon monoxide and dioxide, sulphur dioxide, hydrogen sulphide, ammonia, methane, chlorine, and water and sulphur vapour were plotted up to 2500°, and a simplifying chart is given. The errors range from 1·5 to 10%.
E. A. RYDER.

Vapour pressure of chlorine monoxide. C. F. GOODEVE (J.C.S., 1930, 2733—2737).—Apparatus is described which is suitable for the determination of the vapour pressure of chlorine monoxide without undue decomposition of the gas; at temperatures below −10° decomposition ceases. The vapour pressure p between −96° and 3° accords with the equation $\log p = -1373/T + 7\cdot87$, from which the calculated latent heat of vaporisation is 6200 g.-cal./mol.; Trouton's constant, 22·5, is indicative of little association in the liquid state. The b. p. is 2·0°/760 mm., and the m. p. −116°±1°.
H. F. GILLBE.

Compressibility of nitrogen and hydrogen at pressures of 5000 atm. J. BASSET and R. DUPINAY (Compt. rend., 1930, **191**, 1295—1297).—Data are given for the volumes occupied at 16° and pressures up to 5000 kg. per cm.^{2} by masses of nitrogen and hydrogen occupying (*a*) 1 c.c. at 16° and 1000 kg. per cm.^{2}; (*b*) 1 litre at 0° and 76 cm. The apparatus previously described (this vol., 59) was used and the results for hydrogen (up to 3000 kg. per cm.^{2}) are in agreement with those of Amagat, whilst for nitrogen they are 2—3% lower.
J. GRANT.

Direct connexion between equation of state and inner friction. L. SCHAMES (Physikal. Z., 1931, **32**, 16—20).—Mathematical. It is possible, by means of the friction, to separate the effects of the van der Waals a and b terms, and to determine these quantities as temperature functions.
A. J. MEE.

Measurements with the aid of liquid helium. XII. Plasticity of metal crystals at the lowest temperatures. W. MEISSNER, M. PÓLANYI, and E. SCHMID (Z. Physik, 1930, **66**, 477—489).—Stress-strain curves for the extension of zinc and cadmium crystals at temperatures in the liquid helium range are given. The form of these curves does not change as the temperature is lowered. Plasticity is separated into two parts; one, apparent only in crystals, is independent of temperature, and the other, which may be associated with the self-diffusion of amorphous substances, is dependent on temperature. The first is termed "athermic," the second "thermic," plasticity. The experimental method, and a means of transporting liquid helium, are described in detail.
A. B. D. CASSIE.

Determination of molecular velocities and proof of the cosine law. P. CLAUSING (Ann. Physik, 1930, [v], **7**, 569—578).—An expression derived for the mean time taken by a molecule in its zig-zag path down a long capillary tube (cf. this vol., 34) is tested experimentally for argon and neon at the ordinary temperature. It is necessary to assume that during its passage down the tube the molecule does not collide with another, and that the adsorption time of the molecules on the glass walls of the tube is so small that the time of travel down the tube is independent of it. From the experiments it is shown that the cosine law for diffuse scattering of molecules is correct for argon and neon at glass at the ordinary temperature, and that the mean molecular velocity agrees with the Maxwell velocity distribution.
A. J. MEE.

Critical constants of carbon dioxide–oxygen mixtures. H. S. BOOTH and J. M. CARTER (J. Physical Chem., 1930, **34**, 2801—2825).—The maximum temperatures of condensation, the critical temperatures, and the corresponding pressures have been determined for the following volume mixtures of oxygen and carbon dioxide: 1 : 1, 3 : 2, 7 : 3, 4 : 1, and 9 : 1, respectively, in an apparatus specially designed for the study of critical phenomena at low temperatures. Mixtures containing 50% or less of carbon dioxide should not lose their uniformity under the ordinary conditions of transport or storage. The mixture containing 50% CO_2 cannot be liquefied at all above −8·4° and cannot be completely liquefied above −35·7°. With less carbon dioxide even lower temperatures are required. A discontinuity in the critical curve of the mixtures is shown by those which contain from 62% to 97% O_2. The curve representing the maximum temperatures of condensation also

shows a discontinuity for mixtures containing 88—98% O_2. Solid carbon dioxide is soluble to about 3% in liquid oxygen near its critical temperature. The retrograde phenomena are explained.

L. S. THEOBALD.

Changes in volume and temperature that accompany the mixing of organic liquids. I. E. R. WASHBURN and A. LIGHTBODY (J. Physical Chem., 1930, **34**, 2701—2710).—The changes in temperature and volume which accompany the mixing of methyl, ethyl, and *iso*propyl alcohols with benzene and with toluene, respectively, have been determined. The maximum temperature changes become greater as the homologous series is ascended and the volume changes appear to vary in a regular manner, but no simple relation exists between the temperature and volume changes for a given mixture. The presence of water in the system ethyl alcohol–benzene increases the magnitude of both changes. L. S. THEOBALD.

Application of the Debye dipole theory to binary liquid mixtures. III. Derivatives of ammonia. J. M. FOGELBERG and J. W. WILLIAMS (Physikal. Z., 1931, **32**, 27—31; cf. A., 1928, 578, 1180).—The structure of the ammonium group is discussed. The ammonium model, consisting of a pyramid in which the nitrogen atom is situated at the point of the pyramid, is in agreement with stereochemical observations, and also with the dipole moment data. The dipole moments of a number of aromatic and aliphatic amines have been determined to ascertain whether they can be classed as ammonium derivatives. The binary mixture method, previously developed, was used. Values for the dielectric constants and densities are given. The conditions under which the dipole moments can be calculated are stated.

A. J. MEE.

Theory of orderly structure of solid solutions. C. WAGNER and W. SCHOTTKY (Z. physikal. Chem., 1930, B, **11**, 163—210).—The array of the particles in the lattice of a solid binary compound will be disturbed if an excess of one component is introduced so as to form a solid solution, and some of the particles will be wrongly placed as compared with the original lattice, either through the formation of a solid solution of the interstitial or substitutional type, or by the appearance of empty places in one of the partial lattices. By a combination of thermodynamical and statistical methods it has been possible to determine the number of such points of disarray and the activities and chemical potentials in solid solutions of the various types as functions of the composition. In solid solutions with metallic lattices the relationship between electrical resistance and composition is dependent on the number of points of disarray. It is considered that even when the composition of the solid solution corresponds with a simple stoicheiometric ratio some points of disarray are present, and the ratio of the number of points of disarray to the total number of lattice points in the crystal is termed the "degree of disarray." Various examples of the calculation of this quantity from experimental data are given. R. CUTHILL.

Isomorphism between oxides of quadrivalent metals. Systems CeO_2–ThO_2, CeO_2–ZrO_2, and CeO_2–HfO_2. L. PASSERINI (Gazzetta, 1930, **60**, 762—776).—An *X*-ray examination by the powder method has been made of the various binary solid solutions of the above oxides obtained by calcination at about 800° of the solid solutions of the corresponding hydroxides, which were prepared by precipitation with potassium hydroxide of solutions containing the required amounts of the metallic nitrates or sulphates. The binary solid solutions of the dioxides, like the dioxides of cerium and of thorium, crystallise in the cubic system with a lattice of the fluorite type. In the system CeO_2–ThO_2 the components are soluble in one another in all proportions and the lattice constants and densities vary regularly with the composition of the solid solution. In the other two systems the solubility is only partial, the maximum solubilities being approximately 27% of zirconium oxide in cerium oxide, 23% of cerium oxide in zirconium oxide, 25% of cerium oxide in hafnium oxide, and 32% of hafnium oxide in cerium oxide. By extrapolation from the data for the solid solutions the following lattice dimensions have been obtained for the cubic form of zirconium dioxide and for the probable cubic form of hafnium dioxide: ZrO_2, a 5·065±0·01 Å., v 129·94×10^{-24} c.c., d 6·27; HfO_2, a 5·115±0·01 Å., v 133·82×10^{-24} c.c., d 10·43. These two oxides have a fluorite type lattice. The calculated diameter of the Hf^{++++} ion is 1·79 Å. For the binary systems investigated the solubility in the solid state depends on the difference between the diameters of the metallic ions. O. J. WALKER.

Thermal conductivity of copper alloys. II. Copper–tin. III. Copper–phosphorus. C. S. SMITH (Amer. Inst. Min. Met. Eng. Tech. Pub., 1930, No. 360, 11 pp.).—The addition of tin rapidly reduces the thermal conductivity of copper (0·941 g.-cal. per cm.^{2} per cm. per sec. per 1°) until with 10·41% Sn it is only 0·121 at 20°; 0·93% of phosphorus reduces the value to 0·129. The electrical conductivity decreases more rapidly on alloying than does the thermal conductivity. The Wiedemann–Franz–Lorenz ratio increases rapidly at first, but beyond 2·0% Sn or 0·15% P it remains nearly constant.

CHEMICAL ABSTRACTS.

X-Ray investigation of the system cadmium–magnesium. U. DEHLINGER (Z. anorg. Chem., 1930, **194**, 223—238).—*X*-Ray diagrams of cadmium–magnesium alloys show the existence of two series of mixed crystals, α and β, of which the axial ratios are 1·89 and 1·62, respectively, at all concentrations; no phase having a different lattice type appears to exist. Powder diagrams of the compound $CdMg_3$, which has the β structure, resemble closely those of pure magnesium and indicate a regular distribution of cadmium in the magnesium lattice without appreciable distortion. The cell constants a and c of the compound are 3·13 and 5·07 Å., as compared with 3·19 and 5·16 Å. for magnesium; the observed density of the compound is 3·49, whilst that calculated on an assumption of atomic substitution is 3·45. The compound Cd_3Mg, which is of the α type, is formed in the analogous manner by substitution of magnesium atoms in the cadmium lattice, of which the lattice constants a and c diminish from 2·96 and 5·63 Å. to

2·93 and 5·53 Å. The transformation experienced by cadmium when subjected to pressure (3000 atm.) appears to be reversible, but by hammering a cadmium–magnesium mixed crystal containing 50 at.-% of magnesium a permanent change from the cadmium to the magnesium type of lattice takes place; the presence of magnesium thus lowers the pressure necessary to cause the cadmium transformation. This phenomenon is thermodynamically in accordance with the smaller cell volume of the magnesium type of mixed crystal. H. F. GILLBE.

Electrical conductivity and thermal expansion of magnesium–cadmium alloys. G. GRUBE and E. SCHIEDT (Z. anorg. Chem., 1930, **194**, 190—222).—The variation with composition of the conductivity and thermal expansion of magnesium–cadmium alloys has been determined between 50° and the m. p. The conductivity–composition isotherms at 50° exhibit three sharp peaks corresponding with the compound MgCd and the *compounds* Mg_3Cd and $MgCd_3$; at higher temperatures the maxima become flatter, since the compounds are stable only at relatively low temperatures. $MgCd_3$ separates at 89° on cooling the cadmium-rich α-mixed crystals, and Mg_3Cd at 150° from the magnesium-rich β-mixed crystals; MgCd decomposes at temperatures above 251°. Cadmium and $MgCd_3$, as well as $MgCd_3$ and MgCd, form continuous series of mixed crystals at the ordinary temperature, whereas MgCd and Mg_3Cd have only limited mutual solubility. The α′-mixed crystals, stable at the ordinary temperature, contain from 0% to 65% of magnesium, whilst the β′-mixed crystals contain from 100% to about 60% of magnesium. The heterogeneous region at 61—67% magnesium vanishes at 150°, but at 100° a second heterogeneous region appears at 28—33% magnesium. The transformation of the α′- and β′-mixed crystals into the α- and β-types, stable at higher temperatures, has been investigated, and the limits of co-existence of the various phases have been determined. For alloys containing 40—60% and 70—80% of magnesium the temperature coefficients of the conductivity and thermal expansion are at first constant, and then, at 70—80° below the transition interval, increase slowly; in the transition range the increase becomes abrupt, and finally, after the transition has been completed, the coefficients fall to a small constant value. The transitions thus appear to take place in two stages, of which the first involves the gradually accelerated breakdown of the regular orientation of the atoms and the second the rearrangement of the still partly oriented atoms into the structure of the mixed crystals stable at the higher temperature. H. F. GILLBE.

Equilibrium relations in aluminium–magnesium silicide alloys of high purity. E. H. DIX, jun., F. KELLER, and R. W. GRAHAM (Amer. Inst. Min. Met. Eng. Tech. Pub., 1930, No. 357, 15 pp.).—Aluminium containing 0·14—2·37% of Mg_2Si was investigated. At the eutectic temperature, 595°, the solid-solubility of Mg_2Si is 1·85%; it decreases with falling temperature, being less than 0·27% at 200°. The mechanical properties of the alloys were studied. CHEMICAL ABSTRACTS.

Equilibrium relations in aluminium–antimony alloys of high purity. E. H. DIX, jun., F. KELLER, and L. A. WILLEY (Amer. Inst. Min. Eng. Tech. Pub., 1930, No. 356, 9 pp.).—The solid-solubility of antimony is less than 0·10% at 645°. The eutectic lies at 1·1% Sb and 657°. CHEMICAL ABSTRACTS.

Constituents of aluminium–iron–silicon alloys. W. L. FINK and K. R. VAN HORN (Amer. Inst. Min. Met. Eng. Tech. Pub., 1930, No. 351, 11 pp.).—*X*-Ray examination of the annealed alloys confirms Dix and Heath's results. The α ternary constituent appears to be a solid solution of silicon in the compound $FeAl_3$. The β constituent is a ternary compound which may contain excess of aluminium in solid solution. CHEMICAL ABSTRACTS.

Strontium amalgams. G. DEVOTO and E. RECCHIA (Gazzetta, 1930, **60**, 688—692).—A thermal analysis has been made of strontium amalgams containing up to approximately 20 at.-% Sr. A compound, $SrHg_8$, is formed by a transition which occurs at 262°. A slight arrest is found at 39°, which may be due to the compound $SrHg_{12}$, and a eutectic point occurs at −43°, with approximately 1·1 at.-% Sr. The initial b. p. of mercury in these amalgams is 390°, compared with 337° for calcium amalgams.

F. G. TRYHORN.

Multicomponent systems containing iron. III. System iron–phosphorus–silicon. W. HUMMITZSCH and F. SAUERWALD (Z. anorg. Chem., 1930, **194**, 113—138).—The system $Fe–Fe_2P–FeSi$ has been investigated thermally and microscopically. Fe_2P and FeSi form a quasi-binary system, the components being completely miscible when fused and immiscible when solid; the eutectic mixture formed at 1185° contains Si 15·0, P 12·05%. Fe_3P and FeSi do not form a quasi-binary system; Fe_3P melts incongruently at 1165—1173°, and the liquidus curve which commences at this point rises to a maximum, but there is no evidence for the existence of a compound such as $2Fe_3P,FeSi$; the eutectic formed at 1180° contains P 8·95%, Si 14·42%. Mixtures containing 8% P exhibit two binary eutectics, viz., with mixed crystals and Fe_3P (1027°) and with mixed crystals and FeSi (1147°) as solid phases, whilst at a slightly lower phosphorus content (7·45%) a ternary eutectic mixture containing Si 6·35% separates at 1018°, the phases being ternary saturated mixed crystals of unknown composition, Fe_3P, and FeSi. An invariant point exists at 1110°, corresponding with the transformation liquid + Fe_2P=Fe_3P + FeSi; the liquid phase contains P 6%, Si 13·55%. There is no evidence of a thermal effect due to the compound Fe_3Si_2. H. F. GILLBE.

Peaks in the isotherms of the electrical conductivity of metallic mixed crystals. G. GRUBE and J. HILLE (Z. anorg. Chem., 1930, **194**, 179—189).—The application of measurements of electrical conductivity to the investigation of changes in metallic systems which cannot be studied by thermal methods is described; a particular case is that of transformations in solid alloys, which often take place with extreme slowness. The types of isotherm to be expected when the two components form an undissociated compound which yields mixed crystals with

each component, and when transformations take place in the solid state, are described for the three cases in which the transformation temperature is (1) lowered by each component, (2) raised by each component, (3) raised by one component and lowered by the other. In case (1) the maximum in the conductivity isotherms does not vary with temperature; in the second case, as the temperature falls, secondary, flattened maxima appear at concentrations above and below that of the peak due to separation of the compound, and at low temperatures the isotherm becomes a smooth curve with a pronounced minimum; in case (3) a flattening and displacement of the peak takes place, and flattened secondaries appear. The maximum may be displaced in case (1) if the compound undergoes partial dissociation. Since the conductivity of an alloy is a function of the volume and not of the mass, the composition by volume should, theoretically, be employed; nevertheless, the ordinary weight composition–conductivity curves exhibit the displacement of the maxima, and for the investigation of the limits of existence of the various phases temperature–resistance curves are satisfactory.

H. F. GILLBE.

X-Ray study of the A3 point of iron and some iron–nickel alloys. O. L. ROBERTS and W. P. DAVEY (Met. and Alloys, 1930, **1**, 648—654).—The lattice parameters at the ordinary temperature for alloys containing 0, 0·87, 1·04, 2·78, 4·27, 11·73, and 13·21% Ni are, respectively, 2·858, 2·864, 2·866, 2·851, 2·849, 2·848, and 2·846 Å., indicating that the first 1—2% Ni stretches, whilst 3% or more contracts, the iron lattice. The transition temperature for the change body-centred $\longrightarrow$ face-centred iron lies between 907$\pm$3° and 910$\pm$3°. The Ac3 points for alloys of iron and nickel containing 1·04, 2·78, 4·27, 11·73, and 13·21% Ni lie, respectively, between the limits 820—815, 720—715, 660—655, 525—520, and 520—515°, all $\pm$3°. The Ac3 and Ar3 points do not coincide. The fractional lowering of the Ac3 point is greater for the first 10% Ni than for larger percentages.

CHEMICAL ABSTRACTS.

Transformation of austenite at constant subcritical temperatures. E. S. DAVENPORT and E. C. BAIN (Amer. Inst. Min. Met. Eng. Tech. Pub., 1930, No. 348, 30 pp.).—In all the carbon steels examined, the transformation was most rapid at about 540°. In the range from Ac1 to 500° the transformation time decreases with either increasing or decreasing carbon content as the eutectoid recedes. Manganese retards markedly the transformation. At lower temperatures both carbon and manganese decrease the rate of transformation. The small amount of chromium (0·26%) in a low alloy steel retards the reaction of the austenite. Two methods for determining the rate of transformation, suitable respectively for temperatures above 300° and for low temperatures, are described.

CHEMICAL ABSTRACTS.

Systems of four immiscible liquid layers. E. L. SMITH (Nature, 1931, **127**, 91).—A four-phase system can be produced at the ordinary temperature by mixing hexane (or light petroleum) 12 c.c., aniline 7 c.c., and oleic acid 0·5 c.c., and adding 10 c.c. of 0·8N-aqueous sodium hydroxide to saponify the fatty acid and salt out the soap. The addition of 1·5 c.c. of alcohol, although not essential to the system, greatly reduces the time required for separation into layers. A rise in temperature or an increase in concentration of electrolyte favours the miscibility of the hexane (first layer) and the aniline (third layer) which then form the top layer. L. S. THEOBALD.

Variation with temperature of the solubility of the rare gases in liquids. G. TAMMANN (Z. anorg. Chem., 1930, **194**, 159—161).—The function $(1/\log l)[d(\log l)/dT]$, where l is the solubility of a gas in a liquid at T° Abs., has been calculated for solutions of helium, neon, and argon in a number of non-aqueous solvents at temperatures between 18° and 37°, and is shown to assume an average value equal to $-1/T$, a condition theoretically necessary if the heat change Q corresponding with a chemical reaction between the gas and the solvent molecules is zero. The experimental error in the determination of l is, however, too great to permit a decision as to the actual value of Q in any particular case. The temperature variation of the solubility of argon and neon in water, as determined by a number of observers, indicates that in this solvent Q is not zero.

H. F. GILLBE.

Solubility effects. VII. Thiocarbamide antipyrine, caffeine–antipyrine. E. OLIVERI-MANDALA and L. IRRERA (Gazzetta, 1930, **60**, 872—877; cf. A., 1927, 303).—The solubility of thiocarbamide and of caffeine in water is considerably increased by the addition of antipyrine. Two supposed criteria for the recognition of complex formation in solution are discussed, viz., (*a*) determination of the temperature coefficient of solubility, and (*b*) determination of f.-p. depressions. The former method does not constitute a sure basis for deciding what molecular complexes are present in a solution, and the two methods often give different results. In the case of thiocarbamide and antipyrine the former method suggests that no compounds are formed in solution, whereas for solutions of caffeine and antipyrine both methods indicate the formation of a caffeine–antipyrine compound. O. J. WALKER.

Is there an intermediate horizontal portion between two eutectic points in the fusion curves of binary systems? N. A. PUSHIN and I. I. RIKOVSKI (Z. physikal. Chem., 1930, **151**, 257—268; cf. Kremann and Pogantsch, A., 1924, i, 52).—Thermal analysis of the systems *m*-dinitrobenzene–*o*-phenylenediamine, *m*-dinitrobenzene–*m*-phenylenediamine, benzamide–*m*-nitrophenol, benzamide–*p*-nitrosodimethylaniline, and benzophenone–picric acid affords no indication in any of the existence of a horizontal portion joining two eutectic points, and the molecular compounds assumed by Kremann to account for it do not exist. An equimolecular compound is formed between *m*-dinitrobenzene and naphthalene, but the diagram is of normal type. F. L. USHER.

System thorium nitrate–ether–water between 0° and 20°. P. MISCIATTELLI (Gazzetta, 1930, **60**, 833—838).—The solubility of thorium nitrate in water between 0° and 20° has been determined, and

solubility data and triangular diagrams are given for the ternary system with ether at 0° and 20°.

O. J. Walker.

System uranyl nitrate–ether–water between 0° and 20°. P. Misciattelli (Gazzetta, 1930, **60**, 839—842; cf. preceding abstract).—Solubility data and triangular diagrams are given for the system at 0° and 20°. O. J. Walker.

Extraction of phenols from alkaline solution with ether. G. Vavon and J. Paira (Ann. Off. Nat. Combust. liq., 1929, **4**, 997—1013; Chem. Zentr., 1930, ii, 234—235).—The following phenols were prepared by the Fries displacement from tolyl acetates: *o*-methyl-*p*-ethyl-, b. p. 218—220° (*p*-nitrobenzoate, m. p. 70—71°; dinitrobenzoate, m. p. 137—138°; arylglycollic acid, m. p. 125—126°); *m*-methyl-*o*-ethyl-, b. p. 215—219°, m. p. 44—45° (as above, m. p. 88—89°; m. p. 115—116°; m. p. 94—95°); *m*-methyl-*p*-ethyl-, b. p. 230—233°, m. p. 26—27° (as above, m. p. 116°; m. p. 128°; m. p. 131—132°); *p*-methyl-*o*-ethyl-, b. p. 215—219° (as above, m. p. 95—96°; m. p. 136—137°; m. p. 132—133°). The extraction coefficients of the phenols for ether are, respectively, 65, 66, 43, 74. The hydrolysis of phenoxides and the extractability by ether are not completely parallel. *m*-Cresol and thymol are readily, phenol and *o*-cresol fairly readily, and *m*- and *o*-cresol with difficulty separable by fractional extraction with sodium hydroxide; *p*- and *m*-cresol are not thus separable. With *o*-cresol and α-naphthol separation can be effected with 20% sodium hydroxide and ether, but not by 4% sodium hydroxide. Butyl ether is ineffective; benzene gives slight, and carbon tetrachloride partial, separation. Various phenols were isolated from a crude Saar tar and identified.

A. A. Eldridge.

Sorption of water vapour at low pressures by activated charcoals. I. A. J. Allmand and R. B. King (Proc. Roy. Soc., 1930, **A**, **130**, 210—217).—The sorption of water vapour by six specimens of activated charcoal has been measured at 25° over the pressure range 10^{-1} to 10^{-3} mm., the experimental method used being very similar to that described by Chaplin (cf. A., 1929, 133). The final isothermals obtained are apparently reversible. The influence of traces of residual gas present in the charcoal surface on the nature of the isothermal is discussed. It is found that the heat of adsorption of water vapour rises with decrease in the quantity adsorbed, as in the case of carbon tetrachloride (following abstract). Adsorbed water vapour appears to be less effective than other vapours in freeing a charcoal surface from its residual layer of bound oxygen or adsorbed carbon dioxide. L. L. Bircumshaw.

Sorption of carbon tetrachloride at low pressures by activated charcoals. IV. A. J. Allmand and A. Puttick (Proc. Roy. Soc., 1930, **A**, **130**, 197—209; cf. A., 1930, 1513).—Experiments have been carried out which indicate that the effect of high-temperature degassing can be much greater than was previously found, but support the views already advanced on the part played by adsorbed oxygen (*loc. cit.*). In the case of a chemically-activated charcoal and carbon tetrachloride, a charging pressure of about 0·1 mm. at 25° is insufficient to clean up adsorbed oxygen from the charcoal surface, but this can be effected in practice by a charging pressure of 1·0 mm. An isothermal has been determined over a large pressure range ($3{\cdot}3\times10^{-2}$ to 70·45 mm.) in a single experiment, the higher pressures being read by a mercury manometer and the lower by the Pirani gauge; the results indicate that the readings of the latter instrument are valid. Further evidence of the discontinuous nature of these isothermals has been obtained. L. L. Bircumshaw.

Swelling of charcoal. I. Preliminary experiments with water vapour, carbon dioxide, ammonia, and sulphur dioxide. D. H. Bangham and N. Fakhoury (Proc. Roy. Soc., 1930, **A**, **130**, 81—89).—A form of extensometer is described by means of which simultaneous measurements can be made of the percentage linear expansion (x) of a rod of wood charcoal and the weight (s) of gas taken up per unit weight of the adsorbent. In the case of ammonia, carbon dioxide, and sulphur dioxide the swelling is given by equations of the type $x=k[s/(S-s)]$, where k and S are constants characteristic of each gas. An additional term is necessary to represent the behaviour of water vapour. The values of the constant S represent nearly equal volumes of the normal liquids at the experimental temperature. It is found that for any given value of s the corresponding x is slightly greater at higher temperatures. It is suggested that the expansion is caused by the pressure exerted by the adsorbed molecules at sharp re-entrant angles in the surface of the adsorbent. L. L. Bircumshaw.

Adsorption from solution by ash-free, adsorbent charcoal. VI. Adsorption of invertase. E. J. Miller and S. L. Bandemer (J. Physical Chem., 1930, **34**, 2666—2692; cf. A., 1928, 831).—The adsorption of invertase by blood-charcoal purified as previously described (A., 1927, 821) and the effect of adsorption on the inverting power of the enzyme have been investigated. As is the case with acids adsorbed by charcoal, large amounts of invertase can be adsorbed with complete loss of the power to invert sucrose. Adsorption of still larger amounts results in the retention of some activity by the invertase. Purification of the invertase results in a large decrease in adsorption. Ash-free charcoals from other sources show inactivation, but with unpurified charcoals some activity is retained by the enzyme. Displacement or reactivation of the adsorbed invertase was without success, suggesting that the invertase complex undergoes decomposition when adsorbed on charcoal. The presence of acetic, benzoic, or hydrochloric acid in the invertase solution or of acid adsorbed on the charcoal increases the adsorption of invertase by the latter, but, under these conditions, an inverting activity up to 50% is retained by the enzyme.. The age, concentration, and method of preparation of the invertase, time of contact with adsorbent, the presence of acids, and previous treatment of the charcoal are the main factors controlling adsorptions. Freshly-ignited charcoal adsorbs much larger amounts of invertase and the inactivation after adsorption is less complete. The addition of gum arabic to an invertase solution of low

yeast gum content causes the invertase to show a behaviour on adsorption which is the same as that of an invertase of high yeast gum content. Yeast gum and gum arabic are both considered to function as protective colloids for the invertase. The present work favours the view that the active group of the invertase is of colloidal dimensions.

L. S. THEOBALD.

Adsorbed moisture in Kanbara clay. H. ISOBE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, **14**, 229—274).—Acid, neutral, and alkaline Kanbara clays are found together at different levels, the acid clay being uppermost. The acidity or alkalinity of the clay is due to the presence of soluble acids or alkalis which can readily be washed out, leaving a neutral clay. Measurements of the adsorption coefficient for water by the dried clay give values between the extremes 8·2 and 25·8%; the adsorptive power is not affected by heat treatment below 275°, but decreases as the baking temperature rises above 400°. Neutral clay has the highest adsorbing power. The acidic, neutral, and alkaline clays have different water vapour pressures, but the vapour-pressure curve of neutral clay is the same whether naturally neutral, or neutralised with acid or alkali, or by washing with water. The various ways in which water may be taken up by the dried clay are discussed in relation to the experimental results. The amount of water retained in relatively large crevices depends on the porosity of the sample and varies between 20% and 50%. The water adsorbed by capillary action varies from 20% to 35% and the vapour-pressure curve of this part can be expressed by the equation $a=\alpha P^n$. About 2% to 18% of the water can be ascribed to true adsorption at the surface of the clay, and the vapour-pressure curve is represented by the formula $a=kP^{1/n}$, where $1/n$ has a value between 0·46 and 0·58. When the clay is heated between 600° and 800° a molecule of water of crystallisation is expelled and X-ray investigation shows that the crystal structure of the clay changes from hexagonal to cubic. At the m. p., 1300°, Kanbara clay expels water vapour, which must be water internally combined in the clay. The chemical reactions of Kanbara clay are consistent with the proposed formula, viz., $[Al(SiO_4SiO_2)_3]H_4AlMgH_2O$.

E. S. HEDGES.

Rigidity of adsorption layers. D. TALMUD, S. SUCHOWOLSKAJA, and N. LUBMAN (Z. physikal. Chem., 1930, **151**, 401—412).—The force required to rupture the adsorption layer formed at a solution–air interface has been determined for various capillary-active substances, both soluble and insoluble. The substances studied were palmitic, oleic, heptoic, and octoic acids, cetyl alcohol, ethyl oleate, aniline, and saponin. In every case a well-defined maximum of rigidity was found for a surface concentration lower than that corresponding with a close-packed unimolecular layer. The surface concentrations corresponding with maximum rigidity coincide with those at which air bubbles blown with the respective solutions exhibit their maximum stability. These results support Talmud's theory, according to which the molecules in an unsaturated adsorption layer are only partly oriented and behave as a two-dimensional liquid crystal.

F. L. USHER.

Adsorption time and its measurement by streaming methods. P. CLAUSING (Ann. Physik, 1930, [v], **7**, 521—568).—The apparatus used in the determination is described (cf. this vol., 34), together with the construction of the ionisation manometer employed. The results of the experiments with argon, neon, and nitrogen, with glass as adsorbent, are discussed. It seems that the experiments with argon and nitrogen are not readily reproducible, in spite of the fact that the streaming tube was perfectly cleaned each time. It was found possible, however, to reproduce the temperature coefficient of the adsorption time, and this is determined exactly for the adsorption of argon on glass. The experiments with nitrogen were not so conclusive, and all that can be said is that the adsorption time for the same temperature interval is of the same order as that for argon. These values are also in agreement with those found by Langmuir. For neon and glass between the same temperature interval (78—90° Abs.) the adsorption time is less than 2×10^{-7} sec. The use of the method for similar determinations with different materials is discussed.

A. J. MEE.

Atomic theoretical explanation of adsorptive power. F. LONDON and M. POLANYI (Naturwiss., 1930, **18**, 1099—1100).—Previous theories of adsorption are briefly discussed and a new theory, based on London's conception (A., 1930, 1239) of molecular forces, is put forward to explain adsorptive power.

W. R. ANGUS.

Boedeker's adsorption equation. L. WOHLER and W. WENZEL (Kolloid-Z., 1930, **53**, 273—288).—The adsorption of acetic, propionic, butyric, and valeric acids by charcoal has been studied between 20° and 80°. With rising temperature the exponent n of the adsorption isotherm rises and the constant a falls proportionally. By extrapolating to the b. p. the value of n for acetic acid becomes 1. In the presence of large amounts of carbon the distribution law holds for all four acids when dilute. The adsorption of paraffin from light petroleum by carbon is less, the higher is the b. p. of the petroleum; the exponent is 0·4 for pentane, 0·74 for petroleum of b. p. 143°, and tends asymptotically towards 1·0 with rising b. p. of the solvent. The variation of the adsorption with temperature is small. Ether as a solvent behaves as a saturated hydrocarbon having the same b. p. At high dilutions the adsorption of chloride, thiocyanate, and iodate ions from electrolyte solutions gives the exponent $n=1$, but with increasing concentration the value rapidly falls to a fraction. In very dilute ammonium thiocyanate solution, when the amount of adsorbent is sufficient, solvent and solute are adsorbed in equal amounts and the concentration of the solution does not change. With smaller amounts of carbon the adsorption curve passes through a maximum, which is followed by a minimum, and the maximum of adsorption corresponds with the maximum turbidity of the suspension after shaking. The distribution law, with $n-1$, holds over a wide concentration range for the adsorption of carbon dioxide from aqueous solution by carbon. The tendency of the exponent towards 1 in so many cases leads to the view that adsorption is a modified distribution influenced in velocity and equilibrium

by the solid phase. The factors determining the adsorption exponent are considered to be the structure of the adsorbent surface, and polar properties, degree of solvation, and thermal agitation of the molecules of solute. Saturation of the adsorption layer occurs the more quickly the smaller is the adsorption exponent. The rise of the exponent and fall of the constant with rising temperature are due to the inhibition of the adsorptive force through thermal agitation. The fundamental difference between distribution and adsorption is in the ease of solvation of the solute in the two phases. E. S. HEDGES.

Drop method of measuring surface and boundary tensions. J. TRAUBE (Kolloid-Z., 1930, **53**, 300—303).—A reply to Junker (A., 1930, 1109). The paper cited is said to lead to false ideas of the accuracy of the drop method. E. S. HEDGES.

Electrocapillarity. III. Surface tensions of solutions containing two surface-active solutes. J. A. V. BUTLER and C. OCKRENT (J. Physical Chem., 1930, **34**, 2841—2859; cf. A., 1930, 1514).—Langmuir's adsorption theory has been applied to the simultaneous adsorption of two solutes from solution and the surface tension effects have been evaluated. In the absence of interaction between molecules in the surface layer, the lowering of surface tension produced in the presence of a surface-active substance at a concentration c_1 by a second at concentration c_2 is given by the equation $\Delta\gamma_2=b_2 \log [1+c_2/a_2(1+c_1/a_1)]$, where the lowering of γ of the first substance alone is given by Szyszkowski's equation $\Delta\gamma_1=b_1 \log (1+c_1/a_1)$. Measurements of the surface tensions at the air interface of aqueous solutions of ethyl and propyl alcohols, and of propyl alcohol and phenol, made by the capillary rise method at 20°, are in good agreement with these equations. Electrocapillarity curves have been derived for solutions of caffeine and phenol in $0{\cdot}5M$-sodium sulphate over wide ranges of concentration and the lowerings of surface tension obtained are in satisfactory agreement with a form of Szyszkowski's equation modified to fit the case of highly active solutes. Similar measurements have been made for mixtures of sodium cinnamate and sodium *o*-toluate in $0{\cdot}5M$-sodium sulphate. The effect of the *o*-toluate on the surface tension of solutions of the cinnamate is less than that predicted by theory, and the deviations are ascribed to the effect of the electric charges of the adsorbed cinnamate ions which tend to prevent the adsorption of further ions of the same sign.

L. S. THEOBALD.

Surface tension of soap solutions and its relation to the thickness of adsorbed films. R. BULKLEY and F. G. BITNER (Bur. Stand. J. Res., 1930, **5**, 951—956).—The sharp minimum which has been observed in the surface tension-time curves of certain soap solutions by earlier workers is shown to be due to the action of the carbon dioxide in the air on the dissolved soap and does not occur when the measurements are made in purified air. A. R. POWELL.

Change of the temperature of maximum density of aqueous solutions and of the surface tension in relation to the concentration. G. TAMMANN and A. ROHMANN (Z. anorg. Chem., 1930, **194**, 273—277).—The temperature of maximum density T_m has been calculated for aqueous solutions of a number of volatile liquids which cause T_m to vary with concentration according to a parabolic law. Since in all cases the values obtained are smaller than the observed values, the internal pressure of the solution is diminished by the solute, and by assuming that T_m is influenced to the same extent by a change of internal pressure as by a change of external pressure, the magnitude of the effect has been calculated. At low concentrations the reduction of the internal pressure $\delta\kappa$ produced by the aliphatic alcohols is proportional to the concentration. Although on account of interfacial adsorption and of the influence of the size and form of the molecules the surface tension of a solution is not proportional to the internal pressure, for capillary-inactive solutes such as sodium chloride the lowering of the surface tension $\delta\sigma$ is proportional to the fractional molar concentration of the solute and $\delta\sigma/\delta\kappa$ varies from 13 to 72, whereas for active substances such as propyl alcohol $\delta\sigma/\delta\kappa$ lies between 5000 and 70,000. H. F. GILLBE.

Adherence of quartz powder in electrolyte mixtures. A. VON BUZAGH, H. FREUNDLICH, and J. TAMCHYNA (Kolloid-Z., 1930, **53**, 294—300).—Parallelisms between the adherence of microscopic quartz particles to a quartz plate in the presence of electrolyte solutions, as determined by the angle of tilt method, and the coagulation of hydrophobic sols are pointed out. In mixtures of electrolytes an antagonism of cations has been observed, especially between lithium chloride and aluminium or magnesium chloride. The effect is smaller when the lithium salt is replaced by salts of sodium or potassium. The order of adding the electrolytes has no influence in this case. The angle of tilt in pure electrolyte solutions containing the same cation varies considerably with the nature of the anion, the anion effect being greater for potassium than for lithium salts. With increasing concentration the increase in the angle of tilt becomes less as the valency of the anion increases. The experiments confirm the view that ion-antagonism, coagulation, and the adherence of particles depend mainly on the oppositely charged ion, and not only on its discharging effect, but also on the alteration in the thickness of the boundary layer. The similarly charged ion has also an influence, which is confined mainly to its effect on the properties of the adsorption layer.

E. S. HEDGES.

Reflexion and duration of sojourn of metal atoms at an oil surface. G. VESZI (Z. physikal. Chem., 1930, **B**, **11**, 211—221).—From observations of the displacement on reflexion of atoms incident normally on the surface of a rapidly flowing stream of oil, it appears that atoms of zinc, cadmium, and bismuth show a period of the order of 10^{-5} to 10^{-4} sec. between incidence and reflexion. In the case of thallium and lead, however, no definite evidence of sojourn on the oil surface was obtained.

R. CUTHILL.

Movement of xylene drops on the surface of an aqueous solution of *n*-propyl alcohol. G. G. KANDILAROV (Kolloid-Z., 1930, **53**, 304—306).—When drops of *n*-propyl alcohol are added to water on the surface of which a few drops of xylene have

spread, the xylene collects at the sides of the containing vessel and finally gathers into drops, which execute movements similar to those of camphor particles on a water surface. An explanation in terms of surface tension alterations is given.

E. S. HEDGES.

Structure of thin films formed from solutions of crystallisable and non-crystallisable substances. G. TAMMANN and H. E. VON GRONOW (Z. anorg. Chem., 1930, **194**, 268—272).—The question is discussed as to whether substances such as gums, which do not crystallise from aqueous solution, are capable of forming unimolecular layers composed of oriented molecules when the solutions are slowly evaporated, and experiments are described showing the changes which take place when films of sodium oleate and other soap solutions are slowly evaporated. The thickness of a sodium oleate film assumes values which are multiples of 4·2 $\mu\mu$, in agreement with Perrin's value for the thickness of unimolecular films of sodium oleate; for potassium undecoate the films are 25% thinner. By study of the changes which occur as crystallisation takes place it appears that the films are strongly supersaturated liquid layers in which the soap molecules are already partly oriented. The power of orientation is restricted to those molecules which are able, under the conditions of the experiment, to undergo crystallisation.

H. F. GILLBE.

Dialysis of solutions of sodium hydrogen carbonate. E. CANALS and J. DAUBIAN-DELISLE (Bull. Soc. Chim. biol., 1930, **12**, 1158—1161).—The dialysis of aqueous solutions of sodium hydrogen carbonate of various concentrations through parchment membranes has been investigated. The ions $Na^{\cdot}$ and CO_3'' do not pass through the membrane in equivalent amounts except at a concentration of approximately $0·5N$; solutions more dilute or more concentrated than this have accordingly an excess of one ion. This inequality has a maximum in $0·25N$-solution.

F. O. HOWITT.

Stationary states at non-living membranes. J. STRAUB (Chem. Weekblad, 1930, **27**, 672—674).—The hypothesis previously stated (A., 1929, 264), viz., that the steady concentration differences at living membranes are maintained by electrical forces resulting from metabolism, has been demonstrated by the maintenance of similar conditions in solutions of electrolytes at cellophane membranes and at porous porcelain surfaces by the action of electrical energy. The term "harmony" is proposed to describe conditions of dynamic equilibrium in which constant differences of mechanical and osmotic pressure, electric potential, and concentration are in harmony with constant velocities of chemical reaction, diffusion, and current intensity.

H. F. GILLBE.

Equilibria in osmotic systems in which forces act. I. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 820—826).—A membrane is said to be "inactive" when there are no forces acting in it capable of driving one or more of the substances in some direction or other. Where such forces do occur, as in living membranes, the membrane is said to be "active." A theoretical treatment is given of osmotic systems with an "active" membrane permeable to one substance only.

E. S. HEDGES.

Reaction equilibrium in the cation-exchange of permutits. R. W. BELING (Z. Pflanz. Düng., 1930, **18A**, 292—308).—The course of ionic exchange in permutit is affected by temperature changes which determine the degree of dissociation of the reacting salt solution and of the permutit, both before and after the exchange of ions. Ionic exchange proceeds to completion when the anion of the reacting solution and the cation displaced from the permutit form an insoluble compound. The mathematical formulæ of Jenny and Nageler (A., 1927, 415) are not supported by experimental results.

A. G. POLLARD.

Dependence of base-exchange in permutits on the nature of the anions. E. UNGERER (Z. Pflanz. Düng., 1930, **18A**, 342—346).—The exchange of bases between calcium permutit and the chlorides and sulphates of lithium, sodium, potassium, and magnesium is examined. In all cases the displacement of calcium from permutit is greater with the sulphates than with the corresponding chlorides, the divergence increasing with the concentration of the displacing ion. The effect is ascribed to the dehydrating action of the highly hydrated sulphate ion.

A. G. POLLARD.

***X*-Ray study of the dehydration of heulandite.** J. WYART (Compt. rend., 1930, **191**, 1343—1346).—X-Ray study using copper $K\alpha$ radiation shows that up to 210° the evolution and absorption of water by heulandite is completely reversible, the water molecules being distributed between the recticular (010) planes aperiodically, and the crystal lattice showing the normal Laue diagrams with a relative contraction in one direction of 2%. Above 210° the diagrams show a complete change corresponding with the production of crystalline planes oriented in various directions, although the capacity to reabsorb water and to revert to the original form is not destroyed so long as the heating has not been too prolonged or at too high a temperature (*e.g.*, 24 hrs. at 350°). The recticular intervals of the planes are 8·88 before and 8·00 Å. after dehydration.

J. GRANT.

Relation between the change in the refractive index of a solution of varying concentration and the changes of aggregation which the dissolved substance undergoes. M. FRANKEL (Biochem. Z., 1930, **227**, 304—318).—The magnitude of the refractive index of a solution is strictly proportional to the concentration of the dissolved substance provided that no change occurs in its state of aggregation. If association takes place the value of the index falls below that which would have corresponded with proportionality: conversely, if dissociation occurs, the index increases. Investigation of the way in which the refractive index of a solution changes with its concentration affords a simple, accurate, and rapid method of discovering the state of aggregation of the dissolved substance or substances. Only a few drops of solution are required.

W. MCCARTNEY.

Boric acid problem. W. D. BANCROFT and H. L. DAVIS (J. Physical Chem., 1930, **34**, 2479—2507).—The influence of boric acid on the rotatory power of

tartaric acid and that of glycerol or mannitol in the titration of solutions of boric acid are discussed. In neither case does compound formation afford a satisfactory explanation. The phenomena are attributed to solvent effects involving increased dissociation of the boric acid and to an abnormal influence of the boric acid solutions on the optical properties of the hydroxy-compounds. L. S. THEOBALD.

Viscosity of electrolytes. W. E. JOY and J. H. WOLFENDEN (Nature, 1930, **126**, 994—995).—The relative viscosities of dilute aqueous solutions of potassium chloride have been determined at 18° in silica and glass viscosimeters of the Washburn–Williams type. In both cases, the viscosities are greater than that of water for concentrations up to $0{\cdot}025N$. The limiting slope predicted by the Dole–Falkenhagen equation (A., 1929, 1389) is tangential to the extrapolated curve drawn through the experimental points. A linear curve is obtained by plotting $(\phi-1)/c^{\frac{1}{2}}$ against $c^{\frac{1}{2}}$. L. S. THEOBALD.

Measurement of polarisation of the Tyndall beam of aqueous suspensions as an aid in determining particle size. T. HATCH and S. P. CHOATE (J. Franklin Inst., 1930, **210**, 793—804).—The tedious process of microscopical measurement of individual particles may be supplanted by determination of the degree of polarisation of the Tyndall beam. The relation between the degree of polarisation and particle size has been examined for suspensions of silica, granite, and calcite, having particles ranging from 1 to 50 μ. The degree of polarisation was found to be a function of the arithmetic mean diameter of the particles. Birefringence is another determining factor, the quantitative effect of which has not been studied. By combining the equation expressing the relation between particle size and strength of Tyndall beam with the mathematical relation between degree of polarisation and particle size, an indirect method of obtaining a complete definition of particle size is given. The values obtained in this manner agree to within about 10% with those obtained by direct measurement.
E. S. HEDGES.

Dispersoid synthesis of gold by means of alkaline formaldehyde solutions. II. P. P. VON WEIMARN (Kolloid-Z., 1930, **53**, 352—370; cf. A., 1929, 1142).—A summary of many years' published work on the preparation of colloidal gold solutions. The subjects discussed are the influence of the purity of all the reagents used, especially the water, the influence of the form and material of the reaction vessel and the method of heating, preparation of sols most suitable for accurate quantitative investigation, structure of the dispersed gold particles, the ammonia test, and causes of the stability of gold sols prepared by the formaldehyde method.
E. S. HEDGES.

Rate of formation of gold sols by reduction with dextrose or *d*-galactose. A. L. BERNOULLI, M. SCHENK, and R. PINCZUK (Helv. Chim. Acta, 1930, **13**, 1236—1254).—The reduction of chloroauric acid by dextrose or *d*-galactose in aqueous solution at 83° is a unimolecular reaction, the velocity being independent of the concentration of the acid. Galactose has a much more powerful reducing action than dextrose. R. CUTHILL.

Polyatomic hydroxy-compounds formed during the synthesis of electronegative hydrosols. V. Hydroxy-acids. A. DUMANSKI and A. G. JAKOVLEV (Bull. Soc. chim., 1930, [iv], **47**, 1211—1216, and J. Russ. Phys. Chem. Soc., 1930, **62**, 1665—1670; cf. A., 1930, 1370).—The system $0{\cdot}1N$-ferric chloride–$0{\cdot}1N$-sodium hydroxide–sodium salt of acid ($0{\cdot}1N$) has been studied, using the Gibbs method of triangular co-ordinates. Diagrams are given showing the regions of stability for positive and negative sols, N-solutions, and regions of precipitation. Increase in the number of hydroxyl groups decreases the peptising efficiency of the acids studied, in the order tartaric>glycollic>malic>citric. The ammonium ion favours peptising action to a greater extent than the sodium ion. J. R. I. HEPBURN.

Benzene dispersions of basic soaps of nickel and iron. B. C. SOYENKOFF (J. Physical Chem., 1930, **34**, 2419—2538).—The preparation and properties of dispersions of basic ferric and nickel stearates in benzene are described. Basic ferric stearates are polymerised in benzene, whilst those of nickel form aggregates with the properties of colloids and remain dispersed only when free stearic acid is present. These dispersions of stearates and stearic acid in benzene do not conduct electricity.
L. S. THEOBALD.

Liquid ammonia as a lyophilic dispersion medium. R. TAFT (J. Physical Chem., 1930, **34**, 2792—2800).—The dispersibility of more than 100 substances in liquid ammonia has been qualitatively examined. Good dispersion is obtained with dextrin, cellulose acetate, nitro-cotton, dyes of high mol. wt., and a few proteins such as zein, gliadin, nucleic acid, bactopeptone, and protease peptone. Gums, resins, most proteins, and soaps are not dispersed.
L. S. THEOBALD.

Influence of hydrolysis temperature on some properties of colloidal ferric oxide. III. Viscosity and hydration. G. H. AYRES and C. H. SORUM (J. Physical Chem., 1930, **34**, 2826—2840; this vol., 37).—The viscosities of ferric oxide sols prepared at different temperatures have been determined at 25°±0·02°. Viscosity decreases with a rise in the temperature of preparation. When heated to different temperatures samples of stock sols show viscosity and flocculation values which diminish as the temperature to which they are heated rises. Complete precipitation occurs between 170° and 190°. The addition of alcohol or acetone to the sols lowers the relative viscosity and flocculation value to a similar extent. The results show that hydration is a stability factor in the ferric oxide sols studied and the effects observed can be correlated with corresponding changes in ζ-potential and dielectric constant. L. S. THEOBALD.

Photometric measurement of concentration and dispersity in colloidal solutions. I. Measurement of light weakening. T. TEORELL (Kolloid-Z., 1930, **53**, 322—338).—A study of the diminution of intensity of light as a result of adsorption and scattering has been undertaken with reference

to the thickness of the layer of sol, the concentration, the wave-length of the light, and the particle size. The variation with thickness of the layer is in accordance with Lambert's law between wide limits and the discontinuous variation of the absorption constant with thickness (Soos, A., 1927, 625) has not been confirmed. Beer's law holds for the variation with concentration up to high values, but at higher concentrations the absorption constant per unit of concentration decreases. Rayleigh's law holds only for very highly disperse sols of small extinction; in most cases the wave-length must be raised to a power less than 4. The diminution in intensity of light is greatest at a medium degree of dispersion of the colloid, and the position of the maximum is displaced in the direction of greater particle sizes with increase in wave-length of the light. Beer's law does not hold for hydrophilic colloids, because the degree of hydration varies with the concentration.

E. S. HEDGES.

Spectrophotometric investigations of effect of light on nuclear silver sol. A. GALECKI and R. SPYCHALSKI (Kolloid-Z., 1930, **53**, 338—352).—The changes taking place in silver sols prepared by the nuclear method when irradiated with ultra-violet light have been investigated by optical, viscosity, and electrical conductivity measurements. The first effect of the radiation is on the aqueous dispersion medium, producing hydrogen peroxide, which undergoes oxidation reactions with the silver particles, particularly when the sol is highly dispersed. The sol then loses its colour, silver ions going into solution, and an increase in conductivity and a decrease in viscosity are observed. On further exposure to ultra-violet light the silver ions are partly reduced, the sol again acquires its colour, and the electrical conductivity diminishes. The colour change involved has been observed quantitatively by a spectrophotometric method, which has established that the reaction is of the first order. The temperature coefficient of the reaction involving decolorisation has a mean value of 1·3.

E. S. HEDGES.

Method for following the variation in the number of particles during the evolution of a colloidal solution. Application to blood-serum. A. BOUTARIC (Compt. rend., 1930, **191**, 1332—1334).—Rayleigh's expression for the coefficient of absorption (h) of light by a suspension is applied (a) to simple agglomeration of the particles without participation of the suspending medium (the volume of an aggregate of particles being equal to the sum of the volumes of the particles), and (b) to the increase in size of an aggregate of particles by removal of liquid from the medium, the number of particles remaining constant. The law of mixtures is applied to the resulting expression, and it is shown that h may be taken as proportional to the mean volume of the individual particles for suspensions in which these two phenomena occur simultaneously. Since, further, the processes (a) and (b) result in unchanged and increased viscosities (η), respectively, a comparison of h and η gives an indication of the variation of the number (N) of suspended particles. The method applied to the serum of horse-blood at various temperatures confirms the conclusions reached by other methods, namely, that N does not change with change in temperature, *i.e.*, that the molecules of serum swell by fixation of water.

J. GRANT.

Experiments with precipitated and colloidal manganese dioxide. J. MUKHERJEE, S. R. CHOUDHURY, and M. R. S. RAO (J. Indian Chem. Soc., 1930, **13**, 803—813).—Contrary to the statement of Ghosh and Dhar (A., 1927, 617), a negatively-charged manganese dioxide sol is similar to arsenious sulphide, since, on dilution, it is stabilised against potassium ions and sensitised against barium and aluminium ions; the expected "ionic antagonism" (cf. *loc. cit.*) is completely absent. Cations are adsorbed to a greater extent than anions; the ratio probably remains constant on dilution. The conclusions of Dhar and others (A., 1927, 305, 617, 827) are criticised. A positively-charged manganese dioxide sol obeys the Schulze–Hardy law and the coagulating concentrations for anions are in the order nitrate$>$chloride$>$sulphate, oxalate, phosphate$>$ferrocyanide. The order for the nitrate and chloride is the reverse of that of Ghosh and Dhar (A., 1927, 305). The ratio of adsorption of barium and chloride ions does not alter with dilution. With copper chloride solutions, only copper ions are adsorbed. The ratio of adsorption of barium and chloride ions by precipitated manganese dioxide (negatively charged) also remains constant. For another specimen of precipitated oxide (also negatively charged) the ratio copper : chloride decreased with diminution in the amount of oxide used; this is also contrary to the results of Dhar and others (*loc. cit.*).

H. BURTON.

Lyophilic colloids. I. Hydration of lyophobic colloids. II. Theory of macro- and micro-syneresis. S. LIEPATOV and L. KOROBOVA (Z. anorg. Chem., 1930, **194**, 369—376, 377—382).—I. Although in aqueous solutions of geranin the solute is in a condition of molecular dispersion, gelatinisation takes place on cooling to 0°. Cryoscopic measurements indicate an increase of mol. wt. as the concentration of the solution increases, and although the solute molecule is smaller than, *e.g.*, that of Congo-red, it cannot be dialysed. Measurements of viscosity and of osmotic pressure show that the geranin particles are very considerably hydrated both in the true solutions and in sols prepared by addition of salts or of alcohol to the solutions; the hydration envelope is of multimolecular thickness. The dehydration of lyophilic colloids may be reversible or irreversible. The first is observed when the dehydrating agent acts only on the aqueous envelope and does not alter the composition of the colloidal nucleus; irreversible dehydration, which takes place when, *e.g.*, tannin is added to a geranin sol, involves a change of the chemical nature of the disperse phase. The viscosity of a geranin sol falls rapidly with increase of the tannin concentration, whilst the osmotic pressure falls rapidly to a minimum and thereafter rises slowly.

II. Aqueous geranin sols, prepared in presence of $0{\cdot}1N$-sodium chloride, exhibit complete syneresis even at a concentration of 0·1%. The conductivity of these sols is very small and is independent of the concentration of the associated phase, whereas the

conductivity of geranin sols in 10—25% alcohol increases with the concentration; thus the associated phase carries a charge, and correspondingly syneresis in these sols takes place to only a slight extent. It appears that in both lyophilic and lyophobic systems stability is a function only of the charge on the particles and is independent of hydration. Charged lyophilic and lyophobic colloids differ only in the velocity of the changes which terminate in syneresis, and the differences of velocity are a result of variations of viscosity and of the mobility of the particles. Experiments with geranin are described which demonstrate the four principal characteristics of syneresis: (1) the attractive force between the particles is equal in all directions, (2) the velocity of syneresis is governed by the distance between the particles and the magnitude of the force of attraction, (3) the liquid which separates contains molecules of the colloid at a concentration which is independent of the concentration in the gel, (4) the upper limit of the gel concentration at which syneresis can occur is that at which the particles are in contact, *i.e.*, at which the volume of the disperse phase is equal to the total volume of the system. H. F. Gillbe.

Coagulation of hydrophobic sols by electrolyte mixtures. H. Freundlich and J. Tamchyna (Kolloid-Z., 1930, **53**, 288—294).—No anion antagonism was observed in the coagulation of sols of ferric hydroxide, cupric oxide, and titanium dioxide by mixtures of electrolytes. Antagonism of anions was observed with a sol of arsenious sulphide, positively charged by adsorption of malachite-green, especially between chloride and sulphate ions when the chloride ions were added to the sol first. The ion of similar charge to the colloid also exerts an influence, decreasing in the order $K^{\cdot}>Na^{\cdot}>Li^{\cdot}$, and the antagonism is not observed when the ion with the higher valency is added first. Cation-antagonism has been observed in the coagulation of negatively-charged arsenious sulphide sols, the order of influence of the cations being the reverse of that given above. In this case the anion also has some effect: antagonism is not observed when a cation of higher valency is added first. E. S. Hedges.

Hofmeister series and hydrogen-ion concentration. E. H. Buchner (Rec. trav. chim., 1930, **49**, 1150—1160: cf. A., 1927, 825).—The salting-out capacity of the sodium salts of various acids for gelatin sols at 40° has been studied in relation to the p_H of the liquid. The salts fall into two groups, in one of which (univalent anions) the effect increases, whilst in the other (phosphate, citrate, tartrate) it decreases, with increasing acidity. Sulphate occupies an intermediate position and shows only a small variation over a large p_H range. The reversal of the Hofmeister series in acid solution is not general. The results are discussed theoretically. F. L. Usher.

Vapour pressure of gels. E. H. Buchner (Compt. rend., 1930, **191**, 1323—1324).—Two small glass tubes, one open at both ends and one closed at the top only, were filled with gelatin gel and partly immersed in water for 1 month. The gelatin contents determined by desiccation in a vacuum had then fallen from 21% to 14·5% for the lower (immersed) portion, and 18% for the upper portions of the contents of both tubes. The fact that the (upper) portion of the gel in the closed tube cannot have lost water vapour is considered to contradict the theory of Bary based on a similar experiment (cf. A., 1930, 858, and following abstract). J. Grant.

Vapour tension of gels. P. Bary (Compt. rend., 1930, **191**, 1325—1326).—Polemical against Buchner (cf. preceding abstract). The author's original experiment (A., 1930, 858) was intended to show that continuous distillation of water does not occur through the gelatin, and not to confirm the reality of the swelling of gels in a saturated vapour. J. Grant.

Hysteresis in sol-gel transitions. S. N. Banerji and S. Ghosh (Z. anorg. Chem., 1930, **194**, 305—315).—The time required for the complete solidification and re-melting of sols of sodium palmitate and stearate in methyl, ethyl, propyl, and butyl alcohols has been determined as a function of the temperature. The hysteresis H in degrees is defined as the difference between the solidification and melting temperatures for a specified time interval (12 min.). With increase of concentration H passes first through a minimum and then through a maximum; methyl alcohol sols form an exception. Stirring, inoculation with gel, or addition of free alkali or of sodium or potassium chloride causes a diminution of H; electrolytes at low concentration cause peptisation, but at higher concentrations produce coagulation, their efficiency falling in the order $Li^{\cdot}$, $Na^{\cdot}$, $K^{\cdot}$, $NH_4^{\cdot}$, which, probably as a result of solubility relationships, is the reverse of that which would be anticipated. Gelatin sols behave in a manner similar to that of the soap sols. The experimental results are shown to be in accordance with the view that in sols of this type there exists an equilibrium between single and complex molecules and colloidal micelles. H. F. Gillbe.

State of biochemical substances in anhydrous solutions. J. Loiseleur (Compt. rend., 1930, **191**, 1391—1392).—Biochemical substances, particularly proteins, dissolve in certain aliphatic acids, either alone or with the addition of compounds such as amino-acids, phenol, aniline, etc., to form true solutions which become colloidal on the addition of water. P. G. Marshall.

Properties of biochemical substances, especially proteins, in anhydrous solutions. J. Loiseleur (Compt. rend., 1930, **191**, 1477—1479).—Solutions of proteins in aliphatic organic solvents such as formic acid exhibit no specific colloidal properties, are not flocculated by the addition of high concentrations of metallic ions (in the same solvent) or by heat, and are readily nitrated in such media. The specific colloidal properties are restored on simple dilution of the solution with water. J. W. Baker.

Action of short-wave irradiation on proteins. I. B. Rajewsky. **II. Dependence of the behaviour of protein on the intensity of the ultraviolet irradiation.** W. Gentner and K. Schwerin (Biochem. Z., 1930, **227**, 272—285, 286—303).—I. The effect produced in very dilute aqueous solutions of

paraglobulin by exposure to short-wave radiation has been studied by a modification of the method of Nakashima (Strahlenther., 1926, 24), whose observations on the latent period previous to coagulation and on the rhythmical course of this process have been confirmed. With the shorter wave-lengths the extent of the latent period decreases, but otherwise all the short-wave radiations used have the same effect, the sensitivity of the solutions being parallel to the course of the absorption. The behaviour of the protein towards ultra-violet light is fundamentally independent of temperature, but the effect of Röntgen rays is modified so that an increase in the velocity of the reaction takes place.

II. From the results of the ultramicroscopical examination of 0·01% aqueous paraglobulin solutions which had been exposed to ultra-violet radiation curves have been drawn which show a direct relation between the number of the particles and the energy of the incident radiation. An equation which expresses the relation between this effect and the intensity of irradiation is given. W. McCartney.

Swelling of cellulose in perchloric acid. K. Andress and L. Reinhardt (Z. physikal. Chem., 1930, **151**, 425—432; cf. A., 1928, 1226).—The absorption of perchloric acid by ramie fibre has been measured at various concentrations of the acid. When the normality exceeds 9·3 an additive *compound*, $2C_6H_{10}O_5,HClO_4$, is formed, and on washing out the acid, mercerised fibre remains, whereas with lower concentrations of acid the fibre is recovered unchanged. *X*-Ray analysis, in agreement with absorption experiments, shows a diagram differing from that of cellulose for acid more concentrated than 9·3*N*, and a third diagram, obtained with very concentrated acid, is said to be probably due to a perchloric ester. The unit cell of the additive compound has *a* 16·5, *b* 10·3, *c* 10·7 Å., β 93°. F. L. Usher.

Preparation of cellulose membranes containing proteins. J. Loiseleur and L. Velluz (Compt. rend., 1931, **192**, 43—45).—Solutions (10%) of gelatin and cellulose in cold glacial acetic acid are shaken together in the requisite proportions. The membranes are then prepared by desiccation in the usual way, and are transparent for 5% and opalescent for 25% gelatin. For other proteins (casein, ovalbumin, gliadin, serum-proteins, etc.) the solutions are made in warm or cold formic acid. Earlier investigations (this vol., 166) indicate that these "proteocellulosic" membranes are true solid solutions, the structure of which is dependent on the protein/cellulose ratio. J. Grant.

Structure of celluloid and the swelling function of gelatinising agents for cellulose nitrate. II. *X*-Ray diagrams of camphor-celluloid with varying content of camphor. J. R. Katz, J. C. Derksen, C. A. Kramers, K. Hess, and C. Trogus. **III. Celluloids containing cyclic ketones other than camphor as gelatinising agents. IV. Acid amides and esters as gelatinising agents.** J. R. Katz, J. C. Derksen, K. Hess, and C. Trogus (Z. physikal. Chem., 1930, **151**, 145—162, 163—171, 172—189; cf. B., 1930, 984).—II. The apparently "amorphous" character of *X*-ray diagrams of celluloid prepared without camphor is due to the fusion of a group of contiguous crystal interference rings. By the gradual addition of camphor the interference pattern undergoes a radical alteration and a diagram characteristic of a compound (or compounds) of cellulose nitrate with camphor is obtained. The interference rings become split into segments when the celluloid is stretched, indicating a parallel arrangement of fibrous units in the compound as in the original cellulose nitrate. The experiments support the conclusions based on the optical anisotropy of stretched celluloid.

III. An alteration of the *X*-ray diagram of cellulose nitrate similar to that produced by camphor has been observed with fenchone, menthone, carvone, *cyclo*pentanone, *cyclo*hexanone, and *cyclo*hexanol. It is concluded that compounds are formed with each of these substances.

IV. Both unsymmetrical diphenyldiethylcarbamide and acetethylanilide produce an alteration of the *X*-ray diagram of celluloid resembling that due to ketones and similarly attributable to compound formation. A large number of esters possess the same property, although here the ability to form compounds appears to depend on the size of the alcoholic constituent. Thus methyl phthalate and *iso*amyl phosphate combine with cellulose nitrate, whilst *iso*butyl phthalate and tolyl phosphate do not. It is probable that all good gelatinising agents form compounds, and that combination is effected by the residual valencies of the carbonyl oxygen atom.

F. L. Usher.

Diffusion and distribution in a solvent of graded composition. G. S. Hartley (Trans. Faraday Soc., 1931, **27**, 10—29).—The distribution of a molecular solute in a solvent in which the concentration of a second solute varies from point to point has been studied for several types of gradient. Measurements have been made of the movement of a solute (iodine) in two mutually diffusing solvents, using alcohol–carbon disulphide and benzene–carbon tetrachloride as the solvent pairs. The results indicate that the viscosity effect is included in the solubility effect. Measurements of the diffusion of ethyl ether through an aqueous ferric hydroxide sol show that the gradient of activity in the static component is relatively very much greater in the colloid and therefore depends on the size of the molecules. To determine how far the distribution theory is applicable in a ternary molecular solution where one component is diffusing through the system, the behaviour of ammonium oxalate, lithium carbonate, potassium chlorate, and of succinic acid with respect to a concentration gradient of acetone in water, and of acetone with respect to a gradient of sodium chloride in water, has been studied. There is no evidence that the distribution of a solute free to move in a maintained gradient is influenced by other forces than those internal ones which determine solubility and the dynamic effect of the diffusing components. It seems, therefore, that the statistical effect examined theoretically by Chapman (A., 1928, 588) must be automatically included in the solubility effect, and

that the factors leading to increase of diffusion velocity must also tend to decrease solubility.
O. J. WALKER.

Theories of the Soret effect. G. S. HARTLEY (Trans. Faraday Soc., 1931, 27, 1—10).—Various kinetic theories of the Soret effect are reviewed and the error common to them is pointed out. The mechanism of the phenomenon is considered to be too complicated for the kinetic theory to be a useful method of approach. The phenomenon is also incapable of treatment by use of the ordinary thermodynamic functions, for the temperature gradient is characterised by the freedom of both components and the distinction between solvent and solute is a purely arbitrary one. In fact, the common error of the theories discussed is that they attribute to the solvent no other role than that of vehicle or carrier of the solute. Actually, however, the solvent molecules have a tendency to migrate from the warmer to the colder region also, and the Soret effect is the result of a balance between the two tendencies. Eastman's theory (cf. A., 1928, 365) which connects the "homogeneous effect" in electrolytic thermo-couples with the Soret effect in electrolytes is discussed, and the relation between the Soret effect and the homogeneous thermal *E.M.F.* in electrolytes is derived from more general considerations, thus providing independent support for the conclusions of Eastman's theory.
O. J. WALKER.

Spectrometric determinations of the effect of a neutral salt on the dissociation of acetic acid. N. V. SIDGWICK and L. A. WOODWARD (Proc. Roy. Soc., 1930, A, 130, 1—16; cf. Sidgwick, Worboys, and Woodward, this vol., 39).—Using solutions containing $N/40,000$-methyl-orange, $N/500$-sodium acetate, and a range of concentrations of acetic acid, determinations have been made of c_t (the ratio of the acid to the alkaline colour), from which the values of $[H_{free}]$, $[H_{bound}]$, [OAc], [HOAc], and K_{HOAc} have been calculated. The mean value of the last-named is $1{\cdot}83\times10^{-5}$ at 18°, in agreement with the value obtained from conductivity measurements. In the presence of $2N$-potassium bromide a mean value of $1{\cdot}92\times10^{-5}$ is found for the same constant. Using $N/40,000$-methyl-orange and various concentrations of hydrochloric acid, measurements were made by the wedge-shift method and an improved "flicker" photometer to test the Tizard equation for wave-lengths from 4500 to 5625 Å. The values of K (the apparent dissociation constant of the indicator acid) calculated from this equation show fair agreement, but point to a higher value than that previously obtained with the simpler apparatus. The optimum wave-length is that showing the greatest difference of absorption between the two forms, and for further measurements the wave-length 5125 Å. was selected. Under these conditions the value of K is found to be $3{\cdot}34\times10^{-4}$ at 18°, in good agreement with that obtained by Güntelberg and Schiodt (A., 1928, 1093). In the presence of varying concentrations of potassium bromide (0·0916—1·832N) both K and K_{HOAc} pass through a maximum with increasing salt concentration. The results are discussed from a thermodynamic point of view.
L. L. BIRCUMSHAW.

Formation of complexes of ferric ion and acetate ion in aqueous solution. W. D. TREADWELL and W. FISCH (Helv. Chim. Acta, 1930, 13, 1209—1218).—In the potentiometric titration of ferric chloride solution with sodium acetate the potential of the indicator electrode undergoes an abrupt change when the mol. ratio of acetate to chloride is 8 : 3, corresponding with the reaction $3Fe^{\cdot\cdot\cdot}+2H_2O+8AcO' \longrightarrow [Fe_3(OAc)_6(OH)_2]^{\cdot}+2AcOH$; the liberation of 2 mols. of acetic acid has been demonstrated by a distribution method. The colour of the mixture is also deepest when the composition corresponds with the above ratio. Acetic acid does not affect the titration, but if a mineral acid is present the acetate reacts with this completely before any complex ion is formed.
R. CUTHILL.

Formation of complexes of aliphatic mono- and di-carboxylic acids with ferric chloride. II. W. D. TREADWELL and W. FISCH (Helv. Chim. Acta, 1930, 13, 1219—1227).—The formation of the following *complex ions* in aqueous solution has been detected by potentiometric titration of ferric chloride with the sodium salts of the corresponding organic acids (cf. preceding abstract): $[Fe_3(HCO_2)_6(OH)_2]^{\cdot}$, $[Fe_3(ClCH_2{\cdot}CO_2)_6(OH)_2]^{\cdot}$, $[Fe_3(EtCO_2)_6(OH)_2]^{\cdot}$, $[Fe_3(PrCO_2)_6(OH)_2]^{\cdot}$, $[Fe(O{\cdot}CH_2{\cdot}CO_2)_3]'''$, $[Fe(CO_2{\cdot}CH_2{\cdot}CO_2)_2]'$, $[Fe(CO_2{\cdot}CH_2{\cdot}CO_2)_3]'''$, $[Fe(C_2O_4)_2]'$, $[Fe(C_2O_4)_3]'$, and $[Fe_3(CO_2{\cdot}C_2H_4{\cdot}CO_2)_3(OH)_2]^{\cdot}$.
R. CUTHILL.

Electrometric determinations of dissociation of glycine and simple peptides. P. H. MITCHELL and J. P. GREENSTEIN (J. Gen. Physiol., 1930, 14, 255—275).—The apparent acid and basic dissociation constants of glycine and several peptides, measured potentiometrically by hydrolysis and titration methods with and without potassium chloride and potassium sulphate, show that dissociation decreases as the length of the carbon chain between the basic and acidic groups increases. The constants vary with the hydrogen-ion activity and the ionic strength of the solutions, and exhibit deviations from the Debye-Hückel theory. Specific ion effects are suggested as a possible explanation.
A. COHEN.

Effect of salts on ionisation of gelatin. K. V. THIMANN (J. Gen. Physiol., 1930, 14, 215—222).—Ionised complex salt formation between gelatin and sodium chloride on the basis of the zwitterion theory is demonstrated by applying the Donnan relationship to previously published data on the system. Ionisation is at a maximum at 0·001M-salt concentration. The valency of gelatin in complex positive ion formation is deduced from similar behaviour with calcium and copper chlorides. The bearing of the zwitterion theory on solubility phenomena of proteins in salt solutions is discussed.
A. COHEN.

Debye–Hückel theory and its experimental testing. II. H. VAN VELDHUIZEN (Chem. Weekblad, 1930, 27, 681—685; cf. A., 1930, 1372).—Methods available for the experimental investigation of the validity of the expression for the activity coefficient are reviewed, prominence being given to solubility determinations. A survey is given of the results obtained by a number of workers for solutions of various types of salts.
H. F. GILLBE.

Specific character of the osmotic coefficients of alkali halides. G. KARAGUNIS, A. HAWKINSON, and G. DAMKÖHLER (Z. physikal. Chem., 1930, **151**, 433—466).—F. p. of aqueous solutions of the fluorides and chlorides of potassium, rubidium, and cæsium, lithium and sodium fluorides, and sodium iodide have been determined at concentrations between $0{\cdot}002N$ and $3N$ by a differential method using thermoelectric junctions. The largest fluctuation in the f. p., for solutions more dilute than $0{\cdot}1N$, was 0·0002°. Concentrations were determined interferometrically. Details of the technique, and tables showing the osmotic coefficient at different concentrations for each of the salts, are given.

F. L. USHER.

Thermodynamic action and reaction. W. JAZYNA (JACYNO) (Z. Physik, 1930, **65**, 571—573).—From the fact that the energy equation of a reaction is independent of the initial distribution of energy between the reactants it is possible to deduce the law of thermodynamic equilibrium. J. W. SMITH.

Graphical demonstration of a theory of Roozeboom. A. MAZZUCCHELLI (Gazzetta, 1930, **60**, 719—721).—Le Chatelier's principle is applied to show that the phase change which takes place in a one-component system in the vicinity of an invariant point is that which is associated with the maximum absorption of heat. F. G. TRYHORN.

Heats of distillation. M. BARTHEL (J. Phys. Radium, 1930, [vii], **1**, 411—415).—Theoretical. The equilibrium between binary liquid and vapour mixtures circulating in opposite directions is considered, and an expression is derived for the flow of heat which involves only the initial and final compositions of the vapour. C. W. GIBBY.

Automatic maintenance of solid–liquid equilibrium in a metal. P. A. ANDERSON (Rev. Sci. Instr., 1930, [ii], **1**, 764—767).—A method is described for automatically maintaining a bath of zinc in two-phase equilibrium by making use of the abrupt increase in specific resistance which accompanies isothermal fusion. Applications of the method and its extension to other metals are indicated.

N. M. BLIGH.

System Li_2O–SiO_2. F. C. KRACEK (J. Physical Chem., 1930, **34**, 2641—2650).—This system has been investigated by the heating curve and quenching methods. The system contains the three compounds Li_4SiO_4, Li_2SiO_3, and $Li_2Si_2O_5$. The orthosilicate decomposes at 1255° before its m. p. is reached; the composition of the liquid phase is 50·9 wt.-% SiO_2. The eutectic between the ortho- and meta-silicates corresponds with $1024\pm1°$ and $55{\cdot}3\pm0{\cdot}1$ wt.-% SiO_2, and that between tridymite and the disilicate with $1028\pm0{\cdot}5°$ and $82{\cdot}2\pm0{\cdot}1$ wt.-% SiO_2. The m. p. of the metasilicate is $1201\pm1°$, and its liquidus curve meets the incongruent m. p. of the disilicate at 1033° and 80·1 wt.-% SiO_2. The composition of the liquid at the tridymite–cristobalite inversion at $1470\pm10°$ is 91·0 wt.-% SiO_2. The author's results are incorporated with those of others in a complete phase diagram for the system. The optical properties of the lithium silicates (by H. E. MERWIN) are as follow: disilicate, apparently orthorhombic with three cleavages at 90°, one micaceous and two perfect; optical character positive with $2V$ 50°—60°; α 1·547, β 1·550, γ 1·558: metasilicate, uniaxial apparently with ω 1·591 and ε 1·611; orthosilicate, rounded grains with two lamellar twinnings oblique to extinction directions, α 1·602, γ 1·610, but the optical character and β could not be determined. L. S. THEOBALD.

Fusion diagram of the systems $HgBr_2$–$HgSO_4$ and $HgCl_2$–$HgSO_4$. M. PAIC (Compt. rend., 1930, **191**, 1337—1339; cf. this vol., 50).—The system $HgBr_2$–$HgSO_4$ shows a eutectic at 236° which corresponds with less than 1 mol.-% of the latter, the exact concentration being outside the limits of accuracy of the method. Above this concentration the curve mounts rapidly to 506° for 30 mol.-%. The X-ray diagram shows no evidence of combination. The system $HgCl_2$–$HgSO_4$ shows a eutectic at 240°, the sulphate being less miscible with the chloride than with the bromide. For 10 mol.-% of mercuric sulphate the m. p. is 512°, and there is no evidence of combination. J. GRANT.

Equilibrium $FeS_2 \rightleftharpoons FeS+S$. F. DE RUDDER (Bull. Soc. chim., 1930, [iv], **47**, 1225—1254).—An experimental investigation of the thermal decomposition of pyrites shows that there is no intermediate stage corresponding with the formation of compounds of the type Fe_nS_{n+1} as suggested by earlier workers. Such substances must be regarded as crystalline forms of ill-defined mixtures of the disulphide, ferrous sulphide, and sulphur. The whole of the arsenic present in natural pyrites is expelled as sulphide at the beginning of the decomposition, and the hygroscopic water is evolved as sulphur dioxide and hydrogen sulphide. The reversibility of the reaction has been shown directly by experiment. According to the thermal method employed in studying the dissociation, a sharp break occurs in the time–temperature curve with rising temperature, which corresponds with the point of decomposition at the particular pressure employed. Following this method the dissociation curve has been constructed for pressures from 9 to 768 mm.; the corresponding temperatures are 600° and 689°. The heat of dissociation at atmospheric pressure is calculated as 18·513 g.-cal. The bearing of these results on the industrial roasting of pyrites is discussed, and it is shown that ferrous sulphide is an intermediate product in this process also. J. R. I. HEPBURN.

Affinity of metals for sulphur. I. Thermal equilibria between hydrogen and the sulphides of iron, tin, cadmium, bismuth, and antimony. E. V. BRITZKE and A. F. KAPUSTINSKI [with L. G. TSCHENZOVA and R. A. NEISCHUL] (Z. anorg. Chem., 1930, **194**, 323—350).—The thermal equilibria have been determined at temperatures between 400° and 1000°, and the following data are recorded: affinity (g.-cal.) of sulphur for cadmium 65,380, tin 60,420, iron 58,220, antimony 57,860, bismuth 56,240; heat of formation (g.-cal.) from metal and diatomic sulphur, and heat of dissociation (kg.-cal. per g.-mol.) of CdS 69,140, 19·80, SnS 70,520, 20·51, FeS 65,460, 17·98, Sb_2S_3 57,860, 42·50 (black), and of Bi_2S_3 74,360, 67·20, respectively; normal potential (volts) of

$Sb^{\cdot\cdot}+0\cdot1$, $Bi^{\cdot\cdot\cdot\cdot}+0\cdot2$, $Fe^{\cdot\cdot}-0\cdot43$, $Sn^{\cdot\cdot}-0\cdot10$, and of $Cd^{\cdot\cdot}-0\cdot40$. H. F. GILLBE.

Carbides of high m. p. and the problem of the fusion of carbon. C. AGTE and H. ALTERTHUM (Z. tech. Physik, 1930, **11**, 182—191; Chem. Zentr., 1930, ii, 700).—The following m. p. (° Abs.) have been determined: ZrC 3805°, NbC 3770°, Mo_2C 2960°, MoC 2965°, HfC 4160°, TaC 4150°, W_2C 3130°, WC 3140° Abs. The pairs W_2C–TaC and W_2C–NbC exhibit continuous mixed crystal formation; W_2C–ZrC does not. The systems ZrC–TaC and HfC–TaC exhibit m. p. maxima at the ratio 4TaC : 1Zr(Hf)C, these maxima being 4205° Abs. and 4215° Abs., respectively. Indications of superficial fusion of graphite were obtained. A. A. ELDRIDGE.

Iron–iron carbide–oxygen equilibrium. P. PINGAULT (Compt. rend., 1931, **192**, 45—47).—The equilibrium curve for the reaction $CO_2+Fe_3C \rightleftharpoons 3Fe+2CO$ has been determined at atmospheric pressure both by carburation and decarburation, and concordant results have been obtained. The curve cuts those for the reactions $CO_2+C \rightleftharpoons 2CO$ and $CO_2+Fe \rightleftharpoons FeO+CO$ at 740° and 700°, corresponding with concentrations of 28 and 42% CO_2, respectively. The resulting diagrams provide an interpretation of carburising cementation (temperature above 740° and 0—28% CO_2 in the gas phase), oxidising cementation (740—700° and 28—42% CO_2), and degraphitisation of castings containing both graphite and cementite (oxidation of carbon without decomposition of iron carbide). The calculated heat of reaction for the first equilibrium at 700—1000° is —14·5 g.-cal., whence that of the reaction $3Fe+C=Fe_3C$ is —27·5 g.-cal. J. GRANT.

Dissociation pressure of anhydrous uranyl nitrate and of anhydrous thorium nitrate. P. MISCIATTELLI (Gazzetta, 1930, **60**, 883—885).—The pressures corresponding with $2UO_2(NO_3)_2 \rightleftharpoons 2UO_3+4NO_2+O_2$ and $Th(NO_3)_4 \rightleftharpoons ThO_2+4NO_2+O_2$ have been determined by the dynamic method of Centnerszwer and Krustinson (A., 1927, 21) between 87° and 161°. The results indicate that basic salts are not formed and that only two solid phases are present, viz., anhydrous nitrate and oxide. From the data the heats of dissociation 39,442 and 81,828 g.-cal. are derived for the uranyl and thorium salts, respectively. O. J. WALKER.

Ternary system Na_2SiO_3–Fe_2O_3–SiO_2. N. L. BOWEN, J. E. SCHAIRER and H. W. V. WILLEMS (Amer. J. Sci., 1930, [v], **20**, 405—455; cf. A., 1930, 36).—Equilibria in the system Na_2SiO_3–Fe_2O_3–SiO_2 have been determined by microscopic examination of mixtures quenched from definite temperatures, and the results are expressed graphically. No binary compounds are formed between hæmatite and silica, and the two compounds are almost completely immiscible in the fused state; ferric oxide has probably a higher m. p. than silica. Two ternary compounds exist within the equilibrium triangle, viz., acmite, m. p. 990° (incongruent), and a *compound*, $5Na_2O,Fe_2O_3,8SiO_2$, which forms optically positive hexagonal prisms having n_α 1·609 and m. p. (congruent) 838°; a third ternary *compound*, $6Na_2O,4Fe_2O_3,5SiO_2$, lying outside the equilibrium triangle, forms rounded grains having n_β 1·96, m. p. 1091° (congruent). As in all systems containing silica which have so far been investigated, the lowest eutectic (760°) lies at a high silica content (above 72%), and silica is one of the components of the mixture. The geological significance of the results is discussed. Since the felspars normally associated with acmite in rocks enter only into the liquid phase, acmite can be formed only at temperatures below 990°. The view that the presence of volatile constituents is necessary for the formation of quartz cannot be maintained. The course of crystallisation of mixtures rich in acmite involves an initial separation of hæmatite, followed by its reabsorption by the liquid and ultimate redeposition; alternative courses of crystallisation from one liquid phase are possible as a result of this phenomenon. H. F. GILLBE.

Purification of disodium phosphate. M. LEMARCHANDS and C. TRANCHAT (Compt. rend., 1931, **192**, 50—51).—The equilibrium constants for the reaction $BaHPO_4+Na_2SO_4 \rightleftharpoons Na_2HPO_4+BaSO_4$ are 8·36 (100°) and 100 (18°). The heat of reaction is thus found to be 6528 g.-cal. (calc. 6200 g.-cal.). Since the use at 18° of a saturated solution of disodium phosphate (47·8%) yields a mixture containing 0·478% of sodium sulphate, the reaction may be used for the purification of the former salt prepared commercially from sodium carbonate and natural tricalcium phosphate. J. GRANT.

Stability of complex cobalt and chromium salts as precipitates. II. A. BENRATH and H. STEINRATH. **III.** A. BENRATH and H. PITZLER (Z. anorg. Chem., 1930, **194**, 351—357, 358—368; cf. A., 1929, 256).—II. The nature of the solid phase which is stable in contact with solution has been determined by shaking a number of complex chromium salts with solutions of ammonia, ethylenediamine, and nitric, hydrochloric, and hydrobromic acids. The salts investigated include bromoaquo-, chloroaquo-, hydroxyaquo-, and diaquo-tetramminochromic chlorides and bromides, nitratoaquo- and diaquo-tetramminochromic nitrate, triethylenediaminechromic chloride, 1 : 2- and 1 : 6-dichlorodiethylenediaminechromic chloride, and oxalatotetramminochromic nitrate.

III. The system $[Co(NH_3)_5Cl]Cl_2+2HBr \rightleftharpoons [Co(NH_3)_5Cl]Br+2HCl$ has been investigated at 25° and constant pressure and the phase model has been constructed. Determinations of the equilibria between various hexa-, penta-, tetra-, and tri-amminocobaltic salts and aqueous solutions of ammonia show that the solubility of the complexes in all cases increases with increase of the ammonia concentration. For all except the hexammino-complex the solubility curve rises to a maximum and then falls rapidly, and since the curves do not intersect and lie above that of the hexammine, the latter is the only stable compound, the others being metastable forms. In presence of dilute acids the stability of the complexes increases with increase of the number of ammonia groups in the molecule, whilst the only stable phase is the simple cobalt salt. H. GILLBE.

Heat of formation of water. F. D. ROSSINI (Proc. Nat. Acad. Sci., 1930, **16**, 694—699).—This has been redetermined by finding the amount of electrical

energy required to produce the same rise in temperature of the calorimeter as that produced in the formation of a measured mass of water from combustion of oxygen and hydrogen. Sources of error and their correction are mentioned. The value obtained for the heat of formation of liquid water at 25° and a constant pressure of 1 atm. is 285,890±40 absolute joules. The best values already existing for this quantity are attended by an uncertainty of about ±240 absolute joules. W. GOOD.

Reversible oxidisability of organic substances; thermochemistry of the oxidation of rubrene. C. DUFRAISSE and L. ENDERLIN (Compt. rend., 1930, **191**, 1321—1323).—The heats of formation of rubrene, oxyrubrene, *iso*oxyrubrene, and metrubene or rubrene monoxide are −131, −108·4, −50·4, and −92·4 g.-cal./mol., respectively (cf. Moureu, Dufraisse, and others, A., 1928, 594, 628, 1127). The difference between the values for rubrene and oxyrubrene is less than that which would correspond with the normal introduction of two oxygen atoms into an organic molecule, and less than the differences for the two other oxides. There is therefore no essential difference between the reversible oxidation of rubrene and of respiratory pigments (*e.g.*, hæmoglobin), since the oxidation of the former is catalytic in nature and may be carried out through the agency of light (*i.e.*, photochemically) or of other appropriate catalysts. J. GRANT.

Connexion between ionic mobility and rate of diffusion in solid salts. C. WAGNER (Z. physikal. Chem., 1930, **B**, **11**, 139—151).—Theoretical. Equations have been obtained by a thermodynamic method which permit diffusion coefficients in a binary solid solution composed of two salts with a common ion to be calculated from ionic mobilities. The relationships observed by Tubandt (A., 1929, 255) and by von Hevesy (*ibid.*, 638) may be deduced from these equations. The thermodynamic derivation depends on the assumption that the ions migrate independently of each other. R. CUTHILL.

Electrical conductivity of sulphur dioxide-water mixtures between 8 and 22% SO_2 and from 0° to 40°. M. DE K. THOMPSON and N. PROMISEL (Trans. Amer. Electrochem. Soc., 1930, 58, 101—108).—At 20° the conductivity increases continuously from 0·046 to 0·076 mho/cm. over the concentration range specified. At higher concentrations a two-phase system is formed. For a solution of given concentration the conductivity increases with rise of temperature, reaches a maximum, and then decreases again. This maximum occurs at 30—32° for an 8% solution, but moves to lower temperatures with increasing concentration, reaching 20° for a 20% solution. H. J. T. ELLINGHAM.

[Polarity of] alkali alkyls. F. HEIN and H. SCHRAMM (Z. physikal. Chem., 1930, **151**, 234—256; cf. A., 1925, ii, 217; 1927, 138).—Lithium ethyl, whilst differing from all other alkali alkyls in not possessing the character of a salt, is definitely polar, with an association factor of about 6 in benzene, as calculated from the f.-p. depression. Addition of zinc ethyl causes first depolymerisation, and afterwards combination to form a solvate which in benzene is present in the form of double molecules $(MEt,ZnEt_2)_2$. Sodium, potassium, and rubidium ethyl behave similarly. The molecular conductivity of the sodium ethyl–zinc ethyl complex in benzene decreases with dilution, as expected. The electrolytic nature of rubidium ethyl is confirmed by a study of its conductivity in zinc ethyl solution. Its "salt" character is more pronounced than that of the other alkali alkyls. F. L. USHER.

Determination of electrolytic resistance by the barretter method. J. SCHIELE and M. WIEN (Ann. Physik, 1930, [v], 7, 624—632).—The method is described. It gives more accurate results than the usual Kohlrausch telephone method with platinised electrodes. A. J. MEE.

Gas electrodes. A. C. KRUEGER and L. KAHLENBERG (Trans. Amer. Electrochem. Soc., 1930, **58**, 341—383; cf. A., 1928, 1330).—A systematic investigation has been made of the potentials of gas–metal electrodes consisting of the gases hydrogen, oxygen, nitrogen, helium, and argon in conjunction with more than 20 different metals and a few non-metals such as carbon and silicon in *N*-solutions of hydrochloric acid, potassium chloride, and potassium hydroxide at the ordinary temperature. Nitrogen, helium, and argon, which are normally regarded as electromotively inactive, are reported to give potentials as characteristic as those of hydrogen or oxygen, and these potentials often vary with the nature of the electrolyte in a manner similar to the latter. All the potentials are greatly dependent on the nature of the metal as well as on the electrolyte, and the effects of these factors are largely specific. Thus, although with a given metal and electrolyte the potentials produced by the gases often become increasingly positive in the sequence hydrogen, argon, nitrogen, helium, oxygen, this order is by no means general, and for a given metal may be changed by using a different electrolyte. There are even cases where oxygen gives a more negative potential than hydrogen in a given electrolyte, *e.g.*, with aluminium, electrolytic iron, or graphite electrodes in *N*-potassium chloride, and with cadmium, mercury, iridium, or tungsten electrodes in *N*-hydrochloric acid. The *E.M.F.* of a hydrogen–oxygen cell set up with platinum electrodes in a given solution is far greater than that of a similar cell set up with electrodes of any other metal. All the results are tabulated in various ways so as to indicate the effects due to gas, metal, and electrolyte, and are discussed at length. H. J. T. ELLINGHAM.

Poisoning of hydrogen electrodes. A. H. W. ATEN and (MISS) M. ZIEREN (Trans. Amer. Electrochem. Soc., 1930, **58**, 109—132; cf. A., 1929, 1246).—The effect of oxygen on the potential of a platinum-black or palladium-black hydrogen electrode in a pure sodium hydroxide solution or pure dilute sulphuric acid remains quite small until the partial pressure of oxygen in the gas approaches $\frac{1}{3}$ atm. With a pure hydrogen electrode of this type addition of arsenious oxide to the electrolyte causes the potential to assume somewhat more positive values (2 mg. per litre makes the potential about 2·3 millivolts more positive), but this effect eventually decreases with time. If, however, a small percentage of oxygen be now admitted

with the hydrogen to the poisoned electrode, the potential gradually changes to very positive values (above 800 millivolts more positive with 2% of oxygen) during a period of days. With smooth platinum or palladium electrodes this change occurs much more rapidly, and is even observed in solutions of commercially pure sodium hydroxide or sulphuric acid to which no arsenious oxide has been added. Since preliminary treatment of the solution with platinum-black prevents this action of oxygen, it is concluded that these solutions normally contain traces of some poisoning impurity. This would account for the slightly positive values often given by pure hydrogen electrodes in which smooth platinum plates are used. The effects of varying the proportions of hydrogen and oxygen (0—100%) in the gas supplied to a palladium-black electrode in pure sulphuric acid and sodium hydroxide solutions and in these solutions with various additions of arsenious oxide are shown by a series of curves. In experiments with smooth electrodes it is shown that appreciable poisoning is produced by a quantity of arsenious oxide much less than would be necessary to form a unimolecular layer on the electrode, but the fact that anodic treatment restores the true hydrogen potential indicates that poisoning is due to the deposition of a substance on the electrode surface. The theoretical interpretation of the results is discussed, but a satisfactory quantitative explanation is not yet forthcoming. H. J. T. Ellingham.

Electrode potentials in air-free electrolyte. A. L. McAulay, G. L. White, and E. C. R. Spooner (Nature, 1930, **126**, 914—915; cf. A., 1930, 423).—A summary of the authors' work on the potential assumed by a metal immersed in a salt solution with no sensible concentration of its own ions. When this is the case and when the electrode is not covered by an oxide film, its potential is determined by p_H if the hydrogen overvoltage is positive to the deposition potential which it would have in a solution about $0{\cdot}001N$ with respect to its own ions. When this is not the case, the potential is controlled by the anion concentration probably arising from a film of electrolyte in contact with the metal with a concentration of the electrode metallic ions of the order $0{\cdot}0001N$.
L. S. Theobald.

Electrode properties of stainless steel. E. Newbery (Trans. Amer. Electrochem. Soc., 1930, **58**, 335—340).—The single potential of a sample of stainless steel (containing about 13% of chromium) in N-ferrous sulphate solution is much more positive than that of pure iron in the same solution and approximates to the potential exhibited by a sample of chromium in this electrolyte. On the other hand, the hydrogen overpotential of the stainless steel in N-sulphuric acid, measured by the commutator method, is practically identical with that of pure iron under the same conditions and is much less than that of chromium. The use of stainless steel as cathode in the controlled electrolytic reduction of certain organic substances is suggested and preliminary experiments on these lines are referred to. The oxygen overpotential of stainless steel at low current densities in N-sulphuric acid is comparable with that of chromium, but when the current density exceeds a certain value the overpotential increases suddenly to a value which is intermediate between those of iron and chromium. Partial dissolution of the stainless steel with formation of chromic acid then takes place. A tentative explanation of the phenomena is advanced.
H. J. T. Ellingham.

Electrochemistry of aluminium and aluminium amalgams. H. Gerding (Z. physikal. Chem., 1930, **151**, 190—218).—The potentials of aluminium amalgams of varying composition have been determined in a solution of aluminium acetylacetonate in acetylacetone. There is no indication of compound formation. The mutual solubility of the metals is very small, and a two-phase system with constant potential extends from 0·8 to 99·97 at.-% Hg. A *P.D.* of 0·130 volt exists between the two-phase system and "theoretical" (active) aluminium, which is due to a difference of free energy between the pure metal and the amalgam and is independent of the liquid. It follows that the potential of active aluminium in a $1N$-solution of aluminium chloride in water is $-1{\cdot}47$ volt (H=0). Pure aluminium does not dissolve in the liquid used, but when the content of mercury exceeds 0·2% aluminium acetylacetonate is formed with evolution of hydrogen, which latter causes the potential to become more negative. Oxygen has the opposite effect. The behaviour of aluminium and its amalgams in acetylacetone cannot be explained by assuming the existence of a film of oxide, but is ascribed to a real difference in the metal.
F. L. Usher.

Potential of the iridi-irido-chloride electrode. H. Terrey and H. C. Baker (J.C.S., 1930, 2583—2586).—Potentiometric measurements with the cell $Hg|Hg_2Cl_2+N\text{-}NaCl|N\text{-}NaCl+Na_2IrCl_6+Na_3IrCl_6|Ir$ show that the *E.M.F.* of the concentration cell at 25° is given $E_0=(RT/F)\log(i/o)$, where i and o are the concentrations of the iridi- and irido-salts, and that the electrode reaction is $IrCl_6''+e\longrightarrow IrCl_6'''$; for values of i/o between 2·166 and 8·900 and an iridised iridium electrode E_0 lies between 0·976 and 0·983, and for values of i/o from 0·105 to 11·06 and an iridised glass electrode between 0·968 and 0·970. The *E.M.F.* is a linear function of the temperature, and has a temperature coefficient of about $-0{\cdot}001$ volt per 1°; the calculated heat effect of the cell reaction is 25,400—26,100 g.-cal., and regarding the reaction as $Hg+Cl'+IrCl_6''\longrightarrow HgCl+IrCl_6'''$ the heat of formation of the iridi- from the irido-chloride (Q') is 5600 g.-cal./mol. H. F. Gillbe.

Potentials of unstable oxidation–reduction systems. L. F. Fieser (J. Amer. Chem. Soc., 1930, **52**, 4915—4940).—A "discontinuous titration" method is used which involves the addition of varying amounts of potassium molybdicyanide ($0{\cdot}03M$-solution) to a fixed amount of a well-buffered reductant ($0{\cdot}0003M$) whereby varying quantities of the oxidant become available. The ratio oxidant : reductant is fixed momentarily in each case and the potentials of the solutions are determined after varying intervals. The initial potentials are fixed by extrapolation of the first straight portion of the potential–time curves. A composite titration curve is constructed from the results and the normal oxidation–reduction potentials

are calculated from it. The method is applicable to systems which are so unstable that the half-life period for the decomposition of the oxidant is 0·1—0·5 min. The variation of potential with the hydrogen-ion concentration over the range of p_H 1—8 was determined for the systems *p*-benzylaminophenol–*N*-benzyl-*p*-benzoquinoneimine, *p*-methylaminophenol–*N*-methyl-*p*-benzoquinoneimine, and *p*-aminophenol–*p*-benzoquinoneimine. The following systems were also studied: *p*-phenylenediamine–*p*-benzoquinonedi-imine, methyl-*p*-phenylenediamine–*N*-methyl-*p*-benzoquinonedi-imine, 4 : 4′-dihydroxystilbene–stilbene-4 : 4′-quinone, and 4 : 4′-dihydroxydiphenyl–diphenoquinone.

Application of the method to the following substances was unsuccessful owing to the instability of the oxidised solutions: *o*-aminophenol, *o*-phenylenediamine, pyrocatechol, nitroquinol, and 2 : 6-dihydroxynaphthalene. H. BURTON.

Indirect method of studying the oxidation-reduction potentials of unstable systems, including those from phenols and amines. L. F. FIESER (J. Amer. Chem. Soc., 1930, **52**, 5204—5241).—A method is described for determining the potential at which the velocity of the reaction between an oxidisable substance (*e.g.*, α-naphthol) and an oxidising system (*e.g.*, ferricyanide–ferrocyanide) reaches a small, limiting value. This is called the "critical oxidation potential." For the two examples quoted, oxidation occurs only when the potential exceeds 0·790—0·800 volt. A series of ferricyanide–ferrocyanide solutions is prepared in which the total concentration of the cyanides is the same, whilst the ratio of oxidant to reductant is varied. Following the determination of the potentials of these solutions, α-naphthol (equivalent to the ferricyanide) is added, and the potential changes are noted during 5 min.; the solutions are usually made up in 37% alcohol containing neutral buffer salts (phosphates). The percentage oxidation of the naphthol can be calculated from the results and is found to be a linear function of the initial potential of the solution. Extrapolation of the percentage oxidation–potential curve gives the "critical oxidation potential." The "critical oxidation potentials" of 71 substances (mainly phenols and amines) are recorded, and their relationship to the normal oxidation–reduction potentials and the structural formulæ of the reducing agents are discussed. H. BURTON.

Reduction cells containing alkali chlorites. G. R. LEVI and D. GHIRON (Atti R. Accad. Lincei, 1930, [vi], **11**, 1104—1107).—The *E.M.F.* of cells in which the reduction of potassium chlorite is effected by various substances have been measured at 20° in cells of the type $Pt^{+}|0·1N\text{-}KClO_2|X|Pt^{-}$, in which X represents the reducing solution. The observed *E.M.F.* in volts are: $0·2M\text{-}K_2S$, 1·119; $0·1N\text{-}KNO_2$, 0·3905; $0·025M\text{-}K_4Fe(CN)_6$, 0·476; $0·1M\text{-}Na_2S_2O_3$, 0·437; 0·1*N*-KI, 0·285; $0·1M\text{-}N_2H_4,H_2SO_4$, 0·370; $0·1N\text{-}(NH_2\cdot OH)_2,H_2SO_4$, 0·350. The *E.M.F.* of the cell $Pt^{+}|0·1N\text{-}KClO_2|0·1N\text{-}KCl+Hg_2Cl_2|Hg^{-}$ is 0·363 volt. O. J. WALKER.

Variations of the *E.M.F.* during the formation of alloys in the wet way. E. PACE (Gazzetta, 1930, **60**, 811—818).—Measurements have been made of the *E.M.F.* of voltaic couples of the type A|solution of A^{+}|B during the whole process of dissolution of the more electropositive metal A and the deposition on the metal B to form an alloy of the type A_nB. The following systems have been investigated: copper–tin, copper–antimony, antimony–tin, gold–cadmium, silver–cadmium, gold–tin, and silver–tin. Values of the *E.M.F.* at the ordinary temperature and at 100° are given with closed and open circuit. O. J. WALKER.

High-voltage anodic layer on aluminium. J. E. LILIENFELD, L. W. APPLETON, and W. M. SMITH (Trans. Amer. Electrochem. Soc., 1930, **58**, 285—331).—Anode layers were formed on aluminium sheets by electrolysis in borax–boric acid solutions of various concentrations at various current densities and temperatures, the current being kept constant and the voltage allowed to rise until sparking commenced, at which stage the voltage was kept constant and the current allowed to fall. From calculations based on the estimated thickness of the layer and from direct observation of the amount of oxygen gas evolved, it is concluded that the oxygen which enters into the formation of the layer is only a very small fraction of the total amount released by the current. The behaviour of the formed plates, set up in the electrolyte, as condensers was examined particularly with regard to the variation of leakage current. The condenser was charged to 380 volts and, when the leakage current had decreased to a steady value, it was completely or partly discharged. After being kept idle in this condition for a time it was re-charged to the original voltage and the leakage current redetermined. From these data the extent of the deterioration which had occurred during idleness under various conditions was estimated. The results are not in harmony with the views that deterioration is due to dissolution of aluminium oxide from the layer or to escape of oxygen imprisoned in the layer, but can be explained on the assumption that changes occur in the spatial orientation of particles of oxide in the layer without any loss of material from the layer. The layer behaves as a dielectric containing a large number of polar molecules which are oriented by the electric field during formation, but tend to become disorganised by thermal motion during idle periods. Conduction through the layer is believed to occur by the passage of electrons from molecule to molecule, the resistance depending on the state of organisation. H. J. T. ELLINGHAM.

Passivity of chromium. I. E. MÜLLER and O. ESSIN (Z. Elektrochem., 1930, **36**, 963—972).—The potential of chromium, deposited electrolytically on copper, in contact with solutions of different acids has been determined as a function of time and of temperature. The results indicate that at 0° the metal is passive towards *N*-hydrofluoric, -hydrochloric, -hydrobromic, -sulphuric, -perchloric, -phosphoric, and -nitric acids, but that on warming to a temperature which is characteristic for each acid and increases with the diameter of the anion, the metal becomes active towards the first four acids; in phosphoric, perchloric, and nitric acids it remains inactive at 100°. Treatment such as immersion in chromic acid solution or

heating in a vacuum, which tends to remove hydrogen from the chromium film, reduces its (negative) potential; in contact with non-activating acids the potential increases with time to values greater than the reversible hydrogen potential without the metal losing its passivity. Cathodic polarisation in perchloric and nitric acids causes sudden activation when a certain potential is attained. The activating influence of anions follows the same order as their power of producing cathodic reduction of chromic acid; the influence of hydrochloric acid is hindered by the presence of other acids. It is suggested that the passive metal is covered with a superficial oriented film of oxide molecules through which the anions must penetrate in order to produce activation.

H. F. GILLBE.

Colloidal diaphragm for the electrolysis of water. G. F. JAUBERT (Compt. rend., 1930, **191**, 1447—1449).—If a 25% solution of potassium hydroxide holding in colloidal suspension a hydrogel, *e.g.*, calcium magnesium silicate (colloidal asbestos) or ferric hydroxide, is electrolysed with a nickel anode and an iron cathode, a uniform layer of the colloidal substance, several millimetres thick, is deposited on the anode in the course of some hours or days, according to the fineness of the suspension. If a sheet of iron wire gauze is placed between the electrodes a similar deposit accumulates thereon, and this after about 50 hrs. is absolutely impermeable to the free gases. A diaphragm thus prepared is very cheap, possesses a very low resistance, and enables hydrogen of 100% and oxygen of 99·5% (0·5% hydrogen) purity to be readily prepared. C. A. SILBERRAD.

Thermal transformation of para-hydrogen. A. FARKAS (Z. physikal. Chem., 1930, B, **10**, 419—433). —The conversion of para-hydrogen into ortho-hydrogen when heated in a quartz vessel is a homogeneous reaction, although traces of such impurities as dust or metals exert a powerful catalytic effect. Measurements of the velocity, made chiefly at 600—750° and under pressures of 50—400 mm., show the reaction to be of the order 1·5, which is taken as pointing to the mechanism H+H', the hydrogen atom being of thermal origin. If this reaction is regarded as the exchange of a bound hydrogen atom for a free atom, leading to the formation of para- and ortho-molecules in the equilibrium ratio 1 : 3, it does not contravene the principles of quantum mechanics. The effect of rise in temperature on the velocity is due far more to increase in the number of free atoms than to increase in the proportion of effective collisions. The Arrhenius equation gives 4200 g.-cal. per g.-mol. for the heat of activation, whereas the value of 11,000 g.-cal. is deduced from the absolute velocity.

R. CUTHILL.

Ignition of electrolytic gas by electric sparks. A. KOVALSKY (Z. physikal. Chem., 1930, B, **11**, 56—58; cf. A., 1930, 299).—The limiting pressures at which electrolytic gas can be ignited by a single spark have been determined in relation to the "strength" of the spark, the latter being measured by the capacity of a condenser charged to a constant potential, from which the spark was obtained. The limiting pressure decreases with increasing strength of spark down to 17 mm. for 2 microfarads. The limiting pressure of ignition by a spark at 450° coincides with the lower limit for propagation of ignition in the mixture.

F. L. USHER.

Thermal decomposition of nitrous oxide between 1 and 10 atm. N. NAGASAKO and M. VOLMER (Z. physikal. Chem., 1930, B, **10**, 414—418; cf. A., 1930, 1255; Hinshelwood, *ibid.*, 1528).—The above reaction has been measured at 830—940° Abs., and found to be unimolecular. The heat of activation, 53,000 g.-cal. per g.-mol., is practically independent of the pressure. R. CUTHILL.

Atomic reactions possessing inertia. H. VON HARTEL and M. PÓLANYI (Z. physikal. Chem., 1930, B, **11**, 97—138).—In seeking to account for the apparent absence of inertia in many of the reactions in which free atoms or free radicals participate, it must be noticed that a reaction with a heat of activation below about 15,000 g.-cal. will occur so rapidly as to seem instantaneous. London's theory of chemical reactions (A., 1929, 1397), indeed, indicates that the upper limit of the heat of activation of reactions involving free atoms or radicals corresponds approximately with this figure. The reaction of methyl iodide with sodium vapour at 240° is free from inertia, but the reactions with the bromide, chloride, and fluoride possess inertia, the magnitude of which increases in this order. From the ratio of the number of effective collisions to the total number of collisions it is calculated that in the reaction with methyl bromide the heat of activation is 3200 g.-cal., and in that with the chloride 8800 g.-cal.; similar values are also deduced from the temperature coefficient of the reaction velocity. With the fluoride, the heat of activation must exceed 25,000 g.-cal., and this is the only reaction which would occur at a measurable speed at the ordinary temperature. The order of the reactivities of the halides is what would be expected from London's theory. The reaction of sodium vapour with cyanogen exhibits considerable inertia, which appears, however, to be due, not to the smallness of the heat of activation, but to some steric factor, probably to the shielding of the sensitive region of the C·C linking by the nitrogen atoms. This effect does not vary with the temperature. In the reaction of sodium vapour with cyanogen chloride the proportion of sodium chloride to sodium cyanide formed depends on the temperature, which may be explained by supposing that the inertia of the reaction $Na+CNCl=NaCl+CN$ depends on a low heat of activation and therefore varies with the temperature, whereas the inertia of the reaction $Na+CNCl=NaCN+Cl$ is independent of the temperature. The reactions of a variety of other organic halogen compounds with sodium have been studied. From kinetical considerations and examination of the energy changes involved it may be demonstrated that in all such reactions the primary result of the formation of a molecule of sodium halide is the liberation of the free radical previously combined with the halogen. When sodium reacts with a methyl halide in presence of hydrogen, methane is formed by the reaction $CH_3+H_2=CH_4+H$, the heat of activation of which is about 8000 g.-cal. From this figure it is deduced

that the heat of the reaction $CH_3+H=CH_4$ is 98—110 kg.-cal. R. CUTHILL.

Decomposition of ethylamine. Unimolecular reaction. H. A. TAYLOR (J. Physical Chem., 1930, **34**, 2761—2770).—The decomposition of ethylamine has been investigated over the range 500—540° and at pressures between 50 and 400 mm. The decomposition is a homogeneous, unimolecular reaction with an energy of activation of 43,400 g.-cal.; E/RT is 28·9. The addition of hydrogen, nitrogen, or ammonia has no effect. L. S. THEOBALD.

Effect of neutral salts on the velocity of reaction of ions in low total ionic concentration. A. PARTS (Festschr. Jub. Ver. Estn. Chem., 1929, 44—50; Chem. Zentr., 1930, ii, 687).—When potassium persulphate (0·00625M) and iodide (0·0250M) react in presence of neutral salt (0·0500N) the velocity coefficient (0·317) attains values as follows: potassium chloride, 0·459, sodium chloride 0·374, ammonium chloride 0·417, barium chloride 0·682, calcium chloride 0·485. Values for the reaction $(CHBr{\cdot}CO_2)_2''+OH'$ (each 0·01813M)$\longrightarrow(CO_2{\cdot}CH{:}CBr{\cdot}CO_2)''+Br'+H_2O$ are (1·70), sodium nitrate 2·09, lithium nitrate 2·33, barium chloride 4·83, calcium nitrate 9·61. The results are interpreted by means of Debye and Hückel's theory. A. A. ELDRIDGE.

Hydrolysis of acetamide. T. W. J. TAYLOR (J.C.S., 1930, 2741—2749).—The velocity coefficients K of the hydrolysis of acetamide by 3N-, 4N-, and 5N-hydrochloric acid and 4N- and 5N-hydrobromic and sulphuric acids at 25°, and by 4N- and 5N-hydrochloric acid at 40° and 41°, respectively, have been determined and the influence of the alkali metal halides has been investigated. With increase of the concentration of hydrochloric or hydrobromic acid up to about 3N, K increases to a maximum and thereafter diminishes, but with sulphuric acid K is smaller in 4N than in 5N solution. It appears that at the higher concentrations undissociated molecules of hydrochloric and hydrobromic acids form with the amide complexes which are not capable of undergoing hydrolysis; this view is supported by calculations of the uncombined fraction of the amide based on the assumption that the complexes formed are of the type $2NH_2Ac,HCl$. In 4N-hydrochloric acid solution N-sodium or -potassium chloride accelerates the hydrolysis, but lithium chloride is without effect, whilst in hydrobromic acid solution potassium bromide acts as a positive catalyst, sodium bromide is apparently without effect, and lithium bromide retards the reaction. The salt effect is of the same nature if the hydrolysis be carried out in alkaline (N-sodium or -potassium hydroxide) solution. On account of the specific nature of the salt effect it is suggested that acetamide is able to form with certain salts complexes which are stable in solution. H. F. GILLBE.

Reactions of zero order. A. PARTS (Festchr. Jub. Ver. Estn. Chem., 1929, 23—30; Chem. Zentr., 1930, ii, 687).—A discussion of the hydration of pinene. A. A. ELDRIDGE.

Velocity of dissolution of oxygen in water. III. MIYAMOTO and T. KAYA (Bull. Chem. Soc. Japan, 1930, **5**, 321—325; cf. A., 1930, 1379).—The relationship of the rate of oxidation of sodium sulphite in aqueous solution when air is bubbled through it to the radius of the bubbles has been found to conform to the theoretical considerations previously advanced (*ibid.*, 866). R. CUTHILL.

Passivity phenomena with aluminium in still, dilute acids and alkalis. L. W. HAASE (Hausz. V.A.W. Erftw. Aluminium, 1930, **2**, 53—60; Chem. Zentr., 1930, ii, 976).—Interaction of aluminium with solutions of acids, bases, and salts in concentration corresponding with natural water leads to the gradual formation, not of passivating films, but of a homogeneous protective layer of aluminium oxide or hydroxide of low water content. A. A. ELDRIDGE.

Influence of the azide ion on the catalysis of [the decomposition of] hydrogen peroxide by colloidal platinum. II. E. OLIVERI-MANDALA (Gazzetta, 1930, **60**, 878—882; cf. A., 1930, 170).—The decomposition of hydrogen peroxide by colloidal platinum is also a first-order reaction in presence of azoimide, which acts as a negative catalyst, although there is not a strict proportionality between the values of K and the concentration of the azoimide, which reduces the value of K from 0·0029 to 0·00078. The temperature coefficient of the velocity coefficient for 10° is 1·66. O. J. WALKER.

Slow and induced oxidation of potassium oxalate, sodium nitrite, and sodium sulphite by air. S. N. CHAKRAVARTI and N. R. DHAR (J. Physical Chem., 1930, **34**, 2749—2760; cf. Palit and Dhar, A., 1926, 822).—In the presence of cerous hydroxide, potassium oxalate or sodium nitrite is not oxidised by the passage of air through their solutions at the ordinary temperature, but in the presence of ferrous hydroxide or sodium sulphite oxidation occurs. Oxidation increases with an increase in concentration of inductor and acceptor and with the time of passage of the air. In all the above cases a compound of the peroxide type, liberating iodine from acidified potassium iodide, is formed. Sodium phosphite is oxidised by air in the presence of sodium sulphite, but no peroxide is formed in this case. L. S. THEOBALD.

Autocatalysis in oxidation. IV. Mechanism of antioxygenic action. G. DUPONT and J. ALLARD (Bull. Soc. chim., 1930, [iv], **47**, 1216—1225; cf. A., 1930, 1003).—The proportion of quinol required to prevent the autoxidation of abietic acid in xylene solution increases as the oxidation advances; whilst 1 part in 5000 parts is sufficient at the start, 5 parts are required if the quinol is added when oxidation has already occurred. Similarly, in presence of 1% of cobalt as cobalt abietate addition of 1% of quinol at the start prevents oxidation, but if added when the oxidation has attained its maximum velocity 1·4—1·6% of quinol is required. In presence of 0·5% of cobalt abietate the proportion of quinol necessary is halved. On addition of quinol to a solution of cobalt abietate in abietic acid and of oxidised cobalt abietate in abietic acid the characteristic complementary absorption band at 500 μμ disappears and the solutions give the absorption spectrum of neutral cobalt abietate. Accordingly, it is concluded that the dark absorption band below 500 μμ is due to the formation

of the green complex of cobalt abietate and a constituent of oxidised abietic acid, which is slowly decomposed by the quinol. The antioxygenic action of the latter is observed only when the green complex has been completely decomposed and accordingly this complex acid-oxidised abietate is regarded as the positive catalyst of the oxidation, and the constituent of oxidised abietic acid which forms this complex is the active oxide which catalyses the natural direct oxidation. It is suggested that the quinol acts by combining with this acid oxide, liberating cobalt abietate, the antioxygenic action of quinol with abietic acid itself being attributed to the combination of quinol with this active constituent of the oxidised acid. The greater part of the cobalt abietate is present in the active form when the velocity is at its maximum, whilst in the direct autoxidation of abietic acid a very small proportion of the oxidation product is in the active form. R. BRIGHTMAN.

Activity of surfaces. J. R. PARTINGTON (Nature, 1930, **126**, 917).—The idea underlying many theories concerning the catalytic effect of a surface and its structure was published by the author in a qualitative form in 1911 (cf. J.C.S., 1911, **99**, 475).

L. S. THEOBALD.

Dissolution of metals in acids. G. WALPERT (Z. physikal. Chem., 1930, **151**, 219—233).—The influence of foreign substances on the rate of dissolution of metals in acids has been studied by measuring both the rate of evolution of hydrogen and the potential of the dissolving metal. Dissolution of iron in $8N$-sulphuric acid is retarded by hydrochloric acid, by formic, acetic, propionic, and butyric acids (in order of increasing influence), gelatin, and methyl-violet. Salts have little effect in dilute solution. Chromium, zinc, and cadmium behave similarly, except that salts accelerate their dissolution. The effects observed are attributed to adsorption, which is considered to be the first stage in the process of dissolution.

F. L. USHER.

Catalytic activity of cadmium. R. J. HARTMAN and O. W. BROWN (J. Physical Chem., 1930, **34**, 2651—2665).—The catalytic activity of cadmium in the reduction of nitrobenzene to aniline has been investigated. With catalysts prepared in different ways, the highest yield of aniline is always obtained at 319°±1°. The most active catalyst is that prepared by precipitating the hydroxide on asbestos, roasting at 250°, and then reducing with hydrogen at 300°. When used above its m. p., cadmium gives high yields of aniline and shows less tendency to coalesce in nitrobenzene and hydrogen than in hydrogen alone. A catalyst prepared by reduction of the oxalate roasted at 250° is somewhat more active than that obtained from the unroasted oxalate, whilst that prepared from the hydroxide roasted at 250° is more active than that from the hydroxide roasted at 350°. A rate of flow of 0·3794 g. of nitrobenzene per hr. per g. of supported catalyst gives a quantitative yield of aniline, but the unsupported catalyst does not give quantitative yields at this rate. Support of the catalyst, however, on pumice or asbestos does not increase the yield at suitable rates; it only accelerates reduction. Shredded asbestos is a better support for cadmium than is pumice. The aniline produced at 319° is colourless; at lower temperatures it contains some carbylamine and at higher temperatures the product is slightly coloured. No formation of ammonia has been detected in any of the experiments. L. S. THEOBALD.

Reactions at the surface of hot metallic filaments. B. L. SRIKANTAN (Rec. trav. chim., 1930, **49**, 1146—1149; cf. A., 1930, 550).—A general discussion of previous work. The order of efficiency of different catalysts for the reaction between carbon dioxide and hydrogen deduced from the apparent heats of activation agrees with that given by velocity measurements. F. L. USHER.

Rates and temperature coefficients of the catalytic decomposition of ammonia over molybdenum, tungsten, and promoted iron. C. H. KUNSMAN, E. S. LAMAR, and W. E. DEMING (Phil. Mag., 1930, [vii], **10**, 1015—1037; cf. A., 1929, 520).—The theory of the decomposition of ammonia on hot surfaces is examined kinetically, taking into consideration the condensation on the catalyst surface and the evaporation therefrom of the products of decomposition, and a formula is derived for the "true heat of activation" in terms of the temperature coefficient and the heats of desorption of the reactant and products. Ammonia was decomposed on molybdenum and tungsten in the form of electrically heated filaments, and on promoted iron catalysts applied on electrically heated platinum strips. The adsorption of nitrogen from the gas phase was negligible, but the active surface remained covered with hydrogen and ammonia during a run over a wide temperature range. The heat of activation and the heat of desorption of ammonia less that of hydrogen were computed. Evidence indicates that no nitride exists in presence of hydrogen above 740° in the case of molybdenum, and that decomposition on the iron catalyst may take place on nitrides formed from the nitrogen in the ammonia. N. M. BLIGH.

Catalytic formation of hydrogen cyanide. II. Formation from hydrocarbons and ammonia [with E. DEMME]. **III. Formation from carbon monoxide and ammonia** [with R. K. MÜLLER]. **IV. [Mechanism of the] formation from carbon monoxide and ammonia** [with G. KORTÜM]. G. BREDIG and E. ELOD (Z. Elektrochem., 1930, **36**, 991—1003, 1003—1007, 1007—1023; cf. A., 1927, 838).—II. The reaction between ammonia and ethylene, acetylene, and methane in presence of catalysts such as alumina and quartz has been investigated. At temperatures above 700° hydrogen cyanide is formed and with rise of temperature the yield increases to a maximum and then diminishes. The greatest yield (about 70%) is obtained with mixtures of ammonia and ethylene at equal partial pressures; the reaction is a catalytic surface reaction, the most effective catalysts being pure alumina and a mixture of alumina and quartz. Addition of hydrogen to the gaseous mixture reduces the yield of hydrogen cyanide very considerably, whereas nitrogen produces a much smaller effect, although the quantity of methane formed is reduced. The decomposition of the ethylene proceeds according to the equations $C_2H_4 \longrightarrow 2C+2H_2$ and $2C_2H_4 \longrightarrow 2C+2CH_4$; the ratio of

hydrogen to methane formed depends on the temperature, but although at 800° it is independent of the rate of passage of the mixture over the catalyst, the quantity of ethylene decomposed decreases with reduction of the time of contact, and since the hydrogen cyanide is formed only from the carbon produced according to the first equation, the yield diminishes simultaneously. The yield from ammonia and acetylene is, on the contrary, independent of the time of contact, whilst no yield is obtained when methane is employed until conditions suitable for the formation of acetylene are attained. It appears that in all cases the intermediate formation of acetylene is a necessary condition for the production of hydrogen cyanide.

III. The reaction between ammonia and carbon monoxide when passed over catalysts of alumina, thoria, and ceria at 500°, 600°, and 700° has been studied. The greatest yields of hydrogen cyanide are obtained with alumina and with ceria deposited on alumina; silica catalysts are unsatisfactory. The yield, calculated on the quantity of ammonia initially present in the mixture, increases with rise of temperature and with increasing excess of carbon monoxide, but diminishes as the velocity of the gas stream increases. With a twenty-fold excess of monoxide and a contact period of 6 sec. a 65% conversion of ammonia into hydrogen cyanide is obtained, 14% of ammonia being lost by dissociation: at 500° this loss is only about 2—6%. Since the rate of increase of the hydrogen content of the mixture, expressed as a fraction of the ammonia employed, corresponds with the rate of formation of hydrogen cyanide, it is suggested that the principal reactions concerned are $NH_3+CO \longrightarrow HCN+H_2O$ and $H_2O+CO \longrightarrow H_2+CO_2$, which may either take place as one reaction or be independently catalysed to about the same extents.

IV. The influence of nitrogen, hydrogen, carbon dioxide, and water on the reaction has been studied for various periods of contact and at various temperatures with the object of deciding among a number of possible mechanisms. Increase of the carbon monoxide excess favours the formation of hydrogen cyanide to a greater extent than does increase of the ammonia excess, whilst nitrogen is without appreciable influence except for low contact periods. Hydrogen, and especially carbon dioxide, displace the apparent equilibrium in the direction of less formation of hydrogen cyanide; hydrogen also diminishes the dissociation of the ammonia. The reduction of yield caused by water is due, not to displacement of the equilibrium, but to hydrolysis of the hydrogen cyanide. In the light of these observations the mechanism suggested in III cannot be correct; the most probable mechanism is expressed by $2CO+NH_3 \longrightarrow HCN+CO_2+H_2$ and $CO_2+H_2 \longrightarrow CO+H_2O$, and by the side reactions $2CO \longrightarrow C+CO_2$ and $C+NH_3 \longrightarrow HCN+H_2$. Minor reactions involving the formation and decomposition of formaldehyde may take place to some extent. Attempts to attain equilibrium from the hydrogen cyanide–water side confirm the mechanism suggested, although a true equilibrium is, on account of hydrolysis, not attainable.

H. F. GILLBE.

Catalysis of autoxidation: anti- and pro-oxygenic action of iron and its compounds. C. DUFRAISSE and R. HORCLOIS (Compt. rend., 1930, **191**, 1126—1128).—The catalytic effect as regards autoxidation of metallic iron and 21 of its compounds on acraldehyde, benzaldehyde, furfuraldehyde, styrene, turpentine, and sodium sulphite solution is shown to be, like that of all other catalysts, sometimes pro- and sometimes anti-oxygenic. Examples of anti-oxygenic action are: of ferric chloride on benzaldehyde, ferric acetylacetonate on sodium sulphite, oxy-, carboxy-, and met-hæmoglobin on acraldehyde or sodium sulphite, β-chlorohæmin, hæmin, and β-bromohæmin on acraldehyde, benzaldehyde, or sodium sulphite, and of all the foregoing, as also of ferrous oxide, β-chlorohæmin, and its dimethyl ether on furfuraldehyde. Iron is thus no exception to the general rule in this respect.

C. A. SILBERRAD.

Reaction between vapours of methyl alcohol and water as example of heterogeneous catalysis. J. A. CHRISTIANSEN and J. R. HUFFMAN (Z. physikal. Chem., 1930, **151**, 269—302; cf. A., 1926, 358).—The velocity of the above reaction has been observed at temperatures from 190° to 250°, the catalyst being in every case 0·1 g.-at. of copper dispersed in varying quantities of magnesium oxide. The copper loses its activity in the course of time, but it can be restored by treatment with air. The initial velocity is proportional to the square root of the concentration of methyl alcohol, and the reaction is strongly inhibited by hydrogen and to a smaller extent by carbon dioxide. Formulæ for the velocity and for its variation with temperature are given. The velocity decreases with increasing dispersity of the copper.

F. L. USHER.

Use of oscillating discharges in the formation of gaseous hydrides. B. FORESTI (Gazzetta, 1930, **60**, 745—754).—By passing oscillating discharges between electrodes of tin, of bismuth, and of lead in a current of hydrogen at ordinary pressure it is possible to obtain the respective hydrides of these metals even in the absence of organic substances. The best results were obtained with tin, the yield being the greater the smaller was the distance between the electrodes. If the discharge is aperiodic practically no hydride is formed. The amount of hydride formed is not related to the period of the oscillating discharge. The work of Paneth and his co-workers, who obtained negative results in absence of organic substances, is discussed. The catalytic action of hydrocarbons in the formation of metallic hydrides is probably due to the decomposition of the hydrocarbons by the discharge into free radicals of great chemical activity and atomic hydrogen.

O. J. WALKER.

Electrolytic combination with compressed nitrogen at the ordinary temperature. F. FICHTER, P. GIRARD, and H. ERLENMEYER (Helv. Chim. Acta, 1930, **13**, 1228—1236; cf. A., 1922, ii, 372).—On electrolysis of a solution of lithium chloride in absolute ethyl or butyl alcohol in contact with compressed nitrogen using a platinum cathode lithium nitride is formed and gives rise to ammonia by the reaction $Li_3N+3EtOH=3LiOEt+NH_3$. The current yield with nitrogen under a pressure of 1000 atm. may amount to 12%.

R. CUTHILL.

Electrolytic reduction of acid solutions of vanadium. F. Foerster and F. Bottcher (Z. physikal. Chem., 1930, **151**, 321—400).—The static potentials of platinum, iridium, and gold electrodes in solutions containing equimolecular proportions of $V^{V}O_2^{\cdot}$ and $V^{IV}O^{\cdot\cdot}$, $V^{IV}O^{\cdot\cdot}$ and $V^{\cdot\cdot\cdot}$, and $V^{\cdot\cdot\cdot}$ and $V^{\cdot\cdot}$ have been determined and compared with the cathode potentials measured during the respective electrolytic reductions. The static potentials are independent of the metal of the electrode. The experimental procedure was the same as that previously described in the investigation of molybdenum compounds (A., 1930, 432), and the general results obtained are similar. The reduction of V^{V} to V^{IV} at a platinised gauze cathode proceeds without appreciable polarisation, but at a smooth platinum surface the cathode potential is considerably increased, without, however, giving rise to evolution of hydrogen. Reduction of V^{IV} to V^{III} is accompanied by evolution of hydrogen, but the current yield increases during the reduction. The reaction $V^{III} \longrightarrow V^{II}$ cannot occur at a platinised surface, but may be carried to completion at a smooth platinum surface, the current yield steadily decreasing during the reduction. The irregularities observed in the first two stages of reduction are due to the formation of membranes of insoluble products of hydrolysis on the surface of the cathode, leading to an increased potential and to evolution of hydrogen. No such membrane is formed during the final stage, in which the decreased current yield is due solely to the simultaneous discharge of hydrogen ions. Variations in the amount of free sulphuric acid present affect the results in the sense required by the above explanation.

F. L. Usher.

Vanadous salts. J. Meyer and (Frl.) M. Aulich (Z. anorg. Chem., 1930, **194**, 278—292).—The cause of the discrepancies between the work of Piccini and Marino (A., 1902, ii, 663) and that of Rutter (A., 1906, ii, 366) on the electrolytic preparation of vanadous sulphate has been traced to the influence of the sulphuric acid concentration. The solubility at 25° and 100° of vanadium pentoxide in sulphuric acid of concentrations from 0 to 98·5% exhibits two maxima, between which colloidal solutions are formed. In contradiction of the reports of the earlier observers, the nature of the cathode is without influence on the electrolytic reduction, which in presence of air yields compounds of tervalent vanadium; in presence of sufficient sulphuric acid the solution becomes green and then contains the complex acids $[V(H_2O)_4SO_4]SO_4H$ and $[V(H_2O)_2(SO_4)_2]_4H$. If air be excluded the solution becomes violet owing to the production of vanadous salt, and by concentration over phosphorus pentoxide violet crystals of vanadous sulphate heptahydrate may be isolated. Details are given of the preparation of the relatively stable ammonium, potassium, and rubidium vanadous sulphates. The preparation of the vanadous salts of other acids is difficult owing to their instability; cathodic dissolution of the metal yields always compounds of higher valency. The stability of vanadous sulphate solutions increases with increase of concentration and of the free acid concentration; addition of alcohol, sodium hydrogen sulphite, etc. is without influence.

H. F. Gillbe.

Electrolytic preparation of zinc and lanthanum persulphates. V. Arnal (Helv. Chim. Acta, 1930, **13**, 1254—1257).—Solutions containing zinc and lanthanum persulphates have been obtained by electrolysis of aqueous solutions of the corresponding hydrogen sulphates, but it has not been possible to isolate the solid salts. R. Cuthill.

Electrolytic deposition of gold at high current densities. H. Paweck and R. Weiner (Z. Elektrochem., 1930, **36**, 972—980).—Experiments have been performed on the electrodeposition of gold from alkaline ferrocyanide solutions with the object of establishing a process which may be operated at relatively high current densities. The ferrocyanide concentration is of little consequence; increase of the quantity of sodium carbonate in the solution causes at low gold concentrations an increase of the electrode potential, whereas at higher gold concentrations the reverse effect obtains. Increase of the gold concentration markedly reduces the polarisation, and the potential attains a value which is almost independent of the current density. Dilution of a solution of constant composition causes a considerable increase of chemical polarisation. The ordinary dilute ferrocyanide bath exhibits such a rapid increase of electrode potential, even at low current densities, that passivity results and the employment of a gold anode becomes useless, whereas with a bath containing potassium ferrocyanide (200 g.), hydrochlorauric acid (50 g.), and sodium carbonate (50 g./per litre), the potential remains at a constant low value at current densities up to 10 amp. per dm.^{2} and anodic dissolution proceeds unhindered; such a bath may be successfully employed for rapid cathodic deposition.

H. F. Gillbe.

Electrodeposition of chromium. V. P. Ilinski.—See B., 1931, 25.

Electrolytic production of antimony. F. Vogel.—See B., 1931, 25.

Polarographic studies with the dropping mercury cathode. XVI. Electro-reduction of acetaldehyde. I. Smoler (Coll. Czech. Chem. Comm., 1930, **2**, 699—711).—The cathodic reduction of acetaldehyde in 0·1—0·0001*M*-solutions containing lithium chloride at concentrations from 0·02*N* to 0·01*N* by the dropping mercury cathode has been investigated by means of polarographically recorded current–voltage curves. The reduction potential in *M*-solution is —1·60 volt, and is not influenced by variation of the p_H of the solution within wide limits; with decreasing p_H, however, the reduction is retarded, and in presence of acid at a concentration comparable with that of the aldehyde is entirely inhibited. The electrode potential π is related to the current I by the equation $\pi = -(RT/F) \log I$, whilst the change of π due to a change dC of the aldehyde concentration is given by $d\pi = (RT/F) \log dC$. The insensitivity of the reduction process to changes of p_H indicates that the reaction is irreversible; the most probable product is dimethylglycol. The application of polarographic methods to the determination of traces of acetaldehyde is described; 0·0005 mg. in 1 c.c. may be determined to within 10%. For the determination in ethyl alcohol, 10 c.c. are diluted with 90 c.c. of

water, and to the first 10 c.c. obtained on distillation lithium chloride is added. Vinegar should be neutralised with $2N$-lithium hydroxide, and the first fifth of the distillate treated with lithium chloride until the salt concentration is $0·01N$. Fermentation vinegars suppress strongly the maxima on the current–voltage curves, but synthetic and pyroligneous acetic acid have no such influence. H. F. GILLBE.

Anodic oxidation of acetic acid in sulphuric acid solution. R. SCHREINER (Z. Elektrochem., 1930, **36**, 953—963).—$0·5M$-Solutions of formaldehyde, methyl alcohol, and formic, acetic ($0·5M$ and $5M$), oxalic, glyoxylic, and glycollic acids have been subjected to anodic oxidation in $2N$-sulphuric acid solution at a platinum anode and with constant current density with the object of establishing the mechanism of the oxidation of acetic acid; the observations made include determinations of the variation with time of the nature and quantity of gas evolved and of the anode potential, of the nature of the products formed in solution, and of the change of weight, if any, of the anode. The main process is represented by $CH_3·CO_2H \longrightarrow OH·CH_2·CO_2H \longrightarrow CH(OH)_2·CO_2H \longrightarrow (CO_2H)_2 \longrightarrow 2CO_2$, but at higher potentials there are side reactions commencing with the products of the first and second stages and resulting in the formation of formaldehyde, formic acid, methyl alcohol, and carbon monoxide. Increase of the anode potential favours the true oxidation stages, as compared with those involving removal of hydrogen: the latter takes place most readily from the alcoholic group and least readily from the carboxyl group. Simultaneous removal of two hydrogen atoms which are attached to two different carbon atoms occurs only when they form the end members of a six-membered chain, and to only a small extent if an alternative mode of oxidation is possible. H. F. GILLBE.

Mechanism of the synthesis of the nitrogen oxides. L. A. M. HENRY (J. Physical Chem., 1930, **34**, 2782—2791).—The reaction between oxygen and nitrogen has been investigated at low pressure and temperature in the Geissler, the electrodeless, and the dark electronic discharges. With the Geissler discharge, no reaction occurs at the ordinary temperature, but at the temperature of liquid air the reaction has been followed for mixtures of oxygen and nitrogen in the ratios 1 : 1 and 1 : 2. The best yields of nitrogen dioxide are obtained with the stoicheiometric mixture. With the electrodeless discharge no reaction occurs at the temperature of liquid air unless a luminous discharge of high energy content is present. A mechanism between one molecule of oxygen and one atom of nitrogen is proposed.

L. S. THEOBALD.

Organic reactions in gaseous electrical discharge. I. Normal paraffin hydrocarbons. E. G. LINDER (Physical Rev., 1930, [ii], **36**, 1375—1385).—With the object of investigating chemical action in electrical discharges, an apparatus for subjecting vapours to an electrical discharge at various pressures and currents is described; different fractions of the gaseous reaction products can be collected, and their rates of accumulation have been measured for various discharge currents and vapour pressures. Results reported for n-decane indicate that electric conduction in gases may follow an electrochemical equivalence law similar to Faraday's law of electrolytic conduction in liquids, and that the amount of reaction is proportional to the current and independent of voltage and vapour pressure. Curves are given for the relation between molecular size and rate of production of various gaseous reaction product fractions for n-pentane, hexane, heptane, octane, decane, dodecane, and tetradecane. A theoretical discussion of the results is given. N. M. BLIGH.

Chemical decomposition by radiation. G. HARKER (J. Cancer Res. Comm. Sydney, 1930, **2**, 160—181).—A general survey of contemporary theory and some experimental data. N. M. BLIGH.

Thermal and photochemical decomposition of ozone. H. J. SCHUMACHER and G. SPRENGER (Z. physikal. Chem., 1930, **B**, **11**, 38—44; cf. A., 1930, 425).—A reply to Riesenfeld and Wassmuth (A., 1930, 1135). F. L. USHER.

Photochemical union of hydrogen and chlorine. I. Effect of light intensity. II. Effect of wave-length. Measurements with filtered light. A. J. ALLMAND and E. BEESLEY (J.C.S., 1930, 2693—2708, 2709—2721).—I. The velocity of the photochemical combination of hydrogen and chlorine has been measured under widely varying conditions of illumination. With monochromatic light of wave-lengths 4050 and 4360 Å. the velocity is proportional to the light intensity over intensity ratios of 180 : 1 and 440 : 1, respectively, and with polarised light the same holds for a ratio of 4 : 1, obtained by the use of crossed Nicols. The velocity is proportional also to the average intensity when intermittent monochromatic or complex light is employed, and is independent of the rate of intermission. Under certain conditions there appears to be a destruction of inhibitors present in the gas, and it is suggested that this phenomenon may be the cause of the results obtained by Baly and Barker (J.C.S., 1921, **119**, 653).

II. The quantum efficiencies of the photochemical reaction between moist hydrogen and chlorine at 5460, 4360, 4050, 3650, and 3030—3130 Å. are 0·45, 1·41, 2·06, 1·08, and 1·00, respectively, and the threshold is on the longer wave-length side of 5460 Å., since the green mercury line of this wave-length is active. The velocity of the reaction is considerably greater at 25° than at 19·7°, probably as a result of the increased sensitivity of the gas mixture consequent on the destruction of inhibitors: nevertheless, despite the maximum in the quantum efficiency–wave-length curve, the true temperature coefficient of the quantum efficiency probably increases continuously with increase of wave-length. The effect of radiations of two different wave-lengths appears to be additive; the sum of the effects produced when the two act successively is equal to the total effect when they act simultaneously. H. F. GILLBE.

Photosensitised decomposition of nitrogen trichloride and the induction period of the hydrogen–chlorine reaction. J. G. A. GRIFFITHS and R. G. W. NORRISH (Nature, 1931, **127**, 14).—Mixtures of chlorine and small quantities of nitrogen

chloride give total pressure increments corresponding with the net reaction $2NCl_3=N_2+3Cl_2$. Measurements of quantum efficiency with light of wave-length 366 and 436 $\mu\mu$ indicate that the photosensitised decomposition of the nitrogen trichloride proceeds by short reaction chains, the efficiency falling to a limiting value of 2 as the pressure of chlorine is increased. The addition of helium, argon, nitrogen, and oxygen has specific retarding effects, and as the pressures are increased it depresses the quantum efficiency towards the limiting value. The reaction chains appear to be initiated and controlled in the gas phase. Hydrogen has a retarding influence on the decomposition of nitrogen trichloride numerically equal to that of helium. In the inhibition of nitrogen trichloride on the hydrogen–chlorine reaction, confirmation has been obtained of the view that small quantities of hydrogen chloride, comparable in amount with the nitrogen trichloride destroyed, should be formed during the induction period.

L. S. THEOBALD.

Photo-reaction of hydrogen and iodine monochloride. D. P. MELLOR and T. IREDALE (Nature, 1931, **127**, 93).—Contrary to the conclusions of Rollefson and Lindquist (A., 1930, 1135), hydrogen and iodine monochloride react rapidly in light when the pressure of the hydrogen is large compared with that of the iodine monochloride. The reaction is slow in artificial light, rapid in diffuse daylight, and very rapid in direct sunlight; iodine and hydrogen chloride are the main products. The reaction indicates that conditions favour the greater probability of the reaction $H_2+Cl=HCl+H$ and that excited chlorine atoms may not be necessary for it to take place.

L. S. THEOBALD.

Photochemical reaction between ethylene iodide and iodine in carbon tetrachloride solution. H. J. SCHUMACHER and E. O. WIIG (Z. physikal. Chem., 1930, **B**, **11**, 45—55; cf. A., 1930, 1255).—A solution of ethylene iodide and iodine in carbon tetrachloride is only slightly changed when illuminated with a quartz mercury lamp at the ordinary temperature, but at 100° the photochemical decomposition is considerable. The reaction has been studied in relation to the intensity of the light absorbed and the concentration of the reactants. The reaction is of the "chain" type, the stages being: (1) $I_2+E\longrightarrow I+I$; (2) $I+C_2H_4I_2\longrightarrow I_2+C_2H_4I$; (3) $C_2H_4I\longrightarrow C_2H_4+I$; (4) $I+I\longrightarrow I_2$. The temperature coefficient of the velocity is 1·57 for 10°, and the heat of activation 11·8 kg.-cal., in agreement with the value (11·5 kg.-cal.) previously found for the thermal reaction. The velocity is given by the equation $-d[C_2H_4I_2]/dt$ $[C_2H_4I_2]$, in which $I_{abs.}$ is the intensity of the absorbed light.

F. L. USHER.

Photosensitising action by iodine: isomeric transformation of *allo*cinnamylideneacetic acid into the normal form in methyl alcohol, ethyl alcohol, chloroform, and in mixtures of alcohol, chloroform, and water. J. C. GHOSH, D. N. D. GUPTA, N. C. ROY, and H. K. CHATTERJEE (J. Physical Chem., 1930, **34**, 2771—2781; cf. A., 1926, 400).—The conversion of the *allo*-acid into the normal acid at equilibrium is 90% in the various solvents used and is independent of the concentration of iodine or *allo*-acid, the intensity or wave-length of the light used, and the temperature. The measured velocity coefficients are in agreement with the deduced formula $K-A[1-e^{-\epsilon c}]e^{-\alpha c}$, where A and α are constants and ϵ and c are the molecular extinction coefficient and the molar concentration, respectively, of the iodine.

L. S. THEOBALD.

Point-concentration or centripetal theory of light effect. A. STEIGMANN (Kolloid-Z., 1930, **53**, 318—322).—A discussion of published work.

E. S. HEDGES.

Lattice energies of the silver halides and their photochemical decomposition. II. S. E. SHEPPARD and W. VANSELOW (J. Physical Chem., 1930, **34**, 2719—2748; cf. A., 1929, 408).—Theoretical. The importance of lattice energy for light absorption and photodecomposition of crystals is maintained. Sommerfeld's "electron gas" theory of metals is discussed and criticised in its application to photoionisation in ionic crystals, whilst Pauling's theory and conception of "electron affinity of the crystal" which is based on this is analysed and shown to be inadequate in certain respects. It is suggested that replacement of this electron affinity by the virtual field or lattice potential of the metal gives better agreement between calculated and observed wave-length limits of absorption. Deformation of anions by cations with large external electron sheaths tends to shorten the wave-length limit of absorption rather than to extend it. Adsorption effects supporting the opposite view are ascribed to lattice loosening. The relation of photodecomposition to lattice loosening appears to be more restricted than was previously indicated and photodecomposition may be able to take place irrespective of lattice loosening for waves within the absorption band. The loosening, however, increases the probability of its commencing at a given point and extends the active wave-length region by lowering the potential of the crystal lattice.

L. S. THEOBALD.

New photochemical effect on "celloidin" paper as a radiation problem. H. MEWES (Z. wiss. Phot., 1930, **28**, 311—324).—All substances (except wood and similar dielectrics) are stated to emit a new kind of radiation (*L*-rays) which will affect certain brands of printing-out paper at a short distance. These rays are emitted in a narrow pencil, so that on development (with rodinal etc.) images of exact shape are produced, slightly enlarged, and surrounded by concentric haloes at definite distances and of varying colours. Possible theories are discussed.

J. LEWKOWITSCH.

Action of sodium thiosulphate on a slightly acid solution of potassium iodate. E. CARRIÈRE and JULLIARD (Compt. rend., 1930, **191**, 1133—1135).—The result of the addition of solution of sodium thiosulphate to potassium iodate in (hydrochloric) acid solution may result in the reactions: (i) $HIO_3+6Na_2S_2O_3+2H_2O=5NaOH+NaI+3Na_2S_4O_6$; or (ii) $4HIO_3+3Na_2S_2O_3+3H_2O=4HI+6NaHSO_4$. The results of varying (*a*) temperature, (*b*) concentration of hydrochloric acid, (*c*) concentration of iodate, and

(*d*) speed of addition of thiosulphate show that with (*a*), (*b*), and (*c*) constant the amount of thiosulphate required diminishes, *i.e.*, reaction (ii) is favoured, as (*d*) increases; the same is the case when (*b*) is increased with (*a*), (*c*), and (*d*) constant, or when (*a*) is increased with (*b*), (*c*), and (*d*) constant. With (*a*), (*d*), and the ratio (*b*)/(*c*) constant dilution favours (i).

C. A. SILBERRAD.

Periodic process in a chemical reaction. W. T. GIBSON (Nature, 1931, **127**, 13).—The periodic formation of rings of potassium oxide by the slow oxidation of a layer of potassium is described.

L. S. THEOBALD.

Action of boric acid on alkali chlorides and nitrates. L. HACKSPILL, A. P. ROLLET, and L. ANDRES (Compt. rend., 1931, **192**, 48—50).—Intimate mixtures of alkali chlorides or nitrates with a large excess of boric acid were heated in steam at 100—150°. After 30 min. the hydrochloric acid was completely evolved, leaving a pentaborate ($R_2O,5B_2O_3$) except in the case of sodium salts when, unless there is an excess of sodium chloride, a chloroborate, $(5B_2O_3,Na_2O)NaCl$, is produced, whilst sodium nitrate and excess of boric acid yield a triborate, $Na_2O,3B_2O_3$.

J. GRANT.

Ammonium and potassium dimagnesium acid carbonates. E. URBAIN (Compt. rend., 1930, **191**, 1339—1340).—The salts $MgCO_3,2KHCO_3,4H_2O$, $MgCO_3,KHCO_3,4H_2O$ (cf. Engel, A., 1881, 1087), and *potassium dimagnesium hydrogen carbonate*, $2MgCO_3,KHCO_3,4H_2O$, were prepared by the addition of various quantities of potassium hydrogen carbonate to an aqueous suspension of magnesium carbonate, the mixture being stirred by a stream of carbon dioxide and the crystals separated by cooling to 0°. The reaction $5MgCO_3+2RCl+CO_2+4H_2O$ —— $2(MgCO_3)_2,RHCO_3,4H_2O$ gives quantitative yields. Ammonium behaves analogously to potassium in both reactions, mixtures of isomorphous potassium and ammonium chlorides (" potazote ") giving a mixture of the carbonates.

J. GRANT.

Heterogeneous complex salts. I. G. SPACU and G. SUCIU (Bull. Soc. Stiinte Cluj, 1930, **5**, 191—219; Chem. Zentr., 1930, ii, 534—535).—The following *compounds* have been prepared: [M en$_3$]HgI$_4$ (M=Zn, Cd, Ni); [Cu en$_2$]HgI$_4$; [Ni en$_3$]CdI$_4$; [Co en$_3$]CdI$_4$; [Co en$_3$]$_2$[BiI$_4$]I; [Cu en$_2$][HgCl(CN)$_2$]$_2$; [Ni en$_3$][HgCl(CN)$_2$]$_2$; [Cu en$_2$][HgBr(CN)$_2$]$_2$; [Cu en$_2$][Hg(SCN)(CN)$_2$]$_2$; [Cu en$_2$][Hg(SeCN)(CN)$_2$]$_2$; [Cd en$_2$][HgCl$_2$(CN)$_2$]; [Cu en$_2$][HgCl$_2$(SCN)$_2$] [Co en$_3$][HgI$_4$]Cl; [Cu en$_2$][CdI$_3$(SeCN)].

A. A. ELDRIDGE.

Complex thiosulphates of copper with ammonium, potassium, and sodium. II. G. SPACU and I. G. MURGULESCU (Bul. Soc. Stiinte Cluj, 1930, **5**, 254—272; Chem. Zentr., 1930, ii, 535).—The *compounds* $K_5Cu(S_2O_3)_3,3H_2O$ and $K_7Cu(S_2O_3)_4,2KNO_3$ are described. In solutions more concentrated than *M*, interaction of cupric and thiosulphate ions affords sulphur and sulphur dioxide as well as tetrathionate.

A. A. ELDRIDGE.

Action of carbonic acid under pressure on salts of the alkaline-earth metals. I. Action on calcium phosphate. E. MÜLLER and J. KNÖFEL. **II. Action on alkaline-earth silicates.** E. MULLER and W. LUBBERGER (Z. anorg. Chem., 1930, **194**, 258—260, 261—267).—I. By the action of aqueous solutions of carbon dioxide on calcium phosphate at 60 atm. pressure solutions are obtained in which the ratio CaO : P_2O_5 is less than unity for temperatures above 80°. The reaction appears to be $2CaHPO_4+H_2CO_3=Ca(H_2PO_4)_2+CaCO_3$, followed by the formation of calcium hydrogen carbonate, which decomposes at the higher temperatures. With bone ash, and particularly with phosphorite, markedly smaller quantities enter into solution, probably as a result of the greater compactness of these materials.

II. The quantities *x* of calcium, strontium, and barium dissolved from the corresponding silicates by solutions of carbon dioxide at pressures up to 50 atm. have been determined as functions of the temperature. In all cases *x* diminishes with rise of temperature, the decrease being especially marked above 80° owing to the decomposition of the hydrogen carbonate formed; *x* is not influenced by increase of pressure above 30 atm. Since addition of colloidal aluminium hydroxide solution does not alter the values of *x*, silica, and not free silicic acid, must be formed during the process of dissolution. Experiments with ordinary and ignited silicates demonstrate the great influence of the available surface on the reactivity; approximately the same values of *x* are obtained for ignited artificial calcium silicate as for wollastonite. H. F. GILLBE.

Action of bivalent metals on persulphates of the alkali metals. Synthesis of double salts of the type $M^I_2M^{II}(SO_4)_2$. O. ASCHAN (Z. anorg. chem., 1930, **194**, 139—146).—The exothermic dissociation of a number of metals in solutions of sodium, potassium, and ammonium persulphates has been studied. By crystallisation of the filtered solutions a series of hexahydrated complex *salts* of the type $M^I_2M^{II}(SO_2)_2$, where M^I=K, Na, or NH_4, and M^{II}=Mg, Mn, Fe, Ni, Co, or Cu, have been prepared; the *zinc* and *cadmium* compounds are obtained only with the sodium and potassium persulphates. All these compounds crystallise in well-defined oblique rhombohedra. Their mode of formation is represented by: $(M^IO\cdot SO_2\cdot O)_2+M^{II} \longrightarrow M^IO\cdot SO_2\cdot O\cdot M^{II}\cdot O\cdot SO_2\cdot OM^I$, in accordance with the peroxide constitution of the persulphates. Mercury reacts vigorously with the persulphate solutions, but yields compounds of abnormal composition, and the reaction between ammonium persulphate and zinc and cadmium also yields abnormal compounds. H. F. GILLBE.

Mercury fulminate. F. H. VAN LEENT (Chem. Weekblad, 1930, **27**, 670—671).—The structure of mercury fulminate is discussed. The reaction between the fulminate and sodium thiosulphate has been investigated alkalimetrically and iodometrically: the quantity of alkali liberated is twice the quantity which would be produced by hydrolysis of the sodium salt formed according to the equation $Hg(CNO)_2+2Na_2S_2O_3 \longrightarrow Na_2[Hg(S_2O_3)_2]+2NaCNO$, and it appears that the reaction involves oxidation of the thiosulphate, 2 mols. of oxygen being given up by 1 mol. of the fulminate: $4Na_2S_2O_3+2O+2H_2O \longrightarrow 2Na_2S_4O_6+4NaOH$. Titration with a variety of indicators shows that part of the alkali thus produced

combines with complexes containing mercury which are simultaneously produced and behave as very weak acids. Iodometric titration of the neutralised solution indicates that only one half the quantity of iodine solution is required as compared with the quantity of acid necessary for neutralisation, and it is therefore suggested that the residue of the fulminate, after reduction, reacts additively with iodine according to the equation $Hg(NC)_2+2I+H_2O \longrightarrow Hg(NC{\cdot}HI)(NC{\cdot}I{\cdot}OH)$. The metallic fulminates are to be regarded as carbylamines of the metal peroxides. H. F. GILLBE.

Formation of double ammines in aqueous solution. II. Metallic thiocyanates. R. RIPAN and L. DIMA (Bul. Soc. Stiinte Cluj, 1930, 5, 220—249; Chem. Zentr., 1930, ii, 708—709).—The following *compounds* have been prepared (X = hexamethylenetetramine): $[Hg(SCN)_4][MX(H_2O)_3]$ (M=Co, Ni, Fe, Mn); $[Hg(SCN)_4][MX(C_5H_5N)_4]$ (M=Co, Ni, Mn, Cd); $[Hg(SCN)_4][CoX(C_5H_5N)_3]$; $[Hg(SCN)_4(C_5H_5N)_2][MX(C_5H_5N)(H_2O)_3]$ (M=Ni, Fe, Mn); $[Hg(SCN)_4][CdX]$; $[Co(SCN)_4(H_2O)_3][NiX_2(H_2O)_4]$; $[Co(SCN)_4(C_5H_5N)_2][NiX_2(C_5H_5N)_4],H_2O$; $[Ni(SCN)_6][MnX_2(H_2O)_4][NiX(H_2O)_5]$; $[Ni(SCN)_6][MnX_2(C_5H_5N)_4][NiX(C_5H_5N)_5],12H_2O$. A. A. ELDRIDGE.

Preparation of anhydrous stannous chloride. H. STEPHEN (J.C.S., 1930, 2786—2787).—A rapid and strongly exothermic reaction takes place when 2 mols. of acetic anhydride are added to 1 mol. of hydrated stannous chloride; the anhydrous stannous chloride which separates may be washed free from acetic acid by means of ether, and is then apparently non-hygroscopic. It is readily soluble in acetone and in methyl, ethyl, and amyl alcohols, but is insoluble in benzene and chloroform. Traces of water in the solvents cause the immediate appearance of opalescence, presumably due to the formation of stannous oxychloride. H. F. GILLBE.

Cerium. L. LORTIE (Ann. Chim., 1930, [x], 14, 407—460).—By interaction of ammonium cerinitrate and sodium carbonate in aqueous solution, *sodium cericarbonate*, $Na_6[Ce(CO_3)_5,2H_2O],10H_2O$ (yellow), is formed and the corresponding *thallous* salt (orange-yellow) may be obtained from thallous sulphate in a similar manner. The sodium salt is isomorphous with sodium thoricarbonate and in aqueous solution forms *basic ceric carbonate*, $Ce(OH)_2CO_3$ (yellow). By the action of the halogen acids on cerous tartrate, *cerous tartrate hydrochloride*, $Ce_2(C_4H_4O_6)_3,3HCl,14H_2O$, *hydrobromide*, $Ce_2(C_4H_4O_6)_3,3HBr,14H_2O$, and *hydriodide* may be obtained. Cerous tartrate also reacts with tartaric acid to form *cerotartaric acid*, $H[Ce(C_4H_4O_6)_2,2H_2O]$. The *sodium* salt of this acid, $Na[Ce(C_4H_4O_6)_2,2H_2O]6H_2O$, may be prepared by interaction of cerous nitrate and sodium hydrogen tartrate. Investigation of the oxidation of cerous and ceric salts to the perceric state in presence of alkali-metal salts of hydroxy- and phenolic acids has shown that these compounds exert a stabilising effect on perceric salts. *Perceric salicylate*, $Ce_2O_3(O{\cdot}C_6H_4{\cdot}CO_2)_3,6H_2O$ (red), is formed by the interaction of a mixture of sodium carbonate, sodium salicylate, and ammonium cerinitrate. On passing oxygen through a mixed solution of potassium hydroxide and cerous tartrate, *potassium ceritartrate*, $2CeO(C_4H_2O_6)K_2,K_2C_4H_4O_6,11H_2O$ (red), results. R. CUTHILL.

Mechanism of precipitation processes. I. Reaction between lead chloride and ammonium chromate. Z. KARAOGLANOV and B. SAGORTSCHEV (Z. anorg. Chem., 1930, 194, 151—158).—The quantity of chloride retained by lead chloride when precipitated in presence of chloride has been determined. The chloride content x of the precipitate, when hot ammonium chromate solution is added rapidly to a boiling solution of lead chloride containing hydrochloric acid, bears a linear relationship to the hydrochloric acid concentration, and although this holds also if the order of the addition is reversed, x assumes higher values; precipitation in the cold also leads to higher values of x, which tend to a maximum at high chloride concentrations. With solutions of sodium, potassium, and ammonium chlorides the values of x are relatively small for precipitation in the cold, but with hot solutions high values are attained and a specific influence of the cation becomes evident. In all cases x diminishes as the time of precipitation increases, and increases with increase of the volume of solution used. None of the precipitates contains dichromate, and the chlorine content is non-volatile. The results are compared with those obtained for the interaction of lead chloride and sulphuric acid (A., 1930, 563); the secondary reaction is probably $2PbCl^{\cdot}+CrO_4''=Pb_2Cl_2CrO_4^{\cdot\cdot}$. H. F. GILLBE.

Nitrogen tri-iodide. H. W. CREMER and D. R. DUNCAN (J.C.S., 1930, 2750—2754).—Nitrogen tri-iodide, NI_3, has been isolated by passing dry ammonia over solid cæsium, potassium, and pyridinium iododibromides and washing the black product rapidly with water to remove residual bromides. The process appears to be essentially a reaction between the ammonia and iodine bromide produced by dissociation of the iododibromide, since the more stable compounds of this type, *i.e.*, those of low dissociation pressure, yield with ammonia additive compounds. It is apparently possible to sublime nitrogen tri-iodide in a vacuum at the ordinary temperature, the sublimate being condensed by means of liquid air. H. F. GILLBE.

Reaction between nitrite and aminosulphonic acid. F. L. HAHN and P. BAUMGARTEN (Ber., 1930, 63, [B], 3028—3029).—Nitrite can be removed from aqueous solution by reaction with aminosulphonic acid or precipitation with 2:4-diamino-6-hydroxypyrimidine. If a 4% solution of nitrite "purissimum" is used, the sum of the originally present and newly formed nitrate in the residual solution amounts to 0·002—0·004 mg. per c.c. H. WREN.

Isomorphism and chemical homology. W. LANGE (Nature, 1930, 126, 916).—Priority is claimed for the preparation of monofluophosphates and the discovery that the PO_3F'' ion resembles SO_4'' (cf. Ray, A., 1930 1351; Lange, A., 1929, 662). L. S. THEOBALD.

Reduction by hydrogen of the oxygenated compounds of phosphorus. P. VILLARD (Compt. rend., 1930, **191**, 1035—1038).—Metaphosphoric acid and anhydride are reduced in a stream of hydrogen (50 litres per hr.) at 900—950° to elementary phosphorus which, after condensation in a vessel at 0°, is obtained as ordinary (? white) phosphorus, or is deposited near the heated portion of the tube in an orange-yellow (pyromorphic) form, and in the cooler parts as brilliant gold to violet scales. Both the latter types are transformed into ordinary phosphorus if heated in a vacuum. Similar results are obtained with sodium and barium pyrophosphates, calcium pyrophosphate being converted into tricalcium phosphate, which is not further reduced to an appreciable extent. Trisodium phosphate gives traces of phosphorus at 1200° by indirect reduction resulting from dissociation and subsequent formation of the pyrophosphate (above). At lower temperatures phosphorescence and an odour of garlic are obtained.

J. GRANT.

Action of halogens on ethyldi-iodostibine. Antimony bromodi-iodide. R. E. D. CLARK (J.C.S., 1930, 2737—2739).—By the action of iodine on ethyldi-iodostibine highly coloured unstable products, which on decomposition leave only antimony tri-iodide, are formed. If to 12 g. of ethyldi-iodostibine dissolved in 15 c.c. of chloroform 1·6 c.c. of bromine dissolved in 5 c.c. of chloroform are added, and the liquid is refluxed for a few minutes and cooled, a mixture of iodine and *antimony bromodi-iodide*, m. p. 88°, separates. The action of chlorine on the stibine yields only the tri-iodide. H. F. GILLBE.

Oxidation of trithiocarbonate in alkaline solution. J. G. WEELDENBURG (Rec. trav. chim., 1930, **49**, 1180—1188; cf. A., 1928, 602).—When solutions of sodium trithiocarbonate are oxidised in alkaline solution with bromine, permanganate, or hydrogen peroxide, the sulphate produced is about 9% less than that corresponding with the sulphur content. The discrepancy has been traced, in the case of hydrogen peroxide, to the occurrence of a reaction in which dithionic and formic acids are produced in the molecular ratio of 1 : 4. Addition of nickel nitrate before the oxidation reduced the error to about 3%.

F. L. USHER.

Selenocyanammines. II. G. SPACU and C. G. MACAROVICI (Bul. Soc. Stiinte Cluj, 1930, **5**. 169—187; Chem. Zentr., 1930, ii, 708).—The following *compounds* have been prepared: $[CoAu_2](SeCN)_2$; $[CdAu_2](SeCN)_2$; $[Ni\ en_3](SeCN)_2,KCNSe$; $[Cd\ en_3](SeCN)_2,KCNSe$; $[Zn\ en_3](SeCN)_2,KCNSe$; $[Co\ en_3](SeCN)_2,KCNSe$; $[Co\ en_3](SeCN)_3$; $[Ni\ en_3](SeCN)_2$; $[Cr\ en_2Cl_2]SeCN$.

A. A. ELDRIDGE.

Complex thiocyanates of quadrivalent molybdenum. G. A. BARBIERI (Atti R. Accad. Lincei, 1930, [vi], **12**, 55—61).—Complex thiocyanates of quadrivalent molybdenum may be prepared by oxidising the corresponding compounds of tervalent molybdenum by means of potassium ferricyanide. The pyridine tervalent molybdenum salt, $_5H_5N,H_3Mo(SCN)_6,3H_2O$ (cf. Sand and Burger, A., 1906, i, 487; Sand and Maas, A., 1908, i, 11, 397, 513; Rosenheim and Garfunkel, *ibid.*, 614), prepared by treating an aqueous solution of Chilesotti's salt (A., 1906, ii, 263, 365) with pyridine and acetic acid, yields the *pyridine quadrivalent molybdenum* salt, $2C_5H_5N,H_2Mo(SCN)_6$, on oxidation. The hexamethylenetetramine tervalent molybdenum salt ($+2H_2O$) (cf. Scagliarini and Tartarini, A., 1924, i, 312) gives the corresponding *quadrivalent molybdenum* salt, $(C_6H_{12}N_4)_2H_2Mo(SCN)_6,2H_2O$, on oxidation. The degree of oxidisability of the molybdenum in such compounds as the above may be determined by treating a known weight of the compound, mixed with a known weight of potassium ferricyanide, in ammoniacal solution, with excess of silver nitrate solution and then with a definite volume of standard ferrous sulphate solution, which rapidly reduces the silver ferricyanide to ferrocyanide. Determination of the residual ferrous sulphate by titration with permanganate gives the amount of the potassium ferricyanide converted into silver ferricyanide and hence the amount of ferricyanide reduced to ferrocyanide by the molybdenum. The quadrivalency of the molybdenum in the above compounds is determined in this way. T. H. POPE.

Amphoteric oxide hydrates, their aqueous solutions and crystalline compounds. XI. Molybdates, polymolybdates, and polymolybdic acids as examples of the formation and decomposition of complex inorganic compounds in solution. G. JANDER, K. F. JAHR, and W. HEUKESHOVEN (Z. anorg. Chem., 1930, **194**, 383—428).—A survey is given of previous work on the molybdates and on the products obtained on acidification of alkali molybdate solutions. Measurements have been made of the diffusion coefficients at about 13° of $0{\cdot}2N$-sodium molybdate solutions of p_H from 14 to 0 diffusing into solutions of the same p_H containing sodium nitrate and nitric acid. The diffusion coefficients remain practically constant at 0·58 as the p_H is diminished from 14 to 6·5 and thereafter fall abruptly in a series of stages at p_H 4·5, 1·25, and 1·0, which correspond with the formation of di-, para-, octo-, and deca-molybdates; with further increase of acidity the diffusion coefficients rise steadily as a result of the breakdown of the highly complex aggregates formed at the isoelectric point, which contain at least 24 mols. of molybdic oxide. The change of the absorption coefficients at wave-lengths between 2880 and 3760 Å. of sodium molybdate solutions on gradual addition of acid confirm the results of the diffusion measurements. Conductometric titration shows the paramolybdates to be of the form $M_5(HMo_6O_{21})$, the dimolybdates, $M_3H(Mo_3O_{11})$, and the metamolybdates, $M_3(H_3Mo_6O_{21})$; formation of the other complex molybdates is not apparent on the conductivity curves. The trimolybdates are regarded as tetrabasic salts of hexamolybdic acid, $M_4(H_2Mo_6O_{21})$, and the octomolybdates as tribasic salts of a dodecamolybdic acid, $M_3H_7(Mo_{12}O_{41})$, whilst the higher molybdates are derivatives of an acid, $H_{12}(Mo_{24}O_{-8})$; thus the decamolybdates are $M\text{-}H_7(Mo_{24}O_{78})$ and the hexadecamolybdates $M_3(H_9Mo_{24}O_{78})$. Thermometric titration of neutral and of acidified molybdate solutions indicates that the

process of aggregation is exothermic. The conclusions reached regarding the nature of the aggregates formed are compared with the views of other workers.

H. F. GILLBE.

Reactions with liquid chlorine. J. MEYER and W. AULICH (Z. angew. Chem., 1931, 44, 21—23).—Liquid chlorine was put into sealed tubes containing the other reagent and the tubes were then heated. No reaction occurred with powdered vanadium at low temperatures, but at 0° the mixture exploded, forming vanadium trichloride. No appreciable reaction occurred with platinum, even at 100°, but gold was readily attacked, forming auric chloride. Silver acquired a protective coating of the chloride, but was attacked in the simultaneous presence of water and liquid chlorine. Lead was attacked only by a mixture of liquid chlorine and carbon tetrachloride at 320°, the dichloride being formed. No reaction occurred with dry chromium, but slight attack in the presence of water. Manganese produced manganous chloride at 100° when water was also present. No reaction occurred with silicon or boron. Selenium and tellurium were attacked readily even at −80°, the corresponding tetrachlorides being formed.

E. S. HEDGES.

Oxidation of chlorites to chlorates by permanganates. G. R. LEVI and D. GHIRON (Atti R. Accad. Lincei, 1930, [vi], 11, 1005—1008).—The oxidation of alkali chlorites by neutral potassium permanganate solutions is retarded by the accumulation of hydroxyl ion during the reaction $3ClO_2'+2MnO_4'+H_2O= 3ClO_3'+2MnO_2+2OH'$. The presence of calcium or zinc ion removes the hydroxyl ion formed in the reaction and renders the oxidation to chlorate rapid and quantitative in the cold.

F. G. TRYHORN.

New tetramminocobaltic complexes. P. B. SARKAR and T. DAS-GUPTA (J. Indian Chem. Soc., 1930, 7, 835—837).—By the action of sodium thiosulphate at temperatures below 0° on *trans*-tetramminodichlorocobaltic chloride or on *cis*-tetramminoaquochlorocobaltic chloride, trans-*tetramminoaquothiosulphatocobaltic thiosulphate* is formed as green very soluble crystals; by double decomposition the corresponding *chloride, bromide, sulphate, nitrate, thiocyanate, chromate*, and *dithionate* have been prepared. Aqueous solutions of all these compounds have identical ultra-violet absorption spectra, with two characteristic heads. By keeping a solution of the thiosulphate at 30—35° gradual conversion into the green insoluble trans-*tetramminohydroxythiosulphatocobalt* takes place, and after prolonged hydrolysis, a red *compound* of the structure $[Co^{II}\{(OH)_2Co^{III}(NH_3)_4\}_2(H_2O)_2](S_2O_3)_2$ was isolated. It is suggested that in aqueous solutions of tetramminodichlorocobaltic salts there exists an equilibrium of the type $[Co(NH_3)_4Cl_2]Cl$ $[Co(NH_3)_4H_2OCl]Cl_2$ $[Co(NH_3)_4OHCl]Cl$; at low temperatures the first action of the thiosulphate ion is one simply of substitution, but on raising the temperature hydrolysis causes the formation of the hydroxy-compound, whilst on prolonged hydrolysis the liberated thiosulphuric acid reduces part of the tervalent cobalt.

H. F. GILLBE.

Role of water in the aquotetramminoruthenium compounds. R. CHARONNAT (Compt. rend., 1930, 191, 1453—1455).—Ethylenediamine and potassium ruthenium nitrosoiodide, $K_2Ru(NO)I_5$, interact to form hydroxynitrosodiethylenediaminoruthenium iodide, $[Ru(NO)(OH)\,en_2]I_2$, as pale yellow leaflets. Concentrated hydrochloric acid converts these into orange needles of $Ru(NO)\,en_2ClI_2,H_2O$. Although this loses water fairly readily, the loss is accompanied by change in colour to pale yellow, indicating that the water is constitutional; moreover, silver nitrate precipitates only iodide from a solution. The formula must therefore be $[Ru(NO)(H_2O)\,en_2Cl]I_2$. Pyridine and potassium ruthenochloronitrosodioxalate, $K_2[Ru(NO)Cl(C_2O_4)_2]$ (cf. A., 1924, i, 707), interact to form, besides a soluble monopyridino-derivative, almost insoluble deep red crystals of $Ru(NO)(C_5H_5N)_2Cl(C_2O_4)$. Concentrated hydrochloric acid converts them into red needles of $Ru(NO)(C_5H_5N)_2Cl_3,3H_2O$. This readily loses $2H_2O$, but the third only with decomposition. In contact with water it becomes salmon-coloured in consequence of the reaction $Ru(NO)(C_5H_5N)_2Cl_3(H_2O) \rightleftharpoons Ru(NO)(C_5H_5N)_2Cl_2(OH)+HCl$. The dehydrated product dissolved in alcohol gives no precipitate with silver nitrate until water is added. Its constitution must therefore be $[Ru(NO)(H_2O)(C_5H_5N)_2Cl_3]$. These results indicate, not a co-ordination number 7 for ruthenium, but that the HCl is attached by a secondary valency to the OH, (ClH·OH) occupying one co-ordination position, thus: $[Ru(NO)\,en_2(ClHOH)]Cl_2$, and $[Ru(NO)(C_5H_5N)_2(ClHOH)Cl_2]$. Similarly, aquonitrosotetramminoruthenium chloride is $[Ru(NO)(NH_3)_4(ClHOH)]Cl_2$, and not $[Ru(NO)(NH_3)_4(H_2O)]Cl_3$.

C. A. SILBERRAD.

Adjustment of achromatic indicators. E. L. SMITH (Quart. J. Pharm., 1930, 499—507).—A number of mixtures of indicators (or of an indicator and a dye) are described, such that the colour of one constituent is complementary to that of the other at the mid-point of its colour change, so that the colour at the transition point is grey. These mixtures (for which the term "achromatic indicator" is suggested) are suitable for the titration of coloured, turbid, or very dilute solutions, and for use in artificial light. Mixtures of phenolphthalein with methyl-red and methylene-blue have been prepared with transition points ranging from p_H 8 to 10. A solution of bromocresol-green (0·02 g.), neutral-red (0·0045 g.), *p*-nitrophenol (0·05 g.), and phenolphthalein (0·60 g.) in alcohol (100 c.c.) shows sharp achromatism at p_H 4·5 and 8·5 and may be used for the titration of the first and second hydrogen ions of phosphoric acid.

R. CHILD.

Determination of p_H at temperatures above 100°. S. STONE (Rec. trav. chim., 1930, 49, 1133—1145).—A platinised platinum hydrogen electrode gives reproducible potentials at temperatures above 100° and can be used in conjunction with a suitable standard to determine p_H. Calomel electrodes are unsatisfactory at high temperatures, but good results have been obtained with a silver–silver chloride reference electrode. The construction of the electrodes and electrode vessels is described. The p_H values of a series of buffer mixtures, covering a range of p_H from 1 to 10, have been determined at 150°. The alter-

ation of p_H due to temperature may be either positive or negative and, except with borate buffers, remains approximately constant over a considerable range of p_H. F. L. Usher.

Protective influence of liquid paraffin on the alteration of volumetric solutions. C. J. Blok (Pharm. Tijds. Nederl.-Ind., 1930, 7, 406—408).—Sodium hydroxide solutions (0·1—0·5*N*) when covered with a 3-mm. layer of liquid paraffin and kept in open vessels showed practically no change of concentration after 24 days even when titrated with phenolphthalein as indicator. H. F. Gillbe.

Rapid determination of moisture. T. H. Fairbrother and R. J. Wood (Ind. Chem., 1930, 6, 442—444).—Moisture can rapidly be determined with an accuracy of ±0·5% by measuring the volume of water obtained when the sample is distilled with carbon tetrachloride. The Burton–Pitt method (cf. A., 1928, 712), depending on the change in strength of current when the sample is introduced into a rapidly alternating electric field, and a modification of Berliner and Ruter's method, in which the effect of the sample on the capacity of an electrical condenser is measured, give trustworthy results for the natural moisture content of wheat; added moisture behaves differently. D. K. Moore.

Detection of traces of hydrochloric acid in the presence of hydrobromic acid. G. G. Longinescu and T. I. Pirtea (Bull. Acad. Sci. Roumaine, 1930, 13, 195—196).—The mixed silver halides, obtained by addition of silver nitrate to the solution acidified with nitric acid, are dissolved in 10% ammonia solution and 1 c.c. of 1% potassium bromide is added to the ammoniacal solution, which is then just acidified with nitric acid and filtered. Addition of silver nitrate to the filtrate produces a precipitate which is pure white as long as only chloride is present. The volume of 1% potassium bromide, in c.c., which can be added without giving a yellow precipitate gives the number of mg. of chloride present in the original solution. Potassium bromide can be replaced by hydrobromic acid. P. G. Marshall.

Determination of iodides in presence of other halogens. H. Ditz (Z. anorg. Chem., 1930, 194, 147—150).—The statement of Gorbatschev and Kasatkina (A., 1930, 1143), that iodate should not be employed as an oxidising agent for the determination of iodide in presence of other halides, is criticised, and by reference to earlier work of the author (A., 1902, ii, 12; 1904, ii, 366) it is shown that by suitable choice of the hydrogen-ion concentration the method yields satisfactory results, although if bromide or chloride and bromide be present, only the extraction process at the ordinary temperature is trustworthy. Only in absence of bromide is it permissible to titrate the excess of iodate after heating with 0·1*N*-acid and iodate to remove the liberated iodine. H. F. Gillbe.

Spectrographic determination of various gases. B. de la Roche (Bull. Soc. chim., 1930, [iv], 47, 1326—1331).—An extension of the method previously described (A., 1930, 1145) to other gas mixtures. The spectral lines suitable for determining the gas and the general appearance of the intensity curves have been studied for fluorine (as silicon or boron fluoride), chlorine, bromine, iodine, sulphur, oxygen, nitrogen, boron, and silicon. Precautions must be taken to eliminate effects due to impurities, more particularly water vapour, which superpose a continuous spectrum on that of the gas studied. This effect may render the results untrustworthy. It may be obviated by employing spectral lines in regions not affected by these impurities, or by working with the gas in some standard state—perfectly dry, or having the same degree of humidity, *e.g.*, saturated vapour. The method is applicable to fluorine, chlorine (admixed with dry air), and nitrogen (admixed with hydrogen or carbon dioxide), to an accuracy of 1 in 1000. Bromine and iodine (studied as hydrogen bromide and iodide) give inaccurate values, whilst the gaseous compounds of sulphur, boron, silicon, and phosphorus are decomposed by the spark, the elements being deposited on the electrodes, so that the results are meaningless. Oxygen also behaves anomalously, in that the intensity of the emission lines is independent of the concentration in the gas mixture; the effect is ascribed to oxidation at the electrode. J. R. I. Hepburn.

Determination of small quantities of oxygen in gases. H. R. Ambler.—See B., 1931, 19.

Determination of oxygen in steel. G. Thanheiser and C. A. Müller.—See B., 1931, 24.

Rapid determination of sulphur dioxide in air. K. Zepf and F. Vetter.—See B., 1931, 60.

Titrimetric determination of sulphates. M. Dominikiewicz (Bull. trav. dep. chim. inst. hyg. état [Poland], 1930, 31, No. 1, 3—6).—The solution (100 c.c.) is acidified with hydrochloric acid and heated to the b. p.; 0·1*N*-barium chloride (20—25 c.c.) is added and, after boiling, the solution is neutralised with ammonia. The excess of barium chloride is titrated with 0·1*N*-ammonium potassium chromate, using benzidine as external indicator. Chemical Abstracts.

Rapid determination of selenium. E. Benesch and E. Erdheim (Chem.-Ztg., 1930, 54, 954—955).—The method is applicable to the determination of selenium present as element, selenious or selenic acids. If the selenium is in solution a quantity of this equivalent to 0·1—0·15 g. Se is diluted to 400 c.c., acidified with 5 c.c. of hydrochloric acid, and treated with 30 g. of hydrazine hydrochloride or sulphate. It is boiled in a covered beaker until the red modification of selenium precipitated is converted into the black variety, which is washed, dried, and weighed. If the selenium is present in a powdered substance a weight of the substance containing 0·1—0·15 g. Se is mixed with 3 g. of powdered pure iron oxide, 3 g. of potassium chlorate, and 4 g. of sodium hydrogen carbonate and the mixture is heated in a nickel crucible until it just sinters. It is then washed into a measuring flask and the liquid diluted to 250 c.c. The liquid is filtered through a folded filter and 200 c.c. of it are mixed with 200 c.c. of water; the solution is neutralised and the selenium determined as described above. Directions are given for the reclamation of the hydrazine. Tests of the method on selenic acid

solutions and mixtures of known selenium content gave concordant results. An analysis of selenium sludge is appended. H. E. BLAYDEN.

Separation and determination of selenium and tellurium. K. WAGENMANN and H. TRIEBEL (Metall u. Erz, 1930, **27**, 231—236; Chem. Zentr., 1930, ii, 273—274).—In Keller's method (A., 1900, ii, 573) the selenium is incompletely precipitated; precipitation with ferric acetate leads to an error of 33%. Selenium is preferably precipitated with a hydrazine salt from slightly acid solution; the determination of selenium in metallic and non-metallic substances is described. Separation of selenium and tellurium by means of potassium cyanide is inaccurate; Keller's method is accurate but inconvenient. Lenher and Smith's method (A., 1924, ii, 698), with some modification of the apparatus, is preferred. A. A. ELDRIDGE.

Spot reaction for nitrite. F. L. HAHN (Mikrochem., 1931, **9**, 31—33).—α-Naphthylamine oxalate is a delicate reagent for nitrite and can conveniently be used on paper, a small drop of nitrite solution then giving a red spot on the test-paper. Special directions are given for the preparation of the reagent paper. The limit of sensitivity is 1 in 10^7. E. S. HEDGES.

Argentometric determination of azides. A. MAJRICH (Chem. Obzor, 1930, **5**, 3—4; Chem. Zentr., 1930, ii, 949).—The solution of alkali azide is titrated with $0{\cdot}1N$-silver nitrate solution in presence of potassium chromate. The error is not greater than 0·2%. A. A. ELDRIDGE.

Colorimetric determination of phosphorus. H. B. BENNETT (J. Lab. Clin. Med., 1927, **13**, 251—257).—Modified concentrations of reagents in Briggs' method are recommended. CHEMICAL ABSTRACTS.

Determination of phosphoric acid as ammonium phosphomolybdate and as phosphomolybdic anhydride. A. VON ENDRÉDY (Z. anorg. Chem., 1930, **194**, 239—257).—The conditions of precipitation of ammonium phosphomolybdate in presence of tartaric acid have been investigated. According to the procedure recommended, the solution, containing 0·0003—0·035 g. of P_2O_5, is treated with 8 g. of ammonium nitrate and 20 c.c. of $4N$-nitric acid, diluted to 100 c.c., and heated to boiling; 20 c.c. of the ammonium molybdate reagent are added with stirring, and after 24 hrs. the precipitate is collected, washed with 25 c.c. of cold and 50 c.c. of hot solution containing 50 g. of ammonium nitrate and 40 c.c. of nitric acid per litre, and dried in a current of warm air after washing with 20 c.c. of acetone in several portions. The molybdate solution is prepared by mixing solutions containing 100 g. of tartaric acid in 300 c.c. and 150 g. of ammonium molybdate in 600 c.c., filtering, adding 10—12 drops of hydrochloric acid, and diluting to 1 litre. The precipitate, in which the ratio $P:NH_4$ is 1 : 3, may if desired be weighed as $P_2O_5,24MoO_3$ by heating to constant weight in a porcelain crucible. From the weight of the dried precipitate the empirical factor 0·0355 gives the P_2O_5 content, and for the ignited precipitate the factor is 0·0392; by application of a correction which is approximately −3·0 mg. for dried precipitates weighing 0·05—0·08 g. and for ignited precipitates weighing 0·10—0·80 g., the error may be reduced to ±0·6 and 0·02 mg., respectively. The adsorption of molybdic acid by a precipitate of constant composition is in accordance with the isotherm $a=0{\cdot}863c^{-0{\cdot}328}$. H. F. GILLBE.

Analysis of phosphates. V. VINCENT.—See B., 1931, 60.

Determination of silicon in steel and iron. H. WOLF and R. HEILINGOTTER.—See B., 1931, 24.

Determination of carbon dioxide in sea-water and of carbonate in soils. M. NICLOUX (Compt. rend. Soc. Biol., 1929, **101**, 182—186; Chem. Zentr., 1930, ii, 285).—By the use of a simplified form of the apparatus previously described the carbon dioxide content of sea-water at Roscoff has been found to be 4·93 vol.-% (cf. A., 1927, 996). A. A. ELDRIDGE.

Volumetric determination of sodium. A. BLENKINSOP (J. Agric. Sci., 1930, **20**, 511—516).—Sodium, in solutions containing 0·1—12·0 mg., is determined by precipitation as uranium zinc sodium acetate. The complex salt is dissolved in acid and reduced with excess of titanous chloride, the excess being titrated with iron alum solution using a thiocyanate indicator. Iron, aluminium, and phosphates are removed, prior to the determination, by gentle ignition and extraction of the residue with water. Calcium and magnesium salts in relatively large amounts do not interfere with the reaction, but excessive amounts are sufficiently reduced by a single precipitation with ammonia and ammonium carbonate. A. G. POLLARD.

Micro-determination of silver in oligodynamic water. C. EGG (Schweiz. med. Woch., 1929, **59**, 84—86; Chem. Zentr., 1930, ii, 1256).—The silver is removed electrolytically from an alkaline bath after suitable concentration of the water and is finally determined volumetrically with $0{\cdot}001N$-iodide solution. A. A. ELDRIDGE.

Potentiometric precipitation titration of silver iodide. E. LANGE and R. BERGER (Z. Elektrochem., 1930, **36**, 980—988).—A technique is described whereby the potentiometric precipitation titration of silver iodide may be conducted with an average deviation from the mean of ±0·003%. The influence on the observed equivalence point of adsorption and occlusion of ions has been investigated; on the assumption that the effect is symmetrical on either side of the equivalence point, the probable error is ±0·03 volt. The mean error of a determination is of the order of ±0·01%. Rubbing the electrode with a soft insulating material such as rubber causes on the silver side a negative displacement of potential and on the iodine side a positive displacement, whilst in the neighbourhood of the equivalence point a maximum displacement of −220 millivolts has been observed. The cause of this effect is discussed and the necessity of eliminating possible causes of energy displacement during measurements of *E.M.F.* is emphasised. H. F. GILLBE.

Separation and determination of calcium and strontium. L. SZEBELLÉDY (Magyar Chem. Fol., 1929, **35**, 59—62; Chem. Zentr., 1930, ii, 274).—The

mixed nitrates are dried at 180°, and then extracted first with absolute alcohol and then with *iso*butyl alcohol until not more than 5 mg. are removed. The calcium nitrate solution so obtained is evaporated and the residue dried, whilst the strontium nitrate is dried at 140°. A correction of 0·2 mg. for each extraction is applied. A. A. ELDRIDGE.

Separation and determination of calcium and barium. L. SZEBELLEDY (Magyar Chem. Fol., 1929, **35**, 63—64; Chem. Zentr., 1930, ii, 274).—The procedure employed for the separation of calcium and strontium (preceding abstract) is applicable.
A. A. ELDRIDGE.

Determination of strontium and barium in presence of one another. Separation as bromides. L. SZEBELLEDY (Magyar Chem. Fol., 1929, **35**, 100—105; Chem. Zentr., 1930, ii, 274).—The nitrates (0·5g.) are converted into the bromides by treatment with hydrobromic acid (free from sulphate), dried at 100°, and finely ground with hot *iso*butyl alcohol (10 c.c.). The filtrate containing the strontium bromide is evaporated, the residue being heated with ammonium sulphate, and the strontium weighed as sulphate. The remainder of the salt mixture is dissolved in water, evaporated with hydrobromic acid (1 g. HBr), and the extraction repeated until not more than 5 mg. of strontium sulphate are recorded. The residual dry barium bromide is weighed. A correction of 0·5 mg. is transferred from the strontium sulphate to the barium bromide for each extraction.
A. A. ELDRIDGE.

Volumetric determination of barium. L. ZOMBORY (Magyar Chem. Fol., 1929, **35**, 90—94; Chem. Zentr., 1930, ii, 274).—The salt is titrated with 0·2*N*-ammonium or alkali sulphate (neutral or slightly acidified with hydrochloric acid) or sulphuric acid in presence of sodium rhodizonate as indicator.
A. A. ELDRIDGE.

Volumetric determination of calcium and magnesium in drinking water. M. E. STAS.—See B., 1931, 92.

Spectral analysis of foreign elements in a metal. L. AMY (Compt. rend., 1930, **191**, 1049—1050).—The spark spectra of metals often change during exposure of the plate on account of alterations in the surfaces of the metallic electrodes due to different rates of volatilisation of the elements present. The author therefore makes a number of exposures for 1 sec. only after striking the arc, using a fresh metal surface each time. Lines due to small amounts of magnesium, calcium, and carbon in lead, zinc, or copper, and to magnesium and calcium in iron are thereby reinforced about 100 times, less marked effects being obtained for small traces of tin, copper, antimony, and iron.
J. GRANT.

Determination of cadmium in mill and smelter products. W. E. KECK, G. L. OLDRIGHT, and F. K. SHELTON.—See B., 1931, 25.

Separation of lead from mercury or copper and its determination. H. FUNK and J. SCHORMULLER (Z. anal. Chem., 1930, **82**, 361—365).—The lead is precipitated from a hot 2·5% solution of sodium chloride containing 1—2 g. of sodium acetate and a few drops of acetic acid by the addition of a boiling 5% solution of potassium dichromate in slight excess. The precipitated lead chromate is washed with 1—2% acetic acid, dried at 120°, and weighed. The filtrate is acidified with hydrochloric acid, boiled with alcohol to reduce chromic acid, and saturated with hydrogen sulphide to precipitate copper or mercury sulphide. A. R. POWELL.

Iodometric determination of copper and its application to the determination of reducing sugars. R. INTONTI (Annali Chim. Appl., 1930, **20**, 583—590).—Addition of carbamide serves as a suitable means of removing nitrous fumes from copper solutions prior to determination of the copper by the iodometric method. The copper (0·05—0·3 g.) is dissolved in 15—20 c.c. of 20% nitric acid with only gentle heating. After addition of ammonia in slight excess, the ammonia and nitrous fumes above the liquid are expelled by a current of air. The solution is neutralised with dilute sulphuric acid, 10 c.c. of 20% sulphuric acid and 3 g. of carbamide being added and the liquid stirred vigorously until effervescence ceases. After addition of 3 g. of potassium iodide, the solution is titrated with 0·1*N*-thiosulphate, with continual stirring; starch paste is added towards the end of the titration. The method is applicable to the determination of reducing sugars by means of Fehling's solution, and details of the procedure are given. T. H. POPE.

Electrolytic deposition of copper from tartaric acid chloride solutions. H. HOLEMANN (Z. anal. Chem., 1930, **82**, 273—276).—With increasing concentration of tartaric acid the deposition potentials of copper and antimony from chloride solutions become slightly more positive at 70° and more negative at 0°. With constant concentration of tartaric acid increase in the concentration of hydrochloric acid causes the deposition potentials of the two metals to diverge from one another, but the deposition of copper is accompanied by a strong chemical polarisation and is not complete at a potential below that at which antimony begins to be deposited. A. R. POWELL.

Analysis of copper–zinc and copper–zinc–nickel alloys. E. DI NOLA.—See B., 1931, 68.

Determination of mercury in mercuric cyanide. E. CATTELAIN (J. Pharm. Chim., 1930, [viii], **12**, 529—531).—Although mercuric chloride, sulphate, or nitrate may be determined by reduction to mercurous chloride by hypophosphorous acid in the presence of hydrochloric acid and hydrogen peroxide, under similar conditions the cyanide is reduced to the metal. Quantitative yields of mercurous chloride may be obtained by heating 10 c.c. of approximately 0·1*N*-mercuric cyanide, 10 c.c. of 10% sodium chloride, 2 c.c. of 20% ammonia, and 10 c.c. of saturated potassium permanganate solution on the water-bath for 0·5 hr. in order to convert the cyanide into cyanate. The excess of permanganate is reduced by 2 c.c. of 95—96% alcohol and the manganese dioxide formed is reduced and dissolved by the addition of 5 c.c. of hydrochloric acid (*d* 1·19). After cooling, the addition of 20 c.c. of 10—12-vol. hydrogen peroxide followed by 2 c.c. of 50% hypophosphorous acid gives an immediate precipitate of mercurous chloride.
T. McLACHLAN.

Quinoline as a microchemical reagent for some heavy metals. I. M. Korenman (Pharm. Zentr., 1930, **71**, 769—772).—The characteristics of the crystalline precipitate formed, and the sensitivity of the reaction between quinoline and salts of mercury, copper, bismuth, cadmium, zinc, lead, and tin in presence of alkali halogen salts are described, as also is a reaction between quinoline nitrate solution and salts of iron, zinc, cobalt, and cadmium in presence of ammonium thiocyanate. E. H. Sharples.

Organic reagents in mineral qualitative analysis (cations). B. Tougarinoff (Ann. Soc. Sci. Bruxelles, 1930, **50**, *B*, 145—246).—Methods of detection of aluminium, antimony, arsenic, barium, bismuth, cadmium, calcium, chromium, cobalt, copper, tin, iron, magnesium, manganese, mercury, nickel, lead, strontium, and zinc by means of organic reagents which have been proposed during the last 20 years are summarised and notes are given in each case on the nature of the reaction, conditions favouring the test, and sensitivity. An experimental investigation of the possibilities of using certain organic reagents for the qualitative analysis of cations has been carried out, with the following results. The red lake formed when ammonia and alizarin are added to aluminium salts is recommended as a test for aluminium; it permits the detection of 0·03 mg. of aluminium in 10 c.c. Iron, chromium, and manganese should be absent and the precipitate does not form in the presence of tartaric or citric acid. The violet coloration formed by rhodamine B with antimony forms a useful test. The antimony must be in the quinquevalent state; the presence of tin does not interfere. Tervalent antimony gives a characteristic white crystalline precipitate with pyrogallol up to dilutions of 1 in 50,000, but the reaction is not serviceable in the presence of tin, and the test is considered to be less valuable than that with rhodamine B. The crystalline orange precipitate obtained with feebly acid tervalent antimony and benzidine in the presence of potassium iodide has a low sensitivity (1 in 600), but the form and colour of the precipitate are very characteristic. Hexamethylenetetramine is not recommended as a test for antimony; the test is neither sensitive nor specific. The benzidine test for bismuth is suitable only for microchemical identification. The hexamethylenetetramine test for bismuth is useful only in microchemical analysis; it succeeds best in 15% hydrochloric acid solution and the sensitivity is only 1 in 1000. The dimethylglyoxime test for bismuth is useful for confirmation in the ordinary course of analysis, since it does not succeed with other members of the same analytical group; the sensitivity of the reaction is 1 in 100,000. Rhodamine B is also recommended for the identification of bismuth; the solution should be only feebly acid so that the bismuth salt is partly hydrolysed; the sensitivity is 1 in 6000. In the presence of ammonium thiocyanate, antipyrine gives characteristic precipitates with some metals as follows: zinc, white; copper, brown; ferric iron, reddish-purple; cobalt, blue; nickel, chromium, aluminium, tin, and antimony are incompletely precipitated from concentrated solutions. The reaction with cobalt has been studied in detail. The reagents consist of 5—10% antipyrine and 50% ammonium thiocyanate solutions, the neutral cobalt solution being made feebly acid by the addition of 5 drops of 15% hydrochloric acid to 10 c.c. The sensitivity is 1 in 500,000, but nickel at concentrations greater than 0·1% and traces of iron interfere with the reaction. A sensitive reaction for cobalt, which is not affected by the presence of nickel or iron, is provided by potassium xanthate. It has no particular advantages over other methods except for the qualitative separation of cobalt and nickel; it does not effect a quantitative separation. A new qualitative reagent for magnesium consists of a solution of alizarin in glacial acetic acid. A few drops of the reagent are added to a feebly acid magnesium solution and on the subsequent addition of excess of sodium hydroxide a sky-blue lake is precipitated. Several other metals interfere and the procedure is valueless in the presence of ammonium salts. Benzidine gives a blue coloration with lead compounds, which are first oxidised to lead peroxide by means of hydrogen peroxide. If care is taken to eliminate excess of the oxidising agent the test is useful for ordinary analytical work and detects 0·1 mg. of lead in 10 c.c. The colour reactions given by diphenylamine, diethylaniline, and orange IV, respectively, with zinc salts in the presence of potassium ferricyanide form excellent tests for zinc, particularly as they permit the detection of small quantities of zinc in the presence of aluminium. The red coloration produced with diphenylamine is the most sensitive; 0·004 mg. of zinc may be detected.

E. S. Hedges.

Determination of iron with potassium dichromate. L. Szebellédy (Magyar Chem. Fol., 1930, **36**, 40—44; Chem. Zentr., 1930, ii, 274—275).—The solution diluted to 50 c.c. is treated with 10 c.c. of aqueous sulphuric acid (1 : 3) and 1 c.c. of 1% *p*-phenetidine solution as indicator. After expulsion of air by means of potassium hydrogen carbonate (1 g.), ammonium fluoride (3 g.) is added and the mixture is titrated with 0·1*N*-potassium dichromate from yellowish-green to reddish-violet. A. A. Eldridge.

Determination of iron with ethyl ether. T. Szaffka (Magyar Chem. Fol., 1929, **35**, 44—51; Chem. Zentr., 1930, ii, 275).—Ethyl ether extracts ferric chloride from (hydrochloric) acid solution; 99·8% is extracted in 30 min. in presence of 20·6% of hydrogen chloride. The etherate is of indefinite composition and is unstable, being decomposed by water. A. A. Eldridge.

Determination of iron in aluminium. G. Agamennone.—See B., 1931, 68.

Rapid determination of tin and antimony in alloys with a high copper content. A. M. Belousov.—See B., 1931, 25.

Colorimetric microanalysis. I. Determination of bismuth, aluminium, and zinc. M. Teitelbaum (Z. anal. Chem., 1930, **82**, 366—374).—Bismuth, aluminium, and zinc precipitates obtained by the addition of 8-hydroxyquinoline to feebly acid acetate solutions (containing tartrate also in the case of bismuth) may be determined colorimetrically by

centrifuging the precipitate, dissolving it in 1 c.c. of $4N$-hydrochloric acid, and treating the solution with 6 c.c. of a cold saturated solution of sodium carbonate and 0·5—1 c.c. of a solution of 4 g. of phosphomolybdic acid and 20 g. of sodium tungstate in 150 c.c. of water which has been boiled for 2 hrs. under reflux with 10 c.c. of 85% phosphoric acid, cooled, and diluted to 200 c.c. The resulting blue colour is compared with that produced by standard solutions prepared under similar conditions. Bismuth may also be precipitated with pyrogallol from neutral solution and the precipitate treated similarly for colorimetric determination of the metal. A. R. POWELL.

Determination of bismuth in lead ores by internal electrolysis. E. M. COLLIN.—See B., 1931, 25.

Micro-balance. J. DONAU (Mikrochem., 1931, 9, 1—14).—A description of a new micro-balance, with directions for its manipulation. E. S. HEDGES.

Apparatus for fluorescence microscopy and fluorescence photomicrography. P. METZNER (Mikrochem., 1931, 9, 72—89).—An apparatus for the microscopical examination of fluorescence is described, a parabolic mirror serving as the source of illumination. When an ultra-violet lamp is used with the apparatus photomicrographs can be obtained. E. S. HEDGES.

Micro-m. p. apparatus. L. KOFLER and H. HILBCK (Mikrochem., 1931, 9, 38—44).—The micro-m. p. apparatus described has been tested on a number of substances and the results are compared with those in the literature. For m. p. below 200° the greatest error was $\pm1°$ and for m. p. between 200° and 300° the greatest error was $\pm2°$. The mean errors are less. E. S. HEDGES.

Determination of the m. p. of platinum. G. RIBAUD and P. MOHR (Compt. rend., 1931, 192, 37—38).—Optical extrapolation from the m. p. of gold (1063°) was employed (cf. Ribaud and Nikitine, A., 1929, 366, 967), the mid-point of a hole in the wall of an electrically-heated platinum tube being directed on a potentiometrically-compensated thermoelectric cell calibrated in terms of a pyrometer for 1° intervals 10° below the m. p. The pyrometer was then directed on a black body at a temperature corresponding with the current obtained at the m. p., the brilliance of which was then adjusted by means of a revolving sector to correspond with a temperature approximately equal to that of the m. p. of gold. The difference in temperatures could then be calculated from the effective wave-length of the light concerned and the transmission factor of the sector. The value $1762\pm2°$ was found for platinum (purity 99·99%). J. GRANT.

Electric furnace for elementary micro-analysis according to Pregl. B. FLASCHENTRAGER (Mikrochem., 1931, 9, 15—19).—The advantages of a short type of electric heater for the elementary analysis of organic compounds are pointed out and an apparatus of the type has been constructed. E. S. HEDGES.

Electric tube furnaces, especially for micro-analysis. P. A. THIESSEN (Chem. Fabr., 1930, 493—495).—The furnace comprises a thick-walled hollow cylinder of aluminium silicate refractory, the upper longitudinal half of which is removable to allow the introduction of the combustion tube. Heating is effected by means of longitudinal spirals of nickel-chromium wire laid in a series of longitudinal grooves around the central hole of the refractory cylinder. The use of the furnace in the micro-analysis of organic compounds by combustion is described. A. R. POWELL.

Shelf to increase ashing capacity of laboratory electric furnace. R. HERTWIG (Cereal Chem., 1930, 7, 556).—A removable asbestos shelf is described. E. B. HUGHES.

Immersion liquids for determination of refractive index of solids. A. MAYRHOFER (Mikrochem., 1931, 9, 52—71).—For the determination of the refractive index of solids by the immersion method, the optical properties of some liquid mixtures have been investigated with the object of supplying the widest possible range. Water–glycerol mixtures are available for refractive indices between 1·333 and 1·465, cineole–paraffin mixtures between 1·456 and 1·482, paraffin–1-bromonaphthalene mixtures between 1·482 and 1·658, and 1-bromonaphthalene–methylene iodide mixtures between 1·658 and 1·740. The temperature coefficients of the refractive indices of the mixtures have been determined. E. S. HEDGES.

Interference method for measuring the refractive index of solutions. C. BORTOLOTTI (Nuovo Cim., 1930, 7, 148—152; Chem. Zentr., 1930, ii, 948).—An apparatus for the measurement of small differences in n of dilute solutions with change of concentration is described. A. A. ELDRIDGE.

Conductivity measurements and conductometric determinations. F. L. HAHN (Z. Elektrochem., 1930, 36, 989—991).—A galvanometer employed as a null instrument in conjunction with a copper–cuprous oxide–lead detector affords a convenient and accurate means of measuring the conductivity of electrolytes and is especially suitable for conductometric titrations. H. F. GILLBE.

Apparatus for electrometric analysis employing an electron tube. E. BERL, W. HERBERT, and W. WAHLIG (Chem. Fabr., 1930, 445—446, 458—460).—The electron tube is an ideal voltmeter, as direct readings can be obtained without any compensating device. The bridge, rheostats, etc. formerly necessary are eliminated and only a simple and cheap milliammeter is required. The practical absence of current also gives much more liberty in the construction of the electrodes. The tube used is a vacuum bulb containing three electrodes; the heated element is a tungsten wire covered with alkali oxide. The effect of the screen-grid potential on the anode current is described. Slight changes in this potential produce an easily measured current change. The authors derive the compensating current for the ammeter from the heating battery, thus eliminating one battery and rendering the zero of the instrument almost constant. The anode current must not be less than 100 volts for p_H measurement, but for electrometric titration 50—100 volts is suitable. Measurement of p_H values can be made in a few seconds, using a buffer solution of

known p_H, with an accuracy of 0·05—0·1 p_H. The apparatus requires standardising once a month. For electrometric titration a beaker is mounted on a tripod and supplied with a calomel electrode, agitator, and burette with bent delivery tube. A potential curve is obtained from the first titration, and the exact point of discontinuity obtained by a second one.

C. IRWIN.

Portable p_H apparatus. A. ITANO (Ber. Ohara Inst. Landw. Forsch., 1930, **4**, 471—474).—A combined galvanometer and millivoltmeter has been introduced into a modification of an earlier apparatus (A., 1929, 1034). A. COHEN.

Determination of the fall in potential in a micro-electrophoresis cell. J. GIBBARD (Science, 1930, **72**, 398—399).—Apparatus and method for determining the fall in *P.D.* at any stage of an experiment without loss of time are described.

L. S. THEOBALD.

Automatic mercury still. A. KRETHLOW (Z. tech. Physik, 1930, **11**, 159—160; Chem. Zentr., 1930, ii, 947).—An electrically operated automatic mercury still of pyrex glass is described. A. A. ELDRIDGE.

Micro-sublimation. A. CHALMETA.—See this vol., 246.

Apparatus for measurement of the surface tension of liquids. M. CHOPIN (Compt. rend., 1930, **191**, 1293—1295).—The apparatus is designed for quantities of sap or latex of the order of 0·15—0·3 c.c. It consists of a cylinder suspended from the beam of a balance so that the base is immersed in a thin crown of the liquid placed in the right angle formed at the point of intersection of a slightly smaller cylinder (diameter 40 mm.) and a metallic block, above which the cylinder projects by about 3 mm., and which is perforated to allow access of air to both sides of the film. Increasing weights are applied to the other arm of the balance (*e.g.*, by means of a long, thin glass rod dipping below a water level which is falling continuously), when the top cylinder rises carrying a narrow ring of liquid with it, which eventually breaks. An electrical heater serves to clean the apparatus between experiments, and cold water may be circulated through the metal block for cooling purposes. The weight of the film may be determined from that of the drop adhering to the top cylinder after the experiment. J. GRANT.

Colour measurement. C. SCHAEFER and H. PESE (Physikal. Z., 1931, **32**, 1—16).—The Ostwald method is considered. An indirect test of the method is described involving the neutralisation of opposite colours. A direct test is also arranged, but in many of the examples there is disagreement. The numerical calculation of "white content" and brightness is given. A. J. MEE.

Continuous extraction apparatus. P. A. W. SELF and C. E. CORFIELD (Quart. J. Pharm., 1930, **3**, 408—409).—A perforated glass container rests on a coil of wire at the constriction of the cylindrical outer vessel which connects the flask with the condenser. The apparatus is suitable for general work and for the extraction of vegetable drugs.

R. CHILD.

Integrating photometer for X-ray crystal analysis. B. W. ROBINSON (Proc. Roy. Soc., 1930, **A**, **130**, 120—133).—A detailed account is given of an improved form of Astbury's α-ray photometer (A., 1927, 912; 1929, 745), and the precautions to be observed in order to obtain accurate results are discussed. In practice, the background estimation sets the limit to the accuracy of the instrument. The results obtainable are reviewed. A set of measures made on the equatorial planes of the *c* zone of anthracene are found to be in fair agreement with the corresponding intensities obtained by means of the ionisation spectrometer. It is considered that the α-ray photometer is the best instrument to employ for the complete survey of the intensities of reflexion from a crystal, particularly when the crystal is small or easily volatile. L. L. BIRCUMSHAW.

Optical pyrometry. A. C. EGERTON and M. MILFORD (Proc. Roy. Soc., 1930, **A**, **130**, 111—119).—The advantages of the magnifying pyrometer are discussed. A special composite glass filter has been devised in which use is made of the sharp edge of an absorption band of a "didymium" glass at about 5750 Å.; a band of light 130—140 Å. in visible width is transmitted between 5740 and 5600 Å., about 70% of the energy being within the region 5670±25 Å. Simple methods of calibrating a pyrometer are described, using a wedge as a black-body source or a platinum tube provided with a small hole. The temperatures are determined by melting small pieces of metal on the outside of the tube or wedge, or preferably by hanging a wire down the centre of the tube. It is an advantage to provide two monochromatic glasses for the pyrometer, as observations can then be made in two wave-lengths at a definite temperature.

L. L. BIRCUMSHAW.

Measurement of surface temperatures. W. F. ROESER and E. F. MUELLER (Bur. Stand. J. Res., 1930, **5**, 793—802).—Two types of contact thermometer are described and illustrated. For the measurement of surface temperatures up to 700° a heavily heat-insulated chromel–alumel couple with the hot junction embedded in a gold disc is used; the instrument is calibrated to allow for a standard difference of 10% between the temperature of the surface and that which the gold disc attains in contact with the surface. For surface temperatures up to 250° a compensated thermocouple terminating in a disc of hard bearing metal gives results for moving surfaces, *e.g.*, milk-drying rolls, within 1° of the actual value. A. R. POWELL.

Instantaneous locking clamp for universal stand. A. BARBOT (Bull. Soc. chim., 1930, [iv], **47**, 1331—1332).—A simple form of clamp, suitable for gripping apparatus of very variable dimensions up to 60 mm. diameter, is illustrated.

J. R. I. HEPBURN.

Pyknometer. F. G. HOFFMANN (Chem.-Ztg. 1930, **54**, 936—937; cf. B., 1930, 974).—An open-mouthed pyknometer consists of a small (50-c.c.) beaker in which the level of the liquid is controlled by a gauge-point. The density of solids, powders, etc. can be readily determined; for liquids a sinker of known volume is used in order to avoid error due to meniscus differences. E. LEWKOWITSCH.

Oxygen bomb calorimeter. E. STANSFIELD and J. W. SUTHERLAND (Canad. J. Res., 1930, **3**, 464—472).—An improved type of bomb calorimeter, constructed of acid-resistant steel (Hadfield's Era steel, C.R.2), is described. By improvement of the heat conduction of the crucible and its supports thermal equilibrium is attained within 5 min. of the firing of the charge. The use of a vacuum-insulated calorimeter is criticised, since irregular changes in the water equivalent and rate of cooling of the system have been observed. T. H. MORTON.

***X*-Ray tube to furnish the homogeneous *K* radiations of uranium.** W. MOPPETT (J. Cancer Res. Comm. Sydney, 1930, **2**, 147—152).—A demountable water-cooled glass *X*-ray tube operates at 140 kilovolts continuous current supplied by a Gaiffe-Gallot constant-potential generator, and is designed to give a maximum output of homogeneous penetrating *K* radiation (0·10842—0·13095 Å.) of uranium. The tube has steel end-pieces, one forming the anode, and the target is a copper plate, into which is ground uranium oxide, and is covered by a lead-arsenic alloy shield; the cathode is a Coolidge filament and focussing bowl. The radiation generated is filtered free of *L*-rays and stray secondary radiation, the efficiency being increased by utilising the radiation passing through a thin target of uranium. Experimental energy curves and a spectrogram are reproduced. N. M. BLIGH.

Vacuum evaporation and distillation [in the laboratory]. H. N. NAUMANN (Chem. Fabr., 1930, 505—507).—Continuous vacuum evaporation may be performed by an apparatus with a continuous feed into the distillation flask. The end of a Liebig condenser is connected to a water-jet vacuum pump and the distillate passes away with the water. Two types of collecting vessel are described for distillation purposes when the distillate is to be recovered. One suitable for up to 3 litres of liquid per hr. consists of a double tube with cock connected to a second pump, the lower tube being emptied from time to time. For higher distillation rates a single tube with 3-way cock connected to two receivers used alternately is more suitable. This apparatus requires in all 3 pumps. A boiling capillary of V_2A steel previously described has been improved by increasing the diameter to 0·7 mm.; a wire of the same material is also used. It is resistant to all reagents except concentrated hydrochloric acid and has many advantages over glass capillaries. C. IRWIN.

Arrangement for fractional distillation in the laboratory. W. PRAHL (Chem. Fabr., 1930, 517—519).—The essential feature of the apparatus is a glass tap which regulates the rate at which the vapour enters the receiving condenser, thus providing a control of the equilibrium. E. S. HEDGES.

Resistance thermometers. C. G. MAIER (J. Physical Chem., 1930, **34**, 2860—2868).—A copper resistance thermometer which eliminates hysteresis and drift due to differential thermal expansions is described and a method of calibration is given. A formula giving the resistance of a thermometer of commercial copper wire is recorded and a modified type of thermometer suitable for laboratory use at temperatures below 100° is described. The advantages of copper resistance thermometers are discussed. L. S. THEOBALD.

Geochemistry.

Occurrence of elements of the vanadium group in volcanic minerals. G. VON HEVESY, E. ALEXANDER, and K. WURSTLIN (Z. anorg. Chem., 1930, **194**, 316—322).—The mean niobium, tantalum, and vanadium contents of 282 specimens of volcanic rocks were $3·2\times10^{-7}$, $2·4\times10^{-7}$, and 2×10^{-4} g. per g., respectively. The protoactinium content, calculated from the radium content, was 7×10^{-13} g. The relative frequency of occurrence of the elements of the vanadium group in volcanic rocks and in meteorites is discussed. H. F. GILLBE.

Zeolites. I. General review. M. H. HEY (Min. Mag., 1930, **22**, 422—437).—A review of the literature, with bibliography, on the constitution, dehydration, and base-exchange of the zeolites. L. J. SPENCER.

Simple method of observing the magnetic properties of mineral grains. F. SMITHSON (Min. Mag., 1930, **22**, 419—421).—Two darning needles with their points 0·5—4·0 mm. apart are mounted in a cardboard frame over a horseshoe magnet. This is brought near the grains immersed in a heavy liquid under the microscope; grains of ilmenite, garnet, tourmaline, staurolite, biotite, and monazite can be distinguished by their behaviour. L. J. SPENCER.

Cupriferous melanterite from Skouriotissa mine, Cyprus. M. H. HEY (Min. Mag., 1930, **22**, 413—418).—A fine group of large (18×13 cm.) crystals, transparent and sky-blue in colour, was found in an ancient (Roman?) stope in the cupriferous pyrites ore. In colour and habit the crystals suggest chalcanthite, but a crystallographic and optical examination proves them to be monoclinic, although of unusual habit for melanterite, being tabular parallel to the plane of symmetry and with several new crystal forms. A partial analysis gave CuO 2·15%, corresponding with $CuSO_4,7H_2O$ 7·72% in isomorphous mixture with $FeSO_4,7H_2O$. The amount of copper is not sufficient to refer the mineral to pisanite. L. J. SPENCER.

Tellurium ores. H. BORCHERT (Neues Jahrb. Min., 1930, **A**, **61**, 101—138; Chem. Zentr., 1930, ii, 711).—Corrosion figures and colours, obtained by the use of nitric acid, aqua regia, or ferric chloride solution, are described for the following minerals: calaverite, sylvanite, krennerite, petzite, hessite, nagyagite, altaite, and coloradorite. A. A. ELDRIDGE.

Amethysts and quartz rich in solid inclusions. R. WEIL (Compt rend., 1930, **191**, 1350—1352).—In (*e.g.*) crystals of Brazilian origin, inclusions perpen-

dicular to the ternary axis may be of two types: (*a*) The birefringent compensation planes are parallel to the (1010) face of the prism, and, to some extent, repeated as in ordinary quartz. (*b*) The neutral planes are perpendicular to the prism faces, extending towards the centre at inclinations of 120° or 60°. The two types of plane are analogous to those of *L*- and *S*-quartz, respectively (this vol., 46), and, when they coexist, may exhibit interpenetration. Planes having optical rotation are always present. J. GRANT.

Chemical and crystallographic investigations on Vesuvian litidionite. G. CAROBBI (Rend. Accad. Sci. Fis. Mat. Napoli, 1930, [iii], **36**, 21—31).—The identity of Scacchi's neocianite (A., 1882, 370) with litidionite (cf. Zambonini, Rend. Accad. Sci. Fis. Mat. Napoli, 1909—1910, [ii], **14**) is established, and the formula determined to be $(Cu,Na_2,K_2)Si_3O_7$. The crystallographic and physical constants are given. T. H. POPE.

Infusorial earth from Akhaltzikh (Caucasus). D. WEINBERGER (Masloboino Zhir.-Delo, 1929, No. 1, 16—17).—The infusorial earth, *d* 0·53, contains SiO_2 (soluble in sodium hydroxide solution) 82·30, (insoluble), 4·90, FeO 0·215, Fe_2O_3 0·559, Al_2O_3 0·560, CaO 0·400, MgO 0·072, P 0·008, loss on ignition 4·30, H_2O (105°) 6·70%. It rapidly adsorbs dyes from aqueous solution and decolorises vegetable oils. CHEMICAL ABSTRACTS.

Curtisite, a new organic mineral from Skaggs Springs, Sonoma County, California. F. E. WRIGHT and E. T. ALLEN (Amer. Min., 1930, **15**, 169—173).—The mineral, *H* <2, *d* 1·235—1·237, orthorhombic, yellow to yellowish-green, pleochroic, n_D α 1·557, β 1·734, γ 2·07, when recrystallised from benzene, contained C 93·91, H 5·57%; mol. wt. 292; m. p. about 370°. The probable formula is $C_{24}H_{18}$. CHEMICAL ABSTRACTS.

Moors of Tekir-Ghiol and Agigea. N. T. DELEANU and R. HOFMANN (Bull. Acad. Sci. Roumaine, 1930, **13**, 111—128).—Soil from Tekir-Ghiol is richer in sulphides, organic sulphur compounds, sodium, chlorine, and iodine than that from Agigea, whilst the latter has a larger content of potassium, calcium, iron, and aluminium. The Tekir-Ghiol soil has a greater heat capacity. P. G. MARSHALL.

Physical and chemical characteristics of certain American peat profiles. I. C. FEUSTEL and H. G. BYERS (U.S. Dept. Agric., Tech. Bull., 1930, No. 214, 26 pp.).—Numerous physical and chemical data concerning various types of peat are recorded. Of physical properties the moisture-holding capacity and moisture equivalent are the most definitely indicative of type. In the segregation of peat profiles the most useful chemical characteristics include the ether and alcohol extractives, hemicelluloses and cellulose, lignin–humus complexes, soluble and insoluble nitrogen, and ash composition. No evidence was obtained in support of the theory of lignite formation from present peat deposits. These probably consist of indefinitely preserved layers of plant remains, once permanently submerged, the degree of decomposition of which is indicated by the lignin–humus complexes. A. G. POLLARD.

Development of the soil profile in N. Wales as illustrated by the character of the clay fraction. G. W. ROBINSON (J. Agric. Sci., 1930, **20**, 618—639).—Variations in the composition of the clay fractions in the different horizons of soil profiles are utilised in the classification of soil series. Changes in the ratio silica : sesquioxides throughout a profile are indicative of the course of the eluviation process. In the soils examined there was an accumulation of sesquioxides (notably ferric oxide) in the lower layers at the expense of the surface layers. A. G. POLLARD.

Types of clay in south-west Finland. B. AARNIO (Stat. Markforskningsinst. Agrogeol. Medd., 1928, Nr. 28; Proc. Internat. Soc. Soil Sci., 1930, **5**, 243).—Chemical and physical characteristics, manurial requirement, and cropping power of numerous types of clays are recorded. A. G. POLLARD.

Tuff-soils of Maifeld. P. PFEFFER (Sitzungsber. Preuss. Geol. Landesanst., 1930, [5]; Proc. Internat. Soc. Soil Sci., 1930, **5**, 212).—An examination of pumiceous soil profiles is recorded. The relative ease of decomposition of pumice largely influences chemical variations in the profile, there being a general decrease in hydrochloric acid-soluble constituents from the surface downwards. The molecular ratio $SiO_2 : Al_2O_3$: bases of the acid-soluble material remains practically constant throughout the profile. Magnesium is the most important base in the surface soils. The exchangeability of bases increases from the surface downwards, and univalent bases are more in evidence than is the case with normal soils. A. G. POLLARD.

Principal soils of the Black Sea region and their agricultural characteristics. S. A. ZAKHAROV (Ann. Rep. Soils N. Caucasus, 1929; Proc. Internat. Soc. Soil Sci., 1930, **5**, 245).

Natural acidity of the chief virgin soil types of Roumania. J. F. RADU (Bul. Agric. Bukarest, 1930; Proc. Internat. Soc. Soil Sci., 1930, **5**, 208).

Organic Chemistry.

Physico-chemical organic analysis. M. LECAT Gazzetta, 1930, **60**, 704—719).—A scheme for the recognition of the chemical type of an organic compound is based on the type of azeotropism shown by the compound when mixed with certain test substances, which differ according to the b. p. of the unknown compound. For compounds of b. p. at about 150° glycol, methyl oxalate, and *s*-tetrachloroethane are suggested as test substances; for liquids of b. p. at about 185°, phenol, aniline, and acetamide, and for liquids of b. p. at about 225°, glycol, *o*-nitrotoluene, and pyrocatechol are suggested. The nature of the azeotropism shown by these substances with various classes of compounds is tabulated. F. G. TRYHORN.

Determination of the empirical formula of a hydrocarbon. E. W. WASHBURN (Bur. Stand. J. Res., 1930, 5, 867—890).—Mathematical. Methods and tables are given for deducing the empirical formula of any hydrocarbon containing less than 100 carbon atoms from a determination of the mol. wt. alone (when less than 300) or in conjunction with a combustion analysis; sometimes the determination of the bromine addition number may be used instead of one of the first-mentioned determinations. The determination of a trustworthy "average formula" for a mixture of hydrocarbons and the influence of impurities and of polymerisation are also discussed.

A. R. POWELL.

Formation of methane during the electrolysis of potassium acetate and the mechanism of Kolbe's electrosynthesis. S. N. SHUKLA and O. J. WALKER (Trans. Faraday Soc., 1931, 27, 35—40).—Under certain conditions methane is present together with ethane amongst the gases evolved at a platinum anode during the electrolysis of aqueous potassium acetate solutions of various concentrations. Methane is formed in appreciable amounts only at low current densities (below about 10 milliamp./$cm.^2$), and for a given current density the proportion of methane to ethane is greater the more concentrated is the solution. The mechanism of Kolbe's electrosynthesis and the recent work of Fichter (cf. A., 1929, 1247, 1403) are discussed.

O. J. WALKER.

Synthesis and spectrochemistry of *n*-alkanes. A. KARVONEN (Suomen Kem., 1930, 3, 101—111).—Reduction of γ-iodopentane with zinc dust and a saturated solution of hydrogen iodido in acetic acid at 0° (bath) gives *n*-pentane, b. p. 36·3° (corr.)/758·8 mm., d_4^{20} 0·62783, n_D^{20} 1·35828 (cf. Philipov, A., 1916, i, 551). The density and refractive index are higher than the corresponding values for various specimens of *n*-pentane described in the literature [all of which have been obtained from natural sources (*e.g.*, petroleum)], indicating that these products contain small amounts of impuritics (*e.g.*, *iso*pentane). Comparisons of the molecular and specific refraction or dispersion alone are valueless, as all the samples show the same value. *n*-Heptane, prepared by similar reduction of δ-iodoheptane, has b. p. 98·0—98·2° (corr.)/762 mm., d_4^{20} 0·68480 1·38939 (cf. Tafel and Jürgens, A., 1909, i, 545). The refractivity data are similar to those for *n*-heptane prepared by other methods and obtained from natural sources. Reduction of heptaldehyde (Clemmensen, A., 1913, i, 733) gives impure *n*-heptane.

H. BURTON.

Polymerisation and ring formation. VII. *n*-Paraffins of high mol. wt. prepared by the action of sodium on decamethylene bromide. W. H. CAROTHERS, J. W. HILL, J. C. KIRBY, and R. A. JACOBSON (J. Amer. Chem. Soc., 1930, 52, 5279—5288; cf. Franke and Kienberger, A., 1913, i, 2).—Treatment of decamethylene bromide (0·25 mol.) with powdered sodium (1·52 atoms) in ether affords an ether-insoluble product, m. p. 85—100°, containing about 2% of bromine (removed by treatment with sodium in boiling butyl ether). The halogen-free product, m. p. 87—105°, is separated by fractionation in a molecular still and crystallisation into *n*-eicosane, *n*-triacontane, n-*tetracontane*, m. p. 80·5—81°, n-*pentacontane*, m. p. 91·9—92·3°, n-*hexacontane*, m. p. 98·5—99·3°, n-*heptacontane*, m. p. 105—105·5°, and a non-distillable residue, m. p. 110—114°, which probably contains higher members of the series. The physical properties of the new paraffins are discussed. A mechanism is suggested which involves reaction between the intermediate sodium derivatives and ether. Improved methods of preparation of decamethylene glycol and bromide are given.

H. BURTON.

Errors in analytical bromination. Thermal cleavage of hydrogen bromide from brominated substances. Procedure for determination of organic unsaturation. H. M. BUCKWALTER and E. C. WAGNER (J. Amer. Chem. Soc., 1930, 52, 5241—5254).—An apparatus is described for the bromination of compounds in carbon tetrachloride in absence of moisture at 0—75°; excess of bromine and the hydrogen bromide formed during the experiment are removed in dry nitrogen, absorbed in aqueous potassium iodide, and determined by the usual methods. Under favourable conditions of temperature, the method gives better results (for about 40 substances examined) than does that of McIlhiney (A., 1903, ii, 340); "negative" results (cf. McIlhiney, *loc. cit.*) are completely eliminated. The values obtained for various unsaturated substances are affected greatly by the reaction temperature. This is due to the elimination of hydrogen bromide from the additive compounds first formed (*e.g.*, from the bromides from retene, abietic acid, and phenanthrene); this can be obviated by regulating the temperature at which bromination is carried out.

H. BURTON.

Phosphoric acid. III. Use of phosphoric acid in the preparation of ethylene. A. G. WEBER and J. H. WALTON (J. Physical Chem., 1930, 34, 2693—2700; cf. A., 1930, 537).—In the preparation of ethylene from ethyl alcohol and phosphoric acid, the highest yields are obtained with syrupy phosphoric acid which has been heated for at least 4½ hrs. at 250°. The reaction is continuous at this temperature, giving a yield of 81% of ethylene so long as alcohol is added to the previously-heated acid. The yield decreases by 10—20% at 240° and at 260° is not markedly increased. The addition of metaphosphoric acid decreases the yield by about 15%, but that of the pyro-acid or of phosphoric oxide lowers it only temporarily. Copper oxide, anhydrous copper or aluminium sulphate, silver oxide or sulphate, iron oxide, and animal charcoal give a 10% increase, and ferric chloride, molybdenum or tungsten trioxide, nickel oxide, and silica gel a smaller increase, whilst normal sodium phosphate tends to decrease the normal yield. In each case the yield approaches a maximum and then decreases to a normal value and the yield of the first run of a series is always low owing to the formation of esters. Generally, the gas obtained contains less than 1% of impurity. The catalysts appear to render the intermediate complex of alcohol and acid less stable or to provide a slightly different "pivot" for the reaction.

L. S. THEOBALD.

Pyrolysis of propylene. C. D. Hurd and R. N. Meinert (J. Amer. Chem. Soc., 1930, **52**, 4978—4990).—Propylene decomposes to the extent of 60 and 72·5% when passed through pyrex-glass tubes at 650° and 700° with contact times of 120 and 50 sec., respectively. No decomposition occurs below 600°; at 900—950°/0·5 sec., 90—95% of the propylene is decomposed. The gaseous product consists mainly of hydrogen, methane, ethylene, and other gaseous paraffins (chiefly ethane); the total volume of gaseous products and the amounts of hydrogen and methane increase with rise in temperature and contact time. In pyrex (or quartz) tubes, 20—25% of the propylene used is converted into aromatic hydrocarbons (benzene, toluene, and probably small amounts of naphthalene and anthracene). The reaction in pyrex is predominantly homogeneous and unimolecular, and pyrolysis is of the same type as that of *iso*butylene (A., 1930, 58). Decomposition of a mixture (approximately 1 : 1) of propylene and hydrogen gives increased amounts of methane and ethylene; fission of the propylene molecule occurs.

Decomposition of propylene in monel metal tubes begins at 350° and is almost complete at 375°/30 sec. The reaction is autocatalytic and the products formed are carbon and hydrogen. H. Burton.

Isoprene and caoutchouc. XXXI. Polymerisation of *iso*butylene. H. Staudinger and M. Brunner (Helv. Chim. Acta, 1930, **13**, 1375—1379).—*iso*Butylene is polymerised by Florida earth (cf. Lebedev and others, A., 1925, i, 225; 1930, 316) first at −80° and then at 5°, and the mixture of products separated by distillation and subsequent extraction with alcohol into tri*iso*butylene, penta*iso*butylene, and a poly*iso*butylene, d_4^{17} 0·9007, n_D^{17} 1·5022. The poly*iso*butylene is purified by precipitation from an ethereal solution with alcohol; it is stable towards nitric acid and potassium permanganate but absorbs some bromine. Its physical properties are similar to those of a hemicolloidal hydrocaoutchouc. H. Burton.

Nitrosites and nitrosates. L. Monti (Gazzetta, 1930, **60**, 787—797).—That higher members of the olefine series form additive compounds when treated with nitrous fumes (from arsenious oxide and nitric acid) is shown by the preparation of the nitrosite, $C_8H_{16}O_3N_2$, in this way from di*iso*butylene and by determining the proportion of nitrogen peroxide absorbed by octylene, di*iso*butylene, and hexadecylene when left in contact with the gas; under the latter conditions, hexadecylene yields the compound $C_{16}H_{32}O_4N_2$. When heated in a current of an inert gas, amylene nitrosate and α- and β-styrene nitrosites yield nitrogen and nitric oxide, the total nitrogen thus evolved in the two forms constituting 40·5—41·8% of the nitrogen present in the original compound.

T. H. Pope.

Synthesis of $\Delta^{\alpha\delta}$-pentadiene. P. N. Kogerman (J. Amer. Chem. Soc., 1930, **52**, 5060—5065).—Magnesium is treated with a small amount of allyl bromide in presence of ether and iodine, and after reaction has begun, vinyl bromide (improved method of preparation given) is added. This mixture is treated gradually with allyl bromide; the reaction is carried out in a closed system under a pressure of 260—270 mm. The distillate from this is brominated, whereby *$\Delta^{\alpha\delta}$-pentadiene tetrabromide*, m. p. 85—86°, is obtained in 22% yield (on vinyl bromide used). $\Delta^{\alpha\delta}$-Pentadiene has b. p. 25·8—26·2°/756 mm., d_4^{20} 0·6594, n_D^{20} 1·3883, when regenerated from the tetrabromide by treatment with magnesium in ether containing a little iodine. The hydrocarbon is also formed when ethylene dibromide and allyl bromide are treated with magnesium. Treatment of magnesium allyl bromide with vinyl bromide gives no hydrocarbon. H. Burton.

Action of nitric acid on acetylene. III. A. Quilico and M. Freri (Gazzetta, 1930, **60**, 721—744; cf. A., 1930, 622).—The explosive compound $C_4H_2O_7N_6$ obtained by the action of fuming nitric acid on acetylene is reduced by stannous chloride as follows: $C_4H_2O_7N_6+7H_2 \longrightarrow C_4H_7O_3N_5+NH_2{\cdot}OH+3H_2O$, and the resulting *hydrochloride*, $C_4H_8O_3N_5Cl$, m. p. about 182° (decomp.), has been isolated. The hydrochloride gives a characteristic orange-yellow coloration with alkalis, which is due to the *compound* $C_4H_5O_2N_5$. The above-mentioned explosive compound decomposes when heated in glacial acetic acid as follows: $C_4H_2O_7N_6 \longrightarrow C_4H_2O_3N_4+N_2O_4$. The *compound* $C_4H_2O_3N_4$ has m. p. 108°.

O. J. Walker.

Hexa-ω-*tert*.-butylpropinylethane and acetylenic carbinols. I. L. Ozanne and C. S. Marvel (J. Amer. Chem. Soc., 1930, **52**, 5267—5272).—Magnesium *tert*.-butyl chloride and β-bromoallyl bromide give *β-bromo-δδ-dimethyl-Δ^{α}-pentene*, b. p. 135—138°, d_4^{20} 1·030, n_D^{20} 1·4630, converted by sodamide in high-boiling mineral oil into *δδ-dimethyl-Δ^{α}-pentinene*, b. p. 73—75°, d_4^{20} 0·7154, n_D^{20} 1·4028 [*mercury* derivative, m. p. 125—126·5° (corr.)]. Successive treatment of this with magnesium ethyl bromide and ethyl carbonate (cf. A., 1928, 988) affords *tri-ω-*tert.*-butylpropinylcarbinol*, b. p. 140—142°/0·7 mm., m. p. 50—51°, which with acetyl bromide and "molecular" silver in light petroleum yields *hexa-ω-*tert.*-butylpropinylethane*, m. p. 127·5—128·5°. This is unstable to oxygen, gives a red alkyl with liquid sodium-potassium alloy in ether, is not cleaved by 1% sodium amalgam, and is oxidised by ozone in carbon tetrachloride to ββ-dimethylbutyric acid (p-*bromophenacyl* ester, m. p. 81—81·5°).

Treatment of the reaction product from magnesium ethyl bromide and δδ-dimethyl-Δ^{α}-pentinene (ozonolysis product ββ-dimethylbutyric acid) with benzophenone gives *diphenyl-ω-*tert.*-butylpropinylcarbinol*, m. p. 55—56°, the *bromide* of which is converted by "molecular" silver into s-*tetraphenyldi-ω-*tert.*-butylpropinylethane*, m. p. 116—118°. *Phenyldi-ω-*tert.*-butylpropinylcarbinol*, b. p. 135—137°/0·4 mm., d_4^{20} 0·9325, n_D 1·5080; *diphenyl-ω-*cyclo*hexylpropinylcarbinol*, b. p. 165—166°/0·003 mm., d_4^{20} 1·058, n_D^{20} 1·5750, and *phenyldi-ω-*cyclo*hexylpropinylcarbinol*, b. p. 180—185°/0·017 mm., d_4^{20} 1·014, n_D^{20} 1·5390, are also described. H. Burton.

Preparation of allyl derivatives. R. Breckpot (Bull. Soc. chim. Belg., 1930, **39**, 462—469).—Allyl chloride is prepared in excellent yield by the action of a mixture of concentrated hydrochloric and sulphuric

acids on allyl alcohol in presence of a little cuprous chloride. Instead of allyl alcohol, allyl formate or the mixture of aqueous allyl alcohol and allyl formate obtained from glycerol and formic acid may be used. Δ^{β}-Butenonitrile may be prepared in good yield by the action of cuprous cyanide on allyl chloride, on a mixture of concentrated hydrochloric acid and allyl alcohol, or on a mixture of concentrated hydrochloric acid and allyl formate. J. D. A. JOHNSON.

Stereoisomeric pairs of chloro-*n*-butenes. L. NAVEZ (Bull. Soc. chim. Belg., 1930, **39**, 435—443).—The butenes prepared (*A*) by the action of concentrated sulphuric acid +5% of aluminium sulphate on *n*-butyl alcohol on treatment with chlorine give a mixture of dichlorobutanes of which 41% boils below 121°, whereas the mixture of butenes prepared (*B*) by the catalytic dehydration of *n*-butyl alcohol at 410—420° using alumina as catalyst gives a mixture of dichlorobutanes of which 90% boils below 121°. The mixture of dichlorobutanes is separated by fractional distillation into I, m. p. —80·4+0·1°, b. p. 115·9°, d_4^{15} 1·1147, n_D^{15} 1·4445; II. b. p. 119·5°, d_4^{15} 1·1183, n_D^{15} 1·4458; III, b. p. 124°, d_4^{15} 1·1224, n_D^{15} 1·4474. By the action of alcoholic potassium hydroxide (1·25 mols.) on each of these dichlorobutanes (1 mol.), chlorobutenes are obtained which are separated by fractional distillation of their azeotropic mixtures with alcohol. From III, azeotropes of alcohol with three chlorobutenes are obtained; III (*a*) b. p. 53·6—54°, 0·8945; III (*b*) b. p. 57·8—58·2°, d_4^{15} 0·8946: III (*c*) b. p. 61·2—61·6°, d_4^{15} 0·8912. The chlorobutenes corresponding have the following constants; (*a*) b. p. 58·4—58·6°, d^{15} 0·9107, $n_D^{14·1}$ 1·4166; (*b*) b. p. 63·4—63·6°, d_4^{15} 0·9153, n_D^{15} 1·4194; (*c*) b. p. 68—68·2°, d_4^{15} 0·9205, $n_D^{14·6}$ 1·4225. The azeotropes contain respectively 88·5%, 85·2%, and 79·8% of the corresponding chlorobutene. From I and II, the same azeotropes of two chlorobutenes are obtained; I or II (*d*) b. p. 56·8—57·2°, d_4^{15} 0·8960; I or II (*e*) b. p. 60—60·4°, d_4^{15} 0·8964. The chlorobutenes corresponding had the following constants: (*d*) b. p. 62·4—62·8°, d^{15} 0·9185, $n_D^{13·4}$ 1·4217; (*e*) b. p. 66·6—67°, d_4^{15} 0·9246, $n_D^{13·4}$ 1·4250. The azeotropes contain respectively 84·6% and 81·6% of the corresponding chlorobutene. Since III yields three chlorobutenes, whereas I and II yield two only (all five different), it is considered to be αβ-dichlorobutane, I and II being the *meso*- and *r*-forms of βγ-dichlorobutane, respectively. Method *A* is to be preferred to method *B*, therefore, for the preparation of Δ^{α}-butene from *n*-butyl alcohol. The rates of elimination of hydrogen chloride from (*d*) and (*e*) by means of alcoholic potassium hydroxide are held to show that (*d*) is *trans*-β-chloro-Δ^{β}-butene and (*e*) is the *cis*-form. For similar reasons (*b*) and (*c*) are considered to be the *cis*- and *trans*-forms of α-chloro-Δ^{α}-butene respectively, whilst (*a*), because of its volatility, is considered to be β-chloro-Δ^{α}-butene.

Geometrical inversion of these unsaturated substances under the influence of sunlight does not take place. J. D. A. JOHNSON.

Stereochemistry of organic compounds. II. patial arrangement of the atoms in the pentaerythritol molecule. L. ORTHNER and G. FREYSS (Annalen, 1930, **484**, 131—154).—The specific conductivity of boric acid is not increased by the *iso*propylidene or dimethyl ethers of pentaerythritol or by pentaerythritol dibenzoate. The difficult formation of the di*iso*propylidene ether from the *iso*propylidene ether and the inability of the above compounds to form complexes with boric acid are explained thus: after inactivation of two hydroxyl groups by substitution, the remaining hydroxyl groups become removed from one another in space, owing to their taking up a position of minimal potential energy. Pentaerythritol causes an increase in the conductivity of boric acid; this is ascribed to the formation of the complex

$$\left|(CH_2{\cdot}OH)_2C{<}{\begin{matrix}CH_2{\cdot}O\\CH_2{\cdot}O\end{matrix}}{>}B{<}{\begin{matrix}O{\cdot}CH_2\\O{\cdot}CH_2\end{matrix}}{>}C(CH_2{\cdot}OH)_2\right|H,$$

in which the free hydroxyl groups are arranged so that further reaction with boric acid is not possible. The above points are illustrated by models.

The sodium derivative of pentaerythritol *iso*propylidene ether (A., 1928, 270) and methyl iodide in xylene give *pentaerythritol* iso*propylidene methyl ether*, b. p. 129—130°/12 mm. (p-*nitrobenzoate*, m. p. 90°), hydrolysed by aqueous methyl-alcoholic sodium hydroxide to *pentaerythritol methyl ether*, m. p. 72°. Treatment of the *iso*propylidene ether with methyl sulphate and potassium hydroxide solution at 70—100° gives a mixture of *pentaerythritol dimethyl*, b. p. 139°/12 mm., m. p. 32° (*dibenzoate*, m. p. 70°), and *trimethyl ethers*, b. p. 103—104°/12 mm. (p-*nitrobenzoate*, m. p. 53—54°). *Pentaerythritol dibenzoate*, m. p. 75°, and *diacetate*, b. p. 159°/0·3 mm., are obtained from the corresponding iso*propylidene ethers*, m. p. 110° and 48—49°, respectively, by hydrolysis with dilute hydrochloric acid at the ordinary temperature. *Pentaerythritol tetrabenzoate* has m. p. 94°.

The dipole moments of pentaerythritol tetraacetate and di*iso*propylidene ether are 2·18±0·03×10^{-18} (cf. Ebert, A., 1928, 1308; Williams, *ibid.*, 1180) and 2·26±0·07×10^{-18} c.g.s. unit, respectively.

H. BURTON.

Automatic distillation of ether, alcohol, chloroform, etc. under reduced pressure. C. LAPP (J. Pharm. Chim., 1930, [viii], **12**, 498—502).—The liquid to be distilled is automatically drawn from a reservoir along a glass tube and through a three-way tap into the top of a fractionating column the side arm of which is connected to a condenser and the bottom to another, smaller condenser inclined at an angle of about 20° from the horizontal. This latter condenser, which is of the bulb type and contains pieces of nickel foil in each bulb, is heated to about 80° by means of water, which siphons through the jacket and through a glass spiral enclosing an ordinary 30 c.-p. electric lamp, the whole being insulated by cotton wool. The solvent is volatilised during its passage through this condenser and the vapours pass up the fractionating column, thereby scrubbing the incoming liquid from the receiver, and are condensed and pass into the receiver, which is connected to the vacuum pump. The heavier, unvaporised fractions pass through the heating condenser into a second receiver. The most satisfactory temperature for the distillation of the three above-mentioned solvents is

10—20°, using water at a correspondingly low temperature in the condenser. E. H. SHARPLES.

Catalytic decomposition of gaseous ethers. P. A. K. CLUSIUS (J.C.S., 1930, 2607—2615; cf. A., 1929, 1148).—Methyl ethyl ether is decomposed at 460—550° according to the equations: $Me·O·Et \longrightarrow CH_4 + Me·CHO$, $Me·CHO \longrightarrow CH_4 + CO$, the heat of activation of the former, which has only 1/45th of the velocity of the latter, being 38,000 g.-cal. per mol. The reaction is homogeneous in the presence of iodine vapour (derived from thermal decomposition of *iso*propyl iodide) as catalyst, the velocity being proportional to the partial pressure of iodine, but independent of the initial pressure of ether. The decomposition of methyl *iso*propyl ether at 450—520° is in accordance with the simultaneous reactions: $Me·O·Pr$—— $COMe_2$, and $Me·O·Pr \longrightarrow CH_2O + C_3H_8 \longrightarrow CO + H_2 + C_3H_8$, the heat of activation being 29,500 g.-cal. per mol. for the net reaction, which is homogeneous and independent of the original pressure of ether. Methyl *tert.*-butyl ether is stable at 420°, but is immediately decomposed in presence of iodine to a complex mixture containing unsaturated hydrocarbons but free from aldehydes and ketones. Iodine is without catalytic effect on the thermal decomposition of dimethyl ether. H. A. PIGGOTT.

Preparation of the pure isomerides of amyl nitrite. S. D. WILSON and E. F. YANG (Chinese J. Physiol., 1930, 4, 391—392).—The following isomerides were prepared from the appropriate amyl alcohol, sodium nitrite, and sulphuric acid: *n*-amyl nitrite, b. p. 51·5—52·1°/132 mm., $d^{19·5}$ 0·8817, $n^{16·8}$ 1·3902; *iso*amyl nitrite, b. p. 98·2—99·2°/760 mm., 0·8828, $n^{16·8}$ 1·3909; *sec.*-amyl nitrite, b. p. 96·0—96·5°/760 mm., 0·8626, $n^{16·8}$ 1·3864; *tert.*-amyl nitrite, b. p. 62·0—63·0°/345 mm., $d^{19·5}$ 0·8758, $n^{16·8}$ 1·3904. W. O. KERMACK.

Interaction of ammonium sulphite with certain polybromoparaffins. W. J. POPE and F. B. KIPPING (J.C.S., 1930, 2591—2594).—Interaction of αβγδ-tetrabromo-βγ-dimethylbutane with boiling aqueous ammonium sulphite, followed by successive treatment with barium hydroxide and silver oxide, gives the *barium* salt ($+1H_2O$) of a βγ-dimethylbutenedisulphonic acid (*ammonium* and *sodium* salts; *pyridine* salt, m. p. 215—216°; *chloride*, m. p. 125—126°). βγ-Dibromobutane similarly treated gives two isomeric β-hydroxybutane-γ-sulphonic acids, the brucine salts of which may be separated by repeated crystallisation from 90% alcohol [(A), *brucine* salt, m. p. 270°, $[\alpha]^{20}_{5461}$ −23·9° in water; *barium* salt, $[\alpha]^{20}_{5461}$ −5·4° in water; l-*menthylamine* salt, m. p. 196°. (B), *brucine* salt, m. p. 180—185°, $[\alpha]^{20}_{5461}$ −29·6° in water; *barium* salt, optically inactive].

H. A. PIGGOTT.

Addition of alkali alkoxides to esters. IV. Addition of sodium ethoxide to formic esters. F. ADICKES [with O. LUCKER, A. WACHTEROWITZ, and H. DU MONT] (Ber., 1930, 63, [*B*], 3012—3027).—The author's supposition (A., 1927, 228) that the product obtained by the action of ethyl formate on sodium ethoxide according to Scheibler's first method (A., 1926, 711) has the homogeneous composition $CH(OEt)_2·ONa$ cannot be maintained, although the substance is present to some extent. Contrary to Scheibler, a large proportion of the ester is decomposed into alcohol and carbon monoxide and another portion does not react with the ethoxide. The product consists mainly of sodium ethoxide with more or less alcohol of crystallisation (about 30%), some sodium formate (about 8%), and generally only about 10—20% of the additive compound $CH(OEt)_2·ONa$. Scheibler's second method of preparation in which the product is heated to 40° (A., 1927, 338) involves the more rapid decomposition of ethyl formate, which occurs slowly at the ordinary temperature (Scheibler's "vigorous reaction"). The final product is not sodiumoxyethoxymethylene, but mainly sodium ethoxide more or less free from alcohol of crystallisation according to the duration of heating. In the products obtained by both methods the presence of formic acid is shown quantitatively by titration and by reduction of mercuric chloride. It exists partly as sodium formate (due to incomplete removal of water from the alcohol used) and partly as ethyl formate, which is liberated as such when the ethereal suspension of the product is treated with carbon dioxide. Presumably it is contained as the compound $CH(OEt)_2·ONa$, since sodiumoxyethoxymethylene could not regenerate the ester under these conditions. Homogeneous sodiumoxyethoxymethylene or sodiumoxydiethoxymethane cannot be present in the product obtained by either method; in the first product the last-named substance may occur to the extent of 25%, but not at all in the second. There is no possibility of the existence of sodiumoxyethoxymethylene with the properties recorded by Scheibler, since in no case is evolution of carbon monoxide observed on decomposition with water, and the ester is completely accounted for partly as carbon monoxide evolved during the reaction, partly as sodium formate and regenerated ester. The production of diethoxymethylene from the additive compound according to Scheibler is readily possible on theoretical grounds. The additive compound of ethyl formate (1 mol.) and sodium ethoxide (1 mol.) is easily prepared from the components in ethereal suspension at 0°. It is very hygroscopic and readily decomposed at the ordinary temperature with formation of carbon monoxide. It is not possible to prepare derivatives of ethyl orthoformate from it by means of ethyl chloroformate or benzyl bromide, so that its constitution (as sodiumoxydiethoxymethane) cannot be established directly. When its ethereal suspension is treated with ethyl oxalate, ethyl formate is liberated.

It is certain that sodiumoxyethoxymethylene with the properties indicated by Scheibler cannot be prepared by either of his methods, whereas the production of a differing sodiumoxyethoxymethylene in small amount at the ordinary temperature is not completely negative, although rendered very improbable. H. WREN.

Preparation of ethyl Δ^{ι}-elaidate by partial reduction of ethyl $\Delta^{\theta\kappa}$-linoleate, and the corresponding acid as member of the elaidic acid series. J. BOESEKEN and R. HOEVERS (Rec. trav. chim., 1930, 49, 1161—1164).—Ethyl $\Delta^{\theta\kappa}$-linoleate when catalytically partly hydrogenated gives

ethyl Δ'-elaidate, the position of the double linking acid being proved by ozonolysis. The m. p. of the (42°) is considered to show that the acid has the elaidic acid configuration. J. D. A. JOHNSON.

Polymerisation of the methyl esters of higher unsaturated fatty acids. V. Esters with one 4-carbon ring. K. KINO (J. Soc. Chem. Ind. Japan, 1930, **33**, 444—445B; cf. A., 1930, 577, 741, 1272).—The polymerisation of the methyl esters of the highly unsaturated acids (clupanodonic acid, *loc. cit.*) has been repeated, the products being purified by vacuum distillation; a product having $d_4^{40.5}$ 0·9192, $n_D^{40.5}$ 1·4820 and corresponding almost to $C_{22}H_{33}O_2Me$ was separated, and on hydrogenation yielded a solid fatty acid (lead salt–alcohol separation), m. p. 79—79·3°, probably identical with the acid (m. p. 78—78·2°) obtained previously. The earlier conclusions appear to be confirmed. E. LEWKOWITSCH.

Photochemical oxidation of lactic acid. G. R. BURNS (J. Amer. Chem. Soc., 1930, **52**, 5272—5278; cf. A., 1929, 1424).—Aqueous solutions of lactic acid containing dissolved oxygen are decomposed by radiations of less than 2890 Å. The main products of the decomposition are carbon dioxide, acetic acid (75%; the percentages are based on the amount of carbon dioxide evolved), a peroxide (32%), and acetaldehyde (28%); small amounts of formaldehyde and carbon monoxide, but no alcohol or pyruvic acid, are formed. The quantum yield is several times that of the decomposition in absence of oxygen (cf. *loc. cit.*). H. BURTON.

Hydrogenation of ethyl acetoacetate and its derivatives over nickel. H. ADKINS, R. CONNOR, and H. CRAMER (J. Amer. Chem. Soc., 1930, **52**, 5192—5198).—Ethyl acetoacetate is reduced by the method previously described (this vol., 47) in absence of solvent at 100—150° to a mixture of 2 parts of ethyl β-hydroxybutyrate (I) and 1 part of *ethyl β-(β'-hydroxybutyryloxy)butyrate* (II), $OH{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2Et$, b. p. 154—156°/15 mm., d_{25}^{25} 1·0678, n_D^{25} 1·4360, together with small amounts of alcohol and dehydroacetic acid. When the reduction is carried out in presence of alcohol, I is the sole product; in presence of ether, methyl*cyclo*hexane, or ethyl β-hydroxybutyrate, mixtures of approximately 2 parts of I and 1 part of II are formed, whilst in *n*-butyl alcohol a mixture of 66% of I and 34% of *n*-butyl β-hydroxybutyrate results. The formation of II supports the mechanism postulated by Arndt and Nachtwey (A., 1924, i, 1223) for the production of dehydroacetic acid from ethyl acetoacetate. Ethyl α-methylacetoacetate is reduced to a mixture of ethyl β-hydroxy-α-methylbutyrate and *ethyl β-(β'-hydroxy-α'-methylbutyroxy)-α-methylbutyrate*, b. p. 155—158°/17 mm., d_{25}^{25} 1·0332, n_D^{25} 1·4393, whilst ethyl αα-dimethyl- and α-methyl-α-ethyl-acetoacetates furnish quantitative yields of the corresponding hydroxybutyrates both in absence and presence of solvent. Reduction of dehydroacetic acid in presence of methyl*cyclo*hexane at 185—190°/about 300 atm. gives 40—45% of dipropyl ketone, together with small amounts of alcohol and acetone. Alcoholysis of dehydroacetic acid to ethyl acetoacetate occurs at 190°.

The *α-naphthylcarbimide* derivative of dipropylcarbinol has m. p. 79—80°. H. BURTON.

Decomposition of ethyl *n*-butylacetoacetate to hexoic acid and methyl *n*-amyl ketone. N. L. DRAKE and R. W. RIEMENSCHNEIDER (J. Amer. Chem. Soc., 1930, **52**, 5005—5008).—Optimum yields (about 60%) of hexoic acid are obtained when ethyl *n*-butylacetoacetate is decomposed with 59·5% potassium hydroxide solution (8 mols. of hydroxide) at 75—110°. The best yield of ketone is obtained with approximately 17% alkali at 105° (bath). H. BURTON.

Lævulic acid and its esters. P. P. T. SAH and S. MA (J. Amer. Chem. Soc., 1930, **52**, 4880—4883).—When commercial dextrose (500 g.) is heated with diluted (1 : 1) hydrochloric acid for 24 hrs. (after a preliminary, short treatment and removal of humin substances), lævulic acid is obtained in yields of about 75 g. The following esters of lævulic acid were prepared: methyl, b. p. 191—193°, d_4^{20} 1·05113, n_D^{20} 1·4231 (*semicarbazone*, m. p. 142—143°; *phenylhydrazone*, m. p. 94—96°); ethyl, b. p. 199—201°, d_4^{20} 1·01336, n_D^{20} 1·4225; *n*-propyl, b. p. 214—216°, d_4^{20} 0·98988, n_D^{20} 1·4255 (*semicarbazone*, m. p. 129—130°; *phenylhydrazone*, m. p. 88—90°); iso*propyl*, b. p. 203—205°, d_4^{20} 0·98422, n_D^{20} 1·4220 (*semicarbazone*, m. p. 141—142°; *phenylhydrazone*, m. p. 108—109°); n-*butyl*, b. p. 229—231°, d_4^{20} 0·97452, n_D^{20} 1·4290 (*semicarbazone*, m. p. 102—103°; *phenylhydrazone*, m. p. 79—81°); iso*butyl*, b. p. 222—224°, d_4^{20} 0·97047, n_D^{20} 1·4264 (*semicarbazone*, m. p. 112—113°; *phenylhydrazone*, m. p. 84—86°); iso*amyl*, b. p. 238—240°, d_4^{20} 0·95921, n_D^{20} 1·4310 (*semicarbazone*, m. p. 91—92°; *phenylhydrazone*, m. p. 70—72°). H. BURTON.

Reactivity of atoms and groups in organic compounds. XI. Influence of structure of the substituent on the temperature of decomposition of derivatives of malonic acid. J. F. NORRIS and R. C. YOUNG (J. Amer. Chem. Soc., 1930, **52**, 5066—5069).—The decomposition temperatures of the following acids, determined by a method similar to that previously described (A., 1930, 470), are given in parentheses: malonic, m. p. 129—131° (128°); methylmalonic, m. p. 120—122° (120°); ethylmalonic, m. p. 110—111·5° (110°); *n*-propylmalonic, m. p. 94—96° (99°); *n*-butylmalonic, m. p. 99·5—101·5° (108°); *iso*propylmalonic, m. p. 85—87° (90°). The influence of the alkyl group (R) on the decomposition temperature is the same as that found for the triphenylmethyl alkyl ethers, $CPh_3{\cdot}OR$ (*loc. cit.*). The decomposition temperatures in both series fall in the same order as the velocity coefficients for the reactions between *p*-nitrobenzoyl chloride and the alcohols R·OH (A., 1925, i, 626; 1927, 1166). H. BURTON.

Ether-like compounds. III. Polyether-acids of the type $OR{\cdot}[CH_2{\cdot}CH_2{\cdot}O]_n{\cdot}CH_2{\cdot}CO_2H$. M. H. PALOMAA and T. A. SIITONEN (Ber., 1930, **63**, [*B*], 3117—3120).—The action of chloroacetic acid on the sodium derivative of ethylene glycol monomethyl ether affords *β-methoxyethoxyacetic acid*, $OMe{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CO_2H$, b. p. 121—122°/4 mm., d_4^{20} 1·1634, n_D^{20} 1·43375, in 80% yield; the *ethyl* ester has b. p. 90°/10 mm., d_4^{20} 1·0369, n_D^{20} 1·41908. *β-Ethoxyethoxyacetic acid*, b. p. 125—126°/4 mm., d_4^{20} 1·1103,

n_D 1·43572, and β-n-*propoxyethoxyacetic acid*, b. p. 131°/4 mm., d_4^{20} 1·07415, 1·43652, are described. *n*-Butyl glycol, b. p. 50°/4 mm., d_4^{20} 0·9015, n_D^{20} 1·41980, is transformed into β-n-*butoxyethoxyacetic acid*, b. p. 141°/5 mm., d_4^{20} 1·04635, n_D^{20} 1·43823. β-*Methoxyethylglycol*, b. p. 65°/4 mm., d_4^{20} 1·02695, n_D^{20} 1·42686, yields -*methoxyethoxyethoxyacetic acid*, b. p. 155—156°/4 mm., d_4^{20} 1·1492, n_D^{20} 1·44575. H. WREN.

Additive heteropolymerisation. T. WAGNER-JAUREGG (Ber., 1930, **63**, [*B*], 3213—3224).—The term "homopolymerisation" is applied to the union of several similar molecules, whereas the union of different molecules to a large molecule is designated "additive heteropolymerisation." It is proposed to discriminate between true and false polymerisation according as the process is or is not accompanied by atomic displacement and to apply the term "condensation polymerisation" to processes involving the elimination of water, ammonia, etc.

Additive heteropolymerisation of two ethylenic compounds, one of which is maleic anhydride, has been investigated. Maleic anhydride and stilbene in boiling xylene afford in 45—70% yield an amorphous white, infusible substance, insoluble in most organic media, but sometimes yielding colloidal solutions after swelling, for example, in camphor. Direct determination of mol. wt. is impossible, but the more soluble polymeric homologues dissolved from the product by boiling xylene have mean mol. wt. about 4200 in molten camphor. Dry distillation in absence or presence of barium oxide yields stilbene. The ratio of the components in the polymeride is 1 : 1 when a mixture of hydrocarbon and anhydride in the ratio 2 : 1 is used, falling to 0·95 : 1 (stilbene to anhydride) when the composition of the original mixture is 1 mol. of hydrocarbon to 2 mols. of anhydride. The product has therefore the composition $-\left[\mathrm{CHPh{\cdot}CHPh{\cdot}CH}<\begin{matrix}\mathrm{C\quad CO}\\ \mathrm{CO{-}O}\end{matrix}\right]-$, in conformity with which it does not absorb bromine in boiling *s*-tetrachloroethane. The polymerisation resembles that of acrylic acid, since a little less highly polymerised material is formed in addition to the main polymerisate, whilst the remainder of the initial material remains unchanged. Non-occurrence of polymerisation in boiling benzene or toluene is explicable, since the molecules do not possess the necessary activating energy, but a specific influence of the solvent is involved, since poor yields are obtained in boiling *s*-tetrachloroethane or in a molten mixture of the components at the temperature of boiling xylene. Conversely, benzylidenefluorene and maleic anhydride at about 130°, but not in boiling xylene, yield a white, amorphous *heteropolymeride* which separates from the molten mixture and appears unaccompanied by less complex products. The molecular ratio of hydrocarbon to anhydride is exactly 1 : 1 when that in the initial mixture is 2 : 1, and passes to 0·9 : 1 when the initial ratio is 1 : 2; the tendency towards excess of anhydride is again obvious. Anisylidenefluorene at 130° gives a similar *heteropolymeride*. αδ-Diphenyl-Δ^{α}-butene gives a mixture of products of differing degree of polymerisation and not excessive mol. wt. in which the ratio of the components is displaced in favour of the anhydride. Bromostilbene, tetraphenylethylene, and αδ-diphenyl-Δ^{β}-butene do not react with maleic anhydride, thus indicating a profound influence of substitution; steric influences also operate, since *cis*-stilbene gives a heteropolymerisate only in very poor yield. *as*-Diphenylethylene and maleic anhydride afford the *compound*, $C_{22}H_{16}O_6$, m. p. 279—281° (corr., decomp.), *M*—376. Stilbene does not condense with succinic anhydride, whereas dibenzyl and maleic anhydride yield a *heteropolymeride* (1 : 1) in very poor yield. Amylene and styrene give viscous, gum-like products with maleic anhydride. Certain substances containing the >C:N· group appear to give heteropolymerides with maleic anhydride. Thus fluorenoneimine in benzene or benzylidene- or cinnamylidene-azine in toluene or xylene afford yellow or brown amorphous products. In addition to the amorphous products, benzylideneazine and maleic anhydride yield a crystalline additive *substance*, $C_{22}H_{16}O_6N_2$, m. p. 243—244° (corr.), whilst methyl maleate yields the *product* $C_{26}H_{28}O_8N_2$, m. p. 232—234° (corr.). H. WREN.

Action of maleic anhydride on $\Delta^{\theta\kappa}$-linoleic acid (m. p. 53°) and its ethyl ester. Products of dehydration of ricinoleic acid. J. BOESEKEN and R. HOEVERS (Rec. trav. chim., 1930, **49**, 1165—1168).—Linoleic acid and its ethyl ester combine normally with maleic anhydride to give exclusively *substances* of m. p. 88° and 60°, respectively. The substance, m. p. 88°, is also formed when the product of the reaction between maleic acid and linoleic acid is heated with acetic anhydride. By means of this reaction, the product of the dehydration of ricinoleic acid is shown to contain about 75% of linoleic acid, 15% of $\Delta^{\theta\lambda}$-linoleic acid, and a small quantity of an aldehydic substance.

J. D. A. JOHNSON.

Polymorphism of the saturated dibasic fatty acids as a function of temperature. F. D. LA TOUR (Compt. rend., 1930, **191**, 1348—1350).—Two forms, α and β, of succinic acid exist, the unstable β-*form* being transformed into the α-form at 137°. The spatial arrangement of the carboxyl groups probably corresponds with *cis*- and *trans*-forms.

P. G. MARSHALL.

Highly-polymerised compounds. XLVII. Morphology of substances of high mol. wt. II. Polyoxymethylenes precipitated from solution. H. W. KOHLSCHUTTER (Annalen, 1930, **484**, 155—178).—Polyoxymethylenes (α-, β-, β+γ-; for nomenclature, see Staudinger and others, A., 1930, 579) have been precipitated under various conditions and the genesis and development of the crystals determined; photomicrographs are given. Addition of 1 vol. of sulphuric acid to 1 vol. of an aqueous solution of paraformaldehyde (d^{19} 1·086) gives two types of crystals: (*a*) hexagonal laminæ showing a normal growth, (*b*) round disc-shaped crystals completely penetrated by the mother-liquor (which are not observed until they are fully formed). With 0·7 vol. of acid, the precipitated material consists of prisms (isometric habit) which when treated with 0·1*N*-sodium hydroxide solution, are attacked in the centre of the prism zones. β-Polyoxymethylene, precipitated very

rapidly by 0·4 vol. of acid, consists of granular masses to which are attached sphærolith-like structures; freshly-prepared material is attacked rapidly by 0·1*N*-alkali, but old preparations are attacked only slowly. The polyoxymethylene precipitated by 0·1 vol. of acid can be completely freed from sulphuric acid. Increase in the amount of acid used causes a rise in the velocity of aggregation and the formation of larger crystals. These crystals contain sulphuric acid in the "inner" surfaces; crystallisation begins by the formation of a film of material over a gel-drop, which subsequently grows into a plastic primary part. Two of these parts join to give a prismatic crystal, the centre of which is the weakest part. The crystals shrink on keeping and sulphuric acid can be washed out. There are morphologically continuous transitions between the α-, β-, and $\beta+\gamma$-polyoxymethylenes.

Precipitation of polyoxymethylene from formaldehyde solutions containing methyl alcohol gives preparations which are alkali-stable; this behaviour is ascribed to the formation of polyoxymethylene dimethyl ether. H. BURTON.

Replacement of halogen by hydrogen in α-halogenoketones under the influence of the Grignard reagent. C. H. FISHER, T. S. OAKWOOD, and R. C. FUSON (J. Amer. Chem. Soc., 1930, **52**, 5036—5040).—α-Bromo*iso*butyryl bromide reacts with mesitylene in presence of carbon disulphide and aluminium chloride, forming *α-bromo*iso*butyrylmesitylene*, m. p. 27° (*dinitro*-derivative, m. p. 117·5—118·5°); the *dibromo*-derivative, m. p. 106—107° (corr.), of this is also formed by bromination of *iso*butyrylmesitylene with ice-cold bromine water. Reduction of 4 : 6 - dibromo - 2-α - bromo*iso*butyrylmesitylene with zinc dust and acetic acid gives 4 : 6-*dibromo*-2-*iso*butyrylmesitylene*, m. p. 69—70°, also obtained when the tribromo-compound is treated with magnesium methyl chloride or ethyl bromide and the products are decomposed with dilute hydrochloric acid. The following changes occur during the treatment with the Grignard reagents (cf. Lowenbein and Schuster, A., 1930, 1184): $\cdot CO\cdot CBrMe_2 \longrightarrow \cdot C(OMgBr){:}CMe_2 \longrightarrow \cdot CO\cdot CHMe_2$. H. BURTON.

Dioximes. LXVIII. I. DE PAOLINI (Gazzetta, 1930, **60**, 700—704; cf. A., 1930, 226).—By the action of bromine on the dihydroxytrioxime, $OH\cdot[C{:}N\cdot OH]_3\cdot OH$, on hydroxyglyoximecarboxylic acid, on oximinomalonic acid, and on oximinoacetic acid the *oxime of carbonyl bromide*, $CBr_2{:}N\cdot OH$, m. p. 70—71° (vac.), is obtained due to reaction of bromine with oximinoacetic acid. This oxime represents the most easily obtained derivative of the simpler derivatives of fulminic acid, from which it has also been prepared by the reaction $C{:}N\cdot OH+Br_2 \longrightarrow CBr_2{:}N\cdot OH$, thus confirming its structure. By the action of mercuric nitrate it forms dibromoglyoxime peroxide, $Br(C_2N_2O_2)Br$, or dibromofuroxan, $Br[(C_2N_2O)O]Br$. O. J. WALKER.

Degradations in the sugar group. V. DEULOFEU (J.C.S., 1930, 2602—2607; cf. A., 1929, 427).—Tetra-acetylarabonitrile, m. p. 118°, from *d*-arabinoseoxime, sodium acetate, and acetic anhydride, gave with ammoniacal silver oxide *d*-erythrosediacetamide, m. p. 210°, hydrolysed by 60% sulphuric acid to erythrose, and with less ammonia triacetylerythrose, m. p. 133°. Degradation of the nitrile by sodium methoxide, or sulphuric acid followed by treatment with barium hydroxide and silver carbonate, gave only traces of erythrose. Similar results were obtained with tetra-acetylxylononitrile from *d*-xylose, and the syrup resulting from degradation with sodium methoxide gave tartaric acid on oxidation with nitric acid. *l*-Rhamnonamide (from the lactone and ammonia) gave methylerythrose with hypochlorite and alkali. Degradation of tetra-acetylrhamnononitrile with sodium methoxide or sulphuric acid gave methylerythrose in poor yield, but application of these methods to penta-acetylgalactonitrile gave 30% and 22%, respectively, of the theoretical yields of β-lyxose. Penta-acetylmannononitrile, prepared from *d*-mannoseoxime, gave *d*-arabinosediacetamide with silver oxide and ammonia, and arabinose by degradation with sodium methoxide or sulphuric acid in yields of 33%, 61%, and 56%, respectively. Arabinose was also obtained by oxidation of calcium mannonate with hydrogen peroxide and "colloidal" ferric acetate. H. A. PIGGOTT.

Titration of aldose sugars with standard iodine and alkali. G. M. KLINE and S. F. ACREE (Bur. Stand. J. Res., 1930, **5**, 1063—1084; cf. A., 1930, 1560).—In the titration of aldose sugars with iodine and alkali it is necessary to avoid both oxidation beyond the monobasic acid stage ("over-oxidation") and the exhaustion of the iodine in the formation of iodate before the completion of the oxidation. With the procedure recommended (*loc. cit.*) the iodate content becomes significant only after the completion of the reaction, and over-oxidation is absent unless large excess of reagents is employed.

Sucrose and lævulose are slightly attacked by large excess of reagents; iodine and sodium hydroxide are used up in the ratio of 4 : 5, indicating the oxidation of a primary alcoholic to a carboxyl group. With the oxidation of an aldose sugar the ratio is 2 : 3, and it is suggested that this reaction may be used to titrate iodine against standard alkali, with an error of 0·2%. The reaction is complete at p_H 9—10.

T. H. MORTON.

Cupro-potassium carbonate solution in the determination of reducing sugars. H. A. SCHUETTE and J. N. TERRILL (J. Amer. Chem. Soc., 1930, **52**, 4960—4964).—The dextrose–copper equivalents of the cupro-potassium carbonate solutions of Ost and Nyns have been determined at 48·9° (reduction time 150 min.) by the method of Zerban and Sattler (A., 1930, 1165); the results are presented as mathematical expressions. The solution used by Beyersdorfer (B., 1920, 126) (containing 0·8 mg. Cu per c.c.) is also reduced by dextrose; the solution cannot be regarded as being selective for lævulose. Mathematical expressions are also derived for calculating the lævulose–copper equivalents of a reagent (Beyersdorfer's) containing 4·03 mg. Cu per c.c., using three sets of reduction conditions. H. BURTON.

Transformation reactions in the carbohydrate group. IV. Kinetics of the transformation of 3-acetyl*iso*propylideneglucose. K. JOSEPHSON.

(Ber., 1930, 63, [B], 3089—3102; cf. A., 1929, 912).—Re-examination of the change of specific rotation with time of solutions of 3-acetyl*iso*propylideneglucose (p_H 7·19) at 20±0·02° shows that the reaction constant calculated for a unimolecular change exhibits a decided progressive variation, probably due to the formation of an intermediate product of unknown optical activity. For purposes of comparison, Schmid's method (A., 1926, 480) of calculating the mean reaction coefficient is adopted. Variation of the hydroxyl-ion concentration shows a proportionality between the rate of acyl migration and concentration of hydroxyl ion over a considerable range of acidity. The temperature coefficients of the change are smaller than those generally observed in cases of catalysis by hydroxyl ions, whereas for similar hydrogen-ion concentrations the temperature coefficients are much greater owing to the marked change of the ionic products of water with temperature. H. WREN.

Structure of carbohydrates and their optical rotatory power. W. N. HAWORTH and E. L. HIRST. **I. Introduction. II. 4-Glucosido-α-mannose and derivatives.** [With H. R. L. STREIGHT, H. A. THOMAS, and J. I. WEBB.] **III. 4-Galactosido-α-mannose and derivatives.** [With (MISS) M. M. T. PLANT and R. J. W. REYNOLDS.] **IV. Derivatives of α- and β-methylmannopyranoside.** [With H. G. BOTT and (in part) R. S. TIPSON.] **V. Optical rotatory powers of methylated lactones derived from simple sugars.** [With J. A. B. SMITH] (J.C.S., 1930, 2615—2635, 2636—2644, 2644—2653, 2653—2659, 2659—2663).—I. Polemical. The claim of Hudson (A., 1930, 747) to classify sugars on a basis of optical rotation leads to many inconsistencies and necessitates the postulation of structures at variance with the bulk of experimental evidence. The rotations of a number of derivatives of 4-glucosido- and 4-galactosido-α-mannose do not agree with those calculated by Hudson on the basis of a hypothetical mannose of $[\alpha]_D$ +77°, but conform to ordinary mannose (+30°) as unit. Further experimental evidence indicates that rotation may vary considerably and irregularly according to the solvent where a choice of solvent is possible, *e.g.*, with the fully-methylated lactones derived from monoses. Conclusive proof of the pyranoside structure of the mannoside residue in 4-glucosido- and 4-galactosido-α-methylmannoside and the absence of the hypothetical form is afforded by their hydrolysis by emulsin to α-methylmannopyranoside, $[\alpha]_D$ +79°, a method already tacitly approved by Hudson as a test of structure.

II. The action of perbenzoic acid on carefully-dried cellobial in methyl-alcoholic ethyl acetate gives 4-*glucosido-α-methylmannoside*, m. p. 227—228°, $[\alpha]_D^{17}$ +46° in water (*hepta-acetyl* derivative, m. p. 184°, $[\alpha]_D$ +30° in chloroform, +36° in acetone, +21·5° in benzene), hydrolysed by emulsin to dextrose and α-methylmannopyranoside, $[\alpha]_D$ +79°, the identity of which is confirmed by mixed-m. p. determinations and conversion into acetyl derivative. The pyranoside structure of the glucoside is confirmed by the slow rate of hydrolysis by 0·01*N*-hydrochloric acid. 4-Glucosido-α-methylmannoside is also obtained by interaction of hepta-acetyl-4-glucosido-α-mannosidyl bromide with methyl alcohol in presence of silver carbonate or pyridine. The rate of mutarotation of 4-glucosido-α-mannose, $[\alpha]_D^{18}$ +20° ⟶ +12·5° in water, is comparable with, but rather slower than, that of mannose. 4-Glucosido-β-mannose has $[\alpha]_D^{18}$ −1° determined indirectly (cf. Hudson and Yanovsky, A., 1917, i, 445).

If during the reduction of hepta-acetylcellobiosidyl bromide (cf. Zemplén, A., 1928, 741) the temperature rises to 30—35°, *hexa-acetyl-2-deoxycellobiose*, m. p. 196°, $[\alpha]_D^{20}$ +15° in chloroform, is formed.

III. Oxidation of lactal (cf. Bergmann, A., 1924, i, 265; slight modifications of the preparation described) with perbenzoic acid in methyl alcohol and ether in the cold gives 4-*galactosido-α-methylmannoside*, m. p. 207°, $[\alpha]_D^{19}$ +66° in water (*hepta-acetyl* compound, $[\alpha]_D$ +36° in chloroform, +19° in benzene), hydrolysed by emulsin to galactose and α-methylmannopyranoside, $[\alpha]_D^{17}$ +79·2° in water (identified as above). Neither α-methylmanno-pyranoside nor -furanoside is altered by emulsin under identical conditions. Confirmation of the pyranose structure of the glucoside is afforded by its slow hydrolysis at the biose linking only by 0·01*N*-hydrochloric acid. The action of perbenzoic acid on aqueous lactal (cf. Bergmann, *loc. cit.*) gives 4-*galactosido-α-mannose* (+$1H_2O$), m. p. 150—160° (indefinite), $[\alpha]_D^{20}$ +38°⟶+27° in water, the rate of mutarotation being comparable with that of mannose. 4-Galactosido-β-mannose (*loc. cit.*) has $[\alpha]_D$ +16° in 76% alcohol, calculated by Hudson and Yanowsky's method. Details are given for the separation of α-methylmanno-pyranoside or -furanoside from galactose by precipitation of the last in aqueous solution with lead acetate and ammonia. The yields of recovered mannosides are 30% and 40%, respectively.

IV. When heated with 2% methyl-alcoholic hydrogen chloride, mannose gives a mixture of α- and β-methylmannosides (cf. Hudson, *loc. cit.*); the latter may be separated and characterised as its tetra-acetyl derivative which regenerates β-methylmannopyranoside when treated with 0·5*N*-aqueous alkali or dimethylamine and methyl alcohol. β-Methylmannoside is very slowly hydrolysed by 0·01*N*- or even 0·1*N*-hydrochloric acid at 100°; methylation of it or its acetyl derivative with methyl sulphate and alkali, followed by methyl iodide and silver oxide, gives *tetramethyl-β-methylmannopyranoside*, b. p. 110—112°/0·1 mm., m. p. 36—37°, 1·4531 (supercooled liquid), $[\alpha]_D$ −80° in water, −79° in methyl alcohol, −87° in chloroform, −72° in benzene, −82° in ethyl alcohol, equilibrium value +60° in 1% methyl-alcoholic hydrogen chloride, hydrolysed by 6% hydrochloric acid to tetramethylmannopyranose, identified as anilide and by conversion into 2 : 3 : 4 : 6-tetramethyl-δ-mannonolactone (cf. A., 1927, 750). Methylation of mannose by methyl sulphate and alkali, followed by methyl iodide and silver oxide, gives a mixture of tetramethyl-α- and -β-methylmannopyranosides, containing about 32% of the latter, and free from furanose derivatives as indicated by resistance to hydrolysis with 0·01*N*-hydrochloric acid at 90°. It was identified by conversion into 2 : 3 : 4 : 6-tetramethyl-δ-mannonolactone free from γ-lactone. Simultaneous deacetylation and methylation of

tetra-acetyl-α-methylmannopyranoside by gradual addition of methyl sulphate and alkali to a solution in acetone gives tetramethyl-α-methylmannopyranoside, $[\alpha]_D^{18}$ +43°, converted by hydrolysis into tetramethylmannopyranose.

V. The optical rotations of fully-methylated lactones are not appreciably affected by the nature of the solvent where *cis*-methoxy-groups are absent (dextrose series), are more affected where *cis*-methoxy-groups occur in positions 3 and 4 (galactose series), and vary considerably where such occur in positions 2 and 3 (mannose series). In every case unchanged lactone is recovered by evaporation. The following values of $[\alpha]_D$ in water, chloroform, ether, and benzene, respectively, are recorded for carefully-purified substances: *d*-2 : 3 : 4 : 6-tetramethylmannonolactone, +150°, +59·5°, +35°, +20°; *d*-2 : 3 : 5 : 6-tetramethylmannonolactone, +65°, −9·7°, −36·3°, −49·2°; *d*-2 : 3 : 4-trimethyl-lyxonolactone, +35·5° −60·4°, −87°, −102°; *d*-2 : 3 : 5-trimethyl-lyxonolactone, +82·5°, −28°, −70°, −70°; *l*-2 : 3 : 4-trimethylrhamnonolactone, −130°, −67·5°, −39·3°, −15·0°; *l*-2 : 3 : 5-trimethylrhamnonolactone, −57°, +13°, +65°, +87°; *d*-2 : 3 : 4 : 6-tetramethylgluconolactone, +98°, +103°, +123°, +121°; *d*-2 : 3 : 5 : 6-tetramethylgluconolactone, +62°, +42°, +67°, +68°; *d*-2 : 3 : 4-trimethylxylonolactone, ±0°, +9°, +12°, +17°; *d*-2 : 3 : 4 : 6-tetramethylgalactonolactone, +153°, +101°, +96°, +128°; *d*-2 : 3 : 5 : 6-tetramethylgalactonolactone, −34°, −13°, −11°, −11°; *l*-2 : 3 : 4-trimethylarabonolactone, +181°, +125°, +105°, +166°; *l*-2 : 3 : 5-trimethylarabonolactone, −44°, −9°, −3°, +16°.

H. A. PIGGOTT.

Ring structure of mannose. Optical rotation of 4-glucosido-α-mannose. H. S. ISBELL (Bur. Stand. J. Res., 1930, **5**, 1179—1187).—4-Glucosido-α-mannose has been prepared by the deacetylation of the octa-acetate by means of a small quantity of barium methoxide in dry methyl-alcoholic solution at 0° for 20 hrs. At the close of the reaction the barium methoxide is quantitatively removed by the addition of an equivalent quantity of sulphuric acid. This method of deacetylation is of general application. The mutarotation of 4-galactosido-α-mannose monohydrate in water, $[\alpha]_D$ +14·64° to +5·88°, is a unimolecular reaction. The epimeric difference in molecular rotation between 4-glucosido-α-mannose and cellobiose is 16,900, approximating to the difference, 14,900, between α-*d*-glucose and α-*d*-mannose. This suggests that the ring structures of α-*d*-mannose and 4-glucosido-α-mannose are identical, a result opposed to that of Hudson (A., 1930, 747) derived from a consideration of the epimeric differences of the aceto-halogen derivatives of these sugars. In addition, it is pointed out that the epimeric difference between 4-galactosido-β-mannose and β-lactose corresponds with that between β-*d*-glucose and β-*d*-mannose. It therefore appears that the use of these pairs of sugars as a crucial test (cf. Hudson, *loc. cit.*) of the ring structures of α- and β-mannose is unsatisfactory.

T. H. MORTON.

Structures of acetylmethylmannosides. H. S. ISBELL (J. Amer. Chem. Soc., 1930, **52**, 5298).—The following *hepta-acetyl-4-glucosidomethylmannosides* have been prepared by the Koenigs–Knorr reaction: "α"-, m. p. 185°, $[\alpha]_D$ +26·7° (all rotations in chloroform); "β"-, m. p. 161°, $[\alpha]_D$ −22·3°, and "γ"-, m. p. 167°, $[\alpha]_D^{20}$ −12·7°. These appear to be analogous to the three known acetylmethylmannosides (cf. Hudson, A., 1930, 747). The "γ"-compound can be converted into a hepta-acetyl-4-glucosidomannose, $[\alpha]_D$ +21·7°, which does not exhibit mutarotation, thus indicating that the methoxyl group in the original compound is not in position 1. This supports the *ortho*-ester formula of Freudenberg (A., 1930, 894) and of Bott, Haworth, and Hirst (*ibid.*, 1024) for compounds of the above types.

H. BURTON.

Crystalline α- and β-methyl-*d*-gulosides. H. S. ISBELL (Proc. Nat. Acad. Sci., 1930, **16**, 699—703).—The additive compound of *d*-gulose and calcium chloride is treated with 1% methyl-alcoholic hydrogen chloride, the mixture neutralised with calcium carbonate, and the resulting solution evaporated, whereby the additive compound ($+2H_2O$), [α] about +60°, of 1 mol. of α-methyl-*d*-guloside and 1 mol. of calcium chloride separates. Repeated crystallisation of this affords the additive compound ($+3H_2O$), [α] +83°, of 2 mols. of the guloside and 1 mol. of calcium chloride, which when decomposed with silver oxalate furnishes α-methyl-*d*-guloside ($+H_2O$), decomp. 77° with loss of H_2O, $[\alpha]_D^{20}$ +109°. The mother-liquor from the above preparation deposits the additive compound ($+2H_2O$), m. p. 155°, [α] −46°, of 1 mol. of β-methyl-*d*-guloside and 1 mol. of calcium chloride; this is converted by crystallisation from alcohol into the (2 : 1) compound, [α] −65°, of the guloside and chloride. β-Methyl-*d*-guloside has m. p. 176°, [α] −83°.

H. BURTON.

Synthesis of glucosides. VI. Preparation of β-glucosides of phenols. A. ROBERTSON and R. B. WATERS (J.C.S., 1930, 2729—2733).—The phenol is allowed to interact with *O*-tetra-acetyl-α-glucosidyl bromide and "active" silver oxide in quinoline, and the tetra-acetate produced hydrolysed by methyl-alcoholic ammonia (cf. Takahashi, J. Pharm. Soc. Japan, 1925, **525**, 4; Zemplen and Müller, A., 1929, 1281). This method, which fails with alcohols, produces the β-modification alone. Use of pyridine in place of quinoline gives an impure product. The following were prepared: β-phenyl- and β-naphthyl-glucoside, $[\alpha]_D$ −26·7° in 95% acetone; helicin (from salicylaldehyde); *O-octa-acetyl*-m-*phenylenediglucoside*, m. p. 203°, $[\alpha]_D$ −83·1° in acetone; and *O*-tetra-acetyl-β-glucovanillin. *O-Monobenzoylquinol*, m. p. 161°, is readily converted into its *tetra-acetylglucoside*, m. p. 154—155°, $[\alpha]_D$ −63·97° in acetone, hydrolysed by the standard method to arbutin.

H. A. PIGGOTT.

Synthesis of glucosidoferulic acid. R. M. HANN (J. Amer. Chem. Soc., 1930, **52**, 5049—5051).—Acetobromoglucose reacts with the potassium derivative of methyl ferulate (4-hydroxy-3-methoxycinnamate) in ether and alcohol, forming *methyl tetra-acetyl*-β-d-*glucosidoferulate*, m. p. 142—143° (corr.), $[\alpha]_D$ −32·3° in chloroform, hydrolysed by 6% barium hydroxide solution at the ordinary temperature to β-d-*glucisodoferulic acid*, m. p. 198—199° (corr.), $[\alpha]_D$ −36·6° in alcohol.

H. BURTON.

Varieties of starch and constitution of starch. S. von Naray-Szabó (Z. physikal. Chem., 1930, **151**, 420—424; cf. A., 1928, 1224).—Differences in the X-ray diagrams of starches of different origin are due to variation in the water content. There is no chemical distinction between different starches. Differences between amylose and amylopectin are due partly to admixture of other substances and partly to their physical character. The constitution of starch is briefly discussed. F. L. Usher.

Supposed depolymerisation of glycogen. J. Reilly and H. Pringsheim (Ber., 1930, **63**, [*B*], 3210—3211).—A refutation of the criticism of Berner (this vol., 74). H. Wren.

Constant occurrence of non-reducing disaccharides in hydrolysed inulin. R. F. Jackson and E. McDonald (Bur. Stand. J. Res., 1930, **5**. 1151—1160).—Members of the family *Compositæ*, burdock, golden-rod, dandelion, artichoke, and wild chicory, yield inulin, which after two fractionations gives a mixture of hydrolytic products of very nearly constant composition. The mixture consists of 91·0% of lævulose, 3·7% of dextrose, and 5·3% of non-reducing difructose anhydrides, $[\alpha]_D^{20}$ +49° (cf. Jackson and Goergen, A., 1929, 1280). Dahlia and artichoke inulins have been subjected to 11 "recrystallisations," whereby 85% and 96%, respectively, of the original material was rejected. The composition of the products derived from these materials by acid hydrolysis is similar to the above, with the exception that dahlia inulin yields but 1·9% of dextrose. The non-reducing residue is preformed in the inulin, since polysaccharides related to inulin, soluble in 60—70% alcohol, derived from artichoke and iris yield, under similar hydrolytic conditions, lævulose and dextrose alone. It is considered that these refractory difructose anhydrides form an essential part of the molecule, which therefore contains not less than 110 hexose residues, corresponding with M 18,000. T. H. Morton.

Highly-polymerised compounds. XLVIII. Molecular size of cellulose. H. Staudinger and O. Schweitzer (Ber., 1930, **63**, [*B*], 3132—3154).—Hydrolysis of a series of polytriacetylcelloglucan diacetates, the mol. wt. of which has been determined according to Bergmann and Machemer and by measurement of viscosity (cf. A., 1930, 1415, 1416), yields a polymeric homologous series of polycelloglucan dihydrates. The mol. wt. of the dihydrates is uniformly greater than that of the corresponding acetates owing to removal of the simplest portions of the hydrolysate by the mother-liquors. It may, however, be assumed that the length of the chain of the polycelloglucan diacetates remains intact during conversion into the hydrates and that cellulose derivatives may bo subjected to chemical change without altering the degree of polymerisation. The polycelloglucan dihydrates thus obtained are hemicolloids insoluble in water or formamide but soluble in Schweitzer's reagent; they are identical with the so-called cellodextrins or hydrocellulose. The behaviour of solutions of hemicolloidal polycelloglucan dihydrates in Schweitzer's solution is less complicated than expected, provided that the concentration of the reagent is maintained uniform and it is used in excess so that more than 1 atom of copper is present for each glucose residue. Solutions of a 70-polycelloglucan dihydrate do not change with time and obey the Hagen–Poiseuille law. Within the limits imposed by the volatility of the ammonia, the value $\eta_{sp.}$ is independent of the temperature, so that the hydrates are dissolved as molecules, not micelles. The values $\eta_{sp.}/C$ for different concentrations are constant for the hemicolloids in quite dilute solution, but increase with the concentration when the degree of polymerisation exceeds 150. The viscosity of the hemicolloidal heteropolar polycelloglucan dihydrate complexes in Schweitzer's solution resembles that of hemicolloidal polystyrenes in benzene or tetrahydronaphthalene. With the simpler dihydrates of degree of polymerisation 30—100 the value K_m shows relatively little variation. With more complex products the value is less constant, possibly owing to the imperfect applicability of the Bergmann–Machemer method.

The viscosity of solutions of purified cotton in Schweitzer's reagent diminishes with time without becoming constant after 4 weeks. The change depends on the oxidative degradation of the macromolecules of the cellulose by copper oxide. Comparable values can be obtained only by use of solutions which have been preserved for equal intervals at the same temperature. When rapidly observed, the value $\eta_{sp.}/C$ at different temperatures is approximately constant; the primary colloid particles are therefore macromolecules, not micelles. The value is also independent of concentration and conditions of flow provided that the solutions are quite dilute (sol solutions). Calculation of the mol. wt. of cellulose from the viscosity of its solutions in Schweitzer's reagent shows that a more or less profound degradation of the molecule occurs according to the method of purification. The highest observed value (190,000) is for purified cotton. Slight degradation accompanies mercerisation. Sulphite-cellulose and copper-silk are more appreciably affected (mol. wt. 80,000—65,000 and 35,000, respectively). The apparent discrepancy between the behaviour of more dilute and concentrated solutions of cellulose in Schweitzer's reagent is explained, as in previous cases, by the consideration that the sphere of influence of dissolved thread molecules is much greater than that corresponding with the actual size of the molecules. About 0·2% solutions of cellulose in Schweitzer's reagent are gel solutions which show deviations from the Hagen–Poiseuille law. The swelling of cellulose in Schweitzer's reagent is not evidence of micellary structure, but is equally reconcilable with the presence of long molecules. The stability of macromolecules in the solid state and in solution is discussed. The highest observed value for the mol. wt. of cellulose can be regarded only as a minimum value for native cellulose, since it is not impossible that degradation occurs during swelling and dissolution. Possibly native cellulose is an aggregated compound the macromolecules of which are capable of existence only in the solid state embedded in the crystal lattice. H. Wren.

Action of acids on cellulose. Bouchonnet, Jacquet, and Mathieu (Bull. Soc. chim., 1930, [iv],

47, 1265—1270).—Cellulose obtained from lucerne and from linters when purified and boiled (1) with 10% sulphuric acid for (*a*) 15—20 min. or (*b*) 2 hrs.; (2) with 2% oxalic acid or treated cold with hydrochloric acid, *d* 1·18, for (*a*) 25 hrs. or (*b*) 50 hrs., or with 4% sulphuric acid or with acetic acid in presence of sulphuric acid, is converted into hydrocelluloses, the copper numbers of which vary irregularly from 1·82 to 4·42 with the linters cellulose and from 2·96 to 5·5 with the lucerne cellulose. Examination of the hydrocelluloses in polarised light (Röntgen rays) showed no difference in structure from that of the original cellulose and indicated that the crystalline constituent of cellulose is more developed in linters than in lucerne cellulose. Photomicrographs indicate that the copper number of the hydrocellulose increases with the degree of division of the cellulose under the action of acid. It is suggested that cellulose is a mixture of a crystalline phase enveloped in an amorphous skin which is destroyed under more or less drastic conditions, yielding the crystallite constituent the degradation of which yields polysaccharides. The same cellulose thus yields the same crystallite structure under the action of acid media, but the copper number depends on the extent of the degradation of the amorphous form. The variations in copper numbers are not due to adsorption of reducing products, as prolonged washing did not affect the value obtained. R. BRIGHTMAN.

Chemical changes during the dissolution of cellulose in copper oxide–ethylenediamine and -ammonia solutions. W. TRAUBE (Cellulosechem., 1930, **11**, 249—254).—A review (cf. Traube, Glaubitt, and Schenck, A., 1930, 1417). T. H. MORTON.

Benzylcellulose. H. OKADA (Cellulosechem., 1931, **12**, 11—17).—Benzylcellulose of a high carbon content and viscosity may be made in either a single or a two-stage process by steeping cellulose in aqueous sodium hydroxide, pressing free from excess of alkali, and heating with benzyl chloride at 100°. It forms films of greater extensibility but lower tensile strength than does cellulose nitrate. In the former process alkali concentrations of 30—50% are employed; the use of excessive concentrations reduces the reaction velocity and the viscosity of the product. In general, the products are incompletely soluble in benzene, but readily soluble in benzene–alcohol mixtures. The use of 17·5% alkali and a weight of benzyl chloride rather greater than of cellulose in a first stage, followed by 50% alkali and three to four times the weight of benzyl chloride in a second, gives a product completely soluble in benzene. Use of benzene or toluene as solvent reduces the reaction velocity, and temperatures below 100° favour depolymerisation rather than benzylation. H. A. PIGGOTT.

Nitration of cellulose with a mixture of nitric and phosphoric acids. E. BERL and G. RUEFF (Ber., 1930, **63**, [*B*], 3212).—Since cellulose nitrates are not hydrolysed by phosphoric acid, it is easily possible by use of suitable mixtures to obtain products with 14 0—13·7% N. The process is accompanied by marked swelling of the fibres which facilitates access of the acid to the interior of the material and thus uniform action. After short boiling the nitrates are completely stable and contain no mixed phosphate-nitrate esters. Nitrates with 11·0—11·5% N cannot be obtained by the process in fibrous form. During esterification the lattice of native cellulose is transformed into that of hydrocellulose. With phosphoric and nitric acids, nitration is relatively slow, the nitric acid mercerising the cellulose before esterification commences. The cellulose trinitrates obtained give a clear point diagram if nitration and washing are effected under tension. H. WREN.

Absorption of bases by Willstätter's lignin, and related swelling phenomena. L. KALB, F. NEVELY, and O. TOURSEL (Cellulosechem., 1931, **12**, 1—11).—The absorption of alkali, measured by the decrease in concentration of the solution, from aqueous sodium or potassium hydroxides by Willstatter's lignin (A., 1928, 743) increases rapidly with increasing concentration of the solution to 0·5*N*, and then remains constant at 0·126 g.-equiv. per 100 g. A higher value (0·168) is obtained by direct determination of alkali in the product. Absorption, measured by the first method, is higher (0·154) in presence of sodium chloride (approx. 3*N*). Methyl-alcoholic sodium hydroxide gives abnormally high results, with no evidence of a constant value; from sodium carbonate the absorption is inconsiderable. Barium hydroxide gives a value (0·168) which is regarded as approaching the true value, it being considered that the lower values obtained with the alkalis are the result of masking of the true value by the swelling of the lignin. In general, the results for strong bases are parallel to the swelling of the fibre. They do not vary appreciably between 0° and 30°, and are unaffected by the relative amounts of lignin and solution or by short drying of the lignin at 100°. The effects of the presence of carbohydrates and alkali-soluble material are measured and discussed. Gaseous ammonia is absorbed in quantity by dry lignin, the actual amount depending on a number of physical factors, but much of the gas is rapidly lost on keeping, a final value of 0·130 g.-equiv. per 100 g. being reached. Progressive methylation of lignin leads to a decrease in affinity for bases which eventually disappears completely; in view of its behaviour in this respect, the absorption of bases is regarded as conditioned in part by the presence of alcoholic hydroxyl groups.

Absorption of alkali is not a consequence of the chlorine content, and is unaffected by its partial or complete removal. It is shown by measurements of the p_H of aqueous and aqueous potassium chloride extracts that most samples of lignin contain loosely-bound acid constituents, and it is noteworthy that samples regenerated from the alkali-lignins slowly regain their acidity on keeping.

A standard method is described for determination of the absorption of sodium hydroxide from a 0·5*N*-solution, and the values measured for a number of lignin preparations are given. H. A. PIGGOTT.

Beech-wood alkyl-lignins and their fission. A. VON WACEK (Ber., 1930, **63**, [*B*], 2984—2993; cf. A., 1930, 458).—The oil obtained by treatment of primary beech-wood methyl-lignin with sodium ethoxide consists of a neutral portion (oxidised to 3 : 5-dimethoxybenzoic acid) and a phenolic fraction con-

verted by successive ethylation and oxidation into 3-methoxy-4-ethoxybenzoic acid. Lignin, isolated from beech wood by Freudenberg's method, gives a methyl-lignin with 36·57% OMe which differs from primary methyl-lignin in its methoxyl content and in its behaviour when treated according to Friedrich. Ethylation of the "Freudenberg" lignin gives a product with 34·17% of alkoxyl (as OMe) which when treated with sodium ethoxide affords an oil partly soluble in ether which is divided into neutral and acidic portions. Oxidation of the portions (after ethylation of the acidic material) gives an acid which does not melt below 300° and 3-methoxy-4-ethoxybenzoic acid, respectively. The "residual" lignin differs therefore from primary methyl-lignin. Treatment of beech-wood meal, free from resin and gum, with ethyl sulphate at 60° yields a product with 27·35% OAlk (as OMe) which gives a primary ethyl-lignin with 29·10% OAlk. The product is very sensitive towards heat. When treated with sodium ethoxide it affords an oil almost completely soluble in ether and divisible into neutral and acidic portions, yielding on oxidation only a trace of crystalline material and (after ethylation) non-crystalline substances, respectively. Ethylation of beech wood at 25—30° gives a product with 30·15% OAlk yielding a more stable primary ethyl-lignin with 31·27% OAlk which with sodium ethoxide gives an oil completely soluble in ether. Oxidation of the neutral portion thereof affords 3 : 5-dimethoxybenzoic acid, whereas successive methylation and oxidation of the acidic portion does not yield a crystalline substance. The ethyl groups of the primary ethyl-lignin could not be detected in the phenolic fission products. A free phenolic group does not appear to be present in the phenolic components of genuine beech-wood lignin which contains other groups capable of alkylation. The methoxyl groups are present in genuine lignin. The methoxyl content of isolated beech-wood lignin and methyl-lignin contradicts the hypothesis that lignin contains only the components $\cdot O\cdot C_6H_2(OMe)_2\cdot CH_2\cdot CH{:}CH\cdot$. The assumption that aliphatic hydroxyl groups are present in the side-chain necessitates a much higher methoxyl content than that actually found. It is uncertain whether pyrocatechol derivatives are present in the chain in addition to pyrogallol residues or whether a substance of entirely different constitution participates in the structure.

The synthesis of *3-methoxy-5-ethoxybenzoic acid*, m. p. 145° (corr.), is recorded. H. WREN.

Reaction between propylene oxide and diethylamine. K. A. KRASUSKI and G. T. PILIUGIN (Ukraine Chem. J., 1930, 5, 135—139).—The product of the interaction of 1 mol. of propylene oxide with 2 mols. of diethylamine either in aqueous solution at the ordinary temperature or on heating in a sealed tube is *α-diethylaminopropan-β-ol*, b. p. 157·5—159°/756 mm., d_0^{20} 0·8511, which is the only amino-alcohol obtained in aqueous solution. The *hydrochloride* and *picrate* are described. E. B. UVAROV.

Reaction of ethylamine and diethylamine with *iso*propylethylene oxide. F. F. KRIVONOS (Ukraine Chem. J., 1930, 5, 141—146).—The reaction between *iso*propylethylene oxide (2 mols.) and ethylamine (1 mol.) gives *ethyl-β-hydroxy-γ-methyl-*n*-butylamine*, b. p. 150—152°/25 mm., d_0^{20} 0·8929. The *hydrochloride* and *picrate* were prepared. Using 1·5 mols. of oxide to 1 mol. of ethylamine, *ethyldi-β-hydroxy-γ-methyl-*n*-butylamine*, b. p. 244—247°/20 mm., was obtained. The *hydrochloride* was prepared. The reaction between *iso*propylethylene oxide and diethylamine gave *diethyl-β-hydroxy-γ-methyl-*n*-butylamine*, b. p. 151—154°/15 mm., d_0^{20} 0·8512 (*picrate* and *hydrochloride*). E. B. UVAROV.

Preparation of dimethylamino-aliphatic acids. V. PRELOG (Coll. Czech. Chem. Comm., 1930, 2, 712—722).—*Dimethylammonium hydrogen succinate*, m. p. 159—160°, is converted by heating at 160—180° until steam ceases to be evolved, followed by distillation under reduced pressure, into a mixture of the mono- and bis-dimethylamides, which is reduced electrolytically, using an activated lead cathode (cf. Tafel, A., 1900, ii, 588). The product is made alkaline with barium hydroxide and αδ-tetramethyldiaminobutane (*picrate*, m. p. 188—189°) removed by distillation in steam; from the residue *δ-dimethylamino-*n*-butyric acid*, b. p. 145—150°/2 mm., m. p. 102—104° [hydrochloride, m. p. 145—147° (cf. A., 1915, i, 966); *ethyl* ester, b. p. 78—90°/18 mm., $d^{13\cdot6}$ 0·9187, $n^{14\cdot3}$ 1·4264], may be isolated after removal of inorganic matter. Its methiodide gives with silver oxide in aqueous solution a quaternary *hydroxide* (?), m. p. 77°, converted by prolonged drying at the ordinary temperature into the betaine, m. p. 219° (decomp.) [*chloroaurate*, m. p. 184—185°; *chloroplatinate*, m. p. 225—226° (cf. A., 1902, i, 266)]. Similarly, from *dimethylammonium hydrogen adipate*, m. p. 75°, were prepared: adiptetramethyldiamide, m. p. 85°; αη-tetramethyldiaminohexane [*picrate*, m. p. 163—164°; *chloroplatinate*, m. p. 222° (decomp.); *chloroaurate*, m. p. 169°]; *ξ-dimethylamino-*n*-hexoic acid*, m. p. 107—109° [*hydrochloride*, m. p. 97—99°; quaternary (methyl) *hydroxide*, m. p. 115°; *betaine*, m. p. 254—255° (*chloroaurate*, m. p. 149°)]. The betaine is decomposed at temperatures above its m. p. into *methyl ξ-dimethylamino-*n*-hexoate*, b. p. 209—210°, trimethylamine, and (probably) n-Δ^{δ}-hexenoic acid. H. A. PIGGOTT.

Ability of peptides to combine with acid and alkali. E. STIASNY and H. SCOTTI (Ber., 1930, 63, [*B*], 2977—2983).—Glycine, glycylglycine, di-, tri-, tetra-, and penta-glycylglycine, and glycine anhydride are titrated with sodium hydroxide and hydrochloric acid, respectively, the hydrogen-ion concentration being measured potentiometrically after each addition by aid of the hydrogen electrode. The graphs show that union of hydrochloric acid does not occur with the peptide groups of soluble peptides, which, however, definitely combine with alkali hydroxide. The dissociation constants and the isoelectric points are calculated from the graphs. The introduction of the first peptide group has a more marked effect than that of subsequent peptide groups on the acidic and basic character of the peptides. With increasing number of peptide groups the acidic character steadily increases; the basic properties increase only to the dipeptide. The isoelectric point, confirmed by meas-

urement of the optimal conditions for precipitation with alcohol in the cases of the tri-, tetra-, and penta-peptide and by p_H measurement on solutions of increasing concentration with glycine and dipeptide, wanders into the acidic region with increasing number of peptide groups and in the case of polypeptides attains the value of many proteins. H. WREN.

Synthesis of serine. S. K. MITRA (J. Indian Chem. Soc., 1930, **7**, 799—802).—Ethyl sodiophthalimidomalonate and methyl chloromethyl ether react in ether, forming *ethyl phthalimidomethoxymethylmalonate*, m. p. 127°, hydrolysed to the free *acid*, m. p. 102° (*silver* salt), only by hydrobromic acid (d 1·8) at 48°. When this acid is heated with fuming hydrochloric acid in a sealed tube at 100°, the hydrochloride of α-amino-β-hydroxypropionic acid (serine) (*phenylcarbimide* derivative, m. p. 159°) is obtained in 50% of the theoretical amount. Hydrolysis of the above ester with alcoholic potassium hydroxide affords a *tripotassium* salt, probably $CO_2K{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}C(CH_2{\cdot}OMe)(CO_2K)_2$, which when treated with acid gives carbon dioxide and an oily product (hydrolysed further to serine).

H. BURTON.

Ethyl aminomalonate and its derivatives. R. LOCQUIN and V. CERCHEZ (Bull. Soc. chim., 1930, [iv], **47**, 1274—1279, 1282—1287, 1287—1289).—Reduction of ethyl oximinomalonate with excess of aluminium amalgam gave only 15% of ethyl aminomalonate in place of the 60% yield claimed by Piloty and Neresheimer (A., 1906, i, 146). By using only a slight excess of aluminium ($1\frac{2}{3}$ atoms per mol. of ester), in the form of 0·3-mm. leaves amalgamated with 4% mercuric chloride solution, covering the amalgam with an ethereal solution of ethyl oximinomalonate, and gradually adding to the boiling ethereal solution water equal in weight to six times the weight of aluminium, the aluminium hydroxide separates in pulverulent form and from the clear liquid ethyl aminomalonate, b. p. 122—123°/16 mm., d_4^{16} 1·100, 1·4353, is obtained in 65% yield by direct distillation. It is best isolated for storage as the *oxalate*, m. p. 138°. The carbamide, $NH_2{\cdot}CO{\cdot}NH{\cdot}CH(CO_2Et)_2$, m. p. 173°, is obtained in 50—70% yield with potassium cyanate in acetic acid; hydrolysis with 25% hydrochloric acid yields 90% of hydantoin. The phenylcarbamide m. p. 117°, ethyl carbethoxyaminomalonate, m. p. 61—63°, and diamide, m. p. 197° (yield 90%), are also described.

R. BRIGHTMAN.

Preparation of ethyl oximinomalonate. V. CERCHEZ (Bull. Soc. chim., 1930, [iv], **47**, 1279—1281).—Ethyl oximinomalonate, b. p. 172°/12 mm., d_4^{18} 1·182, n_D^{18} 1·4544, is obtained in 90% yield by the action of a slow current of nitrous fumes or of methyl nitrite on ethyl sodiomalonate in alcoholic solution. Yields of 80—90% are obtained by the action of a concentrated aqueous solution of sodium nitrite (3 mols.) on a solution of ethyl malonate (1 mol.) in 3 mols. of glacial acetic acid. Nitrosyl hydrogen sulphate gives only 40% yields. R. BRIGHTMAN.

Action of magnesium phenyl bromide on ethyl α-cyano-α-ethyl-*n*-butyrate. A. MAVRODIN (Compt. rend., 1930, **191**, 1064—1066).—Magnesium phenyl bromide reacts with ethyl α-cyano-α-ethyl-*n*-butyrate, which is incapable of enolisation (cf. A., 1929, 796), thus: $CEt_2(CN){\cdot}CO_2Et + PhMgBr \longrightarrow PhCN + CEt_2(MgBr){\cdot}CO_2Et$ (I); $PhCN + PhMgBr \longrightarrow CPh_2{:}N{\cdot}MgBr \longrightarrow CPh_2{:}NH \longrightarrow COPh_2$; $2(I) \longrightarrow CEt_2(MgBr){\cdot}CO{\cdot}CEt_2{\cdot}CO_2Et \longrightarrow CHEt_2{\cdot}CO{\cdot}CEt_2{\cdot}CO_2Et$ (II), the final products being benzophenone, a small quantity of ethyl α-ethyl-*n*-butyrate (from I), and *ethyl β-keto-ααγ-triethyl-*n*-hexoate* (II), b. p. 138°/18 mm. The last-named is hydrolysed by alcoholic potassium hydroxide to di-(α-ethyl-*n*-propyl) ketone, b. p. 90°/15 mm. (Zerner, A., 1911, i, 950). Comparable cases of elimination of a group from a quaternary carbon atom by a Grignard reagent are cited. J. W. BAKER.

Polymerisation and ring formation. VIII. Amides from ε-aminohexoic acid. W. H. CAROTHERS and G. J. BERCHET (J. Amer. Chem. Soc., 1930, **52**, 5289—5291).—When ε-aminohexoic acid is heated to 210—220°, water is eliminated and a mixture of 20—30% of the corresponding lactam and 70—80% of a polymeric *amide*, m. p. 212—214°, M 800—1200, is formed. The amide is insoluble in most organic solvents (except hot formamide), is hydrolysed by hydrochloric acid to ε-aminohexoic acid, and when heated in a high vacuum does not give any of the lactam. Its formation probably involves at least 10 mols. of the amino-acid. Partial hydrolysis of the amide gives polyaminohexoylaminohexoic acids of lower mol. wt., indicating that the structure of the original material may be represented as $\cdot NH{\cdot}[CH_2]_5{\cdot}CO{\cdot}[NH{\cdot}(CH_2)_5{\cdot}CO]_x{\cdot}NH{\cdot}[CH_2]_5{\cdot}CO\cdot$. No evidence of the presence of terminal amino- or carboxyl groups could be obtained. H. BURTON.

Determination of unsaturated nitriles. G. HEIM (Bull. Soc. chim. Belg., 1930, **39**, 458—461).—The rates of addition of iodine to αβ- and βγ-unsaturated nitriles (cf. Linstead and May, A., 1927, 1167; Kandiah and Linstead, A., 1929, 1294) do not always differ to a marked degree, since *cis*- (1·7%) and *trans*- (1·4%) -crotononitriles and vinylacetonitrile (7·0%) absorb the quantities of iodine given in parentheses, under comparable conditions. A method is described in which a standard solution of bromine in potassium bromide is added to a chloroform solution of the nitrile, followed by potassium iodide and titration with thiosulphate. The rate of addition of bromine to the αβ-unsaturated nitriles, *cis*- and *trans*-crotononitrile (0·9% and 2·1%), α-methylcrotononitriles (*cis*- 0·6; *trans*- 1·2%), and the nitriles of α-methyl-β-ethyl- (*cis*- 1·8%), α-methyl- (1·2%), α-ethyl- (1·4%), and α-propyl- (3·0%) -acrylic acids is much less than in the case of the βγ-unsaturated vinylacetonitrile (99·8%). The composition of mixtures of αβ- and βγ-unsaturated nitriles may be determined in this way.

J. D. A. JOHNSON.

Unsaturated nitriles. γ-Methyl-Δ$^\alpha$-pentenonitriles. P. BRUYLANTS and H. MINETTI (Bull. Acad. roy. Belg., 1930, [v], **16**, 1116—1128).—*iso*-Amyl alcohol (isolated as barium *iso*amyl sulphate from fusel oil), b. p. 131·5—132°/755 mm., d_4^{20} 0·80788, is oxidised to *iso*valeraldehyde, b. p. 91·9—92·1°/765·5 mm., d_4^{20} 0·79770. The cyanohydrin, b. p. 107°/9 mm., d_4^{20} 0·91852, of the latter is dehydrated by means of phosphoric oxide; careful fractionation of the product affords cis-*γ-methyl-Δ$^\alpha$-pentenonitrile*,

b. p. 137·5—138°/770 mm., d_4^{20} 0·80781, n 1·42493, and a fraction, b. p. 160—160·5°/767 mm., d_4^{20} 0·82491, n_D 1·43620, consisting of a mixture of the *trans*-isomeride and γ-methyl-Δ^{β}-pentenonitrile (20%), inseparable by distillation. Treatment of the mixture with bromine removes the latter compound (which reacts more readily with halogens), leaving trans-*γ-methyl-Δ^{α}-pentenonitrile*, b. p. 48·5—49°/13·5 mm., d_4^{20} 0·82131, n_D 1·43418, distillation of which at atmospheric pressure (b. p. 156—157°/761 mm.) causes some re-isomerisation to the Δ^{β}-compound. The fractions, b. p. above 163°, from the original dehydration appear to contain larger percentages of the Δ^{β}-nitrile.

Addition of hydrogen chloride to either of the geometrical isomerides of γ-methyl-Δ^{α}-pentenonitrile affords γ-methyl-β-chloropentonitrile, b. p. 90·4—91·4°/13 mm., d_4^{20} 1·0186, 1·44375, from which hydrogen chloride is removed in the usual manner by quinoline leading to a mixture containing the Δ^{β}-nitrile and the two Δ^{α}-nitriles. Sodium phenoxide acts on the two geometrical isomerides, with formation of considerable percentages (particularly with the *cis*-compound) of γ-methyl-Δ^{β}-pentenonitrile.

The corresponding amides—cis-, m. p. 80°, and trans-*γ-methyl-Δ^{α}-pentenoamide*, m. p. 87·6—88·2°—are prepared by the action of cold sulphuric acid on the nitriles.

New data are given of the molecular refractivities and dispersions of *iso*amyl alcohol, *iso*valeraldehyde and its cyanohydrin, and the new derivatives.

R. CHILD.

Ultra-violet absorption spectra of γ-methyl-Δ^{α}-pentenonitriles and the corresponding amides. A. CASTILLE and E. RUPPOL (Bull. Soc. roy. Belg., 1930, [v], **16**, 1129—1133).—As has been observed with other members of the series, the absorption of the *trans*-nitrile is greater than that of the *cis*-isomeride, whilst the reverse is the case with amides.

R. CHILD.

Alteration in properties of chemical compounds by complex formation. VI. Methylation of alcohols by diazomethane. H. MEERWEIN and G. HINZ (Annalen, 1930, **484**, 1—25).—The reactivity of a hydroxyl group towards diazomethane may be increased either by the introduction of polar groups in the α-position, or by formation of a polar complex by substances capable of addition to the oxygen atom (catalysts). Use of ether as a solvent tends to prevent methylation, and a similar influence is often exerted by the products of methylation.

Saturated aliphatic alcohols are not methylated by diazomethane, but allyl alcohol accelerates its decomposition, and benzyl alcohol gives 13% of methyl ether. The influence of an electronegative group in the α-position is shown by the methylation of the following: glycol monoacetate; α-monoacetin (*methyl ether*, b. p. 126—129°/18 mm., readily methylated to the dimethyl ether); glycol trichloroacetate (*methyl ether*, m. p. 77—78°); ethylene chlorohydrin; α-monochlorohydrin (*monomethyl ether*, b. p. 171—172°; d_0^0 1·1832; accompanied by the dimethyl ether); αγ-dichlorohydrin; ethylene cyanohydrin [*methyl ether*, b. p. 162—164°; and a base, $C_4H_7ON_3$ (*hydrochloride*)]; and acetaldehyde cyanohydrin. In the last case the methyl ether is accompanied by dimethylethylene oxide, acetone, and methyl ethyl ketone. Acetyl- and benzoyl-carbinols react abnormally, being converted into propionylcarbinol and *phenacylcarbinol*, b. p. 140—145°/11 mm., respectively.

Methylation of saturated aliphatic alcohols may be effected in presence of halogenated alcohols, *e.g.*, ethylene chlorohydrin, αα'-dichlorohydrin, and trichloroethyl alcohol, or of salts such as zinc, ferric, or magnesium chlorides, or of alkoxides or ortho-esters. Catalysts of the first two types, particularly the chloro-alcohols, which lose their activity on methylation, give poor results, but good yields are obtained with the third class. Thus *n*-butyl and *iso*propyl alcohols are readily methylated in presence of the corresponding aluminium alkoxides, or, in the former case, of *n*-butyl antimonite. Alkyl borates are rather less active and fail completely in the case of *iso*propyl and *n*-butyl alcohols. It is suggested that polyhydric alcohols should readily be methylated in presence of boric or arsenious acid, the complexes here being intramolecular. H. A. PIGGOTT.

Electrolysis of Grignard solutions. H. E. FRENCH and M. DRANE (J. Amer. Chem. Soc., 1930, **52**, 4904—4906; cf. A., 1927, 756).—Electrolysis of ethereal magnesium *iso*amyl chloride, using a platinum cathode and an anode of bismuth, gold, silver, nickel, or tin, causes no loss of anode material; the amount of Grignard reagent decomposed is equivalent to the amount of current for the first three anode metals. An anode of aluminium, zinc, or cadmium is attacked. Aluminium, approximately equivalent to the quantity of current used, is found in the ethereal solution; the other metals are found in the solid residue in the cell. H. BURTON.

Reaction between magnesium phenyl bromide and carbon dioxide at elevated temperatures. H. GILMAN and (MISS) N. B. ST. JOHN (Rec. trav. chim., 1930, **49**, 1172—1177).—Since triphenylmethyl peroxide is not formed when the reaction is carried out in phenetole or bromobenzene, its formation when ether is used as the reaction medium is considered possibly due to the presence of diethyl ether peroxide in the latter medium. It is suggested that this might oxidise any triphenylmethyl halide formed by the action of magnesium halide on triphenylcarbinol, produced by hydrolysis of $CPh_3·O·MgBr$. When ethereal benzene solutions of the latter are refluxed for several hours, good yields of triphenylmethane are obtained, and the slow addition of carbon dioxide to heated solutions of magnesium phenyl bromide leads to 36·9—46·8% yields of triphenylcarbinol. J. D. A. JOHNSON.

Magnesium dialkyls. Historical note on the first preparation of a magnesium alkyl halide. H. GILMAN and R. E. BROWN (J. Amer. Chem. Soc., 1930, **52**, 5045—5048).—The properties of magnesium dimethyl, diethyl, and di-*n*-butyl, prepared from the corresponding mercury dialkyls, are given. Magnesium reacts with ethyl iodide in absence of solvent at 120—130° (cf. A., 1930, 1302), forming magnesium ethyl iodide; this observation is recorded by Hall-

wachs and Schafarik (Annalen, 1859, **109**, 206). Magnesium does not react with methyl iodide in absence of a solvent at 140—150° (cf. Cahours, *ibid.*, 1860, **114**, 227, 240); magnesium halides are formed from ethyl bromide and *n*-butyl chloride and bromide.

H. BURTON.

Reactivity of halogens in the halogeno-derivatives of *cyclo*hexane. B. V. TRONOV and L. V. LADIGINA (Ber., 1930, **63**, [*B*], 3060—3067).—The rates of reaction of *cyclo*hexyl chloride, bromide, and iodide and of a *sec.*-hexyl iodide (about 70% of β- and 30% of γ-iodohexane from mannitol with hydriodic acid, iodine, and phosphorus) and the corresponding bromide with sodium methoxide, pyridine, and piperidine, respectively, have been measured at 17—19°, the ionised halogen being determined gravimetrically. The halogeno-derivatives of *cyclo*hexane react less readily than the aliphatic halides with amines and potassium iodide, but very energetically with alkoxides. In their reactivity towards amines they very greatly excel the nuclear-substituted aromatic halogeno-compounds. The closure of the six-membered ring does not invariably diminish the readiness with which halogen is lost, but causes a similarity between the halogenated *cyclo*hexanes and the tertiary alkyl halides. In general, the halogen is not replaced but removed mainly, and often exclusively, as hydrogen halide with production of *cyclo*hexene. An electronic interpretation of the course of the reaction is given.

H. WREN.

Action of hexahalogenobenzenes on organo-magnesium compounds. J. F. DURAND and L. WAI-HSUN (Compt. rend., 1930, **191**, 1460—1463). —Whilst hexachlorobenzene does not react, hexabromobenzene reacts readily and hexa-iodobenzene violently with magnesium methyl iodide and magnesium phenyl bromide to yield, respectively, hexamethylbenzene, m. p. 157—158°, and *hexaphenylbenzene*, b. p. 418—420°/760 mm., m. p. 266°. Fuming nitric acid converts hexaiodobenzene into a *substance*, m. p. 330°, converted by prolonged treatment with nitric acid into a *substance*, m. p. 307—308°, probably $C_6O_3I_6$.

J. W. BAKER.

Sorption of hydrogen sulphide by potassium benzenesulphonate. W. LANGE and G. LEWIN (Ber., 1930, **63**, [*B*], 2954—2959).—Measurement of the heat of formation of the thiohydrate, $4Ph·SO_3K,H_2S$ (cf. A., 1930, 1423), in the ice calorimeter gives the value $10·0\pm0·2$ kg.-cal. for the dehydrated salt. Differential measurements give the value $10·5\pm0·3$ kg.-cal. (calc. for 1 mol. of hydrogen sulphide) for the formation of a 1/8 thiohydrate and the value $9·6\pm0·3$ kg.-cal. for subsequent absorption. When the molten salt is employed, 8·5 kg.-cal. are evolved; the difference is accounted for by the greater energy required by the hydrogen sulphide to penetrate the more compact mass. Mathematical expressions have been derived for the relationship between the amount of hydrogen sulphide absorbed, the temperature, and pressure. Irregularities occur corresponding with a thiohydrate, $8Ph·SO_3K,H_2S$. Since the volume of the hydrogen sulphide molecule is approximately twice that of the water molecule, it appears that the 1/8 mol. of hydrogen sulphide occupies the space of the 1/4 mol. of water previously present zeolitically and that further penetration of hydrogen sulphide into the lattice requires a definite amount of energy.

H. WREN.

Oxidation of organic iodine compounds by organic per-acids. J. BOESEKEN and G. C. C. C. SCHNEIDER (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 827—829).—Numerous organic compounds containing iodide are oxidised by peracetic or perbenzoic acid to iodoso- and iodoxy-compounds. With peracetic acid an iodoso-compound is always obtained, generally in the form of its acetate. With perbenzoic acid the iodoxy-compound is obtained directly; iodoxy-compounds are also produced when the iodoso-products obtained with peracetic acid are subsequently treated with perbenzoic acid. With *o*-iodobenzoic acid and *p*-iodobenzenesulphonic acid the oxidation ceases at the iodoso-stage even when perbenzoic acid is used, probably on account of the pronounced polar character of these compounds. *o*-Iodobenzoic acid is often supposed to have a ring structure, but the analogous properties of p-*iodosobenzenesulphonic acid*, m. p. 156·4° (decomp.), suggest that these compounds should be considered as internal salts without ring structure.

E. S. HEDGES.

Preparation of mesitylene. V. N. IPATIEV, B. DOLGOV, and J. VOLNOV (Ber., 1930, **63**, [*B*], 3072—3078).—At 175° under an initial pressure of 100 atm. the yield of mesitylene from acetone increases rapidly with increasing concentration of hydrochloric acid until a concentration of 5% by volume is reached; simple, oxygenated condensation products are formed to some extent. With increase of concentration of acid between 5% and 50%, a gradual fall in the yield of mesitylene occurs, and terpene-like products with a higher degree of condensation appear. With rise in temperature the graph showing relationship of temperature to yield of mesitylene calculated on the acetone used shows a sharp inflexion at 140°, whereas a similar break is noted at 170° when the yield of mesitylene is calculated on the basis of acetone taken. At 175—190° the graphs coincide, indicating the complete utilisation of the acetone. The yield of mesityl oxide diminishes with rise of temperature. At 140—150° in the presence of 5% of hydrochloric acid the yield of mesitylene is 43% of the weight of acetone which enters into the change; 50% of the acetone remains unaffected and can be used in subsequent operations. At 175—180° almost the whole of the acetone reacts and the yield of mesitylene is 36%. The course of the change is represented by the scheme $2COMe_2 \xrightarrow{-H_2O} CMe_2{:}CH·COMe \xrightarrow{+Me·CO·?} C_6H_3Me_3+2H_2O$ or $CO(CH{:}CMe_2)_2+H_2O$.

H. WREN.

Nitration of s-diphenylethane. W. H. RINKENBACH and H. A. AARONSON (J. Amer. Chem. Soc., 1930, **52**, 5040—5045).—4 : 4′-Dinitrodiphenylethane, m. p. 180·5° (corr.), is obtained in 95% of the theoretical amount when diphenylethane is heated with nitric acid (*d* 1·42) at 70—80°. Sulphonation of 2 : 4 : 2′ : 4′-tetranitrodiphenylethane, m. p. 170·9° (corr.) (obtained in 90—95% yield from diphenylethane and fuming nitric acid, first below 30°, and then at 70°), with fuming sulphuric acid (103%) at

85° for 4 days and treatment of the reaction mixture with 95% nitric acid at 85° for 2 days affords α-2 : 4-*dinitrophenyl*-β-2 : 4 : 5-*trinitrophenylethyl alcohol*, m. p. 187·3° [*benzoate*, m. p. about 200° (decomp.)]; in one case, a small amount of 2 : 4 : 6 : 2′ : 4′ : 6′-hexanitrodiphenylethane was isolated. The above alcohol is oxidised by chromic and acetic acids to a mixture of 2 : 4 : 5-trinitrobenzoic acid and (?) 2 : 4-dinitrobenzyl acetate [(?) 2 : 4-dinitrobenzylidene acetate].

H. BURTON.

Alkali-organic compounds. O. BLUM-BERGMANN (Annalen, 1930, **484**, 26—51).—The constitution of 3-phenyl-1-benzhydrylidenehydrindene, assigned by Wieland and Kloss (A., 1929, 1053) to the product of reduction of 2-chloro-3-phenyl-1-benzhydrylideneindene, is confirmed by synthesis; of the isomerides, "m. p. 171° and 131°" (Schlenk and Bergmann, A., 1928, 1031 *et seq.*), the former is shown by synthesis to be 3-phenyl-1-benzhydrylindene, and the latter from its mode of formation must therefore be 1-phenyl-3-benzhydrylindene; this is confirmed by the reduction of 3-phenyl-1-benzhydrylideneindene to a mixture of these (m. p. 174·5—175° and 133—134·5°) by aluminium amalgam in dioxan and reduction of the last by sodium and amyl alcohol to 3-phenyl-1-benzhydrylhydrindene.

The position of the metal in 1-lithio-3-phenylindene is proved by its condensation with benzophenone to 3-phenyl-1-benzhydrylideneindene. The interaction of methyl chloroformate and lithio-3-phenylindene gives *methyl* 3-*phenylindene*-1 : 1-*dicarboxylate*, m. p. 105—107°, reduced by hydrogen and palladised barium sulphate in propyl alcohol to *methyl* 3-*phenylhydrindene*-1 : 1-*dicarboxylate*, m. p. 102—103·5°. The corresponding *acid*, m. p. 175—177° (decomp.), is decomposed by heating above its m. p. into 3-*phenylhydrindene*-1-*carboxylic acid*, m. p. 143—144·5°, b. p. 227—229°/14 mm. (?) (*methyl* ester, b. p. 204·5—205°/13 mm.). 3-*Phenyl*-1-α-*hydroxybenzhydrylhydrindene*, m. p. 122—124°, results from the action of magnesium phenyl bromide on the last-named methyl ester, and is dehydrated by acetyl chloride to 3-phenyl-1-benzhydrylidenehydrindene, dimorphic, m. p. 130—131° and 115—117°. It is readily hydrogenated to 3-phenyl-1-benzhydrylhydrindene. Bromodiphenylmethane interacts with lithio-3-phenylindene to give 3-phenyl-1-benzhydrylindene, m. p. 174·5—175°, tetraphenylethane, 3 : 3′-diphenyl-1 : 1′-di-indenyl), a *dimeride*, m. p. 207—209°, of 3-phenylindene, and a *hydrocarbon* ($C_{28}H_{22}$), dimorphic, m. p. 166—167° and 162—164·5°, reduced catalytically, or by sodium and amyl alcohol, to a *hydrocarbon* ($C_{28}H_{24}$), m. p. 182—184°. The action of methyl iodide on lithio-3-phenylindene leads to 9-methyl- and 9 : 9-dimethyl-fluorene; the interaction of bromodiphenylmethane with lithioindene gives 1-benzhydrylindene (A., 1915, i, 392) unaccompanied by isomerides, and with lithio-2-phenylindene, 2-*phenyl*-1-*benzhydrylindene*, m. p. 175°, converted by sodium and amyl alcohol into 2-*phenyl*-1-*benzhydrylhydrindene*, m. p. 151°.

The "dihydroanthroic acid" of Schlenk and Bergmann is an additive compound of anthroic and tetrahydroanthroic acids, the methyl esters of which may be separated by repeated fractional crystallisation. As a by-product from the action of carbon dioxide on lithioanthracene (Schlenk and Bergmann, *loc. cit.*), 9 : 10-*dihydroanthracene*-9 : 10 : 10-*tricarboxylic acid* (+1Et_2O), m. p. 289—292° (decomp.) (*trimethyl* ester, m. p. 147·5—148°), is formed. Its ready decomposition by boiling with acetic acid into α- and by heating above its m. p. into α- and β-9 : 10-dihydroanthracene-9 : 10-dicarboxylic acids is proof of the structure assigned.

The interaction of alkali-organic compounds with carbonic esters leads generally to esters of the corresponding carboxylic acid; *e.g.*, sodiotriphenylmethyl gives esters of triphenylacetic acid, but in many cases further action produces ketones. With disodiotetraphenylethylene, the original hydrocarbon is re-formed. Methyl carbonate gives with lithiofluorene methyl fluorenyl-9-carboxylate and *difluorenylacetone*, m. p. 230—232° (decomp.), with sodiodiphenylmethyl *s*-tetraphenylacetone, with disodiotetraphenylbutane 1 : 1 : 4 : 4-tetraphenyl*cyclo*pentan-5-one in quantitative yield, and with disodio- or dilithioanthracene *bisdihydroanthranyl ketone*, m. p. 238—240° with decomp. into carbon monoxide, anthracene, and dihydroanthracene. *s*-Tetraphenylacetone interacts with finely-divided sodium in ether to form an enolic *sodio*-derivative, decomposed by heat into tetraphenylallene and ααγγ-tetraphenylpropene.

H. A. PIGGOTT.

Preparation of 2-naphthalene derivatives. A. BARBOT (Bull. Soc. chim., 1930, [iv], **47**, 1314—1323).—When treated with alkyl bromides at 120—130° in presence of aluminium bromide tetrahydronaphthalene yields 2-alkyltetrahydronaphthalenes, which on dehydrogenation with sulphur at 215—220° are converted into 2-alkylnaphthalenes. Similarly, in presence of aluminium chloride acyl chlorides yield exclusively the β-tetrahydronaphthyl ketones and on dehydrogenation with sulphur the corresponding β-naphthyl ketones. With the lower members of the series the condensation yields are poor. Thus methyl bromide at 140—150° affords only 14% of 2-methyltetrahydronaphthalene, b. p. 99—101°/13 mm., together with octahydrophenanthrene and octahydroanthracene. 2-Methylnaphthalene, b. p. 110—112°/16 mm. (picrate, m. p. 115°), is obtained in 75% yield on dehydrogenation for 3 hrs. at 210°. The following are also described: 2-ethyltetrahydronaphthalene, b. p. 121—122°/10 mm. (yield 28—35%, together with a *substance*, $C_{20}H_{24}$, b. p. 219°/9 mm.), 2-ethylnaphthalene, b. p. 117—118°/10 mm., yield 69%; 2-*iso*propyltetrahydronaphthalene, b. p. 124—126°/13 mm., yield 37%, together with the *substance*, $C_{20}H_{24}$, b. p. 219°/9 mm.; 2-*iso*propylnaphthalene, b. p. 129—130°/14 mm., yield 72·5%; 2-*tert.*-butyltetrahydronaphthalene, b. p. 129°/11 mm., yield 70%; 2-*tert.*-butylnaphthalene, yield 70%; β-tetrahydronaphthyl methyl ketone (yield 90%), b. p. 161°/16 mm. (semicarbazone, m. p. 257—258°); β-naphthyl methyl ketone (yield 77%), m. p. 52°, b. p. 171—173°/17 mm. (oxime, m. p. 142°; semicarbazone, m. p. 234—235°); β-tetrahydronaphthyl ethyl ketone (yield 46%), b. p. 169°/17 mm., d_4^{23} 1·033, n^{23} 1·55 (*semicarbazone*, m. p. 224—225°); β-naphthyl ethyl ketone (yield 71·7%), b. p. 181—183°/18 mm., m. p. 58—59°; β-tetrahydronaphthyl propyl ketone (yield 50%), b. p. 178°/18 mm.,

d_{23}^{23} 1·03, n_D^{23} 1·546; β-naphthyl propyl ketone, m. p. 52°, b. p. 184—185°/16 mm.; β-tetrahydronaphthyl *iso*propyl ketone (yield 54%), b. p. 163°/11 mm., d_4^{21} 1·025, n_D^{22} 1·5444; β-naphthyl *iso*propyl ketone (yield 71·4%), b. p. 180—181°/18 mm. The substance, $C_{20}H_{24}$, yields benzoic acid on oxidation with permanganate and is probably α-phenyl-δ-2-tetrahydronaphthylbutane.

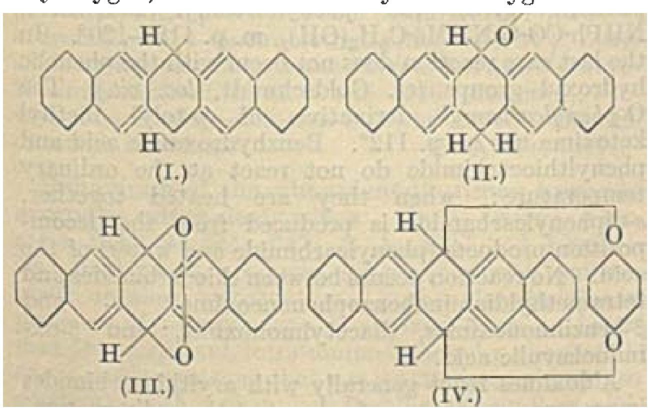
In confirmation of this view, αδ-diphenylbutane, m. p. 52°, is obtained by the condensation of benzene and tetrahydronaphthalene in presence of aluminium bromide and chloride.

With other catalysts substitution in the 2-position does not take place exclusively. R. BRIGHTMAN.

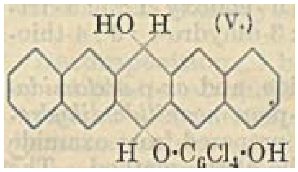
New complex hydrocarbon of the probable formula $C_{16}H_{14}$. C. S. GIBSON and J. D. A. JOHNSON (J.C.S., 1930, 2785—2787).—When chloro-ββ′-dichlorodivinylarsine is treated with benzene in presence of aluminium chloride at 100° (bath), the resulting product contains a small amount of a *hydrocarbon*, probably $C_{16}H_{14}$, m. p. 179—180° (*dibromo*-derivative, not melted at 310° after darkening at 210°), stable to boiling alkaline permanganate. The yellow solution of the hydrocarbon in alcohol exhibits strong bluish-violet fluorescence.

When chloro-ββ′-dichlorodivinylarsine is treated with ethyl sodiomalonate under various conditions, acetylene is produced. H. BURTON.

Polynuclear aromatic hydrocarbons and their derivatives. VII. New class of deeply-coloured radical hydrocarbons and the so-called "pentacene" of Philippi. E. CLAR and F. JOHN (Ber., 1930, 63, [B], 2967—2977; cf. A., 1930, 203).—2 : 3 : 6 : 7-Dibenz-9 : 10-dihydroanthracene gradually passes at the ordinary temperature into 2 : 3 : 6 : 7-*dibenz*-1 : 4-*dihydroanthracene*, m. p. 300—310° when rapidly heated, oxidised by chromic acid in glacial acetic acid exclusively to the diquinone $\left(C_6H_2\left(<^{CO}_{CO}>C_6H_4\right)\right)_2$. The 9 : 10-dihydro-compound is converted by passage over heated copper, by treatment with phenanthraquinone in boiling nitrobenzene, or with chloranil in boiling xylene into 2 : 3 : 6 : 7-dibenzanthracene-9 : 10-diyl (I), blue crystals. When dissolved in xylene the hydrocarbon is not affected by dry oxygen, but is converted by moist oxygen or air



into a mixture of the *peroxides* II, decomp. 335—360°, and III, m. p. 320—330° (decomp.); oxidation is greatly accelerated by light. The suspension of the hydrocarbon in xylene is immediately decolorised by *p*-benzoquinone with production of the quinol *ether* (IV), decomp. 262°, whereas with chloranil it affords a mixture of the analogously constituted *tetrachloroquinyl ether*, decomp. 263°, which dissociates into its components in boiling nitrobenzene and the (3) *monoether* (V), decomp. 267—268°. The last-named compound is converted by aqueous sodium hydroxide into a colourless substance and by glacial acetic acid into a pale red *material*, $C_{28}H_{12}O_2Cl_2$, m. p. 370° (decomp.) after darkening at 300°. Under similar conditions the blue hydrocarbon does not react with phenanthraquinone. It reacts readily with halogens, including iodine, yielding very stable, halogenated diradicals and with boiling aniline containing a little aniline hydrochloride. When sublimed in a vacuum in a current of carbon dioxide above 300° it is transformed into 2 : 3 : 6 : 7-dibenz-9 : 10-dihydroanthracene and a grey residue retaining the crystalline structure of the blue hydrocarbon.



The "*lin*-pentacene" of Philippi (A., 1929, 1436) is oxidisable to 2 : 3 : 6 : 7-dibenzanthraquinone, is dehydrogenated to the blue hydrocarbon, and suffers rise in m. p. when preserved; it is therefore regarded as 2 : 3 : 6 : 7-dibenz-9 : 10-dihydroanthracene.

Reply is made to the criticisms of Scholl and Bottger (A., 1930, 1439). H. WREN.

New colour reaction of aromatic amines. I. DE PAOLINI (Gazzetta, 1930, 60, 859—862).—Addition to neutral alcoholic solution of an aromatic amine of benzoyl peroxide in small doses as long as it dissolves results in the formation of a coloured compound, owing to oxidation of the amine to a quinonoid compound (cf. Gambarjan, A., 1925, i, 1260). Thus, with benzylamine: $3CH_2Ph\cdot NH_2+Bz_2O_2 \longrightarrow CH_2Ph\cdot NHBz + CHPh\!:\!NH + Ph\cdot CO_2NH_3\cdot CH_2Ph + H_2O$. The benzoylating action of benzoyl peroxide is exerted also on other compounds of the type NH_2R; thus, with hydroxylamine and hydrazine hydroxide, *N*-benzoylhydroxylamine and *s*-dibenzoylhydrazine, respectively, are obtained. These actions are probably due to the intermediate formation of perbenzoic acid. In presence of water and of oxidisable substances, this acid may be formed, not only from primary, but also from secondary and tertiary amines, as the result of a hydrolysis analogous to that caused by alkali hydroxides. T. H. POPE.

Preparation of substituted amides and hydrazides. S. M. MISTRY and P. C. GUHA (J. Indian Chem. Soc., 1930, 7, 793—797).—The following diarylcarbamides are prepared in 70—95% yield from carbamide (1 mol.) and the requisite amine (2 mols.) in boiling *iso*amyl alcohol: diphenyl-; di-*m*- and -*p*-tolyl-; di-*m*- and -*p*-nitrophenyl-; di-α- and -β-naphthyl-; di-*p*-acetamidophenyl-; dibenzyl-; *di*-m- and -p-*hydroxyphenyl*-, m. p. 215° (decomp.) and 288° (decomp.), respectively; *o*- and *m*-phenylene-, and diphenylene-carbamides. Similarly, carbamide and *o*-aminobenzoic acid afford 2 : 4-diketo-1 : 2 : 3 : 4-tetrahydroquinazoline; hydrazine hydrate and carb-

amide give semicarbazide (78% yield) preferably in presence of ethyl and *iso*amyl alcohols; diphenyl-, pp′-*dinitrodiphenyl*-, m. p. 361°, and pp′-*dibromodiphenyl-carbohydrazides,* m. p. 236° (decomp.), are obtained from carbamide and the requisite phenylhydrazine, whilst 4-phenylthiosemicarbazide and carbamide yield a mixture of 2-anilino-5-thiol-1-phenyl-1 : 3 : 4-triazole, 2 : 5-endoxy-1 : 3 : 4-triazole, and 5-anilino-2-keto-2 : 3-dihydro-1 : 3 : 4-thiodiazole (A., 1927, 784).

Oxanilide, oxphenylhydrazide, and *ox*-p-*acetamidoanilide*, m. p. above 370° (*ox*-p-*aminoanilide dihydrochloride* is also described), are prepared from oxamide and the requisite amine by the above method. The following are also described: malonanilide; malonphenylhydrazide, m. p. 194—195° (lit. 184° and 187°); *malon*-p-*acetamidoanilide*, m. p. 235° (decomp.); succinanilide; succinphenylhydrazide, m. p. 207—208° [lit. 201° (decomp.)]; *succin*-p-*acetamidoanilide*, m. p. 347° (decomp.); *succin*-p-*aminoanilide*, m. p. 172°. Acetanilide is obtained from aniline and acetamide; *p*-acetamidodiphenylcarbamide from phenylcarbamide and acetyl-*p*-phenylenediamine; di-*p*-acetamidophenylthiocarbamide from thiocarbamide and acetyl-*p*-phenylenediamine; 4-phenylthiosemicarbazide (instead of diphenylthiocarbohydrazide) from phenylhydrazine and thiocarbamide.

o-Nitroamines, hydrazines, and aminobenzenesulphonic acids do not react. Reaction does not occur between arylamines and aromatic acid amides.

H. Burton.

Influence of strength of aromatic amines on their modes of reaction. E. Hertel and K. Schneider (Z. physikal. Chem., 1930, **151**, 413—419).—The extent of the reaction $R\cdot NH_2+H^{\cdot}\leftarrow R\cdot NH_3^{\cdot}$ has been determined by measuring the electrical conductivity of the hydrochlorides of aromatic amines in aqueous acetone in the presence of varying amounts of the free amines. The substances studied were aniline, α- and β-naphthylamines, 4-bromo(chloro)-α-naphthylamine, and 1-bromo-(chloro)-β-naphthylamine. From their relative capacity for combining with hydrogen ions the first three are strong, the fifth is weak, and the fourth of medium strength, "strength" here signifying a property analogous to, but not identical with, the strength of a base in water. The order of strengths is the same when referred to the combination with picric acid in acetone solution. The character of the crystalline compounds formed with nitrophenols depends both on the strength of the amine and on that of the phenol. Thus, aniline, α-, and β-naphthylamine form both with picric acid and with 2 : 6-dinitrophenol compounds of the type $-NO_2\cdots NH_2-$, whereas the two weaker amines form compounds of this type with picric acid only; with the weaker dinitrophenol the linking takes place between a nitro-group and a carbon atom of the nucleus of the amine.

F. L. Usher.

Action of thiocarbimides on oximes. A. Obregia and C. V. Gheorghiu (J. pr. Chem., 1930, [ii], **128**, 239—319; cf. Pavlovski, A., 1904, i, 237).—Reaction between arylthiocarbimides and oximes is less general than with arylcarbimides (Goldschmidt, A., 1890, 251). When reaction does occur, the initial products are probably the normal additive compounds NHAr·CS·O·N:CRR′, but these are unstable and undergo either autoxidation (particularly ketoximes) or self-decomposition (aldoximes). The nature of the final products of the reaction also depends on temperature. Thus, the following changes probably occur between ketoximes and arylthiocarbimides: $2NHAr\cdot CS\cdot O\cdot N{:}CRR' \xrightarrow{heat} 2CRR'{:}N\cdot OH + 2[NHAr\cdot CS\cdot OH] \longrightarrow CS(NHAr)_2 + COS + H_2O$; $2NHAr\cdot CS\cdot O\cdot N{:}CRR'$ (ordinary temperature)$\longrightarrow 2SH\cdot C({:}NAr)\cdot O\cdot N{:}CRR' \xrightarrow{O} [\{\cdot S\cdot C({:}NAr)\cdot O\cdot N{:}CRR'\}_2] \xrightarrow{2H_2O+3O} 2NHAr\cdot CO\cdot O\cdot N{:}CRR' + H_2S_2O_3$.

An equimolecular mixture of phenylthiocarbimide and acetoxime in ethereal solution at the ordinary temperature forms sulphur (produced by decomposition of the intermediate thiosulphuric acid) and the *O*-phenylcarbamyl derivative of acetoxime (Goldschmidt, *loc.* the corresponding o- and p-*tolylcarbamyl* derivatives, m. p. 81—82° and 105—106°, respectively, are obtained similarly, using *o*- and *p*-tolylthiocarbimides. The O-*phenylcarbamyl* derivative, m. p. 135°, of methyl ethyl ketoxime (o- and p-*tolylcarbamyl* derivatives, m. p. 80° and 146—147°, respectively) is obtained from the oxime and phenylthiocarbimide in absence or presence of acetone at the ordinary temperature, or from the oxime and phenylcarbimide. When the reaction is carried out in presence of alcoholic potassium hydroxide, the above phenylcarbamyl derivative and potassium thiosulphate are produced. The separation of sulphur from the reaction mixture of phenylthiocarbimide and methyl ethyl ketoxime is retarded by the absence of air; an attempt to prove the intermediate formation of a disulphide during the autoxidation by Storch's method (A., 1891, 548) was unsuccessful. A small amount of the above carbamyl derivative is formed together with *s*-diphenylthiocarbamide and carbonyl sulphide when phenylthiocarbimide is heated with methyl ethyl ketoxime. The O-*phenylcarbamyl* derivatives of diethyl, methyl propyl, and methyl *iso*butyl ketones, b. p. 175°, d_4^{17} 0·8935, n_D^{20} 1·456 (o-*tolylcarbamyl* derivative, m. p. 184°), have m. p. 96—98°, 146°, and 117°, respectively. Acetophenoneoxime furnishes *O*-phenylcarbamyl, m. p. 131·5° (lit. 126°), and O-o- and -p-*tolylcarbamyl* derivatives, m. p. 109° and 126°, respectively, whilst resacetophenone gives the *phenylcarbamyl* derivative, $NHPh\cdot CO\cdot O\cdot N{:}CMe\cdot C_6H_3(OH)_2$, m. p. 118—120°. In the last case reaction does not occur with the phenolic hydroxyl groups (cf. Goldschmidt, *loc. cit.*). The O-*phenylcarbamyl* derivative of *p*-tolyl methyl ketoxime has m. p. 112°. Benzhydroxamic acid and phenylthiocarbimide do not react at the ordinary temperature; when they are heated together, *s*-diphenylcarbamide is produced from the decomposition products (phenylcarbimide and water) of the acid. No reaction occurs between thiocarbimides and tetramethyldiaminobenzophenoneoxime, α- and β-benzilmonoximes, diacetylmonoxime, and β-oximinolævulic acid.

Aldoximes react generally with arylthiocarbimides in presence or absence of solvent at the ordinary temperature, forming mainly carbonyl sulphide, *s*-diarylthiocarbamides, and the nitriles corresponding with

the oximes used: $2NHAr\cdot CS\cdot O\cdot N{:}CHR \longrightarrow 2R\cdot CN + [2NHAr\cdot CS\cdot OH] \longrightarrow CS(NHAr)_2 + COS + H_2O$. The following secondary reaction also occurs whereby sulphur is formed: $2[SH\cdot C({:}NAr)\cdot O\cdot N{:}CHR] \xrightarrow{O} [\cdot S\cdot C({:}NAr)\cdot O\cdot N{:}CHR]_2 \longrightarrow 2R\cdot CN + [\cdot S\cdot C({:}NAr)\cdot OH]_2 \longrightarrow CS(NHAr)_2 + S + CO$, or $CO(NHAr)_2 + S + COS$. The same products are formed from both *syn*- and *anti*-oximes; the reaction thus differs from that with carbimides (Goldschmidt, *loc. cit.*). Since the nitrile is produced, it follows that the *anti*-additive compound rearranges into the *syn*-form. When reaction is carried out in presence of alcoholic potassium hydroxide, α-benzaldoxime and *anti*-furfuraldoxime afford mainly the *O*-arylcarbamyl derivative of the oxime and potassium thiosulphate; secondary reactions occur as above. α-Anisaldoxime and α-salicylaldoxime undergo the general reactions in presence of alkali. The reactions between phenylthiocarbimide and *o*- and *p*-tolylthiocarbimides and α- and β-benzaldoxime, acetaldoxime, salicylaldoxime (reaction does not occur with the phenolic hydroxyl group), α- and β-anisaldoximes, and *syn*- and *anti*-furfuraldoximes are studied. The O-*o-tolylcarbamyl* derivative of α-benzaldoxime has m. p. 124°.

H. Burton.

New process for preparing tetryl. L. Desvergnes (Chim. et Ind., 1930, **24**, 785—793, 1304—1316).—The solubilities of the oxalates of aniline and mono- and di-methylanilines in 95·7% alcohol, 50% alcohol, and water were determined at various temperatures. By fractional crystallisation of the mixed oxalates from water, methylaniline may be separated in a state of purity from a technical mixture with dimethylaniline, but aniline if present is not completely removed. Methylation of aniline by gradual addition of 1 mol. of methyl sulphate gives a mixture containing dimethylamine, and offers no advantage over ordinary methods of alkylation.

A technical method for the preparation of tetryl by a two-stage nitration of methylaniline is described. In the first stage methylaniline sulphate is added to a diluted mixture of nitric and sulphuric acids at 20—30°, 2 : 4-dinitromethylaniline and a small amount of a new *dinitromethylaniline* being produced. Further nitration of these with more concentrated acids at 70—75° gives tetryl and an isomeric *trinitro*-N-*nitromethylaniline*, m. p. 250—253° (decomp.) [261—262° (decomp.) when pure ?]. From the product of nitration of technical 2 : 4-dinitromethylaniline with 31% nitric acid on the water-bath, a small amount of a new *dinitro*-N-*nitromethylaniline*, m. p. 235—236° (decomp.), converted by further nitration into the above isomeride of tetryl, is isolated.

H. A. Piggott.

Behaviour of the phenylenediamines towards aromatic nitro-derivatives. G. B. Crippa (Gazzetta, 1930, **60**, 644—647; cf. A., 1927, 352, 1205).—The final black product, comparable with aniline-black, obtained by oxidation of *p*-phenylenediamine in presence of nitrobenzene, is derived from an intermediate compound, tetra-aminodiphenyl-*p*-azophenylene. *m*-Nitrotoluene (but not its two isomerides) also condenses with *o*-phenylenediamine, giving 2-m-*tolylbenztriazole*, $C_6H_4{<}\overset{N}{\underset{N}{|}}{>}N\cdot C_6H_4Me$, m. p. 99°, also obtainable as follows. By condensation of *m*-nitrosotoluene and benzoyl-*o*-phenylenediamine, m-*tolueneazo-o'-benzamidobenzene*, m-$CH_3\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NHBz(o)$, m. p. 100°, is obtained, giving on hydrolysis m-*tolueneazo-o'-aminobenzene*, m. p. 81°, which is converted by Zincke's method into the triazole. No condensation occurs between nitrobenzene and *m*-phenylenediamine.

T. H. Pope.

Decomposition of benzenediazonium sulphate by aliphatic alcohols. H. H. Hodgson and A. Kershaw (J.C.S., 1930, 2784—2785).—Dry benzenediazonium sulphate is decomposed by warming with an excess of an alcohol and the amount of aldehyde (=benzene) produced is determined as the *p*-nitrophenylhydrazone. The amounts of aldehyde (as mol.-%) produced from the following alcohols are: benzyl, 19·5; methyl, 0; ethyl, 9·4; *n*-propyl, 4·7; *iso*propyl, 5; *iso*propyl+water, 3·6; *n*-butyl, 1·25. Ether formation is the main reaction.

H. Burton.

Mechanism of the production of hydrazones from diazo-compounds and alkyl derivatives of acetoacetic, malonic, and cyanoacetic esters. G. Favrel (Bull. Soc. chim., 1930, [iv], **47**, 1290—1300).—*m*-Nitrobenzenediazonium hydroxide in acetic acid solution at 0° couples with ethyl ethylacetoacetate in ethereal solution, yielding *ethyl* m-*nitrobenzeneazoethyl acetoacetate*, $NO_2\cdot C_6H_4\cdot N_2\cdot CEtAc\cdot CO_2Et$, m. p. 132—133°, which on reduction in alcoholic solution with acetic acid and sodium amalgam yields *m*-phenylenediamine, and with aqueous alkali isomerises to the *m*-nitrophenylhydrazone, m. p. 77—78°. Ethyl methylacetoacetate similarly gives *ethyl* m-*nitrobenzeneazomethylacetoacetate*, m. p. 122—123°, isomerising to the *m*-nitrophenylhydrazone of ethyl pyruvate, m. p. 102—103°, but the diazonium hydroxides derived from toluidines, chloroanilines, bromoanilines, etc. yield oils which decompose at 110° and could not be purified, but by the action of aqueous alkalis or, more slowly, by water alone are converted into the corresponding hydrazones. With ethyl ethylmalonate or ethyl methylmalonate the condensation product is always an oil. The hydrazones obtained from these compounds by treatment with water or alkalis are identical with those obtained from the same diazo-compounds and alkylacetoacetates and from phenylhydrazine and ethyl pyruvate or its homologue. *pp'*-Diphenyltetrazonium hydroxide in acetic acid and ethyl ethylmalonate in ether at 0° yield the *dihydrazone*, $[\cdot C_6H_4\cdot NEt\cdot N{:}C(CO_2Et)_2]_2$, m. p. 112—114° (decomp.), which on reduction with zinc and acetic acid yields *NN'*-diethylbenzidine. Methyl methylmalonate similarly affords the *dihydrazone*, $[\cdot C_6H_4\cdot NMe\cdot N{:}C(CO_2Me)]_2$, m. p. 103—104° (decomp.), yielding on reduction NN'-*dimethylbenzidine*, m. p. 77—78°. With tetrazotised *o*-tolidine ethyl ethylmalonate yields the dihydrazone, $[\cdot C_6H_3Me\cdot NEt\cdot N{:}C(CO_2Et)_2]$, m. p. 118—120° (decomp.), and with dianisidine the dihydrazone, $[\cdot (OMe)C_6H_3\cdot NEt\cdot N{:}C(CO_2Et)_2]_2$, m. p. 115—116° (decomp.).

Ethyl ethylcyanoacetate in ether at 0° with *p*-bromobenzenediazonium hydroxide yields both the

hydrazone, $C_6H_4Br\cdot NEt\cdot N\colon C(CN)\cdot CO_2Et$, m. p. 56—57°, and the *azo*-compound, $C_6H_4Br\cdot N\colon N\cdot CEt(CN)\cdot CO_2Et$, m. p. 111—112°, which on reduction yield ethylaniline and *p*-bromoaniline with a little aniline, respectively. The same compounds are obtained from *p*-bromophenylhydrazine and ethyl cyanomalonate. *m*-Nitrobenzenediazonium hydroxide and ethyl methylcyanoacetate yield both the hydrazone, $NO_2\cdot C_6H_4\cdot NMe\cdot N\colon C(CN)\cdot CO_2Et$, m. p. 148°, and the *azo*-derivative, $NO_2\cdot C_6H_4\cdot N\colon N\cdot CMe(CN)\cdot CO_2Et$, m. p. 197—198°; benzenediazonium hydroxide and ethyl ethylcyanoacetate give the *hydrazone*, m. p. 72°, and *azo*-compound, m. p. 126°. Ethyl cyanoacetoacetate and benzenediazonium hydroxide yield only the *azo*-compound, $Ph\cdot N\colon N\cdot C(CN)(COMe)\cdot CO_2Et$, m. p. 129—130°.

R. BRIGHTMAN.

Labile compound of benzeneazo-β-naphthol and β-naphthol. H. H. HODGSON and W. ROSENBERG (J.C.S., 1930, 2787).—When diazotised aniline is coupled with β-naphthol in aqueous sodium hydroxide (1 equiv.) containing an excess of sodium carbonate and the resultant product crystallised from benzene, an additive *compound* ($+C_6H_6$), m. p. 62—64°, m. p. (benzene-free) 79—80°, of 1 mol. of benzeneazo-β-naphthol and 1 mol. of β-naphthol is frequently produced. Crystallisation of the benzene-free product from acetic acid, pyridine, or alcohol gives benzeneazo-β-naphthol, m. p. 133—134° (lit. 131°). When coupling is effected in aqueous sodium hydroxide, hydrogen carbonate, acetate, or borate, only benzeneazo-β-naphthol results. Equimolecular amounts of benzenediazonium sulphate and aqueous sodium β-naphthoxide give the double compound, and unchanged diazonium salt remains in solution; with excess of the oxide a quantitative yield results.

H. BURTON.

Preparation of unsaturated ethers from acetals. A. JOHANNISSIAN and E. AKUNIAN (Bull. Univ. Etat R.S.S. Armenie, 1930, No. 5, 245—251; Chem. Zentr., 1930, ii, 552).—Toluene-*p*-sulphonic acid is a good catalyst for the preparation of alkoxy*cyclo*hexenes from the corresponding acetals. On long heating the reaction takes place in absence of a catalyst.

A. A. ELDRIDGE.

Preparation of *p*-nitrophenol from *p*-chloronitrobenzene. A. M. POPOV (Ukraine Chem. J., 1930, 5, [Tech.], 105—111).—The usual method of obtaining *p*-nitrophenol by nitrating phenol and separating the *o*- and *p*-isomerides by steam-distillation is slow and gives a poor yield. By heating *p*-chloronitrobenzene with sodium hydroxide a 93% yield is obtained after 30 min. at 160—162°. Excess of alkali has no influence on the yield, temperature being the chief factor. A theoretical relationship is given connecting temperature and yield. On the semi-technical scale 83% of the theoretical yield was obtained under the same conditions.

E. B. UVAROV.

[Preparation of] picramic acid. E. CLAYTON (J. Soc. Dyers and Col., 1930, 46, 365).—In the preparation of picramic acid by partial reduction of picric acid with sodium sulphide the initial p_H of the reaction mixture is a governing factor; the best yields are obtained when the concentration of alkali is low. The highest yields (90%) result from reduction of an aqueous solution of sodium picrate with sodium hydrosulphide at 50—66% (details given), and high yields are favoured by the use of a reducing agent the aqueous solution of which has a low hydrolysis constant. Confirmation is obtained of the view that in the reduction of polynitro-compounds the presence of hydroxyl ions in the reaction mixture leads to the production of azoxy-compounds, whilst their absence favours the formation of amino-compounds. The highest yields of picramic acid appear to result when the reaction proceeds thus: picric acid $\longrightarrow$ nitroso-derivative $\longrightarrow$ hydroxylamino-derivative $\longrightarrow$ picramic acid, and it follows that the formation of azoxy-derivatives should be avoided.

A. J. HALL.

Syntheses of aceto-*p*-phenetidide. A. KOSS and Z. KWIATKOWSKI (Rocz. Farm., 1928, 15—28; Chem. Zentr., 1930, ii, 549).—A criticism.

A. A. ELDRIDGE.

Action of trichloromethyl chloroformate on phenols. N. MELNIKOV (J. pr. Chem., 1930, [ii], **128**, 233—238, and J. Russ. Phys. Chem. Soc., 1930, **62**, 1671—1675; cf. A., 1930, 738, 1019, 1270).—Trichloromethyl chloroformate (1 mol.) reacts with sodium aryloxides (1 mol.) in aqueous solution, forming aryl trichloromethyl carbonates; with 4 mols. of the aryloxide, diaryl carbonates are produced. The following are new: p-*tolyl*, b. p. 162°/10 mm., m. p. 47°; β-*naphthyl*, m. p. 128°; p-*chlorophenyl*, m. p. 109°, and p-*nitrophenyl trichloromethyl carbonates*, m. p. 132°. Treatment of these mixed carbonates with aniline in ether affords a mixture of diphenylcarbamide and the appropriate aryl phenylcarbamate.

H. BURTON.

Sulphur derivatives of *o*-methoxytoluene. G. B. KOLHATKAR and K. V. BOKIL (J. Indian Chem. Soc., 1930, 7, 843—850).—The compound, m. p. 138°, obtained by Meldrum and Shah (J.C.S., 1923, **123**, 1992) as a by-product during the sulphonation of *o*-methoxytoluene is also formed from 2-methoxytoluene-5-sulphonyl chloride and *o*-methoxytoluene in presence of aluminium chloride and carbon disulphide; it is, therefore, 6 : 6′-*dimethoxydi*-m-*tolylsulphone*. This is oxidised by alkaline potassium permanganate to 4 : 4′-*dimethoxydiphenylsulphone*-3 : 3′-*dicarboxylic acid*, m. p. 250° (decomp.) after sintering at 245°, which when heated with calcium oxide gives 4 : 4′-dimethoxydiphenylsulphone. Demethylation of the above sulphone and acid with hydriodic acid (*d* 1·7) at 165° furnishes 6 : 6′-*dihydroxydi*-m-*tolylsulphone*, m. p. 263° (corr.), and 4 : 4′-*dihydroxydiphenylsulphone*-3 : 3′-*dicarboxylic acid*, m. p. 306—307° (decomp.), respectively. Benzenesulphonyl chloride and *o*-methoxytoluene react as above, forming 4-*methoxy*-3-*methyldiphenylsulphone*, m. p. 112—112·5°, also obtained from benzene and 2-methoxytoluene-5-sulphonyl chloride. This is demethylated to 4-*hydroxy*-3-*methyldiphenylsulphone*, m. p. 226°, and oxidised to 4-*methoxydiphenylsulphone*-3-*carboxylic acid*, m. p. 176° (the corresponding 4-*hydroxy-acid* has m. p. 216—217°). *p*-Toluenesulphonyl chloride and *o*-methoxytoluene

yield 4-*methoxy*-3 : 4′-*dimethyldiphenylsulphone*, m. p. 109·5—110°, also formed from toluene and 2-methoxytoluene-5-sulphonyl chloride. 4-*Hydroxy*-3 : 4′-*dimethyldiphenylsulphone* and 4-*methoxydiphenylsulphone*-3 : 4′-*dicarboxylic acid* have m. p. 200—201° and 283°, respectively. *p*-Methoxybenzenesulphonyl chloride and *o*-methoxytoluene give 4 : 4′-*dimethoxy*-3-*methyldiphenylsulphone*, m. p. 126°, also produced together with an *isomeride*, m. p. 102°, from anisole and 2-methoxytoluene-5-sulphonyl chloride. 4 : 4′-*Dimethoxydiphenylsulphone*-3-*carboxylic acid* has m. p. 186—187°. *o*-Anisolesulphonyl chloride and *o*-methoxytoluene afford (?) 2′ : 4-*dimethoxy*-3-*methyldiphenylsulphone*, m. p. 145°.

Treatment of *o*-methoxytoluene with sulphur dioxide in presence of aluminium chloride yields a mixture of *tri*-o-*methoxytolylsulphonium chloride* ($+3H_2O$), m. p. 69—70°, m. p. (anhydrous) 140—141°, and 6 : 6′-*dimethoxydi*-m-*tolylsulphoxide*, m. p. 87—87·5°. This sulphoxide is reduced by zinc dust and acetic acid to 6 : 6′-*dimethoxydi*-m-*tolyl sulphide*, m. p. 37·5—38°. When 2-methoxytoluene-5-sulphonyl chloride is reduced with alkaline sodium sulphite a mixture of 2-methoxytoluene-5-sulphinic acid (*sodium* and *silver* salts) and 6 : 6′-*dimethoxydi*-m-*tolyldisulphone*, m. p. 206·5° (decomp.), is produced. The sulphinic acid changes spontaneously into 6 : 6′-*dimethoxydi*-m-*tolyldisulphoxide*, m. p. 118°, which is prepared by oxidising 6 : 6′-*dimethoxydi*-m-*tolyl disulphide*, m. p. 44—45°, with hydrogen peroxide in acetic acid. This disulphide is produced when 5-*thiol*-2-*methoxytoluene*, b. p. 236—237°, m. p. 42—43°, is oxidised by iodine. H. BURTON.

Preparation of β-*p*-hydroxyphenylethylamine. T. KONDO and Y. SHINOZAKI (J. Pharm. Soc. Japan, 1929, 49, 267—269).—Electrolytic reduction of *p*-methoxy-ω-nitrostyrene (obtained by treatment of alcoholic anisaldehyde and nitromethane with methyl-alcoholic potassium hydroxide) gave β-p-*methoxyphenylethylamine hydrochloride*, m. p. 210° (*hydroxy*-compound, m. p. 268—269°).

CHEMICAL ABSTRACTS.

β-Phenylethylamines. I. Mezcaline and substances resembling mezcaline. K. H. SLOTTA and H. HELLER (Ber., 1930, 63, [*B*], 3029—3044).—*o*-Methoxybenzaldehyde is condensed with malonic acid in pyridine containing piperidine at 100° to *o*-methoxycinnamic acid, m. p. 183° (yield 80%), which is reduced by sodium amalgam to β-*o*-methoxyphenylpropionic acid, m. p. 92° (yield 99%), converted by thionyl chloride in chloroform into the corresponding chloride and thence by sodium hydroxide and ammonia into β-o-*methoxyphenylpropionamide*, m. p. 111° (yield 86·3%). The amide is transformed by successive treatment with sodium hypochlorite and potassium hydroxide into β-*o*-methoxyphenylethylamine (yield 35·2%) (*hydrochloride*, m. p. 143°; *sulphate*, m. p. 230°). *m*-Nitrobenzaldehyde is transformed by the usual methods into *m*-methoxybenzaldehyde, which is converted successively into *m*-methoxycinnamic acid, m. p. 177°; β-*m*-methoxyphenylpropionic acid, m. p. 50°, and β-*m*-methoxyphenylpropionamide, b. p. 222—225°/12 mm. The amide is converted by sodium hypobromite into β-*m*-methoxyphenylethylamine, b. p. 182°/112 mm., in 61% yield, whereas with hypochlorite the yield is only 19%. Anisaldehyde is similarly transformed into β-*p*-anisylpropionamide, transformed by hypochlorite into β-*p*-anisylethylamine hydrochloride, m. p. 210°, in 43% yield. Cuminaldehyde and malonic acid yield successively *p*-*iso*propylcinnamic acid, m. p. 165°; β-*p*-*iso*propylphenylpropionic acid, m. p. 73°, and β-p-iso*propylphenylpropionamide*, m. p. 142°, degraded by hypochlorite at 65° to β-p-iso*propylphenylethylamine hydrochloride*, m. p. 270°, in small yield. Vanillin ethyl ether, m. p. 63°, affords successively 3-*methoxy*-4-*ethoxycinnamic acid*, m. p. 205° (yield 89%); β-3-*methoxy*-4-*ethoxyphenylpropionic acid*, m. p. 130° (yield 79%); β-3-*methoxy*-4-*ethoxyphenylpropionamide*, m. p. 124° (yield 33·9%), and (by sodium hypochlorite, but not hypobromite) β-3 methoxy-4-ethoxyphenylethylamine, b. p. 165°/15—18 mm. (*hydrochloride*, m. p. 120°). 2 : 4-Dimethoxybenzaldehyde gives 2 : 4-dimethoxycinnamic acid and β-2 : 4-dimethoxyphenylpropionic acid, m. p. 105°, which could not be transformed into the corresponding amide. Piperonal is converted into β-3 : 4-methylenedioxyphenylethylamine (hydrochloride, m. p. 206°). 2 : 3 : 4-Trimethoxybenzaldehyde, b. p. 170°/12 mm., is obtained in 53% yield by the addition of pyrogallol trimethyl ether and hydrogen cyanide to aluminium chloride in benzene and treatment of the product with steam. It affords successively 2 : 3 : 4-*trimethoxycinnamic acid*, m. p. 172° (yield 94%); β-2 : 3 : 4-*trimethoxyphenylpropionic acid*, m. p. 76° (yield 65%); β-2 : 3 : 4-*trimethoxyphenylpropionamide*, m. p. 171° (yield 63·5%), and (by sodium hypobromite) β-2 : 3 : 4-*trimethoxyphenylethylamine*, b. p. 167°/12 mm. (yield 71·5%) (*hydrochloride*, m. p. 146°). 3 : 4 : 5-Trimethoxybenzoyl chloride is converted by hydrogen in boiling xylene in presence of palladised barium sulphate into 3 : 4 : 5-trimethoxybenzaldehyde, m. p. 74° (yield 80%). The aldehyde yields successively 3 : 4 : 5-trimethoxycinnamic acid, m. p. 124°; β-3 : 4 : 5-*trimethoxyphenylpropionic acid*, m. p. 98° (yield 88%); β-3 : 4 : 5-*trimethoxyphenylpropionamide*, m. p. 106° (yield 60%), and (by sodium hypobromite) β-3 : 4 : 5-trimethoxyphenylethylamine (mezcaline), b. p. 180°/12 mm. (yield 66%).

Anisole in glacial acetic acid is converted by bromine vapour into *p*-bromoanisole, b. p. 120°/12 mm. (yield 82·9%), transformed by successive treatment with activated magnesium in ether and ethylene oxide into β-*p*-anisylethyl alcohol, in 31·1% yield. With 47·5% hydrobromic acid the alcohol gives β-*p*-anisylethyl bromide (yield 45%), transformed by successive treatment with phthalimide and potassium carbonate and hydrazine hydrate into β-*p*-anisylethylamine in 11·8% yield. 4-Bromoveratrole, *p*-bromophenol, *p*-bromophenyl acetate, *o*- and *p*-bromonitrobenzene, and *o*-dichlorobenzene could not be caused to react with magnesium in ethyl or *iso*amyl ether.

H. WREN.

Derivatives of *m*-xylenols. I. Intermediate products from *m*-5-xylenol (5-hydroxy-1 : 3-dimethylbenzene). F. M. ROWE, S. H. BANNISTER R. R. SETH, and R. C. STOREY (J.S.C.I., 1930, 49, 469—473T).—Direct nitration of *m*-5-xylenol in

acetic acid is accompanied by much resinification, but gives volatile 4-nitro-*m*-5-xylenol, m. p. 66° (29%), and non-volatile 2-nitro-*m*-5-xylenol, m. p. 107—108° (18%). Monosulphonation of *m*-5-xylenol under all conditions appears to occur solely in *o*-position to the hydroxyl group, and *m*-5-xylenol-4-sulphonic acid is best made with cold monohydrate. There is a confusion in the properties of this acid as described by Raschig (G.P. 283,306). The sulphonic acid is very soluble in water, but does not separate as crystals, m. p. 102—103°, on adding concentrated hydrochloric acid to a concentrated solution. A sulphur-containing *by-product*, m. p. 111—112°, however, is formed in sulphonations with chlorosulphonic acid at 100°. Nitration of *m*-5-xylenol-4-sulphonic acid in monohydrate gives a little 4-nitro-*m*-5-xylenol, but mainly nitrosulphonic acids, from which 4-nitro- (total 38%) and 2-nitro-*m*-5-xylenol (29%) are obtained by acid hydrolysis. Nitration of 2-nitro-*m*-5-xylenol in acetic acid gives volatile 2 : 4-dinitro-*m*-5-xylenol, m. p. 115—116° (85%), but nitration of 4-nitro-*m*-5-xylenol in monohydrate gives some non-volatile 2 : 4 : 6-trinitro-*m*-5-xylenol, m. p. 107—108°, and mainly 2 : 4-dinitro-*m*-5-xylenol-6-sulphonic acid, from which the sulphonic group is eliminated by boiling with aqueous sulphuric acid. Non-volatile 4 : 6-*dinitro*-m-5-*xylenol*, m. p. 126—127°, was obtained only as a by-product of the nitration of a sulphonation mixture probably containing 4 : 6-disulphonic acid. *Toluene*-p-*sulphonyl*-m-5-*xylenol*, m. p. 83°, is nitrated satisfactorily only to a *trinitro*-derivative, m. p. 148—149° (70%), readily hydrolysed by boiling aqueous-alcoholic potassium hydroxide to 2 : 4-dinitro-*m*-5-xylenol (97%).

Diazotised aniline couples with *m*-5-xylenol under all conditions to give a mixture of mono- (maximum 73%) and dis-azo-compounds, alkaline coupling favouring formation of the latter. Reduction of benzeneazo-*m*-5-xylenol, m. p. 104—105°, with alkaline sodium hyposulphite gives 2-amino-*m*-5-xylenol, m. p. 182° (96%), which is obtained also by a similar reduction of 2-nitroso-*m*-5-xylenol, m. p. 182° (decomp.), and forms a *diacetyl* derivative, m. p. 182°. Attempts to prepare 2 : 4-dinitro-4′-hydroxy-2′ : 6′-dimethyldiphenylamine always gave its 2″ : 4″-*dinitrophenyl ether*, m. p. 283—284° (23%).

Reduction of 4-nitro-*m*-5-xylenol with alkaline sodium hyposulphite gives 4-amino-*m*-5-xylenol, m. p. 163° (72%) (*diacetyl* derivative, m. p. 87—88°).

m-5-Xylenol and methyl sulphate give the methyl ether, b. p. 194—195° (87%), which could not be mononitrated. Methyl sulphate with the corresponding nitroxylenols gives the volatile 4-*nitro*-5-m-*xylenol methyl ether*, m. p. 45—46°, and the non-volatile 2-*nitro-methyl ether*, m. p. 53°. Dinitration of *m*-5-xylenol methyl ether gives the 2 : 4-*dinitro*-derivative, m. p. 172°, identical with the methylation product of 2 : 4-dinitro-*m*-5-xylenol, and some 2 : 4 : 6-*trinitro*-derivative, m. p. 124—125°.

Reduction of 4-nitro-*m*-5-xylenol methyl ether with acid stannous chloride gives volatile 4-*amino*-m-5-*xylenol methyl ether*, m. p. 36—37° (80%) (*diacetyl* derivative, m. p. 80—81°), but reduction with alkaline sodium hyposulphite is accompanied by the introduction of a sulphonic group, giving *sodium* 4-*amino*-m-5-*xylenolsulphonate*. Reduction of 2 : 4-dinitro-*m*-5-xylenol methyl ether with sodium sulphide gives, presumably, 2-*nitro*-4-*amino*-m-5-*xylenol methyl ether*, m. p. 91° (76%).

Alkamine and ether-bases of the tetralin and hydrindene series. J. von Braun and K. Weissbach (Ber., 1930, **63**, [*B*], 3052—3059).—When the product of the action of ammonia, methylamine, or dimethylamine on 2-bromo-1-hydroxy-1 : 2 : 3 : 4-tetrahydronaphthalene (cf. A., 1923, i, 105) is treated with methyl sulphate and sodium hydroxide and subsequently with potassium iodide it yields 2-*methoxy*-1 : 2 : 3 : 4-*tetrahydronaphthyltrimethylammonium iodide*, m. p. 168°. When heated at 170° it is decomposed into trimethylamine hydriodide and 2-*methoxy*-3 : 4-*dihydronaphthalene*, b. p. 136°/15 mm., d_4^{27} 1·0674, converted by 2*N*-hydrochloric acid into 2-keto-1 : 2 : 3 : 4-tetrahydronaphthalene, b. p. 132—133°/12 mm. The ether is relatively slowly hydrogenated in presence of palladium to 2-*methoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b. p. 123—124°/16 mm.; in carbon disulphide it readily adds bromine and loses hydrogen bromide with production of β-naphthyl methyl ether.

2-Bromo-1-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene and dimethylamine in benzene at 100° afford 2-*dimethylamino*-1-*methoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b. p. 147—149°/13 mm. (*hydrochloride*, m. p. 184°; *picrate*, m. p. 192°; *methiodide*, m. p. 210°). 2-*Methylamino*-1-*methoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b. p. 144—146°/14 mm., yields a *hydrochloride*, m. p. 228°; a *picrate*, m. p. 150°, and a *methiodide*, m. p. 210°. 2-*Piperidino*-1-*methoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b. p. 191—193°/15 mm., its *hydrochloride*, m. p. 230°, and *picrate*, m. p. 153°, are described. 1-Methoxy-1 : 2 : 3 : 4-tetrahydro-2-naphthyltrimethylammonium iodide decomposes only to a slight extent when heated about 10° above its m. p., but yields 2-dimethylamino-1-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene when subjected to dry distillation. 2-Methylamino-1-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene is transformed by 66% hydrobromic acid at 55—60° into 2-*methylamino*-1-*hydroxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m. p. 77—79°, b. p. about 122°/0·2 mm. (*hydrochloride*, m. p. 206°; *picrate*); if the treatment with hydrobromic acid is conducted at 100° the product is 2-*methylamino*-3 : 4-*dihydronaphthalene*, b. p. 162—164°/12 mm. (hygroscopic *hydrochloride*, m. p. 148—150°; *picrate*, m. p. 149°). Similar treatment of the 2-dimethylamino- and 2-piperidino-derivatives with hydrobromic acid at 40—45° affords, respectively, 2-*dimethylamino*-3 : 4-*dihydronaphthalene*, b. p. 102—104°/0·4 mm. (non-crystalline *hydrochloride*; *picrate*, m. p. 148°), and 2-*piperidino*-3 : 4-*dihydronaphthalene*, b. p. 168—170°/0·4 mm., m. p. 40° (*picrate*, m. p. 149°).

1-*Methylamino*-2-*hydroxyhydrindene*, m. p. 130° (*hydrochloride*, m. p. 175°; *picrate*, m. p. 153°), is prepared by the action of 33% aqueous methylamine on bromohydroxyhydrindene (cf. A., 1923, i, 107). If the product of the action of methylamine, dimethylamine, or ammonia on 2-bromo-1-hydroxyhydrindene is treated with methyl sulphate and, subsequently, potassium iodide, 2-*methoxyhydrindyltrimethylammon*-

ium iodide, m. p. 187°, is formed. It decomposes when heated above its m. p. or, preferably, when distilled in a vacuum into 1-*dimethylamino-2-methoxyhydrindene*, b. p. 132°/14 mm. (*picrate*, m. p. 159°), hydrolysed by acid to 2-hydrindone. 2-*Dimethylamino*-1-*methoxyhydrindene*, b. p. 128—129°/14 mm. (*methiodide*, m. p. 176°), is obtained by the action of dimethylamine in benzene at 100° on 2-*bromo*-1-*methoxyhydrindene*, b. p. 134°/11 mm., prepared by the action of boiling methyl alcohol on 1 : 2-dibromohydrindene. 2-*Methylamino*-1-*methoxyhydrindene*, b. p. 127—128°/14 mm. (*picrate*, m. p. 118°; *hydrochloride*, m. p. 173°), is described. Replacement of methoxyl by hydroxyl is more difficult than in the tetrahydronaphthalene series owing to the tendency of the products towards polymerisation, but treatment of the methylamino-base with fuming hydrobromic acid at the ordinary temperature and subsequently at 45—50° affords 2-*methylamino*-1-*hydroxyhydrindene*, m. p. 77—79° (*picrate*, m. p. 171°), in small amount. The base loses water with great readiness, whereby in presence of hydrochloric acid a *compound*, $C_{10}H_{13}NCl_2$, m. p. 165—166°, is produced. Replacement of methoxyl by hydroxyl does not appear possible in the case of the dimethylamino-base. H. WREN.

Course of substitution reactions. Aromatic and hydroaromatic halogen compounds from β-naphthol. K. FRIES and K. SCHIMMELSCHMIDT (Annalen, 1930, 484, 245—300).—The reaction $C_{10}H_7{\cdot}OH(\beta)+Br_2 \rightleftharpoons C_{10}H_6Br{\cdot}OH+HBr$ is shown to be reversible, since treatment of 1-bromo-β-naphthol with 10 parts of a saturated solution of hydrogen bromide in acetic acid in presence of 1 part of potassium iodide (saturated aqueous solution diluted with 3 parts of acetic acid) gives, after some hours at the ordinary temperature or after a few seconds at 100°, β-naphthol. Potassium iodide may be replaced by stannous chloride and hydrogen bromide by hydrogen chloride. 1 : 6-Dibromo-β-naphthol is converted similarly into 6-bromo-β-naphthol. 1-Chloro- and 1 : 4-dichloro-β-naphthols afford β-naphthol and 4-chloro-β-naphthol, respectively, when treated with a solution of hydrogen chloride in acetic acid in presence of stannous chloride at 100°.

Further evidence is now brought forward supporting the formation of ketobromides during the bromination of β-naphthol derivatives. Various discrepancies in the literature are also explained, the chief of which is that bromination of β-naphthol gives successively the 1-bromo-, 1 : 6-dibromo-, and 1 : 4 : 6-tribromo-derivatives (cf. Franzen and Stauble, A., 1922, i, 450). The tetrabromo-β-naphthols, formed by bromination in acetic acid, consist of the 1 : 3 : 4 : 6-, 1 : 3 : 5 : 6-, and 1 : 3 : 6 : 8-derivatives; the last two compounds are not produced by simple substitution processes. Different derivatives are produced when the ketobromides are brominated (and the products then reduced) from those formed when bromo-β-naphthols are brominated. Thus, 1 : 3 : 6-tribromo-β-naphthol is produced when 1 : 1-dibromo-2-keto-1 : 2-dihydronaphthalene is brominated and the resultant product reduced. Extensions of the changes previously suggested (A., 1924, i, 1187) are given which explain the formation of the polybromo-β-naphthols now described.

2 : 3-Hydroxynaphthoic acid and a large excess of bromine in acetic acid at 100° give the 1 : 5 : 6-*tribromo*-derivative, m. p. 320°, oxidised by boiling nitric acid (*d* 1·4) to 3 : 4-*dibromophthalic acid*, m. p. 196° (decomp.) (*anhydride*, m. p. 148·5°). When bromination is carried out in cold acetic acid containing sodium acetate, 1 : 1 : 3 : 3-*tetrabromo-2-keto-4-acetoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m. p. 140°, decomp. 155°, is produced; carbon dioxide is eliminated. This is reduced by stannous chloride and alcoholic hydrochloric acid to 1 : 3-*dibromo-2-hydroxy-4-acetoxynaphthalene*, m. p. 148° [the 2 : 4-diacetoxy-derivative, m. p. 122°, is identical with that described by Meyer and Wolfsleben (A., 1911, i, 631)], which is converted by alkaline sodium stannite into 1 : 1′-*dibromo*-2 : 4 : 2′ : 4′-*tetrahydroxy*-3 : 3′-*dinaphthyl*, m. p. 242° (decomp.) (*tetra-acetate*, m. p. 222—223°). Treatment of the above tetrabromo-derivative with hydrogen bromide in acetic acid gives 1 : 3 : 6-tribromo-2 : 4-dihydroxynaphthalene, whilst reduction with zinc dust and acetic acid affords 1 : 3-*dibromo*-β-*naphthol*, m. p. 75° (*acetate*, m. p. 102°), which with nitric acid (*d* 1·52) in cold acetic acid yields 1 : 3-*dibromo*-1-*nitro*-2-*keto*-1 : 2-*dihydronaphthalene*, m. p. 98° (decomp.). When a solution of this nitro-compound is boiled for a short time, there is obtained 3-bromo-1 : 2-naphthaquinone, m. p. 179°, converted by alcoholic hydrochloric acid into 3-bromo-2-hydroxy-1 : 4-naphthaquinone, m. p. 202° (lit. 196°) (4-*anil*, m. p. 233°, prepared by the action of alcoholic aniline on the 1 : 2-quinone), by an excess of aniline into 2-anilino-1 : 4-naphthaquinone-anil, and by sulphurous acid into 3-*bromo*-1 : 2-*dihydroxynaphthalene*, m. p. 117° (*diacetate*, m. p. 160°). Bromination of 1 : 3-dibromo-β-naphthol in acetic acid and sodium acetate affords 1 : 1 : 3-*tribromo*-2-*keto*-1 : 2-*dihydronaphthalene*, m. p. 102—105°, which with hydrogen bromide in acetic acid gives some 1 : 3 : 6-tribromo-β-naphthol. Reduction of 1 : 3-dibromo-β-naphthol with tin and alcoholic hydrochloric acid furnishes 3-*bromo*-β-*naphthol*, m. p. 83° (*acetate*, m. p. 94°; *methyl ether*, m. p. 77—78°, converted by the Grignard method into 3-methoxy-β-naphthoic acid). 4-*Bromo*-β-*naphthol*, m. p. 122°, is prepared by the usual method from the bromonaphthylamine.

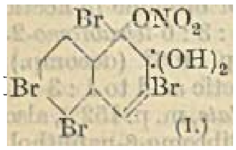
The sulphate of 4-*bromo*-2-*amino*-α-*naphthol*, m. p. 128° (*diacetyl* derivative, m. p. 231°), is oxidised by nitric and acetic acids to 4-*bromo*-1 : 2-*naphthaquinone*, m. p. 154°. Treatment of 1 : 6-dibromo-β-naphthol with nitric and acetic acids yields 1 : 6-*dibromo*-1-*nitro*-2-*keto*-1 : 2-*dihydronaphthalene*, m. p. 100° (decomp.) after sintering at about 75°, converted by heating in benzene into 6-*bromo*-1 : 2-*naphthaquinone*, m. p. 168° (decomp.) after darkening at 145° and sintering at about 150°.

β-Naphthol and a large excess of bromine in acetic acid and sodium acetate give 1 : 1 : 3 : 6-*tetrabromo*-2-*keto*-1 : 2-*dihydronaphthalene*, m. p. 168° (decomp.), reduced by stannous chloride in acetic acid to 1 : 3 : 6-*tribromo*-β-*naphthol*, m. p. 132° (*acetate*, m. p. 152°), also prepared by brominating 1 : 3-dibromo-β-naphthol. Reduction of this with tin and hydrochloric acid affords 3 : 6-*dibromo*-β-*naphthol*, m. p. 127° (*acetate*, m. p. 127°), whilst treatment with nitric and acetic acids yields 1 : 3 : 6-*tribromo*-1-*nitro*-2-*keto*-1 : 2-*dihydronaphthalene*. When this is heated in benzene, 3 : 6-

dibromo-1 : 2-*naphthaquinone*, m. p. 176°, is produced.

1 : 4 : 6-Tribromo-β-naphthol [described as the 1 : 3 : 6-derivative by Franzen and Stauble (*loc. cit.*)] and nitric acid (*d* 1·52) in chloroform give 1 : 4 : 6-*tribromo*-1-*nitro*-2-*keto*-1 : 2-*dihydronaphthalene*, m. p. about 145° after reddening at 110°, convertible into 4 : 6-*dibromo*-1 : 2-*naphthaquinone*, m. p. 153°. This reacts with aniline (2 mols.) in alcohol, forming 6-*bromo*-2-*hydroxy*-1 : 4-*naphthaquinoneanil*, m. p. 276° (also obtained similarly from 6-bromo-1 : 2-naphthaquinone), and is converted by alcoholic hydrochloric acid into 6-*bromo*-2-*hydroxy*-1 : 4-*naphthaquinone*, m. p. 203° (also formed similarly from the 6-bromo-1 : 2-quinone).

1 : 3 : 4 : 6-Tetrabromo-β-naphthol, the main product of bromination of β-naphthol with 4 mols. of bromine in acetic acid at 100°, is oxidised by nitric and acetic acids to 3 : 4 : 6-tribromo-1 : 2-naphthaquinone, m. p. 191° (*quinoxaline* derivative, m. p. 250°, from *o*-phenylenediamine), reduced by stannous chloride and acetic acid to a mixture of 3 : 6-dibromo-1 : 2-dihydroxynaphthalene and probably 3 : 6 : 3′ : 6′-*tetrabromo*-1 : 2 : 1′ : 2′-*tetrahydroxy*-4 : 4′-*dinaphthyl*, m. p. 293°. Treatment of the tribromoquinone with sulphuric acid at 175° gives 3 : 6-*dibromo*-2-*hydroxy*-1 : 4-*naphthaquinone*, m. p. 219° (the *anil*, m. p. 185°, is prepared by the action of alcoholic aniline on the tribromoquinone), whilst with a large excess of aniline 6-*bromo*-2-*anilino*-1 : 4-*naphthaquinoneanil*, m. p. 211° (decomp.), results. The tribromoquinone and warm nitric acid (*d* 1·52) give 3 : 3 : 6-*tribromo*-1 : 2 : 4-*triketo*-1 : 2 : 3 : 4-*tetrahydronaphthalene* ($+H_2O$), m. p. 157°, reduced by stannous chloride and acetic acid to 3 : 6 - dibromo - 1 : 2 : 4 - trihydroxynaphthalene. 1 : 3 : 5 : 6-*Tetrabromo*-β-*naphthol*, m. p. 186° (*acetate*, m. p. 155°), is best prepared by brominating 1 : 5 : 6-tribromo-2-hydroxy-3-naphthoic acid in acetic acid and sodium acetate, and reducing the 1 : 1 : 3 : 3 : 5 : 6-*hexabromo*-2-*keto*-4-*acetoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m. p. 170—175°, so produced with zinc dust and acetic acid. 1 : 3 : 5 : 6-*Tetrabromo*-1-*nitro*-2-*keto*-1 : 2-*dihydronaphthalene* passes at 85° into 3 : 5 : 6-*tribromo*-1 : 2-*naphthaquinone*, m. p. 184°, and is reduced by stannous chloride and acetic acid to 3 : 5 : 6-*tribromo*-1-*nitro*-β-*naphthol*, m. p. 159° (decomp.). This quinone is converted by alcoholic aniline (3 mols.) and hydrochloric acid into 5 : 6-*dibromo*-2-*anilino*-1 : 4-*naphthaquinoneanil*, m. p. 221° (decomp.), and 3 : 5 : 6-*tribromo*-2-*hydroxy*-1 : 4-*naphthaquinone*, m. p. 232°, respectively. Oxidation of 1 : 3 : 5 : 6-tetrabromo-β-naphthol with nitric and acetic acids furnishes a mixture of the tribromoquinone and the *compound* (I) (+Ac·OH), m. p. 115° (decomp.), m. p. (solvent-free) 121° (decomp.); I is reduced by stannous chloride and acetic acid to 3 : 5 : 6-*tribromo*-1 : 2-*dihydroxynaphthalene*, m. p. 181° (*diacetate*, m. p. 171°), and converted by boiling with alcohol into the tribromoquinone.

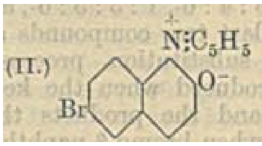


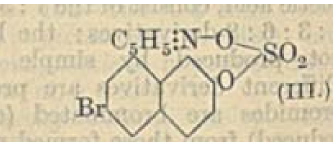
1 : 1-Dibromo-2-keto-1 : 2-dihydronaphthalene (improved preparation given) (A., 1924, i, 1187) is brominated in chloroform at −15° to 1 : 1 : 3 : 4 : 6 : 7-*hexabromo* - 2 - *keto*-1 : 2 : 3 : 4 : 6 : 7 - *hexahydronaphthalene*, m. p. 173°, converted by stannous chloride in acetic acid or potassium iodide in aqueous acetic acid into 1 : 3-dibromo-β-naphthol, and acetylated to 1 : 1 : 3 : 4 : 6 : 7 - *hexabromo* - 1 : 4 : 6 : 7 - *tetrahydro*-β-*naphthyl acetate*, m. p. 178° after previous sintering. This acetate is reduced by zinc dust and acetic acid to 1 : 3-dibromo-β-naphthyl acetate, and converted by warming with pyridine into the *acetate*, m. p. 221°, of 1 : 3 : 6 : 7-*tetrabromo*-β-*naphthol*, m. p. 174° (oxidised by nitric and acetic acids to 4 : 5-dibromophthalic acid).

Bromination of 1-methyl-β-naphthol in acetic acid gives first the 6-bromo- and then the 4 : 6-dibromo-derivatives [previously described (A., 1906, i, 190) as the 3 : 6-compound]. Reduction of the product formed by bromination in acetic acid and sodium acetate with zinc dust and acetic acid affords 3-*bromo*-1-*methyl*-β-*naphthol*, m. p. 76° (*acetate*, m. p. 77°), converted further into the 3 : 6-*dibromo*-, m. p. 110° (*acetate*, m. p. 136°), and the 3 : 4 : 6-*tribromo*-derivatives, m. p. 158° (*acetate*, m. p. 202°); the 3 : 6-dibromo-derivative is also obtained by reduction of the ketobromide from 6-bromo-1-methyl-β-naphthol. 1 : 4 : 6-*Tribromo* - 2 - *keto*-1-*methyl*-1 : 2-*dihydronaphthalene*, m. p. 124° (decomp.), prepared from the 3 : 6- and 4 : 6-dibromo-1-methyl-β-naphthols, reacts with aniline, forming the 6-*bromo*-1 : 4-*dianilino*-derivative, m. p. 250° (decomp.).

1 : 1 - Dichloro - 2 - keto - 1 : 2 - dihydronaphthalene, m. p. 54° (cf. Zincke, A., 1889, 265), is converted by hydrogen chloride and bromide into 1 : 4-dichloro- and 1-chloro-6-bromo-β-naphthol, respectively. Chlorination of 1-bromo-β-naphthol or bromination of 1-chloro-β-naphthol in acetic acid and sodium acetate gives 1-*chloro*-1-*bromo*-2-*keto*-1 : 2-*dihydronaphthalene*, m. p. about 90°, reduced by zinc dust to 1-chloro-β-naphthol and converted by hydrogen chloride or bromide in acetic acid into 1-chloro-6-bromo-β-naphthol. Prolonged treatment of 2 : 3-hydroxynaphthoic acid with chlorine in acetic acid yields 1 : 1 : 3 : 3 : 4-pentachloro-2-keto-1 : 2 : 3 : 4-tetrahydronaphthalene, m. p. 116° (Zincke, *loc. cit.*), reduced by zinc dust and acetic acid to 1 : 3-dichloro-β-naphthol. 1 : 6-Dibromo-β-naphthol is obtained from 1 : 1 : 6-tribromo-2-keto-1 : 2-dihydronaphthalene (A., 1924, i, 1187) and hydrogen bromide in acetic acid.

[With B. Heinemann.] Treatment of 1 : 1-dibromo-2-keto-1 : 2-dihydronaphthalene with pyridine below 40° gives 1-(6-*bromo*-2-*hydroxy*-α-*naphthyl*)-*pyridinium bromide*, yellow, m. p. 320° (decomp.) after becoming colourless at 310°, converted by sodium acetate solution into the *compound* (II), orange-red, m. p. 250° (decomp.). Treatment of II with acetic





anhydride and sulphuric acid at the ordinary temperature affords the *substance* (III), m. p. 330° after blackening at 325°, which when heated with acetic acid passes into 1-(6-*bromo*-2-*hydroxy*-α-*naphthyl*)-*pyridinium sulphate*, m. p. 245° (decomp.); III is converted by aqueous sodium acetate into II.

1-Bromo-2-keto-1-methyl-1 : 2-dihydronaphthalene (A., 1924, i, 1187) and sodium 1-methyl-β-naphthyl-oxide in benzene give dehydro-1-methyl-β-naphthol (Pummerer and Cherbuliez, A., 1919, i, 440).

H. BURTON.

Derivatives of dinaphthylene dioxide. II. A. CORBELLINI and A. PASTURINI (Gazzetta, 1930, **60**, 843—851; cf. A., 1929, 193).—Dibromination of β-dinaphthol in acetic acid solution yields 6 : 6′-*dibromo*-2 : 2′-*dihydroxy*-1 : 1′-*dinaphthyl*, m. p. 202—203° (not 155°, as given by Fosse, A., 1899, i, 818), which forms a *dimethyl* derivative, m. p. 239·5° (uncorr.), gives 2-[2-*hydroxy*-6-*bromonaphthoyl*(1)]-5-*bromobenzoic acid*, m. p. 346° (uncorr.), when oxidised by alkaline permanganate and 4-bromophthalic acid when oxidised by chromic acid and alkaline permanganate successively, and is obtained also by oxidising 6-bromo-β-naphthol by means of ferric chloride. When heated with cupric oxide or when its basic copper salt is heated, 6 : 6′-dibromo-2 : 2-dihydroxy-1 : 1′-dinaphthyl undergoes cyclisation, giving 2 : 7-*dibromodinaphthylene dioxide*, m. p. 361° (uncorr.), and a red *compound*, m. p. about 421°, of lower bromine content, this being possibly formed from 2 mols. of the preceding compound with loss of two bromine atoms. The m. p. of the dibromo-derivative obtained by brominating dinaphthylene dioxide in carbon disulphide (cf. Corbellini and Vietti. A., 1929, 193) was given erroneously as 277°; it should be 335°.

T. H. POPE.

Halogen derivatives of acyl- and alkyl-resorcinols. C. M. BREWSTER and J. C. HARRIS (J. Amer. Chem. Soc., 1930, **52**, 4866—4872).—4-Propionyl-resorcinol, m. p. 96° (2 : 6-dibromo-, m. p. 151—152°; *tribromo*-, m. p. 157—158°, and *dichloro*-, m. p. 146—147°, -derivatives), and 4-butyrylresorcinol, m. p. 68—70° (*dichloro*-derivative, m. p. 110·5—111°), are obtained when resorcinol, the appropriate fatty acid (technical), and zinc chloride are heated to 160—165° and the mixture is cooled. A substance, m. p. 111—112°, accompanies the butyryl derivative when the mixture is kept at 165° for 2—5 min. Reduction (Clemmensen) of resacetophenone gives 4-ethyl-resorcinol (2 : 6-*dibromo*-derivative, m. p. 73·5—74·5°, also prepared by the Clemmensen reduction of 2 : 6-dibromo-4-acetylresorcinol); *dichloro-4-ethylresorcinol*, m. p. 78—79°, is obtained from dichlororesacetophenone, m. p. 190—193°. Bromination of resacetophenone in acetic acid containing a little iodine gives the ωω : 3 : 5-*tetrabromo*-derivative, m. p. 110—110·5°, reduced to 2 : 6-dibromo-4-ethylresorcinol. Tribromoresacetophenone (Segalle, A., 1896, i, 613) could not be prepared.

H. BURTON.

Naphthols. I. Bromination of 1 : 5-dihydroxynaphthalene. A. S. WHEELER and D. R. ERGLE (J. Amer. Chem. Soc., 1930, **52**, 4872—4880).—Bromination of 1 : 5-dihydroxynaphthalene with 2 mols. of bromine in acetic acid containing a little iodine at 80° gives the 2 : 6-*dibromo*-derivative, ar ens at -00°, not melted at 300° (*diacetate*, m. p. 228°; *dibenzoate*, m. p. 262°; *dimethyl ether*, m. p. 161°; *diethyl ether*, m. p. 148°), oxidised by chromic and acetic acids to 2 : 6-*dibromo*-5-*hydroxy*-1 : 4-*naphthaquinone*, m. p. 202° (*acetate*, m. p. 148°), which is not identical with 2 : 3-dibromojuglone (A., 1922, i, 1165). Reduction of the quinone with zinc dust and acetic acid affords 2 : 6-*dibromo*-1 : 4 : 5-*trihydroxynaphthalene*, decomp. 157° after darkening at 110°, whilst treatment with alcoholic aniline yields 6-*bromo*-2-*anilino*-5-*hydroxy*-1 : 4-*naphthaquinone*, m. p. 249°. 2 : 6 : 8-*Tribromo*-1 : 5-*dihydroxynaphthalene*, m. p. 189° (decomp.) (*diacetate*, m. p. 174°; *dibenzoate*, melts at 185° to a turbid liquid which clears at 189°; *dimethyl ether*, m. p. 149°; *diethyl ether*, m. p. 125°), is oxidised similarly to a small amount of 2 : 6 : 8-*tribromo*-5-*hydroxy*-1 : 4-*naphthaquinone*, m. p. 196° (*acetate*, m. p. 234°), which is isomeric with tribromojuglone (A., 1919, i, 490). This quinone gives a *boroacetate*, not melted at 300° after evolution of red vapour at 200°, indicating that it is an *o*-hydroxyquinone (cf. Dimroth, A., 1926, 297); it reacts with aniline in acetic acid forming 6 : 8-*dibromo*-2-*anilino*-5-*hydroxy*-1 : 4-*naphthaquinone*, m. p. 206°, and is reduced by zinc dust and dilute sulphuric acid in presence of ether to 2 : 6 : 8-*tribromo*-1 : 4 : 5-*trihydroxynaphthalene*, decomp. about 140° (*triacetate*, m. p. 185°).

Treatment of 1 : 5-diacetoxynaphthalene with bromine (6 mols.) in chloroform containing iodine gives 2 : 4 : 6 : 8-*tetrabromo*-1 : 5-*dihydroxynaphthalene*, not melted at 300° (*dimethyl ether*, m. p. 226°; *dibenzoate*, m. p. 268°), oxidised by chromic and acetic acids to 2 : 6 : 8-tribromo-5-hydroxy-1 : 4-naphthaquinone. Bromination with 5 mols. of bromine in acetic acid at the ordinary temperature gives a mixture of 2 : 6-*dibromo*-5-*acetoxy*-α-*naphthol*, m. p. 173° (*benzoate*, m. p. 164°), and the above tetrabromo-compound.

H. BURTON.

Condensation products of methylolamides with phenolic ethers. L. MONTI (Gazzetta, 1930, **60**, 777—786; cf. A., 1930, 598).—Interaction of chloroacetamide with formaldehyde in presence of potassium carbonate yields *hydroxymethylchloroacetamide*, m. p. 102° (cf. Einhorn, A., 1905, i, 344), which condenses with veratrole in presence of zinc chloride to form (1) 3 : 4-dimethoxy-*N*-chloroacetylbenzylamine, m. p. 116—118° (Jacobs and Heidelberger, A., 1915, i, 667, gave m. p. 117—117·5°), which gives 3 : 4-dimethoxybenzylamine hydrochloride, m. p. 246° (decomp.) (Douetteau, A., 1911, i, 973, gave m. p. 257°), when heated with 20% hydrochloric acid, and (2) ωω′-*dichloroacetamido*-4 : 5-*dimethoxy*-o-*xylene*, $C_6H_2(OMe)_2(CH_2{\cdot}NH{\cdot}CO{\cdot}CH_2Cl)_2$, m. p. 169—170°, which gives ωω′-*diamino*-4 : 5-*dimethoxy*-o-*xylene* [*picrate*, m. p. 216—218° (decomp.) (anhydrous)] when boiled with 20% hydrochloric acid. Condensation of hydroxymethylchloroacetamide with pyrogallol trimethyl ether yields 2 : 3 : 4-*trimethoxychloroacetylbenzylamine*, m. p. 98—99°, which gives 2 : 3 : 4-*trimethoxybenzylamine* [*picrate*, m. p. 208—210° (decomp.); *chloroplatinate*, blackening at 200° and not melting at 300°] when boiled with 20% hydrochloric acid. Hydroxymethylbenzamide (cf. Einhorn, A., 1905, i, 344) and pyrogallol trimethyl ether condense in presence of zinc chloride to form (1) 2 : 3 : 4-*trimethoxybenzoylbenzylamine*, m. p. 125—126°, which yields 2 : 3 : 4-trimethoxybenzylamine (see above) when boiled with alcoholic potassium hydroxide, and (2) ωω′-*dibenzamido*-2 : 3 : 4-*trimethoxy*-o-*xylene*, m. p.

189—190°, which gives ωω′-diamino-2 : 3 : 4-trimethoxyxylene (*picrate*, m. p. 215—217°) with alcoholic potassium hydroxide. Condensation of hydroxymethylchloroacetamide and hydroxyquinol trimethyl ether yields 2 : 4 : 5-*trimethoxychloroacetylbenzylamine*, m. p. 115—116°, this giving 2 : 4 : 5-*trimethoxybenzylamine* (*picrate*, m. p. 200—202°) with 20% hydrochloric acid. 3 : 4 : 5-*Trimethoxy-2-chloroacetylbenzylamine*-1-*carboxylic acid*, m. p. 189—190°, formed by condensing hydroxymethylchloroacetamide with trimethylgallic acid, gives 3 : 4 : 5-*trimethoxy-2-benzylamine*-1-*carboxylic acid* [*hydrochloride*, m. p. 153—154° (decomp.); *picrate*, m. p. 150—152°] on hydrolysis with 20% hydrochloric acid. T. H. POPE.

Aliphatic diazo-compounds. II. A. SCHONBERG and T. STOLPP (Ber., 1930, **63**, [*B*], 3102—3116; cf. this vol., 84).—Gradual addition of *o*-nitrochlorothiolbenzene to an ethereal solution of diazomethane yields o-*nitrophenylthiolmethyl chloride*, $NO_2\cdot C_6H_4\cdot S\cdot CH_2Cl$, m. p. about 95°. Diazodiphenylmethane and *o*-nitrobromothiolbenzene yield *o-nitrophenylthioldiphenylmethyl bromide*, m. p. (indef.) 108°. p-*Chloro*-o-*nitrophenylthioldiphenylmethyl chloride*, m. p. 121°, is prepared analogously. Phenylthioldiphenylmethyl chloride in ether is transformed by silver benzoate into *phenylthioldiphenylmethyl benzoate*, m. p. 148—149°; o-*nitrophenylthioldiphenylmethyl benzoate*, m. p. 132°, and *phenylthioldiphenylenemethyl benzoate*, m. p. (indef.) 132° (from 9-chloro-9-phenylthiolfluorene), are described. *p*-Nitrophenylthioldiphenylmethyl chloride is converted by water at the ordinary temperature into benzophenone and di-*o*-nitrophenylthioldiphenylmethane, m. p. 146°; 9-chloro-9-*o*-nitrophenylthiolfluorene similarly yields fluorenone and di-*o*-nitrophenylthioldiphenylenemethane, m. p. 159°. With ammonia in ether at the ordinary temperature phenylthioldiphenylmethyl chloride affords benzophenoneimine and diphenylthioldiphenylmethane, m. p. 173°. In benzene under similar conditions *o*-nitrophenylthioldiphenylmethyl chloride gives benzophenone and di-*o*-nitrophenylthioldiphenylmethane, whilst 9-phloro-9-phenylthiolfluorene yields fluorenoneimine and diphenylthioldiphenylenemethane.

Di-*o*-anisyl thioketone and mercuric chloride in ether give the *compound* $C_{15}H_{14}O_2S,HgCl_2$, whilst xanthione and silver perchlorate in benzene afford the *substance*, $C_{13}H_8O_5ClSAg$. The complex compounds from xanthione and silver nitrate and from di-*o*-anisyl thioketone and cadmium iodide are too unstable to permit analysis.

Diphenyldiazomethane and phenyl *o*-nitrophenyl disulphide in boiling benzene in the absence of light and in an atmosphere of carbon dioxide afford *phenylthiol*-o-*nitrophenylthioldiphenylmethane*, m. p. 134°, and benzophenoneketazine. Di-*o*-nitrophenylthioldiphenylmethane, m. p. 146°, di-β-naphthylthioldiphenylmethane, m. p. 133°, and *diphenylthioldi*-β-*naphthylmethane*, m. p. 160°, are prepared similarly. The methane derivatives from di-*p*-tolyldiazomethane and diphenyl disulphide and from diphenyldiazomethane and di-*p*-tolyl disulphide could not be obtained pure.

Xanthione is converted by hydrazine hydrate in alcohol into *xanthonehydrazone*, m. p. 128—130°, which is oxidised by mercuric oxide to *xanthoneketazine*, m. p. 285°, prepared also from xanthione and hydrazine hydrate or, preferably, by the action of xanthone dichloride on xanthonehydrazone. Thioxanthione is converted by hydrazine hydrate in alcoholic benzene into *thioxanthonehydrazone*, m. p. 115°, oxidised by mercuric oxide in presence of light petroleum at 12° to *diazothioxanthen*, m. p. 105°. *Thioxanthoneketazine*, m. p. 284°, is prepared from thioxanthone dichloride and thioxanthonehydrazone. The preparation of *chromonehydrazone*, m. p. 96°, from chromone or 4-thiochromone is recorded.

H. WREN.

Organic compounds of selenium. I. S. KEIMATSU and K. YOKOTA (J. Pharm. Soc. Japan, 1930, **50**, 531—539).—Diazotisation of *p*-anisidine, followed by addition of selenophenol, sodium hydroxide, and copper powder, and keeping the mixture at 0—5° in an atmosphere of carbon dioxide, affords p-*methoxyphenyl selenide*, m. p. 46·3° (corr.), in 70% theoretical yield; *o*-methoxyphenyl selenide, from *o*-anisidine, was also prepared. p-*Acetoxyphenyl selenide* has m. p. 55°, and the *selenocyanate* has m. p. 67°. *Selenoquinol*, m. p. 56—57°, from alcoholic *p*-acetoxyphenyl selenocyanate, dextrose, and aqueous sodium hydroxide at 100° in hydrogen, affords on oxidation pp′-*dihydroxydiphenyl diselenide*, m. p. 134° (*diacetoxy*-compound, m. p. 90·5°). Treatment of selenophenol in alcoholic potassium hydroxide with chloropicrin gave diphenyl diselenide, m. p. 63·5°.

CHEMICAL ABSTRACTS.

Preparation of α-*p*-methoxyphenyl-β-aminoethyl alcohol. Y. SHINOZAKI (J. Pharm. Soc. Japan, 1930, **50**, 666—667).—Catalytic reduction of *p*-methoxyphenylnitroethanol (from anisaldehyde, nitromethane, and potassium hydrogen carbonate) gave α-p-*methoxyphenyl*-β-*aminoethyl alcohol hydrochloride*, m. p. 171—172°. Electrolytic reduction also afforded an amine. CHEMICAL ABSTRACTS.

Optically active diphenylhydroxyethylamines and *iso*hydrobenzoins. IV. Di-*p*-methoxyphenylhydroxyethylamine and di-3 : 4-methylenedioxyphenylhydroxyethylamine. V. β-Hydroxy-β-phenylethylamine and some derivatives. J. READ and (MISS) I. G. M. CAMPBELL (J.C.S., 1930, 2674–2681, 2682—2685).—IV. Aminoacetic acid reacts with anisaldehyde in presence of aqueous-alcoholic sodium hydroxide at 50° (cf. Erlenmeyer, A., 1905, i, 131), forming the *anisylidene* derivative, m. p. 116°, of *dl*-di-*p*-methoxyphenylhydroxyethylamine, m. p. 135·5° [*chloroplatinate*, m. p. 171° (decomp.); *monoacetyl* derivative, m. p. 145—147°; *diacetyl* derivative, m. p. 169—171°; *benzylidene* derivative, m. p. 125—126°; salicylidene derivative, m. p. 134—135°]. Treatment of the amino-alcohol with *d*-tartaric acid in alcoholic ethyl acetate gives the *hydrogen* d-*tartrate* ($+H_2O$), m. p. 110—111°, $[M]_D$ −294° in water, of *l*-di-*p*-methoxyphenylhydroxyethylamine, m. p. 111—112°, $[\alpha]_D$ −150° in alcohol (hydrochloride, $[M]_D$ −307° in water; *monoacetyl* derivative, m. p. 128—129°, $[\alpha]_D$ −16·9° in alcohol; *diacetyl* derivative, m. p. 160—161°, $[\alpha]_D$ +44·6° in alcohol; *benzylidene* derivative, m. p. 136°, $[\alpha]_D$ −88·1° in alcohol). Treatment

of the *l*-base with nitrous acid affords a 30% yield of cis-αβ-*di*-p-*methoxyphenylethylene oxide*, m. p. 142—143°, and oily material which appears to contain some hydroanisoin. The oxide is also obtained when l-, m. p. 145° (decomp.), $[\alpha]_D$ −34·6° in methyl alcohol, or dl-*di*-p-*methoxyphenylhydroxyethyltrimethylammonium iodide*, m. p. 155° (decomp.), is treated with silver oxide (A., 1930, 1576). Aminoacetic acid and piperonal react as above, forming the *piperonylidene* derivative, m. p. 177°, of *dl*-di-3 : 4-methylenedioxyphenylhydroxyethylamine, m. p. 159° [*chloroplatinate*, m. p. 184° (decomp.)], resolved by tartaric acid into the *d*-amino-alcohol, m. p. 164°, $[\alpha]_D$ +196° in alcohol (*hydrogen* d-*tartrate* $+H_2O$, m. p. 145°, $[M]_D$ +549° in water), and the *l*-amino-alcohol, m. p. 164°, $[\alpha]_D$ −196° in alcohol {*hydrogen* d-*tartrate*, m. p. 208° (decomp.), $[M]_D$ −470° in water; hydrochloride, $[M]_D$ −442° in water; *diacetyl* derivative, m. p. 222—224° (decomp.), $[\alpha]_D$ −38·5° in alcohol}.

V. In the preparation of *dl*-β-hydroxy-β-phenylethylamine {hydrochloride, m. p. 213° (decomp.); benzoyl derivative, m. p. 148°; *benzylidene* derivative, m. p. 111—112°; the d-*methylenecamphor* derivative, m. p. 106—108°, $[\alpha]_D$ +230° in alcohol, and the d-*camphor*-10-*sulphonate*, m. p. 125—126°, $[M]_D$ +52·8° in water, are partly racemic compounds} from styrene by the method previously described (A., 1928, 866), a small amount of a *base*, C_8H_7N, m. p. 191—193°, is produced; when a specimen of styrene containing cinnamyl alcohol was used, a small amount of basic *substance*, $C_9H_{12}O_2N_2$, m. p. 192°, was formed. The above *dl*-amino-alcohol absorbs carbon dioxide, yielding a carbamate. It is resolved by tartaric acid into the *d*-base (d-*tartrate*, m. p. 210°, $[M]_D$ +195° in water), which with methyl iodide and methyl-alcoholic sodium methoxide (cf. *loc. cit.*) gives d-β-*hydroxy*-β-*phenylethyltrimethylammonium iodide*, m. p. 223—224°, $[\alpha]_D$ +4·5° in methyl alcohol. Treatment of this with silver oxide furnishes a small amount of acetophenone and a dextrorotatory oil, which appears to consist mainly of *d*-phenylethylene oxide (or a polymeride) together with a little phenylethylene glycol.

H. Burton.

Manufacture of optically active β-aralkylmethylamino- and β-methylamino-α-hydroxy-*n*-propylbenzenes. I. G. Farbenind. A.-G.—See B., 1931, 13.

Manufacture of β-methylamino-α-phenylpropyl alcohol ("diephedrine"). Knoll A.-G. Chem. Fabr. and W. Klavehn.—See B., 1931, 58.

Esters of phenyltribromomethylcarbinol. J. W. Howard (J. Amer. Chem. Soc., 1930, 52. 5059—5060).—Phenyltribromomethylcarbinol, m. p. 72·5—73°, is obtained when powdered potassium hydroxide (4 g.) is added with constant stirring to a mixture of benzaldehyde (37 g.) and dry bromoform (130 g.), the reaction mixture diluted with ether, filtered, distilled up to 155°/680 mm., and the residue distilled with steam. The yield is 16—18 g. The following esters were prepared: acetate, m. p. 133°; *propionate*, m. p. 70·5°; *butyrate*, b. p. 205—207°/220 mm., 1·779, and *benzoate*, m. p. 146°.

H. Burton.

Di-αβ-diphenylethyl ether and di-β-phenyl-α-anisylethyl ether. C. R. Kinney and W. G. Bywater (J. Amer. Chem. Soc., 1930, 52, 4893—4895).—*Di*-β-*phenyl*-α-*anisylethyl ether*, m. p. 148—149°, isolated during the attempted oxidation of β-phenyl-α-anisylethyl alcohol with nitrogen trioxide in ether, is also formed (in small amount) when the alcohol is treated with hydrochloric acid in presence of ether and calcium chloride, and when the product from magnesium benzyl chloride and anisaldehyde is decomposed with ice and concentrated hydrochloric acid. In the last case none of the above alcohol is produced. 4-Methoxystilbene is obtained when the alcohol is treated with ethereal hydrogen chloride. Distillation of the ether gives a substance, m. p. 107—108°. *Di*-αβ-*diphenylethyl ether*, m. p. 129·5—130·5°, is formed in small amount when αβ-diphenylethyl alcohol is treated with nitrogen trioxide or concentrated hydrochloric acid in ether; it is not obtained when the product from magnesium benzyl chloride and benzaldehyde is decomposed.

H. Burton.

Action of chloral and trichloroacetic acid on cholesterol. E. Montignie (Bull. Soc. chim., 1930, [iv], 47, 1323—1325).—When heated with chloral at 100° cholesterol is partly isomerised to metacholesterol [acetate, m. p. 110°; bromide, m. p. 105° (decomp.)]. Trichloroacetic acid at 60—70° and at 100° affords two fractions, m. p. 121° and 140°, mixtures of isomeric cholesteryl trichloroacetates, the latter fraction being anhydrous. Attempts to condense cholesterol with α- or β-penta-acetylglucose in chloroform solution in presence of hydrogen chloride did not yield a glucoside.

R. Brightman.

Sterol group. X. Relationship of the fully saturated derivatives of ergosterol and sitosterol. F. S. Spring (J.C.S., 1930, 2664—2667).—Hydrogenation of ergosterol, m. p. 160°, $[\alpha]_D^{22}$ −131° (all rotations are in chloroform), in presence of palladium-black and ethyl acetate at 40—50° affords, in addition to α-ergostenol, some γ-*ergostenol*, m. p. 129—130°, $[\alpha]_D^{2}$ +5·1°. The new sterol gives a green colour with the Tortelli–Jaffe reagent and resists further hydrogenation. Fractionation of the ergosterol from alcohol–benzene (2 : 1) and hydrogenation of the less and more soluble fractions shows that more γ-ergostenol is obtained from the latter fraction. The ergosterol used is probably a mixture of isomerides. γ-*Ergostenyl acetate*, m. p. 140°, is isomerised by treatment with hydrogen chloride in chloroform into iso-γ-*ergostenyl acetate*, m. p. 103—104°, $[\alpha]_D^{25}$ +4·05°. iso-γ-*Ergostenol*, m. p. 129°, $[\alpha]_D^{22}$ +3·7°, is reduced catalytically (palladium-black) in ether to γ-*ergostanol*, m. p. 137°, $[\alpha]_D^{23}$ +29°, which gives no Liebermann–Burchard reaction, is isomeric with *allo*-α-ergostanol (Reindel and Walter, A., 1928, 295), and appears to be identical with the sitostanol, m. p. 136°, $[\alpha]_D$ −26°, obtained from sitosterol, m. p. 137—137·5°, $[\alpha]_D$ +38°, from cotton-seed oil.

H. Burton.

Carbithioic acids. II. *cyclo*Hexylcarbithioic [*cyclo*hexanedithiocarboxylic] acid. R. W. Bost and W. W. Williams (J. Amer. Chem. Soc., 1930, 52 4991—4992).—*cyclo*Hexanedithiocarboxylic acid, an oil [*silver* salt, m. p. 163°; *methyl*, b. p. 90°/3 mm., and *ethyl*, b. p. 106°/5 mm., esters (both prepared from the sodium salt and the alkyl sulphate); n-*propyl*, b. p. 106°/3 mm., and n-*butyl*, b. p. 145°/5 mm., esters (from

the sodium salt and the alkyl bromide); p-*toluidide*, m. p. 160°], is obtained from magnesium *cyclo*hexyl bromide and carbon disulphide by the method previously described (A., 1930, 340). The acid decomposes when distilled or exposed to air, does not give an acid chloride or amide, and when treated with nitric acid in ether is oxidised to hexahydrobenzoic acid. H. BURTON.

Preparation of benzamide. C. H. KAO and S. MA (J.C.S., 1930, 2788).—A mixture of benzoic acid (200 g.), ammonium carbonate (180 g.), and 95% acetic acid (300 c.c.) is heated gradually to boiling and then distilled through a column of glass tubing (160×2 cm.) at 100 c.c. per hr. until the temperature at the head of the column is 150°. The residue is poured into water (2 vols.), neutralised with ammonia, and crystallised. Two crystallisations from water give 96—98 g. of benzamide. About half the benzoic acid is recovered. H. BURTON.

Decomposition of benzoyl peroxide by ultra-violet light. F. FICHTER and A. SCHNIDER (Helv. Chim. Acta, 1930, 13, 1428—1433).—Ultra-violet irradiation of benzoyl peroxide in a quartz vessel gives as much as 70% of the theoretical amount of diphenyl: $(\cdot CO_2Ph)_2 \longrightarrow 2CO_2 + Ph\cdot Ph$. Resinous material is also produced. Decomposition also occurs in chloroform solution. H. BURTON.

Formation of a complex mixture of RMgX compounds from the reaction between a simple RX compound and magnesium. H. GILMAN and N. B. ST. JOHN (J. Amer. Chem. Soc., 1930, 52, 5017—5023).—Treatment of the reaction product from magnesium and bromo- or chloro-benzene (prepared in absence of solvent) with carbon dioxide gives 30—33% of benzoic acid and small amounts of diphenyl-4-carboxylic acid. The last-named acid probably arises owing to intermediate formation of free phenyl radicals; it could not be isolated when the Grignard reagent was prepared in ether. The various reactions which can occur as the result of radical formation are discussed. H. BURTON.

Configuration of norvaline. P. KARRER and H. SCHNEIDER (Helv. Chim. Acta, 1930, 13, 1281—1291).—*dl*-Allylhippuric (α-benzamido-Δ^γ-pentenoic) acid, prepared by Sorensen's method (A., 1908, i, 981; 1917, i, 89), is resolved by brucine into *d*(—)-, m. p. 89° (potassium salt, $[\alpha]_D^{20}$ −32·11° in water), and *l*(+)-allylhippuric acids, m. p. 90° (potassium salt, $[\alpha]_D^{20}$ +32·9° in water). Oxidation of these active acids by potassium permanganate gives *d*(—)-, m. p. 175°, and *l*(+)-α-benzamidosuccinic acids, m. p. 176° (potassium salt, $[\alpha]_D$ +22·4° in water) (cf. Fischer, A., 1899, i, 888), respectively. *d*(—)-α-Benzamidosuccinic acid is also obtained by benzoylating *d*-α-aminosuccinic acid. Oxidation of *dl*-allylhippuric acid with potassium permanganate or ozone furnishes *dl*-α-benzamidosuccinic acid (+H_2O), m. p. 119° after sintering at 70°. N-($\alpha\alpha$-*Dicarboxy*-Δ^γ-*butenyl*)*phthalamic acid*, m. p. 156° (decomp.), is a by-product in the preparation of *dl*-allylhippuric acid.

Reduction of *d*(—)- and *l*(+)-allylhippuric acids with hydrogen in presence of platinum and the theoretical amount of *N*-potassium hydroxide affords *d*(—)-, m. p. 97° (potassium salt, $[\alpha]_D^{18}$ −13·1° in water), and l(+)-*benzoylnorvalines* (α-*benzamido*-n-*valeric acids*), m. p. 95° (*hydrate*, m. p. 64° after sintering at 40—50°; potassium salt, $[\alpha]_D^{20}$ +14·0° in water), respectively. Benzoylation of the ethyl ester of *d*(—)-norvaline in pyridine gives *ethyl* α-*benzamido*-n-*valerate*, m. p. 59° $[\alpha]_D^{18}$ +7·98° in alcohol, hydrolysed by aqueous-alcoholic sodium hydroxide to the above *d*(—)-benzoylnorvaline. H. BURTON.

Derivatives of anesthesin [ethyl *p*-aminobenzoate]. L. CONIGLIO (Rend. Accad. Sci. Fis. Mat. Napoli, 1930, [iii], 36, 56—60).—The action of α-bromo*iso*valeryl chloride on anesthesin in presence of 2% sodium potassium hydroxide solution yields *ethyl* p-α-*bromoisovaleramidobenzoate*, $CO_2Et\cdot C_6H_4\cdot NH\cdot CO\cdot CHPr^{\beta}Br$, m. p. 115°. Similarly, the action of benzoyl chloride gives *ethyl* p-*benzamidobenzoate*, m. p. 15°; that of phthalyl chloride, *ethyl phthalidobenzoate*, m. p. 152°, and that of acetyl chloride, *ethyl* p-*acetamidobenzoate*, m. p. 181°. T. H. POPE.

Electrochemical oxidation of *p*-toluenesulphonic acid. M. YOKOYAMA (Helv. Chim. Acta, 1930, 13, 1257—1264; cf. Sebor, A., 1903, i, 554).—Oxidation of a *M*-solution of *p*-toluenesulphonic acid at a lead dioxide or platinum anode (current density 0·05 amp./cm.²) at 70—75° gives a small amount of a quinone together with formic, mesaconic, *p*-sulphobenzoic, and 4-sulpho-2 : 3-dihydroxybenzoic acids. Similar oxidation of *o*-cresol-4-sulphonic acid (0·66*N*-solution; lead dioxide anode) affords mesaconic and 4-sulpho-2 : 3-dihydroxybenzoic acids. Various mechanisms are suggested (cf. A., 1929, 1052) to explain the formation of the above compounds. H. BURTON.

3-Chloro-*o*-toluic acid and its conversion into 3-chloro-α-hydroxyphthalide. L. F. LEVY and H. STEPHEN (J.C.S., 1930, 2788).—3-*Chloro-o-toluic acid*, m. p. 91·5°, prepared by the usual method from 3-amino-*o*-toluic acid, is treated with bromine in the fused state and the resultant product warmed with dilute sodium hydroxide solution; 3-*chloro*-α-*hydroxyphthalide*, m. p. 138°, is thereby produced. H. BURTON.

Stereochemistry of diphenyl compounds. XI. Preparation and resolution of 6-nitro-2-methyldiphenyl-2′-carboxylic acid. R. W. STOUGHTON and R. ADAMS (J. Amer. Chem. Soc., 1930, 52, 5263—5267).—A mixture of methyl *o*-iodobenzoate and 2-bromo-3-nitrotoluene is treated with copper-bronze at 270—280° (bath), the resulting mixture heated at 300°, and then hydrolysed with 10% sodium hydroxide solution, whereby 27% of the theoretical amount of 6-*nitro*-2-*methyldiphenyl*-2′-*carboxylic acid*, m. p. 171—172°, is obtained. This is resolved by brucine into the d-, m. p. 171—173° after softening at 167°, $[\alpha]_D^{20}$ +63·1° in methyl alcohol [*brucine* salt (+1·5H_2O), m. p. (anhydrous) 172° after softening at 145°, $[\alpha]_D^{20}$ −57·3° in chloroform], and l-*modifications*, m. p. 174—175° after softening at 168°, $[\alpha]_D^{20}$ −67·7° in methyl alcohol [*brucine* salt (+H_2O), m. p. (anhydrous) 173—175°, $[\alpha]_D^{20}$ +30·4° in chloroform]. The active acids racemise slowly in boiling alkali and more slowly in boiling butyl alcohol or acetic acid. H. BURTON.

Fulminic acid. XI. Triphenylmethyl chloride and silver fulminate. H. Wieland and B. Rosenfeld (Annalen, 1930, **484**, 236—245).—When triphenylmethyl chloride is treated with silver fulminate in benzene with complete exclusion of moisture, an intense yellow coloration is produced owing to the formation of the halochromic additive compound of silver and triphenylmethyl chlorides; this disappears during the reaction provided an excess of the chloride is not used. The main product of the reaction is *triphenylacetonitrile oxide* (I), $CPh_3\cdot C⋮N⋮O$, m. p. 153—154°, probably formed thus: $CNOAg+CPh_3Cl \longrightarrow CPh_3\cdot CCl⋮N\cdot OAg \longrightarrow AgCl+I$. Treatment of I with alcoholic hydrochloric acid gives *triphenylacethydroxamyl chloride*, $CPh_3\cdot CCl⋮N\cdot OH$, m. p. 178—180° (decomp.), which when heated at 190° passes into I, and with methyl-alcoholic potassium hydroxide yields triphenylacethydroxamic acid, m. p. 165—167° (lit. 175—176°), and its *methyl* ester, m. p. 204°. Reduction of I with tin and alcoholic hydrochloric acid affords *triphenylacetonitrile*, m. p. 129°, whilst treatment with magnesium phenyl bromide furnishes *phenyl triphenylmethyl ketoxime*, m. p. 210° (*benzoyl* derivative, m. p. 175°). Treatment of the oxime with sulphuric acid at 100° gives benzamide and triphenylcarbinol (formed from the intermediate benztriphenylmethylamide). Nitrous acid converts the oxime into the *nitroimine*, $CPh_3\cdot CPh⋮N\cdot NO_2$, m. p. 160° (decomp.), which when heated at 160—180° in an atmosphere of carbon dioxide decomposes to nitric oxide, benzonitrile, and triphenylcarbinol. The nitroimine is reduced by 2% sodium amalgam and 96% alcohol to the *hydrazone*, m. p. 189° (iso*propylidene* derivative, m. p. 144—145°), of phenyl triphenylmethyl ketone, which is converted by treatment with mercuric oxide in boiling xylene (by way of the unstable, red diazo-derivative) into tetraphenylethylene. Reduction of the nitroimine with tin and aqueous alcoholic hydrochloric acid gives *phenyl triphenylmethyl ketimine*, m. p. 165°.

When silver fulminate reacts with an excess of triphenylmethyl chloride, a mixture of I and *triphenylacethydroxamyl chloride triphenylmethyl ether* (II), $CPh_3\cdot CCl⋮N\cdot O\cdot CPh_3$, m. p. 174—175°, is formed: $CPh_3\cdot CCl⋮NOAg+CPh_3Cl \longrightarrow AgCl+II$. This ether is reduced by tin and alcoholic hydrochloric acid to a mixture of triphenylacetonitrile and triphenylmethane. H. Burton.

New halogenated sulphonephthaleins. W. C. Boyd [with A. W. Rowe] (J. Amer. Chem. Soc., 1930, **52**, 4951—4959).—Phenols are condensed with tetrabromo- and tetraiodo-*o*-sulphobenzoic anhydrides, prepared by the method of Pratt and Shupp (A., 1918, i, 177), in presence of stannic chloride, whereby phenol-tetrahalogenosulphonephthaleins are produced. The following are described: *phenoltetraiodosulphonephthalein* (*tetrabromo-*, *tetraiodo-*, *tetranitro-*, and *diacetyl*, m. p. 136°, derivatives), o-*cresoltetraiodosulphonephthalein*, *resorcinoltetraiodosulphonephthalein* (*tetraiodosulphonefluorescein*), o-*carboxyphenoltetraiodosulphonephthalein*, *phenoltetrabromosulphonephthalein* (*tetrabromo*-derivative), *resorcinoltetrabromosulphonephthalein*, and o-*cresoltetrabromosulphonephthalein*; these decompose gradually at high temperatures. The p_H ranges of these compounds are given.

*Tetraiodo-*o*-benzoicsulphinide*, not melted at 345°, is also described. H. Burton.

Preparation of salicylyl chloride. A. Kirpal (Ber., 1930, **63**, [*B*], 3190).—Salicylic acid (10 g.) mixed with thionyl chloride (7 c.c.) and aluminium chloride (0·02 g.) is warmed at 45—50° until dissolution is complete. Excess of thionyl chloride is removed in a vacuum, leaving crystalline salicylyl chloride, m. p. 18°. H. Wren.

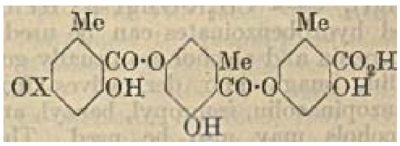
Manufacture of arylamides of 4-arylaminosalicylic acids. I. G. Farbenind. A.-G.—See B., 1931, 58.

Manufacture of 5-arylaminosalicylic acids. I. G. Farbenind. A.-G.—See B., 1931, 58.

Stability of magnesium *r*-mandelate. A. Findlay and A. N. Campbell (J.C.S., 1930, 2721—2724).—Determinations of the solubility of magnesium *l*- and *r*-mandelates in water at 0—40° by the method previously described (A., 1930, 406) show that the solubility curve for the *l*-salt is simple and it ascends rapidly above about 30°; the *r*-salt gives a three-branched solubility curve, indicating the existence of a monohydrate (stable up to about 12°), a semihydrate (stable at 12—29°), and, above 29°, an anhydrous salt. The composition of the hydrates is confirmed by vapour-pressure measurements. The composition of the solution in equilibrium with the *l*- and *r*-salts as solid phases was determined polarimetrically and plotted in rectangular co-ordinates. The *r*-salt exists as a stable, solid phase throughout the range of temperature used. H. Burton.

Benzylidenepyruvic acid. L. Musajo (Gazzetta, 1930, **60**, 669—672).—The m. p. of the dibromide of benzylidenepyruvic acid (βγ-dibromo-α-keto-γ-phenyl-*n*-butyric acid), for which various values are given in the literature, is 124° for the product crystallised from a concentrated solution in benzene. If the substance is kept for some time in a vacuum it then melts at 142—143°. By crystallising from benzene, fractions which melt at 147—150° can also be obtained. A preliminary study has been made of the action of bromine on the oily variety of benzylidenepyruvic acid, which has also been obtained as a solid amorphous product. O. J. Walker.

Lichen substances. VI. Gyrophoric acid. Y. Asahina and M. Watanabe (Ber., 1930, **63**, [*B*], 3044—3048; cf. A., 1929, 818).—Gryophoric acid (I, X=H), m. p. about 220° (decomp.), is obtained in 1·4% yield by successive extraction of *Gryophora*

(I.) 

esculenta with ether and acetone. It is converted by acetic anhydride containing a trace of concentrated sulphuric acid into the corresponding *tetra-acetate*, m. p. 228°, and by chloroacetyl chloride in presence of chloroacetic acid and pyridine into the *tetrachloroacetate* ($+2H_2O$), m. p. 163—164°. It affords a

characteristic *quinine* salt, $C_{44}H_{44}O_{12}N_2,H_2O$, m. p. 162°. With diazomethane it gives *methyl tetramethylgyrophorate*, m. p. 196—197°. Analysis and determinations of mol. wt. of the acid and its derivatives confirm the structure I. Umbilicaric acid has the similar constitution (X = Me). H. WREN.

Reaction between the binary system magnesium+magnesium iodide and aromatic aldehydes. M. GOMBERG and W. E. BACHMANN (J. Amer. Chem. Soc., 1930, **52**, 4967—4972).—When benzaldehyde (3 mols.) is treated with magnesium (1 atom) and magnesium iodide in ethereal benzene and the resulting solution hydrolysed with dilute acid, a mixture of unchanged aldehyde, benzyl alcohol, benzoin, and resinous material is obtained. The use of an excess of magnesium leads to the consumption of 1·5 atoms per 3 mols. of aldehyde; benzyl alcohol and resinous material are the sole products of the reaction. The changes taking place are probably: (*a*) $2Ph{\cdot}CHO+Mg+MgI_2 \longrightarrow 2[CHPh{\cdot}OMgI] \longrightarrow (CHPh{\cdot}OMgI)_2$ (I); (*b*) $(CHPh{\cdot}OMgI)_2+Ph{\cdot}CHO \longrightarrow CHPhBz{\cdot}OMgI$ (II) $+ CH_2Ph{\cdot}OMgI$; (*c*) $2CHPhBz{\cdot}OMgI+Mg+MgI_2 \longrightarrow [CHPh(OMgI){\cdot}CPh(OMgI)]_2$. Magnesium methyl iodide (2 mols.) and hydrobenzoin (1 mol.) afford I, which reacts with benzaldehyde, forming (after hydrolysis) benzoin and benzyl alcohol; the presence of II in the reaction mixture is established by treatment with magnesium phenyl bromide, whereby triphenylethylene glycol is produced. These results support change *b*. Treatment of II, prepared from benzoin (1 mol.) and magnesium ethyl iodide (1 mol.), with a mixture of magnesium and magnesium iodide in ethereal benzene gives, after hydrolysis, a small amount of αβγδ-tetraphenylerythritol and much resinous material which is apparently identical with that obtained from benzaldehyde. These results support equation *c*.

α-Naphthaldehyde, *p*-tolualdehyde, anisaldehyde, and *p*-chloro- and *p*-bromo-benzaldehydes react with the system magnesium–magnesium iodide in essentially the same manner. H. BURTON.

Reducing action of compounds containing the group >CH·OMgI. R. V. SHANKLAND and M. GOMBERG (J. Amer. Chem. Soc., 1930, **52**, 4973—4978).—Treatment of 18 aldehydes (mainly aromatic) with magnesium iodohydrobenzoinate, $(CHPh{\cdot}OMgI)_2$, in ethereal benzene gives, after hydrolysis of the reaction mixture, benzoin and the primary alcohol formed by reduction of the aldehyde: $R{\cdot}CHO+(CHPh{\cdot}OMgI)_2 \longrightarrow CH_2R{\cdot}OMgI + CHPhBz{\cdot}OMgI$. Substituted hydrobenzoinates can be used and the yields of benzoin and alcohol are usually good. The corresponding magnesium derivatives from benzhydrol, benzopinacolin, *iso*propyl, benzyl, and chlorobenzyl alcohols may also be used. The hydrobenzoin derivatives are the most effective. The results favour Marshall's explanation (J.C.S., 1914, **105**, 527; 1915, **107**, 509; A., 1925, i, 1428) of the production of primary alcohols and ketones during the interaction of aldehydes and Grignard reagents. H. BURTON.

Beckmann rearrangement. V. Substituted cinnamaldoximes and cinnamonitriles. K. VON AUWERS and M. SEYFRIED (Annalen, 1930, **484**, 212—235).—When α-bromocinnamaldoxime, m. p. 144°, previously described as probably the *syn*-oxime (A., 1925, i, 1428), is treated with phosphorus pentachloride in ether, trans-α-*bromocinnamonitrile*, b. p. 148—150°/12 mm., m. p. 33—35°, d_4^{20} 1·476, n_{He}^{20} 1·6308, is produced. Treatment with boiling acetic anhydride gives *cis*-α-bromocinnamonitrile, b. p. 143—145°/15 mm., d_4^{20} 1·461, n_{He}^{20} 1·6294 (cf. *loc. cit.*). These results are understandable when α-bromocinnamaldehyde, m. p. 73°, is regarded as the *cis*-derivative; oximation causes no change in configuration. *cis*-α-Bromocinnamamide, prepared from the *cis*-chloride and ammonia (unless precautions are taken, the *trans*-amide results), is dehydrated by phosphoryl chloride at 100° (bath) to the *cis*-nitrile, also formed from αβ-*dibromo*-β-*phenylpropionitrile*, m. p. 92—93°, and cold alcoholic potassium hydroxide (1 mol.). *trans*-α-Bromocinnamamide is dehydrated by phosphorus pentachloride and oxychloride at 100° to the above *trans*-nitrile. Treatment of the *cis*- and *trans*-α-bromocinnamonitriles with alcoholic potassium hydroxide causes considerably more elimination of bromine from the *trans*-form; under suitable conditions both modifications yield the same β-*ethoxycinnamonitrile*, b. p. 152—154°/12 mm., d_4^{20} 1·056, n_{He}^{20} 1·5666, hydrolysed by very dilute sulphuric acid to benzoylacetonitrile. The β-*ethoxycinnamonitrile*, b. p. 163—165°/11 mm., d_4^{20} 1·052, n_{He}^{20} 1·5507, prepared from phenylpropiolonitrile and alcohol by Moureu and Lazennec's method (A., 1906, i, 240) is a stereoisomeric form. Both forms show no difference in the rates of hydrolysis or reaction with bromine.

Treatment of phenylpropiolaldehyde with hydrogen bromide in cold acetic acid gives the unstable β-*bromocinnamaldehyde*, b. p. 138—140°/11 mm., d_4^{20} 1·492, n_{He}^{20} 1·6383, which with hydroxylamine hydrochloride yields a mixture, m. p. 81°, of *oximes*, m. p. 63—66° and 103°, separable through the differing solubilities of their sodium salts. The elimination of bromine (by treatment with alcoholic potassium hydroxide) from the aldehyde occurs much more readily than from the oxime mixture. Acetylation of the mixture of oximes gives the *acetyl* derivative, m. p. 68—69°, of the form of m. p. 103°.

Oxidation of *cis*-α-bromocinnamaldehyde with silver oxide in presence of aqueous-alcoholic sodium hydroxide affords *trans*-α-bromocinnamic acid, also formed (in one case only) when the aldehyde is shaken with oxygen in chloroform.

Spectrochemical data are given for most of the above compounds. H. BURTON.

Condensation of aldehydes with hydrazones. II. Condensation of anisaldehyde and salicylaldehyde with the respective phenylhydrazones. III. Condensation of salicylaldehyde, anisaldehyde, and *p*-nitrobenzaldehyde with benzaldehydephenylhydrazone. A. GIACALONE (Gazzetta, 1930, **60**, 818—821, 821—824; cf. A., 1930, 213).—II. In presence of zinc chloride, anisaldehyde (3 mols.) condenses with its phenylhydrazone (2 mols.)

to form pp′-4 : 4′-*dimethoxybenzylidenedihydrazino*-p″-*methoxytriphenylmethane*, $OMe\cdot C_6H_4\cdot CH(C_6H_4\cdot NH\cdot N{:}CH\cdot C_6H_4\cdot OMe)_2$, m. p. 215—216°. Similarly, salicylaldehyde and its phenylhydrazone give pp′-2 : 2′-*dihydroxybenzylidenedihydrazino*-o″-*hydroxytriphenylmethane*, $OH\cdot C_6H_4\cdot CH(C_6H_4\cdot NH\cdot N{:}CH\cdot C_6H_4\cdot OH)_2$, m. p. 240° (decomp.).

III. When condensed with benzaldehydephenylhydrazone in presence of zinc chloride, (1) salicylaldehyde yields pp′-*dibenzylidenedihydrazino*-o″-*hydroxytriphenylmethane*, $OH\cdot C_6H_4\cdot CH(C_6H_4\cdot NH\cdot N{:}CHPh)_2$, m. p. 185°, which forms a *triacetyl* derivative, m. p. 109—110°; (2) anisaldehyde gives pp′-*dibenzylidenedihydrazino*-p″-*methoxytriphenylmethane*, m. p. about 125°, and (3) *p*-nitrobenzaldehyde gives pp′-*dibenzylidenedihydrazino*-p″-*nitrotriphenylmethane*, m. p. 213—214°. T. H. POPE.

Dioximes. LXIX. LXX. G. PONZIO (Gazzetta, 1930, **60**, 825—832, 886—893; cf. A., 1930, 1409).—LXIX. The extension to the glyoximes of the differentiation, proposed by Hantzsch for the monoximes, into forms stable towards acid and those stable towards alkali has resulted only in the supposed discovery of new forms of glyoximes which have no actual existence. The methods of Scholl (A., 1891, 315), Russanoff (A., 1892, 321), and Wieland and Semper (A., 1908, i, 108) yield, not α-phenylglyoxime, but mixtures of this with the β-form, and the three phenylglyoximes described by Russanoff represent one and the same compound in more or less impure condition. With regard to the action of ethereal hydrogen chloride solution on glyoximes, it is now established that this reagent isomerises a form of benzildioxime that does not give a complex nickel salt into one that does, a form of chloroglyoxime giving no such salt into another also giving none, a form of phenylglyoxime giving a nickel salt into one giving no salt, a form of *p*-tolylglyoxime giving no nickel salt into one giving such salt, and the form of *p*-tolylglyoxime giving a nickel salt into a form giving no nickel salt. These results are not in accord with the configurations which would be attributed to the two forms of these glyoximes on the basis of Hantzsch and Werner's thery.

LXX. Experimental results show that replacement of one or both oximinic hydrogen atoms of a glyoxime by one or two acyl groups does not necessarily yield an acyl derivative of the original glyoxime form, even although this may be obtained by subsequent hydrolysis of the acyl derivative. Hantzsch and Werner's hypothesis is found to be inapplicable to the acyl derivatives of chloro- and amino-glyoxime. Thus, when treated with chlorine, α- and β-phenylglyoximes yield one and the same phenylchloroglyoxime, from which, by conversion into the 2-benzoyl or the dibenzoyl derivative, followed by the action of ammonia, both α- and β-phenylaminoglyoximes are obtained. 2-*Benzoyl*-α-*phenylchloroglyoxime*, NOBz:CPh·CCl:NOH, m. p. 177—178° (slight decomp.); *dibenzoylphenylchloroglyoxime*, NOBz:CPh·CCl·NOBz, m. p. 148—149°; 2-*benzoyl*-α-*phenylaminoglyoxime*, m. p. 171—172° (slight decomp.), and 2-*benzoyl*-α-*phenylacetamidoglyoxime*, NOBz:CPh·C(NOH)·NHAc, m. p. 190—191° (slight decomp.), were prepared. T. H. POPE.

[**Aromatic thioketones.**] E. BERGMANN (Ber., 1930, **63**, [*B*], 3225).—The reaction of aromatic thioketones with sodium (A., 1930, 1584) has been observed previously by Schonberg (A., 1925, i, 1300). H. WREN.

Behaviour of stereoisomeric oximes of αβ-unsaturated ketones when hydrogenated. K. W. MERZ (Ber., 1930, **63**, [*B*], 2951—2953).—3-Hydroxy-4-methoxystyryl methyl ketone is converted by hydroxylamine hydrochloride in 50% methyl alcohol into 3-*hydroxy*-4-*methoxystyryl* syn-*ketoxime hydrochloride*, m. p. 174° (decomp.). The free syn-*oxime*, m. p. 168—169°, is transformed in hot glacial acetic acid into the anti-*oxime*, m. p. 142—143°. Both forms yield the same *dibenzoyl* derivative, m. p. 148—149°, hydrolysed by alcoholic sodium hydroxide to the *anti*-variety. Hydrogenation of the *syn*-oxime in presence of palladised charcoal gives a mixture of β-3-hydroxy-4-methoxyphenylethyl methyl ketone, its oxime, and γ-amino-α-3-hydroxy-4-methoxyphenylbutane, whereas the *anti*-oxime is unchanged under these conditions. Phenyl styryl *syn*-ketoxime is converted into αγ-diphenylpropylamine and phenyl β-methylstyryl *syn*-ketoxime into αγ-diphenylbutylamine, whereas the corresponding *anti*-oximes are unaffected. H. WREN.

Beckmann rearrangement. IV. Unsaturated ketoximes. K. VON AUWERS and M. SEYFRIED (Annalen, 1930, **484**, 178—211).—Hydroxylamine reacts with various phenyl styryl ketones in alkaline solution, forming *iso*oxazolines or *iso*oxazoles, whereas in acidic solution the corresponding oximes are produced. Thus, phenyl styryl ketone and hydroxylamine react in alkaline solution, yielding a mixture of 3 : 5-diphenyl*iso*oxazoline, m. p. 75°, and alkali-soluble hydroxylamino-oximes (cf. Claus, A., 1897, i, 189); with hydroxylamine hydrochloride (cf. Henrich, A., 1907, i, 324), phenyl styryl ketoxime, m. p. 115—116° (lit. 107—108°), results. This oxime is unaffected by boiling alkali; it adds bromine in chloroform, forming phenyl αβ-dibromo-β-phenylethyl ketoxime, m. p. 156°, which when heated at 160° gives hydrogen bromide and 3 : 5-diphenyl*iso*oxazole, and with phosphorus pentachloride in ether undergoes rearrangement to αβ-*dibromo*-β-*phenylpropionanilide*, m. p. 179°. Phenyl α-bromostyryl ketoxime (A., 1929, 816) undergoes the Beckmann rearrangement, yielding an impure substituted benzamide (hydrolysis product benzoic acid). Anisyl styryl ketone furnishes an *oxime*, m. p. about 140° (*acetyl* derivative, m. p. 134—135°), rearranged to *cinnam*-p-*anisidide*, m. p. 152—153°; in alkaline solution, 5-*phenyl*-3-*anisyliso*-*oxazoline*, m. p. 104·5—105·5°, results (cf. Stockhausen and Gattermann, A., 1893, 163). Oxidation of this *iso*oxazoline with chromic and acetic acids gives 5-phenyl-3-anisyl*iso*oxazole, m. p. 121°, also formed from anisoylphenylacetylene and hydroxylamine (cf. Weygand and Bauer, A., 1928, 187). 1 : 5-*Diphenyl*-3-*anisylpyrazoline*, m. p. 140·5—141·5°, is prepared from anisyl styryl ketone and phenylhydrazine in alcohol containing a little acetic acid.

Anisyl α-bromostyryl ketone, b. p. 250—253°/13 mm. (cf. Weygand and Bauer, *loc. cit.*), is converted into 5-phenyl-3-anisyl*iso*oxazole or the corresponding *oxime*, m. p. 153°, which undergoes the Beckmann rearrangement, yielding resinous material (hydrolysed to anisic acid). Treatment of anisoylphenylacetylene with hydrogen bromide in acetic acid gives *anisyl β-bromostyryl ketone*, m. p. 65—66°, also convertible into 5-phenyl-3-anisyl*iso*oxazole; the *oxime*, m. p. 115—116°, is converted by phosphorus pentachloride in ether into trans-β-*bromocinnam*-p-*anisidide*, m. p. 144°. Whilst the above (*syn*) oxime, m. p. 153°, is readily decomposed by aqueous-alcoholic sodium hydroxide to the phenylanisyl*iso*oxazole, the oxime of m. p. 115—116° is only partly hydrolysed under the same conditions (the *iso*oxazole is also produced), indicating that it is an *anti*-derivative. p-*Ethoxyphenyl αβ-dibromo-β-phenylethyl ketone* has m. p. 151—152°.

The mechanism of the formation of the *iso*oxazole derivatives is discussed; they are formed presumably through the *syn*-oximes. The addition of hydroxylamine to aryl α-methoxystyryl ketones (Weygand and Bauer, *loc. cit.*) is considered to give oximinoketones and not hydroxylaminoketones. Meisenheimer's views on the Beckmann rearrangement are criticised and it is considered that the rearrangement is not a method for determining configuration.

H. BURTON.

ω-Alkoxyalkylaminopropiophenones. R. T. MAJOR (J. Amer. Chem. Soc., 1930, 52, 5294).—ω-*Methoxymethylamino-*, b. p. 159°/23 mm. (*hydrochloride*, m. p. 155°), and ω-*ethoxyethylamino-propiophenones*, b. p. 151—153°/9 mm., are prepared in 50% and 18% yield, respectively, from acetophenone, the requisite *ON*-dialkylhydroxylammonium chloride, and trioxymethylene by Mannich's method (A., 1917, i, 634). These compounds have only a slight anæsthetic action. H. BURTON.

Synthesis of aromatic hydroxyketones. I. o- and p-Acylphenols with normal chains of four to nine carbon atoms. G. SANDULESCO and A. GIRARD (Bull. Soc. chim., 1930, [iv], 47, 1300—1314).—Mixtures of *o*- and *p*-hydroxyaryl ketones are obtained in yields of 80—90% of theory when the reaction product $ArO\cdot AlCl_2$(?) from equimolecular proportions of aluminium chloride and a phenol is treated with an acyl chloride at 120—140° in the absence of a solvent. In presence of nitrobenzene or other solvent, the yields are lower and operating difficulties are greater, heptoyl chloride and phenol in nitrobenzene affording 33% of *o*- and 46% of *p*-hydroxyphenyl hexyl ketone. In the absence of solvent about 45—60% of *o*- and 30—40% of *p*-derivative are formed, together with a little *op*-disubstituted derivative. The *o*-hydroxyaryl ketones are liquids or easily fusible solids, readily soluble in light petroleum and volatile in steam, the *p*-isomerides being non-volatile solids and sparingly soluble. In contrast to the *p*-compounds, the *o*-hydroxyaryl ketones have little tendency to form alkali derivatives and only *o*-butyrylphenol is completely soluble in the equivalent amount of *N*-sodium hydroxide. The *o*-compounds are benzoylated only with difficulty in presence of pyridine, and attempts at methylation with methyl iodide or methyl sulphate failed. The *o*-hydroxyaryl ketones are reduced with difficulty, increasing with the mol. wt., whilst the *p*-compounds with zinc and hydrochloric acid readily give the alkylphenols in 75—90% yields; the *o*-compounds require the presence of acetic acid.

The following are described, the yields being indicated in parentheses: *o*- (45%), m. p. 10·5—10·6°, b. p. 119°/9 mm., d^4 1·0683, $n_D^{23.5}$ 1·5375 (*semicarbazone*, m. p. 192—193°), and p-*hydroxyphenyl* n-*propyl ketone* (30%), m. p. 91—91·5°, b. p. 187—188°/9 mm. (benzoate, m. p. 107—107·5°), *o*- (56%), b. p. 130°/10 mm., d^4 1·0435, $n_D^{25.5}$ 1·5309 (*semicarbazone*, m. p. 204—204·5°), and *p*-hydroxyphenyl *n*-butyl ketone (29%), m. p. 63°, b. p. 197·5—198·5°/10 mm. (benzoate, m. p. 92°); *o*- (56%), b. p. 142—143°/10 mm., m. p. 17·2—17·4°, d^{21} 1·026, $n_D^{23.5}$ 1·5254 (*semicarbazone*, m. p. 179°), and *p*-hydroxyphenyl *n*-amyl ketone (34%), m. p. 61°, b. p. 207—208°/10 mm. (benzoate, m. p. 105·5°); *o*- (48%), m. p. 9·8°, b. p. 155—156°/10 mm., d^{24} 1·011, $n^{25.5}$ 1·5209 (*semicarbazone*, m. p. 162°), and *p*-hydroxyphenyl *n*-hexyl ketone (41%), m. p. 91—91·5° (benzoate, m. p. 96·5—97°; *acetate*, m. p. 46·5°, b. p. 194—195°/9 mm.); *o*- (45%), m. p. 22·3°, b. p. 169—170°/11 mm., d^{24} 0·9989, $n_D^{25.5}$ 1·5169 (*semicarbazone*, m. p. 157—158°), and p-*hydroxyphenyl* n-*heptyl ketone* (38%), m. p. 62°, b. p. 224—225°/10 mm. (*benzoate*, m. p. 107—108°); *o*- (55%), m. p. 18·4°, b. p. 180°/10 mm., d^{24} 0·9887, $n_D^{25.5}$ 1·5139 (*semicarbazone*, m. p. 164°), and p-*hydroxyphenyl* n-*octyl ketone* (35%), m. p. 54·5°, b. p. 232°/10 mm. (*benzoate*, m. p. 99·8°); o-n-*butylphenol* (83%), b. p. 109·5—110°/10 mm., d^{23} 0·9774, $n_D^{25.5}$ 1·518 (*phenoxyacetic acid*, m. p. 105·5°); *p*-*n*-butylphenol (86%), m. p. 22°, $n^{23.5}$ 1·5165, $n_D^{45.5}$ 1·5082 (*benzoate*, m. p. 27°), o-n-*amylphenol* (72%), b. p. 122—124°/10 mm., d^{23} 0·9635, $n_D^{23.5}$ 1·5132 (o-n-*amylphenoxyacetic acid*, m. p. 77—77·5°), p-n-*amylphenol* (79%), m. p. 23°, b. p. 134—136°/10 mm., $n_D^{23.5}$ 1·5119, $n_D^{45.5}$ 1·5038 (*benzoate*, m. p. 51—51·5°); o-n-*hexylphenol* (80%), m. p. —2°, b. p. 135—136°/10 mm., d^{23} 0·9524, $n_D^{23.5}$ 1·5089 (o-n-*hexylphenoxyacetic acid*, m. p. 89·5—90°), *p*-*n*-hexylphenol (77%), m. p. 28°, b. p. 146—147°/10 mm., $n_D^{45.5}$ 1·4996 (*benzoate*, m. p. 26·5°); *o*-*n*-heptylphenol (90%), m. p. 3°, b. p. 147—148°/10 mm., d^{23} 0·9432, $n_D^{23.5}$ 1·5058 (o-n-*heptylphenoxyacetic acid*, m. p. 71·5°); *p*-*n*-heptylphenol (73%), m. p. 26°, b. p. 157°/9 mm., $n_D^{45.5}$ 1·4969 (*benzoate*, m. p. 40·5—41°); o-n-*octylphenol* (79%), m. p. 18—18·5°, b. p. 160—162°/11 mm., d^{23} 0·9362, $n_D^{23.5}$ 1·5029 (o-n-*octylphenoxyacetic acid*, m. p. 88—88·5°); p-n-*octylphenol* (85%), m. p. 41—42°, b. p. 169°/10 mm., $n_D^{45.5}$ 1·4938 (*benzoate*, m. p. 40·5°); o-n-*nonylphenol* (85%), m. p. 19·5°, b. p. 176—177°/13 mm., d^4 0·9309, $n_D^{23.5}$ 1·5005 (o-n-*nonylphenoxyacetic acid*, m. p. 75·5°); and p-n-*nonylphenol* (80%), m. p. 42·5°, b. p. 180—181°, $n_D^{45.5}$ 1·4920 (*benzoate*, m. p. 36·2°). R. BRIGHTMAN.

Structure of p-dimethylaminobenzoin. S. S. JENKINS [with L. A. BIGELOW and J. S. BUCK] (J. Amer. Chem. Soc., 1930, 52, 5198—5204).—*p*-Dimethylaminomandelonitrile, prepared from *p*-dimethylaminobenzaldehyde and dry hydrogen cyanide in presence of a small amount of calcium oxide, is

hydrolysed by sulphuric acid at the ordinary temperature to *p*-dimethylaminomandelamide, m. p. 184—186°, which reacts with ethereal magnesium phenyl bromide, forming *benzoyl*-p-*dimethylaminophenylcarbinol* (α-p-*dimethylaminobenzoin*), m. p. 159—160° (corr.). This is oxidised by Fehling's solution to 4-dimethylaminobenzil and reduced by tin and alcoholic hydrochloric acid containing a little copper sulphate to α-*p*-dimethylaminodeoxybenzoin, m. p. 127—128° (this vol., 92).

p-Dimethylaminobenzoylphenylcarbinol (β-*p*-dimethylaminobenzoin), m. p. 161—162° (corr.), prepared from mandelamide and magnesium *p*-dimethylaminophenyl bromide, is identical with the supposed α-derivative, m. p. 163—164°, of Staudinger (A., 1913, i, 1353). It is reduced as above to a mixture of α- and β-*p*-dimethylaminodeoxybenzoins (cf. *loc. cit.*). Similar reduction of *p*-dimethylaminohydrobenzoin gives 4-dimethylaminostilbene. H. BURTON.

Dioximes. LXXI. G. PONZIO and G. LONGO (Gazzetta, 1930, **60**, 893—899).—The action of Grignard's reagent on isomeric arylmethylglyoxime peroxides confirms the view, deduced from the action of phosphorus pentachloride or sodium ethoxide and from physico-chemical investigations (cf. A., 1929, 334, 1316; 1930, 226, 581, 621), that the peroxides with the higher m. p. are furoxans, whilst those with the lower m. p. are dioxdiazines. T. H. POPE.

Anthrone series. I. Condensation of phthalide with aromatic compounds. II. Synthesis of hydroxymethylanthrones. A. STEYERMARK [with J. H. GARDNER] (J. Amer. Chem. Soc., 1930, 52, 4884—4887, 4887—4892).—I. The Friedel-Crafts reaction between benzene and phthalide gives 28% of the theoretical amount of anthrone (cf. King, A., 1927, 358). The oily product obtained similarly, using toluene, is oxidised by chromic and acetic acids to 2-methylanthraquinone; it forms some 2-methylbenzanthrone when treated with glycerol and 82% sulphuric acid, indicating that 2-methyl-10-anthrone is formed in the original condensation. 2-Chloroanthraquinone is obtained when the product from chlorobenzene and phthalide is oxidised; no benzanthrone derivative could be isolated. The above method is not suitable for synthesising anthrones of definite structure.

II. The following benzylbenzoic acids are prepared by reducing the corresponding benzoylbenzoic acids with zinc dust and ammonia: o-2′-*hydroxybenzyl*-, m. p. 133·8—134·5°; o-2′-*hydroxy*-3′-*methylbenzyl*-, m. p. 158·2—159°; o-2′-*hydroxy*-4′-*methylbenzyl*-, m. p. 123—124°, and o-2′-*hydroxy*-5′-*methylbenzylbenzoic acids*, m. p. 129—130°. These are converted by dissolution in sulphuric acid at the ordinary temperature into 1-hydroxy-; 1-*hydroxy*-2-*methyl*-, m. p. 207·2—208°; 1-*hydroxy*-3-*methyl*-, m. p. 258—259°, and 1-*hydroxy*-4-*methyl*-10-*anthrones*, m. p. 226·2—227°, respectively. Reduction of 1-hydroxyanthraquinones, prepared from the corresponding *o*-benzoylbenzoic acids, with tin and hydrochloric acid in acetic acid gives 1-hydroxy-9-anthrones in agreement with the work of Cross and Perkin (A., 1930, 607). The following are described: 1-hydroxy-; 1-*hydroxy*-2-*methyl*-, m. p. 136·2—137°; 1-*hydroxy*-3-*methyl*-, m. p. 158·2—159°, and 1-*hydroxy*-4-*methyl*-9-*anthrones*, m. p. 167·4—168·2°. These anthrones are bright yellow (? benzenoid–quinonoid tautomerism), whilst their isomerides are colourless. The main product formed when 2-methylanthraquinone is reduced by Barnett and Goodway's method (A., 1929, 1171) is 2-methyl-10-anthrone (cf. *loc. cit.*). H. BURTON.

Munjisthin. II. P. C. MITTER and H. BISWAS (J. Indian Chem. Soc., 1930, 7, 839—841).—6-Methoxy-*o*-toluidine is converted by the usual method into 2-*hydroxy*-6-*methoxytoluene*, b. p. 242—244°, and thence into 2 : 6-*dimethoxytoluene*, m. p. 35°, which reacts with phthalic anhydride in presence of aluminium chloride and carbon disulphide, forming o-2 : 4-*dimethoxy*-m-*toluoylbenzoic acid*, m. p. 180°. When this is heated with a mixture of concentrated (1 part) and fuming sulphuric acid (20% SO_3; 5 parts) at 100° (bath), *rubiadin methyl ether*, m. p. 188—189°, is produced. This is demethylated by aluminium chloride at 200° to rubiadin. The above acid could not be oxidised to the corresponding benzophenonedicarboxylic acid, which, on ring closure, should yield munjisthin. The above methyl ether may be identical with the 3-*O*-methylrubiadin of Jones and Robertson (A., 1930, 1167). H. BURTON.

Synthesis of munjisthin. P. C MITTER and H. BISWAS (Nature, 1930, **126**, 761; 1931, **127**, 166).—The synthesis of munjisthin, a dihydroxyanthraquinonecarboxylic acid occurring in *Rubia munjistha*, starting with 2-chloro-6-methoxytoluene and phthalic anhydride, is recorded. L. S. THEOBALD.

Anthracene derivatives. II. E. DE B. BARNETT and N. F. GOODWAY (Ber., 1930, 63, [*B*], 3048—3051).—1 : 5-Dimethoxyanthraquinone, m. p. 241°, prepared by the action of boiling methyl-alcoholic sodium hydroxide on sodium anthraquinone-1 : 5 disulphonate, could not be reduced to the corresponding anthrone. 1 : 5-Diphenoxyanthraquinone is transformed by stannous chloride and concentrated hydrochloric acid in boiling glacial acetic acid into 1 : 5-*diphenoxyanthrone*, $X<{CO \atop CH_2}>X$ or $X<{C(OH) \atop CH}>X$, ($X{=}C_6H_3{\cdot}OPh$), m. p. 166°, which is recovered unchanged after treatment with magnesium methyl iodide or magnesium benzyl chloride and does not afford a mono- or di-benzylanthrone when boiled with benzyl chloride and sodium hydroxide. 1 : 5-*Diphenoxyanthranyl acetate* has m. p. 165°. Bromine in carbon disulphide converts the anthrone into 10-*bromo*-1 : 5-*diphenoxyanthrone*, m. p. about 180—183° (decomp.), from which the following compounds are derived by the usual methods: 1 : 5-*diphenoxy*-10-*ethoxyanthrone*, m. p. 148° (whence the corresponding *acetate*, m. p. 238°); 10-*piperidino*-1 : 5-*diphenoxyanthrone*, m. p. 136°; 10-*anilino*-1 : 5-*diphenoxyanthrone*, m. p. 159° (decomp.); 10-*methylanilino*-1 : 5-*diphenoxyanthrone*, m. p. 159° after softening; 1 : 5-*diphenoxy*-10-p-*dimethylaminophenylanthrone*, m. p. 250° (decomp.). Phthalic anhydride is converted by diphenyl ether in presence of aluminium chloride and carbon disulphide into o-4′-*phenoxybenzoylbenzoic acid*, m. p. 162°, which is not transformed into the corresponding anthraquinone by sulphuric acid; it is reduced by zinc dust and ammonia to o-4′-*phenoxy*-

benzylbenzoic acid, m. p. 128°, which could not be converted into the corresponding anthrone.

H. Wren.

Derivatives of hydroxyaminomethylanthraquinones and dihydroxydianthraquinonylethylenes. III. H. de Diesbach, P. Gubser, and H. Spoorenberg (Helv. Chim. Acta, 1930, **13**, 1265—1274; cf. A., 1929, 70; 1930, 607).—1-Chloro-2-aminoanthraquinone is converted by short treatment with nitrosyl sulphate at 180—200° into 1-chloro-2-hydroxyanthraquinone, m. p. 224°, which reacts with *N*-methyloltrichloroacetamide in cold sulphuric acid, forming 1-*chloro-2-hydroxy-3-trichloroacetamidomethylanthraquinone*, m. p. 204°. Hydrolysis of this with boiling 10% sodium hydroxide solution gives, instead of the expected amine (or its oxidation product) (cf. *loc. cit.*), probably impure β-*amino*-αβ-*di*-(1-*chloro*-2-*hydroxy*-3-*anthraquinonyl*)*ethyl alcohol*, m. p. about 250°; ammonia is evolved during the hydrolysis. Alizarin reacts with dimethylolcarbamide and *N*-methylolphthalimide, forming α-(1 : 2-*dihydroxy*-3-*anthraquinonyl*)*methyl* - γ - *hydroxymethylcarbamide*, m. p. 204°, and 1 : 2-*dihydroxy*-3-*phthalimidomethylanthraquinone*, m. p. 310°, respectively. Hydrolysis of the former of these with 65% sulphuric acid at 160° gives 1 : 2-*dihydroxy*-3-*aminomethylanthraquinone* (the *acetate* is formed by hydrolysis of the carbamide with a saturated solution of hydrogen chloride in acetic acid at 170° and partial neutralisation of the resulting product), whilst treatment of the latter first with boiling 23% sodium hydroxide solution and then with 90% acetic acid at 170° furnishes β-*amino*-αβ-*di*-(1 : 2-*dihydroxy*-3-*anthraquinonyl*)*ethyl alcohol*.

2-Hydroxyanthraquinone condenses with dimethylolcarbamide, forming s-*di*-(α-2-*hydroxyanthraquinonyl*)*methylcarbamide*, m. p. 250°, which is stable towards alkaline hydrolysis, but is converted by hydrochloric acid at 150° into a mixture of the reduced form of *s*-di-(α-2-hydroxyanthraquinonyl)-ethylenediamine and the corresponding glycol (cf. *loc. cit.*). s-*Di*-(α-2-*hydroxy*-3-*carboxyanthraquinonyl*)-*methylcarbamide*, decomp. 318°, is hydrolysed by boiling hydrochloric acid to a mixture of 2-*hydroxy*-1 : 9(N)-iso*pyrroleanthrone*-3-*carboxylic acid* and 2-*hydroxy*-1-*aminomethylanthraquinone*-3-*carboxylic acid*. The former of these is obtained when the latter is heated. Neither of these substances is oxidised to the corresponding ethylene derivative by nitrous acid or oxygen in alkaline solution (cf. *loc. cit.*).

3-Chloroalizarin, anthragallol, and 1-hydroxynaphthacenequinone condense normally with *N*-methylolamides (no details given); the resulting products could not be hydrolysed.

H. Burton.

Derivatives of veratrole and of methylvanillin. III. 2 : 3 : 6 : 7-Tetramethoxyanthraquinone. B. L. Vanzetti and A. Oliverio (Gazzetta, 1930, **60**, 620—632; cf. A., 1927, 462).—Contrary to von Konek and Szamak's statement (A., 1922, i, 458), the preparation of *m*-hemipinic acid from methylvanillin (veratraldehyde) by Perkin and Robinson's method (J.C.S., 1907, **91**, 1073) does not give good results. A more satisfactory procedure consists in converting veratraldehyde, by treatment with sodium in ethyl acetate solution, into 3 : 4-dimethoxycinnamic acid, reducing this with sodium amalgam to obtain 3 : 4-dimethoxydihydrocinnamic acid, condensing the latter by means of phosphoric anhydride to hydrindone, and oxidising the hydrindone with dilute nitric acid (1 : 3). Condensation of *m*-hemipinic anhydride with veratrole in carbon disulphide solution in presence of aluminium chloride yields 4 : 5 : 3′ : 4′-*tetramethoxy*-2-*benzoylbenzoic acid*, m. p. 217—218° (uncorr.), which gives (1) 4 : 5-*dimethoxy*-2-(3 : 4-*dimethoxyphenyl*)-*phthalide*, m. p. 238°, when reduced with zinc dust in sodium hydroxide solution, (2) 4 : 5 : 3′ : 4′-*tetramethoxy*-2-*benzylbenzoic acid*, m. p. 165—166°, when reduced with zinc dust in acetic acid solution, and (3) 2 : 3 : 6 : 7-*tetramethoxy*-9-*anthrone*, m. p. 282—284° (decomp.), when treated with concentrated sulphuric acid at a low temperature. Oxidation of the anthrone by either chromic acid or hydrogen peroxide yields 2 : 3 : 6 : 7-*tetramethoxyanthraquinone*, m. p. 345°, which may also be obtained, in small yield, by oxidising 2 : 3 : 6 : 7-tetramethoxydihydroanthracene with sodium dichromate in acetic acid solution. Demethylation of 2 : 3 : 6 : 7-tetramethoxyanthraquinone by treatment with hydrobromic acid gives 2 : 3 : 6 : 7-*tetrahydroxyanthraquinone*, decomp. above 360°, which forms a *tetra-acetyl* derivative, m. p. 300° (decomp.).

T. H. Pope.

5 : 6 : 5′ : 6′-Dibenzo-*NN*′-dihydro-1 : 2 : 1′ : 2′-anthraquinoneazine. E. Schwenk and H. Waldmann (J. pr. Chem., 1930, [ii], **128**, 320—326).—Treatment of 4-chloro-2-α-naphthoylbenzoic acid with sulphuric acid at 58—60° gives 2-*chloro*-5 : 6-*benzanthraquinone*, m. p. 222—223°, converted by ammonia and cuprous chloride at 180° mainly into 2-*amino*-5 : 6-*benzanthraquinone*, m. p. 283—285°, together with a small amount of probably the 2-amino-1-hydroxy-derivative. Fusion with potassium hydroxide of a mixture of the amino-derivative and potassium acetate at 250—270° affords 5 : 6 : 5′ : 6′-*dibenzo*-NN′-*dihydro*-1 : 2 : 1′ : 2′-*anthraquinoneazine*. This gives a deep blue vat with alkaline hyposulphite, which passes readily, on further reduction, into a dirty brownish-violet; cotton is dyed blue.

The Friedel–Crafts reaction with naphthalene-2 : 3-dicarboxylic anhydride and chlorobenzene yields 3-*p*-chlorobenzoyl-β-naphthoic acid, m. p. 215—220°, converted by treatment with zinc chloride and a little acetic acid at 200—250° into 2-chloro-6 : 7-benzanthraquinone; ring closure can be effected by *p*-toluenesulphonyl chloride at 180°. This chloro-compound gives a green vat with alkaline hyposulphite.

H. Burton.

Monosubstitution derivatives of retene. G. Komppa and E. Wahlforss (J. Amer. Chem. Soc., 1930, **52**, 5009—5017).—Treatment of retene with chlorine in cold carbon tetrachloride containing a little iodine gives a mixture, b. p. 195—205°/10 mm., of chloro-derivatives, part of which distils at 350—351°/747·6 mm. (the remainder resinifies), oxidised by chromic and acetic acids to retenequinone. Introduction of a carboxyl group into retene by Liebermann and Zsuffa's method (A., 1911, i, 202, 387) affords a *retenecarboxylic acid*, m. p. 229—231° (cf. *loc. cit.*) [*sodium* salt (+5H_2O); *methyl* ester, m. p. 96—97°; *amide*, m. p. 224—226°], oxidised to *retenequinone-*

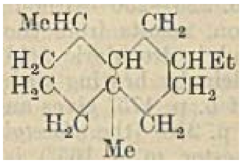
carboxylic acid, m. p. 237—240°; the carboxyl group does not enter the 9- or 10-position, whereas chlorine does. Addition of sulphuric acid (*d* 1·84), with vigorous stirring, to retene at 99° (bath) gives a *retenesulphonic acid*, m. p. 188—189° (*methyl* ester, m. p. 164—166°, prepared from the *potassium* salt and methyl sulphate; *ammonium* salt); when sulphonation is effected at 200°, an isomeric *retenesulphonic acid*, m. p. 121—123° [*ammonium*, *sodium* ($+3H_2O$), *potassium*, *barium* ($+2H_2O$), *strontium* ($+4H_2O$), *calcium* ($+4H_2O$), and *copper* ($+5H_2O$) salts; *sulphonyl chloride*, m. p. 146·5—148°; *sulphonamide*, m. p. 206—207·5°; *methyl* ester, m. p. 117—119°], results. Mixtures of the acids are separable through the differing solubilities of their ammonium, potassium, or sodium salts in water. Both acids are oxidised by chromic and acetic acids to retenequinonesulphonic acids (*potassium* salts). Potassium hydroxide fusion of the less fusible acid gives a *retenol*, m. p. 200—202° (*picrate*, m. p. 151—152°); the more fusible acid yields a *retenol*, m. p. 158·5—159° (*picrate*, m. p. 145—146°; *acetate*, m. p. 132—134°), which couples with diazobenzenesulphonic acid. H. BURTON.

Solutions of gallic acid and tannin; influence of colloids on the crystal form and solubility of gallic acid. L. E. STEENHUISEN (Pharm. Weekblad, 1930, **67**, 1269—1281).—The inhibition of crystallisation of solutions containing 2% of gallic acid, and variations in form of crystals obtained from solutions containing 3% of the acid, as a consequence of the presence in varying quantities of different colloids, are described. When tannin is present, the separated crystals contain very much smaller proportions than correspond with the ratios of tannic to gallic acid in the solution. A modification of Fleck's copper acetate method suitable for determination of tannin and gallic acid together in solution is described. S. I. LEVY.

Rotenone. IX. Alkali fusion of derivatives of rotenone. H. L. HALLER and F. B. LAFORGE. **X. Cleavage of derritol and rotenol.** L. E. SMITH and F. B. LAFORGE (J. Amer. Chem. Soc., 1930, **52**, 4505—4509, 4595—4598).—IX. Fusion of derritol, *iso*derritol, dehydrorotenone, rotenol, dihydroxyrotenonic acid, or *iso*dihydroxyrotenonic acid with potassium hydroxide at 200—210°, gives, in each case, *iso*tubaic acid (cf. A., 1930, 1043). All the above compounds and dihydroderritol methyl ether (potassium hydroxide fusion product dihydrotubaic acid) contain either the lactone group or its hydrolysis group; cleavage does not occur at the keto-group. Similar fusion of dehydrodihydrorotenonic and dihydrorotenolic acids affords unidentified phenolic acids, m. p. about 175° and about 159°, respectively, whilst rotenonic and dihydrorotenonic acids give non-crystalline products.

X. Oxidation of methylderritolic acid (A., 1930, 781) with alkaline hydrogen peroxide affords a *trimethoxyphenylacetic acid*, m. p. 93°, oxidised further by alkaline potassium permanganate to a *trimethoxybenzoic acid*, m. p. 78—80° (*amide*, m. p. 173°). These results make probable Butenandt's suggestion (A., 1928, 1017) that derritol contains the 2-hydroxy-5 : 6-dimethoxyphenylacetyl group. Oxidation of dihydrorotenolic acid (*loc. cit.*) with alkaline hydrogen peroxide furnishes a *dimethoxy-acid*, $C_{12}H_{14}O_5$, m. p. 91—92°. H. BURTON.

Constitution of santonin. III. Proof of positions of methyl groups. G. R. CLEMO and R. D. HAWORTH (J.C.S., 1930, 2579—2582; cf. A., 1930, 919; Ruzicka and Eichenberger, A., 1930, 1442).—Reduction of tetrahydrosantonin by Clemmensen's method gives *deoxytetrahydrosantonin*, m. p. 141—142°, which is further reduced by hydrogen iodide and red phosphorus to an iodine-containing oil, which, after treatment with sodium amalgam and alcohol, followed by distillation over soda-lime, gives 1 : 4(a)-*dimethyl-7-ethyldecahydronaphthalene* (annexed formula), b. p. 120—125°/20 mm.



This could not be successfully dehydrogenated by selenium, but deoxytetrahydrosantonin is readily dehydrogenated to 1-methyl-7-ethylnaphthalene (A., 1930, 593), the 5-methyl group being thereby removed. The location of the second methyl group in the 5-position is therefore proved, and the structure previously assigned (*loc. cit.*) confirmed. H. A. PIGGOTT.

Oxidation of abietic acid with mercuric acetate. G. ROUIN (Bull. Inst. Pin, 1930, 155—157).—Abietic acid, $[\alpha]_D$ −92°, when heated under reflux with 3 mols. of mercuric oxide in acetic acid, gives a monocarboxylic *acid*, $C_{20}H_{28}O_4$, m. p. 198—200°, $[\alpha]_D$ +29·8°, probably diketonic but yielding no oxime, phenylhydrazone, semicarbazone, or quinoxaline. C. HOLLINS.

Fungus dyes. X. Xylindein, the dye of the green mould of decayed wood. F. KOGL, H. ERXLEBEN, and (in part) G. DE VOSS (Annalen, 1930, **484**, 65—84; cf. A., 1925, i, 1440).—Xylindein is converted by aqueous sodium hydroxide into the *tetrasodium* salt of xylindeic acid, which, with silver nitrate, even in excess, gives a *disilver* salt, convertible by methyl iodide into a *dimethyl* ester. This forms a *tetra-acetyl* derivative and a *disemicarbazone*, and is reduced by zinc dust in presence of sodium acetate and acetic anhydride to a *hexa-acetyltetrahydroleuco-dimethyl ester* which no longer forms a semicarbazone. As xylindein itself gives a tetra-acetyl derivative, but has no free carbonyl groups, the occurrence of such in xylindeic acid, which still contains only four hydroxyl groups, may be explained by the presence in xylindein of two lactonic systems derived from enolic structures: $C_{28}H_{22}O_3(OH)_4(CO{\cdot}O{\cdot}O{\cdot}C{:}C{<})_2 + 2H_2O \longrightarrow C_{28}H_{22}O_3(OH)_4(CO_2H)_2(CO{\cdot}CH{<})_2$ This is supported by the catalytic hydrogenation of xylindein, the product of which, when treated with sodium hydroxide, gives the sodium salt of tetrahydroxylindeic acid which contains two carboxylic and two secondary alcoholic groups; thus the crude sodium salt gives a *tetrasilver* salt, which with methyl iodide forms a *dimethyl ether dimethyl ester* (*tetra-acetyl* derivative, not reduced by zinc dust).

Reduction of xylindein with sodium hyposulphite gives a yellow leuco-compound by addition of 1 mol. of hydrogen, the *tetra-acetyl* derivative of which, like the hexa-acetyltetrahydroleuco-ester, shows two reactive hydrogen atoms by Zerewitinov's method. Quantit-

ative oxidation with potassium permanganate of the sodium salt of xylindeic acid occurs with absorption of 36 atoms of oxygen, and yet catalytic reduction of its methyl ester at 80—120° and 120—180 atm. of hydrogen leads only to a hexahydro-compound (isolated as *tetramethyl ether*, m. p. 247°). The hexaacetyl-leuco-ester, alone among the derivatives tried, is degraded to phenanthrene by distillation with zinc dust, and it is suggested that the colour of the dye is due to a 2 : 7-phenanthraquinone structure, the failure to acetylate the hydroxyl groups produced by reduction being ascribed to steric hindrance, probably by *ortho*-substituents.

An *acid*, $C_{32}H_{26}O_{12}Cl_4$, decomp. 225—230° without melting, of unknown constitution, results from the action of hydrogen peroxide and hydrochloric acid on xylindein. Fission of xylindein by heating with alcoholic potassium hydroxide of b. p. 175° gives an *acid*, $C_{13}H_8O_{10}$ or $C_{13}H_{10}O_{10}$, m. p. 216° [the *diacetyl* derivative, m. p. 199° (*trimethyl* ester, m. p. 165°), is converted by catalytic reduction into a substance of m. p. 180—184°], *n*-butyric, and acetic acids.

H. A. PIGGOTT.

Chondridin. V. V. SAVJALOV and P. P. MILOVANOV (Jahrb. Univ. Sofia Med. Fak., 1928, 7, 14; Chem. Zentr., 1930, ii, 249—250).—When a solution of chondrosin is heated with barium hydroxide solution barium chitonate and lutidine are formed. The hydrolytic products of chondrosin afford with benzoyl chloride chitose tribenzoate; when heated under pressure with dilute oxalic acid solution they yield hydroxymethylfurfuraldehyde. Dry distillation of chondroitinsulphuric acid or dried cartilage with calcium oxide affords lutidine. The formula $C_{14}H_{17}O_6N$ is attributed to chondrosin. Chondridin was obtained from tracheal cartilage chondrosin syrup by treatment, after dilution, with ammonium oxalate, evaporation, and extraction with alcohol and ether, followed by decolorisation and crystallisation at 40°. The composition of the chondridin crystals indicated the formula $C_{12}H_{19}O_{10}N,H_2O$. Chondridin is not considered to be a lactone. Chondrosin is regarded as a lutidinecarboxylic ester of chitose.

A. A. ELDRIDGE.

Isoprene and caoutchouc. XXIV. Reduction of caoutchouc with hydriodic acid. H. STAUDINGER and J. R. SENIOR. **XXV. Polymeric homologous hydrocaoutchoucs.** H. STAUDINGER. **XXVI. Hemicolloidal hydrocaoutchouc.** H. STAUDINGER, E. GEIGER, E. HUBER, W. SCHAAL, and A. SCHWALBACH. **XXVII. Relation between viscosity and mol. wt. for hydrocaoutchoucs.** H. STAUDINGER and R. NODZU. **XXVIII. Fractionation and cracking of hydrocaoutchouc.** H. STAUDINGER and W. SCHAAL. **XXIX. High molecular hydrocaoutchouc.** H. STAUDINGER and W. FEISST. **XXX. Hydromethylcaoutchouc.** H. STAUDINGER, M. BRUNNER, and E. GEIGER (Helv. Chim. Acta, 1930, 13, 1321—1324, 1324—1334, 1334—1349, 1350—1354, 1355—1360, 1361—1367, 1368—1374).—XXIV. When caoutchouc is heated with red phosphorus and hydriodic acid (*d* 1·96) at 245—250° and 280°, the products formed are saturated hydrocarbons with M=1760 and 1220, respectively. These products cannot be distilled (cf. Berthelot, Bull. Soc. chim., 1868, [ii], 10, 436; 1869, [ii], 11, 33). They are probably formed by reduction of partly cyclised fragments of the original caoutchouc molecule which result from the cracking process; cyclisation occurs under the influence of the acid.

XXV. The physical properties of the various hydrocaoutchoucs described in the literature and the following papers are discussed. Hydrocaoutchoucs prepared by hydrogenation in absence of solvents at relatively high temperatures are hemicolloids (a 5% solution in carbon tetrachloride is a sol); at lower temperatures in presence of solvents eucolloidal hydrocaoutchoucs are produced (5% solutions in carbon tetrachloride are gels).

XXVI. Hydrogenation of caoutchouc in presence of varying amounts of different catalysts at 275—285° by the method previously described (A., 1922, i, 1043) gives products of widely differing character according to the amount and the activity of the catalyst used. Thus the hydrocaoutchouc obtained with only a small amount of an active nickel (or cobalt) catalyst is much less complex than that formed using equal parts of caoutchouc and catalyst. In the last case reduction occurs at a greater rate than thermal fission of the caoutchouc molecule. Platinum catalysts (cf. *loc. cit.*) give the simpler products, but with copper catalysts abnormal reduction occurs. The products formed during abnormal reduction are hydropoly*cyclo*caoutchoucs; cyclisation of the hemicolloidal polyprene chains occurs before reduction. Reduction of a caoutchouc which has been allowed to swell in *cyclo*hexane (the solvent is removed before reduction) in presence of half its weight of a very active nickel catalyst at 270°/55 atm. affords a hydrocaoutchouc of very high mol. wt., which is stable at 270°. In this case, reduction occurs before any fission. Guttapercha and balata are reduced in presence of equal amounts of nickel catalysts to products similar to the hydrocaoutchouc obtained under the same conditions.

XXVII. The same relationship exists between the viscosity and mol. wt. of pure hydrocaoutchoucs (prepared by rapid reduction on a small scale) as for polyprenes (A., 1930, 609, 782). With technical products (obtained by large-scale processes using little catalyst), it is found that the mol. wt. calcuated from the expressions $M=\eta_{sp.}/cK_m$ and $M=K_cK_{em}$ (cf. *loc. cit.*) are much greater than those determined in benzene.

XXVIII. An ether-soluble hydrocaoutchouc (M=14,000) is fractionally precipitated from its ethereal solution by alcohol. Viscosity determinations of the 5 fractions obtained show that the original product is a mixture of polymeric homologues (M ~5000—21,000); the viscosity of 0·5M-solutions in carbon tetrachloride increases with rise in mol. wt.

Contrary to the statement of Pummerer and Koch (A., 1924, i, 1214), unsaturated compounds are obtained when hydrocaoutchouc is distilled in a high vacuum. The various fractions obtained from a hydrocaoutchouc of M=16,000 have b. p. below 100°/0·1 mm. to above 300°/0·1 mm., and the corresponding mol. wt. vary from about 180 to 960 Iodine chloride titration of the various fractions shows that they contain 2·6—13·7 isoprene units per double linking.

XXIX. Reduction of the ether-soluble caoutchouc of Pummerer and Koch (*loc. cit.*) with hydrogen in presence of platinum oxide and hexahydrotoluene in the cold gives a hydrocaoutchouc with a mol. wt. of about 30,000. A similar product is obtained from a caoutchouc (M=70,000) using an active nickel catalyst at 180—200°/100 atm. The hydrocaoutchoucs are purified by precipitation from solutions in hexahydrotoluene by methyl alcohol. The specific viscosity of 0·1M-solutions of these products in tetrahydronaphthalene is the same at 20° and 60°; with 0·5M-solutions the specific viscosity is greater at the lower temperature owing to strong association. Solutions of the high-molecular hydrocaoutchoucs show only slight deviations from the Hagen–Poiseuille law.

XXX. Hydrogenation of methylcaoutchouc in presence of an active nickel catalyst at 260—270°/90 atm. gives a hemicolloidal hydromethylcaoutchouc with a mean mol. wt. of only 1600. Reduction in presence of 0·025 part of platinum-black at 270—280°/80—100 atm. gives a mixture of products separable by ether–alcohol and distillation into fractions with M=168—1000; the fraction of lowest mol. wt. is probably a tetramethyloctane. The ease of fission of methylcaoutchouc, caoutchouc, and butadiene caoutchouc during reduction under the same conditions is in the order quoted. H. BURTON.

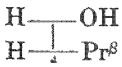
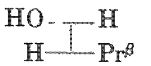
Synthesis of menthyl hydrogen phosphates. K. P. JACOBSOHN and J. TAPADINHAS (Compt. rend. Soc. Biol., 1930, **104**, 432—434, 434—436; Chem. Zentr., 1930, ii, 1221).—The preparation of the *esters* $C_{10}H_{19}{\cdot}O{\cdot}PO(OH)_2$, $(C_{10}H_{19}{\cdot}O{\cdot})_2PO{\cdot}OH$, and $C_{10}H_{19}{\cdot}O{\cdot}PO(OH){\cdot}O{\cdot}PO(OH){\cdot}O{\cdot}C_{10}H_{19}$ is described.

A. A. ELDRIDGE.

Menthone series. VIII. Characterisation of the optically active menthylamines. J. READ and R. A. STOREY (J.C.S., 1930, 2761—2769).—The four stereoisomeric menthylamines have been prepared in quantity and various physical properties of the free bases and of a large number of their acyl derivatives (prepared by the action of the appropriate acid chloride or anhydride in dry benzene) have been determined. The following new or revised physical data are recorded, the values for $[\alpha]_D$ being for the homogeneous state and in chloroform, respectively: *l*-, b. p. 81—82°/12 mm., d_4^{25} (corr.) 0·8525, n_D^{25} 1·4600, $[\alpha]^{25}$ −44·53°, −38·2°; *d-neo-*, b. p. 84°/13 mm., d_4^{25} (corr.) 0·8551, n_D^{25} 1·4614, $[\alpha]_D^{25}$ +15·12°, +8·7°; *d-iso-*, b. p. 87°/13·5 mm., d_4^{25} (corr.) 0·8632, n_D^{25} 1·4659, $[\alpha]_D$ +28·96°, +29·4°; and *d-neoiso-*, b. p. 89°/14·5 mm., d_4^{25} (corr.) 0·8636, n_D^{25} 1·4670, $[\alpha]_D$ +2·32°, +10·7°, -menthylamines. The density and refractive index are higher for the *iso*-bases than for the others, thus supporting the supposed derivation of the former from the *cis*-ketone, *d-iso*menthone. Striking alterations in rotatory power occur when the bases are dissolved in chloroform, decreases of 14% and 42% being shown by the *l*- and *d-neo*-base, respectively, and increases of 1·6% and 360% for the *d-iso-* and *d-neoiso*-base, respectively. The following acyl derivatives are described, all rotations being in chloroform at 25°: formyl-, m. p. 102—103°, $[\alpha]_D^{25}$ −83·8°; acetyl-, m. p. 145°, $[\alpha]_D^{25}$ −81·7°; propionyl-, m. p. 88°, $[\alpha]_D$ −76·6°; *n*-butyryl-, m. p. 73°, $[\alpha]_D^{25}$ −70·9°; *iso*butyryl-, m. p. 128°, $[\alpha]_D^{25}$ −66·5°; iso*valeryl-*, m. p. 110°, $[\alpha]_D^{25}$ −64·7°; *n*-hexoyl-, m. p. 60°, $[\alpha]_D^{25}$ −71·2°; *n*-octoyl-, m. p. 57°, $[\alpha]^{25}$ −53·2°; chloroacetyl-, m. p. 76°, $[\alpha]_D^{25}$ −71·9°; *bromoacetyl-*, m. p. 103°, $[\alpha]_D^{25}$ −61·6°; benzoyl-, m. p. 157°, $[\alpha]^{25}$ −62·8°; phenylacetyl-, m. p. 106°, $[\alpha]_D^{25}$ −60·4°; 2-naphthalenesulphonyl-, m. p. 135°, $[\alpha]_D^{25}$ −53·3°; and anisoyl-, m. p. 183°, $[\alpha]^{25}$ −57·7°, -l-*menthylamine*; formyl-, m. p. 117—118°, $[\alpha]_D^{25}$ +53·8°; acetyl-, m. p. 169—170°, $[\alpha]_D^{25}$ +53·0°; propionyl-, m. p. 149°, $[\alpha]_D^{25}$ +48·3°; *n*-butyryl-, m. p. 104°, $[\alpha]^{25}$ +46·8°; *iso*butyryl-, m. p. 160—161°, $[\alpha]_D^{25}$ +47·5°; *iso*valeryl-, m. p. 132°, $[\alpha]_D^{25}$ +42·8°; n-*hexoyl-*, m. p. 65°, $[\alpha]_D^{25}$ +40·0°; *n*-octoyl-, m. p. 78°, $[\alpha]_D^{25}$ +36·7°; *chloroacetyl-*, m. p. 150°, $[\alpha]_D$ +50·7°; bromoacetyl-, m. p. 160°, $[\alpha]_D^{25}$ +40·9°; benzoyl-, m. p. 121·5°; $[\alpha]^{25}$ +22·7°; phenylacetyl-, m. p. 120°, $[\alpha]^{25}$ +34·5°; 2-naphthalenesulphonyl-, m. p. 208°, $[\alpha]_D$ +43·7°; and anisoyl-, m. p. 130°, $[\alpha]_D^{25}$ +21·1°, -d-neo*menthylamine*; formyl-, m. p. 45—46°, $[\alpha]_D^{25}$ +31·3°; acetyl-, m. p. 77—79°, $[\alpha]_D^{25}$ +30·7°; propionyl-, m. p. 83°, $[\alpha]^{25}$ +27·7°; *n*-butyryl-, $[\alpha]^{25}$ +23·9°; iso*butyryl-*, m. p. 116°, $[\alpha]_D^{25}$ +22·8°; *iso*valeryl-, m. p. 82°, $[\alpha]_D^{25}$ +27·0°; n-*hexoyl-*, $[\alpha]_D^{25}$ +24·9°; n-*octoyl-*, $[\alpha]_D^{25}$ +23·3°; chloroacetyl-, m. p. 82°, $[\alpha]_D^{25}$ +30·0°; bromoacetyl-, m. p. 80°, $[\alpha]^{25}$ +30·3°; benzoyl-, m. p. 97—98°, $[\alpha]_D^{25}$ +18·3°; *phenylacetyl-*, m. p. 103°, $[\alpha]_D^{25}$ +33·3°; 2-naphthalenesulphonyl-, m. p. 80—81°, $[\alpha]_D^{25}$ −2·8°; and anisoyl-, m. p. 121°, $[\alpha]^{25}$ +25·3°, -d-iso*menthylamine*; formyl-, $[\alpha]_D^{25}$ −3·9°; acetyl-, m. p. 99—100°, $[\alpha]_D^{25}$ −2·6°; *propionyl-*, m. p. 103°, $[\alpha]^{25}$ 0°; n-*butyryl-*, $[\alpha]_D^{25}$ −1·0°; *iso*butyryl-, m. p. 128°, $[\alpha]^{25}$ −3·7°; *iso*valeryl-, m. p. 99°, $[\alpha]_D^{25}$ −4·1°; *n*-hexoyl-, m. p. 50°, $[\alpha]_D^{25}$ 0°; *n*-octoyl-, m. p. 55°, $[\alpha]^{25}$ −1·2°; chloroacetyl-, m. p. 80°, $[\alpha]^{25}$ −9·8°; bromoacetyl-, m. p. 100°, $[\alpha]_D^{25}$ −7·5°; benzoyl-, m. p. 151°, $[\alpha]^{25}$ −10·4°; phenylacetyl-, m. p. 109°, $[\alpha]_D^{25}$ −3·4°; 2-naphthalenesulphonyl-, m. p. 120°, $[\alpha]^{25}$ −10·7°; and anisoyl-, m. p. 156°, $[\alpha]_D^{25}$ −9·5°, -d-neoiso-*menthylamine*. The rotatory powers of these derivatives conform in general to the numerical relationship *l*->*l-iso*>*l-neo* >*l-neoiso*, whilst the m. p. observe the sequence *d-neo*>*l*->*d-neoiso*>*d-iso*. The comparative velocity of reaction of the stereoisomeric bases with various acid chlorides, anhydrides, and aldehydes, has been determined by allowing equimolecular mixtures of pairs of the bases to react with an insufficient quantity of the reagent, and determination of the composition of the product by its rotatory power. The results indicate the sequences *d-neo*, *d-iso*, and *d-neoiso*>*l*-; and *d-neo*, and *d-neoiso*>*d-iso*. Condensation of the menthylamines with *d*-, *l*-, and *dl*-camphor-10-sulphonyl chloride indicates that the reaction is more rapid between molecules which display rotation in opposite senses. Thus are obtained: d-*camphor*-10-*sulphonyl*-l-*menthylamine*, m. p. 139°, $[\alpha]_D$ −28·0°, -d-neo*menthylamine*, m. p. 113°, $[\alpha]_D$ +33·1°, and -d-iso*menthylamine*, m. p. 169°, $[\alpha]_D$ +29·7°; l-*camphor*-10-*sulphonyl*-l-, m. p. 143°, $[\alpha]_D$ −60·9°, -d-neo-, m. p. 115°, $[\alpha]_D$ +7·3°, and -d-iso-, m. p. 140°, $[\alpha]_D$ −15·8°, -*menthylamine* (all rotations in benzene at about 16°); and dl-*camphor*-10-*sulphonyl*-d-neo*menthylamine*, m. p. 115°, $[\alpha]_D$ +21·3°. The rotations of the products obtained by the interaction of active with *dl*-reagents and of the hydrochlorides of the unchanged base in such reactions are recorded.

J. W. BAKER.

Piperitone. XI. Synthesis of optically inactive and active piperitylamines, piperitols, and α-phellandrenes. J. Read and R. A. Storey (J.C.S., 1930, 2770—2783).—Interaction of *l*-piperitone and hydrazine under appropriate conditions affords a syrupy *product*, $[\alpha]_D$ +201·1°, possibly a hydrated azine, which is reduced by zinc and glacial acetic acid to *dl*-piperitylamine, b. p. 97·5—98·5°/16 mm., n_D^{1} 1·4802, d_4^{25} (vac.) 0·8801 (*hydrochloride*, m. p. 191°), exhibiting only feeble optical activity and yielding inactive *acetyl*, m. p. 108°, *benzoyl*, m. p. 130°, and *anisoyl*, m. p. 161°, derivatives. Fractional crystallisation of the hydrogen tartrate obtained with *d*-tartaric acid affords l-*piperitylamine hydrogen* d-*tartrate*, m. p. 217°, $[\alpha]_D$ −43·0° in water, from which *l*-piperitylamine, b. p. 101—102°/19 mm., d_4^{25} (vac.) 0·8789, n_D^{25} 1·4770, $[\alpha]^{25}$ −80·35 (homogeneous) and −70·0° in chloroform [*hydrochloride*, m. p. 213° (decomp.), $[\alpha]_l^{16}$ −83·5°; *acetyl*, m. p. 102—103°, $[\alpha]_l^{25}$ −153° in chloroform; *benzoyl*, m. p. 102—103°, $[\alpha]^{25}$ −173° in chloroform; *anisoyl*, m. p. 142—143°, $[\alpha]_D^{1}$ −175° in chloroform; and *phenylacetyl*, m. p. 89—90°, $[\alpha]^{25}$ −130·5° in chloroform, derivatives], is obtained. Its *cis*- or *trans*-configuration has not yet been ascertained. Methylation of *dl*-piperitylamine with methyl iodide and sodium methoxide under conditions precluding decomposition of the quaternary salt affords dl-*piperityltrimethylammonium iodide*, m. p. 88° with decomp. to *dl*-α-phellandrene and α-terpinene, separated and characterised as their nitrosites. From the products obtained when the *dl*-iodide is steam-distilled with silver oxide (trimethylamine being evolved) can be isolated dl-neo*piperitol*, b. p. 94—96°/15·5 mm., $n_l^{19.5}$ 1·4740 (oxidised by Beckmann's reagent to piperitone), dl-*piperitol*, b. p. 100—106°/19·5 mm., n_D^{18} 1·4769 (also obtained by the action of nitrous acid on *dl*-piperitylamine), and *dl*-α-phellandrene, b. p. 63—65°/15·5 mm., $n_D^{19.5}$ 1·4772, identified as its α-nitrosite: α-terpinene could not be detected. Similarly methylation of *l*-piperitylamine and degradation of the quaternary hydroxide affords d-neo*piperitol*, b. p. 96·5—98·5°/15·5 mm., n_D^{25} 1·4729, d_4^{25} (vac.) 0·9119, $[\alpha]_D^{18}$ +21·22°, d-*piperitol*, b. p. 101—104°/16 mm., n_D^{14} 1·4770, d_4^{25} (vac.) 0·9200, $[\alpha]_D^{18}$ +40·22° (both oxidised to *d*-piperitone), and almost pure *d*-α-phellandrene, b. p. 66—68°/16 mm., n_D^{25} 1·4777, d_4^{25} (vac.) 0·8463, $[\alpha]_D^{16}$ +86·4°. These degradations afford a ready passage directly from a Δ^1- to a conjugated $\Delta^{2:6}$-derivative and establish a chemical and stereochemical connexion between *d*-piperitol, *d*-piperitone, and *d*-α-phellandrene, and nake it possible to proceed from *l*-piperitone of *Eucalyptus* oils to *d*-piperitol and *d*-piperitone of *Andropogon* species by the stages *l*-piperitone ⟶ *dl*-piperitylamine ⟶ *l*-piperitylamine ⟶ *d*-α-phellandrene+*d*-piperitols ⟶ *d*-piperitone. The stereochemical relationships of the piperitols are discussed and the relative molecular configurations I and II

(I.)   (II.)

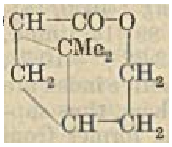
are assigned to *d*(or *l*)- and *d*(or *l*-)-*neo*-piperitol, respectively, on the basis of physical properties.

J. W. Baker.

Pinene and nopinene. G. Brus (Bull. Inst. Pin, 1929, 271—276, 293—300; 1930, 7—16, 33—38, 63—68, 87—96, 109—112, 131—136, 151—157, 175—178, 199—205, 225—228, 244—247, 270—274).—A comprehensive review of pinene, nopinene, and their derivatives, with details of preferred practical methods. *d*-Nopinene probably does not occur in conifer essences, but has been found (Rutovski and Vinogradova, A., 1928, 1377) in *Ferula galbaniflora*, Boiss., and has b. p. 162—163°, d_0^{15} 0·8702, n_D^{20} 1·4755, $[\alpha]_v$ +24·01°. Pure *l*-nopinene (Darmois, Diss., Paris, 1910) has d_0^{15} 0·8740, n_{578}^{15} 1·4874, $[\alpha]_{578}$ −22·44°. The poor yield of crystallisable pinonic acids from oxidation of pinene with neutral permanganate is due largely to racemisation; the presence of *d*-pinonic acid greatly diminishes the rate of crystallisation of the racemic acid, and conversely. The use of an inactive pinene, produced by mixing the calculated quantities of *l*- (Bordeaux) and *d*- (Aleppo) -pinene fractions, leads to a 50% yield of crystalline *r*-pinonic acid. Racemisation is largely prevented and a good yield (50%) of *d*-pinonic acid, m. p. 69°, $[\alpha]_v$ +116·45°, is obtained by neutralising the *d*-pinene oxidation liquors with acetic acid before concentration. A similar effect results from the removal of hydroxyl ions by means of ammonium chloride or magnesium sulphate present during oxidation; the latter reagent retards oxidation, and heating at 40° is necessary.

The yield of nopinic acid by oxidation of pure nopinene is more than doubled by using neutral in place of alkaline permanganate, and neutralising with carbon dioxide the caustic alkali formed. Purified *l*-nopinic acid has m. p. 127° and $[\alpha]_v$ −17·51° in chloroform; it yields a nopinone, m. p. 0—1°, d^{15} 0·9815, n_D^{15} 1·47785, $[\alpha]_{578}$ +19·6° (semicarbazone, m. p. 188°; trihydrochloride, decomp. 148°; dihydrochloride, m. p. 125°). Compounds of nopinic acid with $0{\cdot}5C_6H_6$, $0{\cdot}5C_6H_5Me$, $0{\cdot}5C_6H_4Me_2$, and $0{\cdot}5H_2O$ are described, with crystallographic data.

The ozonisation of pinene and nopinene in chloroform is followed by determinations of unabsorbed ozone in every sixth litre of gas passed. The resulting curves show a period of complete absorption (formation of ozonide), followed by a sudden fall, and finally a slowly decreasing absorption by the solvent. *Nopinene ozonide* provides the best route to nopinone, the yield on decomposition with boiling 5% potassium hydroxide being 50%, together with formaldehyde and a *compound*, $C_9H_{14}O_2$, m. p. 126—127°, which is probably



a lactone (annexed formula) and gives on hydrolysis an *acid* not obtained crystalline. Nopinene is readily detected in mixtures by the production of nopinone from the ozonide, and may be approximately determined by measurement of the carbon dioxide produced by oxidation of the formaldehyde formed with mercuric oxide. Pinene yields a small amount of carbon dioxide on ozonisation and causes an error in this method when applied to mixtures of nopinene and pinene. Pinane gives about 3% of its molecule as carbon dioxide on ozonisation, but is otherwise unaffected.

Fractional crystallisation of solid pinene hydrochloride fails to show any trace of *iso*bornyl chloride of m. p. 161°, and capillary experiments prove the

absence of a racemic compound. By sublimation at 15° over a period of two years pinene hydrochloride is obtained in cubic octahedra, m. p. 132°. Fractional distillation of commercial liquid pinene hydrochloride, from Bordeaux turpentine, yields about 40% of solid pinene hydrochloride, 8—10% of dipentene dihydrochloride, m. p. 49°, about 2% of terpenes (pinene, dipentene, and terpinolene), a little limonene monohydrochloride, and a mixture of fenchyl, bornyl, and *iso*bornyl chlorides. The tertiary hydrochloride of pinene (or nopinene) appears to be a similar mixture, decomposing, however, at 10°; removal of hydrogen chloride by sodium ethoxide yields γ-pinene, nopinene, α-pinene, limonene, dipentene, and terpinolene.

The camphene problem is discussed. By careful fractionation at 10 mm. of distilled *d*-camphene, b. p. 156—161°, obtained in 77% yield by Reychler's method from *d*-pinene hydrochloride and potassium phenoxide, a series of fractions is obtained which increase, at first rapidly and then more slowly, in m. p. (15·6—45·1°), b. p. (148—161° or 47—52°/10 mm.), rotatory power ($[\alpha]_v$ +5·25° to +35·05°), and mol. refraction (42·72—44·10), the density remaining almost constant. *l*-Camphene shows similar variations. In both cases this is due to the presence of a low-boiling (148—153°), inactive, liquid constituent, apparently *s*-tricyclene (m. p. 65°) kept liquid by a little fenchene (?). *l*-Pinene hydrochloride is conveniently converted by sodium resinate at 160° into *l*-camphene, m. p. 43—45°, $[\alpha]_v$ —66° (see also Gammay, F.P. 595,036; B., 1927, 156).

By the action of 1 mol. of chlorine on dry *d*-pinene at —15° to —20° there is obtained a mixture of bornyl chloride, 2 : 6-dichlorocamphane (by isomerisation of 1 : 2-dichloropinane), and liquid di- and polychloro-compounds. 2 : 6-Dichlorocamphane is converted by sodium in ether into tricyclene, m. p. 65°, and is reduced by sodium and alcohol to *i*-camphane, m. p. 150—151°, b. p. 159—160°; potassium phenoxide at 160—170° yields *p*-cymene and a chlorocamphene. Bromine reacts similarly, giving as main product 2 : 6-dibromocamphane, m. p. 169° [crystallographic data by Duffour], from which are obtained tricyclene by the action of sodium, camphor by action of sodium and alcohol, *p*-cymene and a bromocamphene, b. p. 195—200°, by action of potassium phenoxide. Under similar conditions the chlorination of nopinene yields bornyl chloride and liquid products; bromination also fails to give crystalline products except bornyl bromide. The liquids probably contain ω : 2-dichloro- and -dibromo-camphanes, respectively.

C. Hollins.

Derivatives of pinene. G. Gallas and J. M. Montañés (Anal. Fis. Quím., 1930, 28, 1163—1213).—Unsuccessful attempts have been made to convert pinene into camphene by passing the vapour over various catalysts. A considerable amount of dipentene is found in the products.

Pinene dichloride, m. p. 170°, is obtained in 18% yield by shaking an emulsion of pinene and water in a flask containing chlorine and distilling the product in steam. Addition of acid to a mixture of pinene with a solution of sodium bromide and bromate yields a mixture of two forms of pinene dibromide, m. p. 150° and 169°; the first is converted into the second by heating at 120°. Attempts to isolate a di-iodide, either by direct action of iodine or from the chloride by the action of magnesium or aluminium iodides, were unsuccessful.

Unsuccessful attempts were made to oxidise bornyl iodide to an iodoso-compound by the action of hydrogen peroxide.

The oxime of pinonic acid is reduced by sodium and amyl alcohol to the corresponding *amine*, separated as the *hydrochloride*, m. p. 260° (decomp.). The *benzoyl* derivative, m. p. 210°, yields with acetic anhydride, by dehydration and ring-closure, the *acetate*, m. p. 151°, of an *amino-ketone* (*hydrochloride*, m. p. 78°; *oxime*, m. p. 120°).

A preliminary investigation of the conversion of pinene into esters of borneol indicates that the reaction with acids does not proceed in this direction in the absence of catalysts.

Oxidation of bornyl chloride with benzoyl peroxide, hydrogen peroxide, barium peroxide, or permanganate in alkaline solution gives complex mixtures. With benzoyl peroxide, camphoric and ketopinic acids are formed.

R. K. Callow.

Dependence of optical rotatory power on chemical constitution. IX. (*a*) Rotatory dispersion of the stereoisomeric oxymethylenecamphors, *p*-phenylene- and 1 : 4-naphthylenebisaminomethylenecamphors. (*b*) Structure of oxymethylenecamphor and the kinetics of its mutarotation. B. K. Singh and B. Bhaduri (J. Indian Chem. Soc., 1930, 7, 771—791).—The rotatory powers of *d*- and *l*-oxymethylenecamphor and their condensation products with *p*-phenylene- and 1 : 4-naphthylene-diamine have been measured in various solvents for different wave-lengths at 35°. The molecular rotations of the condensation products are lower than those of the analogous compounds from camphorquinone (A., 1930, 1441); this is ascribed to the difference in conjugation. The dispersion data can be expressed by a simple equation of the Drude type. d-, m. p. 269—271°, and l-, m. p. 269—271°, -p-*Phenylenebisaminomethylenecamphor* (the dl-*isomeride* has m. p. 273—275°) do not exhibit mutarotation; d-, m. p. 203—204°, and l-, m. p. 203—204°, -1 : 4-*naphthylenebisaminomethylenecamphor* (the dl-*isomeride* has m. p. 220—222°) show slight mutarotation in chloroform but not in acetone, alcohol, benzene, or pyridine.

The (unimolecular) velocity coefficient for the mutarotation of *d*- and *l*-oxymethylenecamphor in benzene at 35° is almost identical with that deduced by the progressive determination of the amount of enol form under the same conditions, using Meyer's method (A., 1911, i, 832). The chemical change involved in the mutarotation is of the keto–enol type; the keto-form is unstable in benzene solution. Mutarotation is very rapid in benzene at 45°.

H. Burton.

Higher terpene compounds. XLII. Dehydrogenation and isomerisation of agathicdicarboxylic acid. L. Ruzicka and J. R. Hosking (Helv. Chim. Acta, 1930, 13, 1402—1423).—Agathicdicarboxylic acid (A., 1929, 572) is isomerised when heated with 95% formic acid at 120—130° to the tricyclic

iso*agathicdicarboxylic acid*, m. p. 287—288° (decomp.), $[\alpha]_D$ +12·84° (all rotations are in alcohol) (*dimethyl* ester, m. p. 121—122°, $[\alpha]_D$ +6·09°, prepared either by the silver salt method or from the sodium salt and methyl sulphate; *diethyl* ester, m. p. 102—103°, d_4^{111} 1·014, 1·483, $[\alpha]_D$ +9·67°). This is reduced catalytically (Adams) in acetic acid or ethyl acetate at 60° to *dihydroisoagathicdicarboxylic acid*, m. p. 308—310° (decomp.), $[\alpha]_D$ +16·03° (*dimethyl* ester, m. p. 110—111°, d_4^{131} 1·027, n_D^{120} 1·477, $[\alpha]_D$ +9·11°), and when heated at 290°/12 mm., eliminates carbon dioxide forming iso*noragathic acid*, b. p. 181—184°/0·2 mm., m. p. 177—178°, $[\alpha]_D$ +2·13° (*methyl* ester, m. p. 98—99°, d_4^{112} 0·978, n_D^{112} 1·4864, $[\alpha]_D$ +2·65°). Catalytic reduction (Adams) of the last-named acid gives an amorphous dihydro-acid (*methyl* ester, m. p. 80—81°, d_4^{111} 0·9714, 1·4793, $[\alpha]_D$ +35·34°). Dehydrogenation of *iso*agathicdicarboxylic acid with selenium at 250—340° affords pimanthrene and a small amount of a hydrocarbon (unstable *picrate*, m. p. 163—164°). Agathicdicarboxylic acid is dehydrogenated by sulphur at 180—250° to pimanthrene and 1 : 2 : 5-trimethylnaphthalene [previously described (*loc. cit.*) as a methylethylnaphthalene]; the same products are also obtained similarly from the amorphous resin acid from Manila copal (cf. A., 1927, 60). When agathicdicarboxylic acid is dehydrogenated with selenium at 290—340°, small amounts of the hydrocarbon $C_{17}H_{20}$ (I) (cf. *loc. cit.*) and an impure hydrocarbon (II) (unstable *picrate*, m. p. 210°) are formed in addition to pimanthrene and the trimethylnaphthalene. A mixture of the last-named substance, I, and II is obtained by dehydrogenating tetrahydroagathicdicarboxylic acid with selenium at 250—340°; in this case, pimanthrene is not produced.

Energetic oxidation of 1 : 2 : 5-trimethylnaphthalene, m. p. 31—32° (when regenerated from its pure picrate), with alkaline potassium ferricyanide affords some naphthalene-1 : 2 : 5-tricarboxylic acid (*methyl* ester, m. p. 90—91°) (cf. Heilbron and Wilkinson, this vol., 80).

The hydrocarbon $C_{17}H_{20}$ (*loc. cit.*), m. p. 42°, d_4^{70} 0·992, n_D^{70} 1·5847 (crystallographic data by NANNINGA), is reduced catalytically (Adams) in acetic acid (not in ethyl acetate) to a *tetrahydro*-derivative, m. p. 70—72°, dehydrogenated by selenium to the original compound. Oxidation of the hydrocarbon (which probably contains a naphthalene ring and a third saturated ring) with alkaline potassium ferricyanide at 60°, affords a *ketodicarboxylic acid*, $C_{16}H_{12}O_5$, m. p. 304—305° (decomp.) (*oxime*, m. p. 240°) when regenerated from its *dimethyl* ester, m. p. 155—156°. The hydrocarbon could not be dehydrogenated further with selenium at 340°.

[With L. EHMANN, P. JENSEN, and O. T. LIEN.] β-*o*-Tolylethyl bromide reacts with ethyl sodiomethylmalonate in benzene forming *ethyl β-o-tolylethylmethylmalonate*, b. p. 192—193°/16 mm., converted by the usual procedure into *γ-o-tolyl-α-methylbutyric acid*, b. p. 179—180°/16 mm. The chloride, b. p. 146—147°/16 mm., of this, when treated with aluminium chloride in light petroleum, gives 5-keto-1 : 6-dimethyl-5 : 6 : 7 : 8-tetrahydronaphthalene, b. p. 153—155°/16 mm., m. p. 41—42° (semicarbazone, m. p. 194—195°). This is treated with magnesium methyl iodide, water is eliminated from the resulting carbinol by distillation, and the 1 : 5 : 6-trimethyl-7 : 8-dihydronaphthalene, b. p. 130—131°/11 mm., d_4^{20} 0·9760, n_D^{20} 1·5672, so obtained dehydrogenated by selenium at 280—340° to 1 : 2 : 5-trimethylnaphthalene. H. BURTON.

Furan derivatives. II. I. J. RINKES (Rec. trav. chim., 1930, **49**, 1169).—The "3-nitrofuran" obtained by Marquis (A., 1905, i, 224) is shown to be 2-nitrofuran, and the dinitrofuran obtained therefrom the 2 : 5-derivative. Direct substitution in the furan nucleus yields 2- or 5-derivatives, if these positions are vacant or filled by labile groups. Nitration of pyromucic acid yields 2-nitrofuran and 5-nitropyromucic (5-nitrofuran-2-carboxylic) acid.

J. D. A. JOHNSON.

Unsaturated compounds. XII. Action of hydroxylamine on furfurylidenehippuric acid and its esters and on furylacrylic esters. T. POSNER and I. SICHERT [nee MODROV] (Ber., 1930, **63**, [*B*], 3078—3088).—In comparison with the phenyl residue, the furyl group enhances the dissociation of acids and very considerably increases the difficulty of addition. Towards hydroxylamine, cinnamic acid, furylacrylic acid, and furfurylidenehippuric acid are placed in order of diminishing activity. The products of the reaction are the hydroxylamino-acid, R·CH(NH·OH)·CH_2·CO_2H, which is gradually oxidised to the oxime, R·CMe:N·OH. The formation of *iso*oxazolone, $R\cdot C{<}{\genfrac{}{}{0pt}{}{CH_2\cdot CO}{N\cdot O}}$, and of the amino-acid, R·CH(NH_2)·CH_2·CO_2H, is irregular. The esters add hydroxylamine more readily than the corresponding acids, the methyl compounds being usually more reactive than the ethyl analogues. In contrast to the acids they add more than 1 mol. of hydroxylamine, this ability increasing with decreasing acidity of the parent acid. The yields of oxime and *iso*oxazolone increase with increasing dissociation constant of the parent acid, and, generally, the amino-acids are produced in greater amount with the weaker acids.

The following compounds are incidentally described: furfurylidenehippuric acid (cf. Erlenmeyer and Stadlin, A., 1905, i, 238); *methyl furfurylidenehippurate*, m. p. 141°; furylacrylic acid, m. p. 139—140°; *benzimidodiacetic acid*, NBz(CH_2·CO_2H)$_2$, m. p. 68° (obtained as by-product of the preparation of hippuric acid by the successive action of ammonia and benzoyl chloride on chloroacetic acid); β-amino-β-2-furylpropionic acid, m. p. 206°; *2-furyl methyl ketoxime*, m. p. 102°; *furyl*iso*oxazolone*, ${\genfrac{}{}{0pt}{}{CO\cdot CH_2}{O\!-\!-\!N}}{\gg}C\cdot C_4H_3O$, decomp. 147°; *β-amino-β-2-furylpropionyl chloride hydrochloride*; *β-amino-β-2-furylpropionanilide*; *β-amino-α-benzamido-β-2-furylpropionic acid*, m. p. 173·5°; *benzamidofuryl*iso*oxazolone*, decomp. 181·5°; (?) *β-methoxyamino-α-benzamido-β-2-furylpropionic acid*, m. p. 203°; *2-furyl benzamidomethyl ketoxime*, m. p. 157°; *β-carbamido-α-benzamido-β-2-furylpropionic acid*, m. p. 196°. H. WREN.

Coumaryl-2-aldehyde [2-aldehydocoumarone] and coumarone derivatives. T. REICHSTEIN and I. REICHSTEIN (Helv. Chim. Acta, 1930, **13**, 1275—1281).—Coumarilyl chloride reacts with dry hydrogen

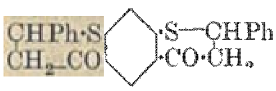
cyanide in presence of cold ethereal pyridine forming *coumarilyl cyanide*, b. p. about 115°/1 mm., m. p. 100—101° (corr.), which on prolonged hydrolysis with hydrochloric acid at the ordinary temperature gives a mixture of coumarylglyoxylic acid (cf. Stoermer and Calov, A., 1900, i, 650) and its *amide*, m. p. 187—188° (corr.); the amide is readily hydrolysed to the acid by alkali hydroxide. When the acid is heated with aniline for a short time, 2-aldehydocoumarone, b. p. 130—131°/13 mm., m. p. 9—9·5° [*semicarbazone*, m. p. 245—246° (corr.; decomp.); *cyanohydrin*, m. p. 66·5—68°; phenylhydrazone, m. p. 136—138° (corr.)], is produced. The aldehyde is also obtained when the above cyanide is reduced with zinc dust and acetic acid and the resulting compound decomposed by potassium hydroxide. The aldehyde undergoes the Cannizzaro reaction yielding coumarylcarbinol, b. p. 105—110°/1 mm., m. p. about 26° [p-*nitrobenzoate*, m. p. 145—146° (corr.)]. Reduction of coumarylglyoxylic acid with hydrazine hydrate and sodium ethoxide (Wolff–Kishner method) gives *coumarylacetic acid*, b. p. about 145°/1 mm., m. p. 98—99° (corr.). H. BURTON.

New modes of formation of coumarone and diphenylene oxide. N. A. ORLOV and V. V. TISTSCHENKO (Ber., 1930, **63**, [*B*], 2948—2951).—When coumarin vapour is passed through a tinned iron tube at about 860°, the gaseous product is mainly carbon monoxide with smaller amounts of hydrogen, ethylenes, and carbon dioxide. The condensate consists of coumarone with unchanged coumarin and small amounts of phenols and benzenoid hydrocarbons. A resin, closely resembling coumarone resin, is also obtained. The change occurs only under atmospheric pressure. In an autoclave at 420° or below the main products are coke and gases. Similarly, at about 880° xanthone affords diphenylene oxide and carbon monoxide mixed with a little methane and hydrogen. Dimethylpyrone affords carbon monoxide and furan derivatives apparently mixed with hydrocarbons. Under like conditions, open-chain ketones do not lose carbon monoxide smoothly. H. WREN.

Use of titanous chloride for the reduction of ethylenic linkings, flavones, and flavanones. P. KARRER, Y. YEN, and I. REICHSTEIN (Helv. Chim. Acta, 1930, **13**, 1308—1319).—Unsaturated compounds are reduced by titanous chloride in aqueous-alcoholic ammoniacal solution at 100° (bath) only when a carbonyl group is adjacent to the double linking. Thus, cinnamic acid, cinnamamide, and styryl methyl ketone are reduced to the corresponding saturated derivatives; cinnamylideneacetic acid affords much δ-phenyl-Δ^{β}-pentenoic acid and a little δ-phenyl-Δ^{γ}-pentenoic acid. Similar reduction of flavone at 100° gives amorphous products, but at the ordinary temperature a small amount of the *pinacol*, $\left[O{<}{\begin{smallmatrix}CPh=C\\C_6H_4\cdot C(OH)\end{smallmatrix}}\right]_2$, m. p. 220—220·5° (corr.), is produced. Flavanone affords a mixture of the isomeric flavanols, m. p. 120—120·5° (corr.) (cf. Freudenberg and Orthner, A., 1922, i, 757) and 148—149° (corr.) [*acetate*, m. p. 97—98° (corr.)], and a small amount of the corresponding pinacol (*loc. cit.*). 6-Chloro- and 4′-methoxy-flavanones are reduced to 6-*chloro*- and 4′-*methoxy-flavanols*, m. p. 114—115° (corr.) and 144—145° (corr.), respectively. Treatment of 4′-methoxyflavanone with phosphorus pentachloride in benzene and decomposition of the resulting product with alcohol gives 4′-*methoxyflavone*, m. p. 160—161° (corr.), reduced to a small amount of the corresponding *picanol* (+EtOH), m. p. 147—148° (decomp.). Pentamethylcyanidin is obtained in small amount by the reduction of quercetin pentamethyl ether. H. BURTON.

Fluoran derivatives. I. Isomeric dihydroxyfluorans. M. DOMINIKIEWICZ (Rocz. Chem., 1930, **10**, 667—685).—1 : 8-*Dihydroxyfluoran*, m. p. 190°, is prepared by the fusion of phthalic anhydride with resorcinol, 1 : 6-*dihydroxyfluoran*, m. p. 204—205°, by fusing together dihydroxybenzoylbenzoic acid and resorcinol, 2 : 6-*dihydroxyfluoran*, m. p. 179°, by substituting quinol for resorcinol in this reaction, and 4 : 6-*dihydroxyfluoran*, m. p. 180°, by using pyrocatechol in place of quinol. The following dyes, substantive for wool, are prepared: 2 : 7-*dinitro*-3 : 6-*dihydroxyfluoran*, 3 : 6-*dinitro*-2 : 7-*dihydroxyfluoran*, 2 : 7-*dinitro*-1 : 6- and -1 : 8-*dihydroxyfluoran*, 3 : 7-*dinitro*-2 : 6- and -4 : 6-*dihydroxyfluoran*. Impure amines are obtained by the reduction of these dinitro-derivatives. R. TRUSZKOWSKI.

Thiophenols: linear dithioflavone and dithioflavanone. C. FINZI (Gazzetta, 1930, **60**, 798—811; cf. A., 1926, 309, 948).—Treatment of dithioresorcinol with cinnamic or β-bromo-β-phenylpropionic acid in acetic acid solution saturated with hydrogen bromide yields β-*thioresorcinol*-β-*phenylpropionic acid*, which was obtained only as a pitchy mass and gives m-*phenylene*-β-*disulphonyl*-β-*phenylpropionic acid*, $C_6H_4(SO_2\cdot CHPh\cdot CH_2\cdot CO_2H)_2$, m. p. 192°, on oxidation with permanganate and *linear dithioflavanone* (annexed formula), softening at 65—70°, m. p. 120—125°, when treated with phosphorus pentachloride or oxychloride in presence of aluminium chloride.



Ethyl phenylpropiolate and dithioresorcinol react additively, forming a mixture of ethyl esters, corresponding with: (1) m-*phenylene*-β-*dithiolcinnamic acid*, $C_6H_4(S\cdot CPh{:}CH\cdot CO_2H)$, m. p. 224°, which is converted into *linear s-dithioflavone*, (annexed formula), m. p. 255—256°, when treated with phosphorus pentachloride in presence of aluminium chloride or with concentrated sulphuric acid, and, on hydrogenation by means of sodium amalgam, gives an oily product oxidisable by permanganate to *m*-phenylenedisulphonyl-β-phenylpropionic acid; (2) m-*phenyl*-α-*dithiolcinnamic acid*, $C_6H_4[S\cdot C(CO_2H){:}CHPh]_2$, m. p. 70—73°, which loses carbon dioxide at about 190°, with formation of a pitchy compound, reducible by sodium amalgam to *thioresorcinoldi*-β-*phenylethyl ether*, $C_6H_4(S\cdot CH_2\cdot CH_2Ph)_2$; this ether, which does not distil at 300°, even under reduced pressure, is also obtained by the interaction of thioresorcinol and β-phenylethyl chloride. T. H. POPE.

Condensation products from aryldithioglycollic acids. E. Gebauer-Fülnegg and H. Jarsch (Monatsh., 1930, **56**, 317—321).—Thioindigoid dyes, probably thioindigotindithioglycollic acids, are obtained when benzene-1 : 2-, -1 : 3-, -1 : 4-, 4-chlorobenzene-1 : 3-, and 2 : 5-dichlorobenzene-1 : 3-dithioglycollic acids are treated with chlorosulphonic acid at 50—60° (cf. A., 1930, 1039). These dye wool and cotton with red to violet shades; they are usually better when used in an acid bath.

H. Burton.

Relationships between dipyrylenes and *meri*- or *holo*-dipyrylium salts. Action of halogens on fulvenes. F. Arndt and L. Lorenz (Ber., 1930, **63**, [*B*], 3121—3132).—In reply to Bergmann and von Christiani (A., 1930, 1569) evidence is adduced in favour of the view that the behaviour of xanthens and dipyrylenes towards halogen is not comparable with that of the open and carbocyclic fulvenes. The hexabromide of dixanthylene contains the total bromine as two anions $BrBr_2$. The mode and readiness of the addition of bromine are possibly greatly influenced by the possibility of the transition of the quinonoid pyrone form into the benzenoid pyrylium form. The relationships between dipyrylenes and *meri*- and *holo*-dipyrylium salts are discussed in detail. The following observations appear new. *Dithioxanthylene*, m. p. 365°, is prepared by heating thioxanthione with copper powder in a current of carbon dioxide at 200°. *Dithioxanthylenedisulphone*, gradual decomp. 380—500°, which is prepared from dithioxanthylene and hydrogen peroxide in boiling glacial acetic acid, is unaffected by bromine. *Dixanthionium perbromide*, $C_{26}H_{16}S_2Br_6$, decomposes at 245° after darkening and softening at 220°. Tetraphenyldipyrylene is converted by perchloric acid in acetic acid into the meri-*perchlorate*, decomp. 287—288°, whereas with 70% perchloric acid at about 200° it yields the holo-*perchlorate*. The meri-*perchlorate* of ethyl dipyrylenetetracarboxylate, $C_{22}H_{24}O_{10},HClO_4$, is described. Tetraphenyldithiopyrylene is transformed by chlorine in chloroform and carbon tetrachloride into black and red *substances*, $C_{34}H_{24}Cl_2S_2$, m. p. 300—310° after softening at 100°. Under similar conditions tetraphenyldipyrylene gives a black *compound*, $C_{34}H_{24}O_2Cl_2$, m. p. 305° after softening at 100°; the red compound appears to be formed transitorily. Tetraphenyldithiopyrylene and bromine yield the substance $C_{34}H_{21}S_2Br_6$.

H. Wren.

Residual affinity and co-ordination. XXXII. Complex salts of bivalent silver. G. T. Morgan and F. H. Burstall (J.C.S., 1930, 2594—2598).—Stable compounds of bivalent silver are prepared in the following manner. When hot aqueous-alcoholic solutions of silver nitrate and of αα′-dipyridyl (prepared by Hein and Retter's method; A., 1928, 1262) (*mercuri-iodide*, sufficiently insoluble for use in the gravimetric determination of the base) are mixed, *bis-αα′-dipyridylargentous nitrate* [Ag2dipy]′NO_3, decomp. 155°, is obtained. This is converted by a cold, saturated solution of potassium persulphate into *bis-αα′-dipyridylargentic persulphate*, [Ag2dipy]″S_2O_8, decomp. 137°. Trituration of this with 60% nitric acid affords a filtrate from which is obtained *pentakis-αα′-dipyridyldiargentic persulphate*, $[Ag_25dipy](S_2O_8)_2$, decomp. 159°, and a residue of *tris-αα′-dipyridylargentic nitrate*, [Ag3dipy]″$(NO_3)_2$, decomp. 176°, from which the corresponding *chlorate*, decomp. 171°, and *perchlorate*, detonates when heated, are obtained by double decomposition. The nitrate is converted by further action of nitric acid into the complex *argento-argentic nitrate*, $[Ag_22dipy](NO_3),AgNO_3,HNO_3$, decomp. 161°, some of the univalent silver of which is removed by repeated extraction with cold alcohol. Cold 40% sulphuric acid converts bis-αα′-dipyridylargentic persulphate into the corresponding *hydrogen sulphate*, decomp. 157°. All these complex salts are crystalline and highly coloured and their solutions are strong oxidising agents. Their composition indicates that bivalent silver has co-ordination numbers of 4 and 6.

J. W. Baker.

Equilibrium and "intermediate stage." F. Arndt (Ber., 1930, **63**, [*B*], 2963—2966).—In connexion with his views on the constitution of 1-alkyl-4-pyridones and similar compounds the author defines a tautomeric equilibrium as characterised by the difference of the point of union of a hydrogen nucleus in the two formulæ. An "intermediate stage" is assumed when the two formulæ show the same relative position of all atomic nuclei and differ only by "linkings" or "charges."

H. Wren.

Pyridine derivatives. VIII. Isomerism of derivatives of 2-hydroxypyridine. C. Rath (Annalen, 1930, **484**, 52—64).—A study of the influence of electronegative substituents on the alkylation of 2-hydroxypyridines. 5-Nitro-2-hydroxypyridine is converted by methyl sulphate and alkali mainly into 5-*nitro*-1-*methyl*-2-*pyridone*, m. p. 175°, accompanied by a little 5-*nitro*-2-*methoxypyridine*, m. p. 108—109°; these are separated by distillation in steam, in which the *O*-ethers alone are volatile. The potassium salt of the nitrohydroxypyridine with methyl iodide gives similar results, but the *silver* salt gives considerably more (16%) of the *O*-ether, the constitution of which is proved by synthesis from 2-iodo-5-nitropyridine and sodium methoxide, and by its inertness towards phosphorus pentachloride. The *N*-methyl compound is converted by phosphorus pentachloride into 2-chloro-5-nitropyridine (cf. O. Fischer, A., 1898, i, 382), and by cyanogen bromide into 3-*bromo*-5-*nitro*-1-*methyl*-2-*pyridone*, m. p. 124—125°. Attempts at interconversion of the isomerides by the method of Haitinger and Lieben (A., 1885, 965) failed. 5-*Amino*-1-*methyl*-2-*pyridone*, m. p. 125—126° (decomp.) (*dihydrochloride*) and 5-*amino*-2-*methoxypyridine*, m. p. 135—136° (*dihydrochloride*), are obtained by reduction.

The behaviour of 5-iodo-2-hydroxypyridine (*silver* salt) on methylation is similar to that of the 5-nitro-compound. The following are described: 5-*nitro*-2-*ethoxy*-, m. p. 91—92°; 5-*nitro*-2-*benzyloxy*-, m. p. 107—108°, and 5-*iodo*-2-*methoxy-pyridine*, b. p. 109—110°/15 mm. [*hydrochloride*, m. p. 145—150° (decomp.)]; 5-*nitro*-1-*ethyl*-, m. p. 142—143°; 5-*nitro*-1-*benzyl*-, m. p. 105—106°; 5-*nitro*-1-n-*propyl*-, m. p. 76—77°; 5-*nitro*-1-isopropyl-, m. p. 86—90°; 5-*nitro*-1-n-*butyl*-, m. p. 46—47°; 5-*iodo*-1-*methyl*-, m. p. 73—74°, b. p. 185°/12 mm.; 5-*iodo*-1-*ethyl*-, m. p.

75—76°, b. p. 180—185°/22 mm.; *5-iodo*-1-n-*propyl-*, b. p. 185—188°/15 mm. [*hydrochloride*, m. p. 112° (decomp.)]; *5-iodo*-1-iso*propyl-*, m. p. 110—111°; *5-iodo*-1-n-*butyl-*, b. p. about 185°/12 mm. [*hydrochloride*, m. p. 125° (decomp.)]; *5-iodo-1-octyl-*, b. p. 221—222°/12 mm. [*hydrochloride*, m. p. 85° (decomp.)], and *5-iodo-1-benzyl-2-pyridone*, m. p. 100—101°.

H. A. Piggott.

β-Diketones in ring formation. II. U. Basu (J. Indian Chem. Soc., 1930, **7**, 815—824; cf. A., 1930, 1443).—Alcoholic sodium ethoxide condensation of cyanoacetamide and dibenzoylmethane affords 5—20% of 3-cyano-4 : 6-diphenyl-2-pyridone; prolonged interaction in presence of alcoholic diethylamine results in a much improved yield. The difference in these results may be due to the greater reversibility of the Michael reaction with sodium ethoxide (cf. Ingold and others, J.C.S., 1922, **121**, 1416, 1770). The pyridone is also obtained in 75% yield from phenyl β-ethoxystyryl ketone and sodiocyanoacetamide. The inhibiting effect of aryl groups on the condensation is established by the isolation of 3-cyano-4-phenyl-6-*p*-tolyl-2-pyridone as the main product of the reaction between benzoyl-*p*-toluoylmethane and cyanoacetamide; the *p*-tolyl group has a greater retarding action than the phenyl group. *3-Cyano-6-phenyl-4-*p*-tolyl-2-pyridone*, m. p. 311—312°, formed also in the above condensation, is hydrolysed by 80% sulphuric acid to *6-phenyl-4-*p*-tolyl-2-pyridone*, m. p. 237—239°. Since the former of the cyano-*p*-tolylpyridones is also obtained from *p*-tolyl β-methoxystyryl ketone, condensation must occur through the enolic form of the diketone. Dipropionylmethane and cyanoacetamide in presence of aqueous-alcoholic diethylamine give a 90% yield of *3-cyano-4 : 6-diethyl-2-pyridone*, m. p. 186°, hydrolysed by hydrochloric acid at 150° to *4 : 6-diethyl-2-pyridone*, m. p. 61—62°. Reaction (condensation) does not proceed so readily as with diacetylmethane; this is ascribed to the bulkier ethyl group. The isolation of only one condensation product from benzoylacetone and cyanoacetamide (*loc. cit.*) is in agreement with the theory that the phenyl group inhibits the reaction between the amide and the form OH·CPh:CHAc. The results described are in harmony with Ingold, Perren, and Thorpe's views (J.C.S., 1922, **121**, 1770) regarding the Michael reaction.

Acetylacetone and malonamide afford 60% of the theoretical amount of 4 : 6-dimethyl-2-pyridone-3-carboxylamide after 3—4 days; with malononitrile reaction occurs more readily and 3-cyano-4 : 6-dimethyl-2-pyridone is produced in 77% yield. Benzoylacetone and ethyl cyanoacetate give *ethyl 6-phenyl-4-methyl-2-pyridone-3-carboxylate*, m. p. 216—217° (decomp.); with malononitrile, reaction is again more rapid and 3-cyano-6-phenyl-4-methyl-2-pyridone is obtained as the main product. The influence of the groups present in the addendum is further illustrated by the observation that chloroacetamide, phenylacetamide, and phenylacetonitrile do not react with acetylacetone under the usual conditions.

H. Burton.

Reactivity of conjugated systems. II. Condensation of acetylenic ketones with cyanoacetamide. C. Barat (J. Indian Chem. Soc., 1930, **7**, 851—862).—The Michael or Knoevenagel condensation of benzoylphenylacetylene and cyanoacetamide gives *3-cyano-4 : 6-diphenyl-2-pyridone*, m. p. 320° (*1-methyl* derivative, m. p. 175°, prepared either by methylation or condensation of the ketone with cyanoacetmethylamide), hydrolysed by 75—80% sulphuric acid to 2-hydroxy-4 : 6-diphenylpyridine, m. p. 208°. This pyridine is identical with the product obtained by dehydrogenation of the tetrahydropyridine derivative prepared from phenyl styryl ketone and cyanoacetamide (A., 1930, 925). Reaction probably occurs by addition to the triple linking with subsequent cyclisation and rearrangement. p-*Toluoylphenylacetylene*, m. p. 72° (from *p*-toluoyl chloride and sodiophenylacetylene), and cyanoacetamide give *3-cyano-4-phenyl-6-*p*-tolyl-2-pyridone*, m. p. 268° (*1-methyl* derivative, m. p. 136—138°), hydrolysed to 2-hydroxy-4-phenyl-6-*p*-tolylpyridine. *p*-Toluoylphenylacetylene and ethyl malonate condense in presence of a trace of sodium ethoxide yielding *ethyl 4-phenyl-6-*p*-tolyl-2-pyrone-3-carboxylate*, m. p. 85°, hydrolysed to *4-phenyl-6-*p*-tolyl-2-pyrone*, m. p. 133° (decomp.). The following compounds are prepared similarly to the above: p-*nitrobenzoylphenylacetylene*, m. p. 161—162°; *3-cyano-4-phenyl-6-*p*-nitrophenyl-2-pyridone*, m. p. 332—333° (*1-methyl* derivative, m. p. 322—324°); *2-hydroxy-4-phenyl-6-*p*-nitrophenylpyridine*, m. p. 275—276°; *ethyl 4-phenyl-6-*p*-nitrophenyl-2-pyrone-3-carboxylate*, m. p. 148°; *4-phenyl-6-*p*-nitrophenyl-2-pyrone*, m. p. 235°; *3-cyano-4-phenyl-6-methyl-2-pyridone*, m. p. 275—276° [*1-methyl* derivative, m. p. 146°; the substance described by Sen (J.C.S., 1915, **107**, 1347) is probably identical with this]; *ethyl 4-phenyl-6-methyl-2-pyrone-3-carboxylate*, m. p. 92°; *4-phenyl-6-methyl-2-pyrone*, m. p. 185—186°; 3-cyano-4-phenyl-6-ethyl-2-pyridone, m. p. 267—268° (lit. 260°) (*1-methyl* derivative, m. p. 158°).

H. Burton.

Synthesis of contrast media for pyelography. I. Y. Sugii, I. Shimoya, and H. Shindo (J. Pharm. Soc. Japan, 1930, **50**, 727—733).—2-Aminopyridine when treated with potassium iodide solution gave 5-iodo-2-aminopyridine, m. p. 129°, diazotised to 5-iodopyridone, m. p. 192°; this when treated with chloroacetic acid forms 5-iodopyrid-2-one-1-acetic acid, decomp. 240° (*ethyl* ester, m. p. 113—114°), the sodium salt of which is employed in *X*-ray photography of organs.

Chemical Abstracts.

***Py*-Alkylquinolines. Generalisation of the Skraup reaction to α-alkylglycerols.** R. Delaby and J. Hiron (Bull. Soc. chim., 1930, [iv], 1395—1400).—See this vol., 98. *2-Ethylquinoline iodoantimonate*, m. p. about 180°, is described, and a modified method of preparing alizarin-blue from 3-aminoalizarin and nitrobenzene in presence of vanadic acid is given.

Quinoline compounds. II. Derivatives of 4-phenyl-2-methylquinoline. U. N. Brahmachari and T. Bhattacharyya (J. Indian Chem. Soc., 1930, **7**, 831—834).—Acetophenone and paraldehyde condense with *p*-nitroaniline under the conditions of the Beyer reaction to give *6-nitro-4-phenyl-2-methylquinoline*, m. p. 141°. This with *p*-dimethylaminobenzaldehyde forms *6-nitro-4-phenyl-2-*p*-di-*

methylaminostyrylquinoline, m. p. 64°, and is reduced by stannous chloride and hydrochloric acid to 6-*amino*-4-*phenyl*-2-*methylquinoline*, m. p. 188°. 8-*Nitro*-4-*phenyl*-2-*methylquinoline*, m. p. 94°, is prepared similarly from *o*-nitroaniline. 8-*Nitro*-4-*phenyl*-2-p-*di-methylaminostyrylquinoline* and 8-*amino*-4-*phenyl*-2-*methylquinoline hydrochloride* have m. p. 129° and decomp. above 210°, respectively. H. BURTON.

Imide and amide chlorides of non-aromatic acids. VI. New method in the quinoline series. J. VON BRAUN and A. HEYMONS [with L. SCHNITZSPAHN] (Ber., 1930, **63**, [*B*], 3191—3203; cf. A., 1930, 613).—The conversion of the imide chlorides of acetarylides into amidines by loss of 1 mol. of hydrogen chloride (*loc. cit.*) is not exhibited by those derived from chloroacetarylides which, under similar conditions, smoothly lose 2 mols. of hydrogen chloride and pass into quinolines. The compounds of propionic and phenylacetic acid resemble those from chloroacetic acid, so that the process appears general for arylamides of all non-aromatic acids with the exception of acetic acid.

The action of phosphorus pentachloride (1 mol.) on chloroacetanilide (1 mol.) at the ordinary temperature gives 3-*chloro*-4-*anilino*-2-*chloromethylquinoline hydrochloride*, decomp. 222°, in 90—95% yield. The free base is most readily prepared by the addition of ammonia or sodium carbonate to the solution of the salt in cold pyridine; the corresponding *picrate*, m. p. 193°, is described. The base is converted by four times its weight of concentrated hydrochloric acid at 160—165° and subsequently at 175—180° mainly into 3-*chloro*-4-*hydroxy*-2-*chloromethylquinoline*, m. p. 303° (yield 80%), accompanied by 3 : 4-*dichloro*-2-*chloromethylquinoline*, m. p. 119—120° (also prepared from 3-chloro-4-hydroxy-2-chloromethylquinoline and phosphorus pentachloride in presence of phosphoryl chloride at 130—140°). With a smaller proportion of hydrochloric acid at 165°, the base is transformed into 3-*chloro*-4-*hydroxy*-2-*hydroxymethylquinoline*, m. p. 283°. Moderated hydrolysis of the trichloro-base by aqueous-alcoholic alkali hydroxide affords 3 : 4-*dichloro*-2-*hydroxymethylquinoline*, b. p. 150—154°/0·2 mm., m. p. 44°. Reduction of 3-chloro-4-anilino-2-chloromethylquinoline with tin and hydrochloric acid yields 3-*chloro*-4-*anilino*-2-*methylquinoline*, m. p. 172° (*picrate*, m. p. 229°). 3-Chloro-4-hydroxy-2-chloromethylquinoline is reduced by zinc dust in boiling glacial acetic acid to 3-*chloro*-4-*hydroxy*-2-*methylquinoline*, m. p. 340°, transformed by phosphorus pentachloride into 3 : 4-*dichloro*-2-*methylquinoline*, m. p. 322°. Transformation of 3 : 4-dichloro-2-chloromethylquinoline into 2-methylquinoline is effected by treatment with hydrogen iodide in glacial acetic acid at 220—240°; reduction with sodium and alcohol affords 2-methyl-1 : 2 : 3 : 4-tetrahydroquinoline. 3-Chloro-4-anilino-2-chloromethylquinoline is converted by cautious treatment with aqueous-alcoholic potassium hydroxide into 3-*chloro*-4-*anilino*-2-*hydroxymethylquinoline*, m. p. 93—94°, and by aqueous-alcoholic potassium cyanide into 3-*chloro*-4-*anilino*-2-*cyanomethylquinoline*, m. p. 156° (*benzylidene* derivative, m. p. 192°). With aniline 3-chloro-4-anilino-2-chloromethylquinoline gives 3-*chloro*-4-*anilino*-2-*anilinomethylquinoline*, m. p. 192° (*hydrochloride*; *acetyl* derivative, m. p. 209°). 3-*Chloro*-4-*anilino*-2-*dimethylaminomethylquinoline*, m. p. 93° (*picrate*, m. p. 190—193°), is reduced by sodium and alcohol to aniline and 2-*dimethylaminomethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m. p. 148—152°/15 mm. 3 : 4-*Dichloro*-2-*dimethylaminomethylquinoline*, m. p. 62°, and its *picrate*, m. p. 177°, are described. 3-*Chloro*-4-*hydroxy*-2-*piperidinomethylquinoline* has m. p. 233—235°. With pyridine and *iso*quinoline, respectively, 3-chloro-4-anilino-2-chloromethylquinoline yields the additive *products*, $C_{21}H_{17}N_3Cl_2$ and $C_{25}H_{19}N_3Cl_2$, m. p. 245° and 258°.

Chloroacet-p-*iodoanilide*, m. p. 193°, is converted by phosphorus pentachloride into 3-*chloro*-6-*iodo*-4-p-*iodoanilino*-2-*chloromethylquinoline*, m. p. 184° (*hydrochloride*, m. p. 232°; *picrate*, m. p. 202°), converted by diethylamine into 3-*chloro*-6-*iodo*-4-p-*iodoanilino*-2-*diethylaminomethylquinoline*, m. p. 152° (*picrate*, m. p. 178°).

Chloroacet-*m*-chloroanilide affords 3 : 7-*dichloro*-4-m-*chloroanilino*-2-*chloromethylquinoline*, m. p. 179°, transformed by *p*-phenetidine into 3 : 7-*dichloro*-4-m-*chloroanilino*-2-p-*ethoxyanilinomethylquinoline*, m. p. 131°. *Chloroacet*-3-*chloro*-4-*methylanilide*, m. p. 102°, yields a homogeneous quinoline *base*, $C_{18}H_{14}N_2Cl_4$, m. p. 174°. The following *compounds* isolated previously as by-products (*loc. cit.*) are recognised as quinoline derivatives: $C_{18}H_{16}N_2Cl_2$, m. p. 160°, from *o*-toluidine; $C_{18}H_{16}O_2N_2Cl_2$, m. p. 196°, from *o*-anisidine; $C_{16}H_{10}N_2Cl_4$, m. p. 116°, from *o*-chloroaniline; $C_{16}H_{10}N_2Cl_2Br_2$ (*hydrochloride*, m. p. 135°) from *o*-bromoaniline.

Propionanilide and phosphorus pentachloride afford 4-*anilino*-3-*methyl*-2-*ethylquinoline*, m. p. 178° (hydrochloride, m. p. 219—220°; *picrate*, m. p. 220—221°), converted by hydrochloric acid under different conditions into 4-*chloro*-3-*methyl*-2-*ethylquinoline*, m. p. 40—43°, and 4-*hydroxy*-3-*methyl*-2-*ethylquinoline*, m. p. 284°, transformed by phosphorus pentachloride and phosphoryl chloride into the 4-chloro-compound. Reduction of 4-anilino-3-methyl-2-ethylquinoline by sodium and alcohol gives aniline and 3-methyl-2-ethyl-1 : 2 : 3 : 4-tetrahydroquinoline, b. p. 136—140°/12 mm. (*hydrochloride*, m. p. 193°).

Phenylacetanilide is more slowly transformed by phosphorus pentachloride into 4-*anilino*-3-*phenyl*-2-*benzylquinoline*, m. p. 172° (*picrate*, m. p. 188°; *hydrochloride*, m. p. 209°), converted into 4-*hydroxy*-3-*phenyl*-2-*benzylquinoline*, m. p. 308°, and reduced to aniline and 3-*phenyl*-2-*benzyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, b. p. 190—192°/0·3 mm. H. WREN.

ω-Cyano-ω-arylideneacetanilides and the conversion of their *o*-nitro-derivatives into quinoline derivatives. M. ISHAQ and J. N. RAY (J.C.S., 1930, 2739—2741).—Cyanoacetanilide condenses with *o*-nitrobenzaldehyde in presence of pyridine and a small amount of piperidine at 60—70° forming ω-*cyano*-ω-o-*nitrobenzylideneacetanilide* [o-*nitro*-α-*cyanocinnamanilide*], m. p. 206°, reduced by zinc dust and acetic acid to 2-*anilino*-3-*cyanoquinoline*, m. p. 208°. The nitro-compound could not be converted into a naphthinoline derivative under any of the conditions tried. The following ω-*cyano*-ω-*arylideneacetanilides* are also de-

scribed: *piperonylidene*, m. p. 182°; m-*methoxybenzylidene*, m. p. 141°; 3 : 4-*dimethoxybenzylidene*, m. p. 168°; 6-*nitro*-3 : 4-*methylenedioxybenzylidene*, m. p. 227°, and 6-*nitro*-3 : 4-*dimethoxybenzylidene*, m. p. 169°. Reduction of the last two nitro-derivatives gives 2-*anilino*-3-*cyano*-6 : 7-*methylenedioxy*-, m. p. 287°, and 2-*anilino*-3-*cyano*-6 : 7-*dimethoxy-quinolines*, m. p. 237°, respectively. The following ω-*cyano*-ω-*arylideneaceto*-p-*toluidides* are obtained similarly from cyanoaceto-*p*-toluidide and the appropriate aldehyde: 3 : 4-*dimethoxybenzylidene*, m. p. 198°; piperonylidene, m. p. 183°; m-*methoxybenzylidene*, m. p. 144°; o-*nitrobenzylidene*, m. p. 182°; 6-*nitro*-3 : 4-*methylenedioxybenzylidene*, m. p. 216°, and o-*nitro*-3 : 4-*dimethoxybenzylidene*, m. p. 174°. 2-p-*Toluidino*-3-*cyano*-, m. p. 221—222°, and 2-p-*toluidino*-3-*cyano*-6 : 7-*dimethoxyquinoline*, m. p. 253°, are also prepared.

H. BURTON.

Quinoline derivatives. XIII. Degradation of 6-methoxyquinoline-4-carboxylic acid. XIV. Derivatives of quinic and xanthoquinic acids. XV. 6-Hydroxy-4-aminoquinoline. XVI. 6-substituted 4-halogenoquinolines. XVII. 6-Methoxy-4-quinolylhydrazine, 6-methoxy-4-thiolquinoline, and 6-methoxyquinoline-4-sulphonic acid. H. JOHN [with E. ANDRASCHKO] (J. pr. Chem., 1930, [ii], **128**, 180—189, 190—200, 201—210, 211—217, 218—222).—XIII. Degradation of 6-methoxyquinoline-4-carboxylic acid by the Curtius method is studied (Hofmann degradation; cf. Hirsch, A., 1896, i, 626). *Methyl* 6-*methoxyquinoline*-4-*carboxylate* has m. p. 84°. The ethyl ester (*loc. cit.*) is converted by the usual methods through the *hydrazide*, m. p. 151° (*picrate*, m. p. 205°; iso*propylidene*, m. p. 135°; *methylbenzylidene*, m. p. 201°, and p-*dimethylaminobenzylidene*, m. p. 132°, derivatives), into the *azide*, decomp. 106°. The latter is converted by boiling alcohol into 6-*methoxyquinolyl*-4-*urethane*, m. p. 170°, and by controlled thermal decomposition into 6-*methoxyquinolyl*-4-*carbimide*, m. p. 171°, which is not attacked by boiling alcoholic potassium hydroxide. Boiling water converts the azide into NN′-*bis*-(6-*methoxy*-4-*quinolyl*)*carbamide*, m. p. 205°, and acid hydrolysis yields 4-amino-6-methoxyquinoline, m. p. 120° (cf. *loc. cit.*) (sulphate; nitrate; picrate, m. p. 192°). The *diacetyl* derivative of the latter has m. p. 242° (*picrate*).

XIV. β-*Chloroethyl* 6-*methoxyquinoline*-4-*carboxylate* [from quinoyl chloride hydrochloride (Karrer, A., 1918, i, 40) and β-chloroethyl alcohol] has m. p. 71°; from the foregoing acid chloride and the corresponding amine are obtained β-(6-*methoxyquinoline*-4-*carboxylamido*)*ethanol*, m. p. 143°, and αβ-*bis*-(6-*methoxyquinoline*-4-*carboxylamido*)*ethane*, m. p. 269° (*hydrochloride*; *sulphate*; *picrate*).

An improved method is described for the preparation of 6-hydroxyquinoline 4-carboxylic acid by the action of hydriodic acid (*d* 2·0) on the methoxy-compound and numerous salts are described but not characterised [*chloride* (from the acid and thionyl chloride), m. p. 158° (decomp.); *amide*, m. p. 264°; *diethylamide*, m. p. 119°; β-*chloroethyl* ester, m. p. 150°].

6-Ethoxyquinoline-4-carboxylic acid (from the hydroxy-acid and ethyl iodide) has m. p. 278° (cf. the acid obtained by Karrer, *loc. cit.*, from ethyl dihydrocupreine) (*methyl* ester, m. p. 58°). Numerous salts of this acid are also described.

XV. The Curtius degradation of 6-hydroxyquinoline-4-carboxylic acid follows the same lines as that of the methoxy-acid (cf. XIII).

The *methyl*, n-*propyl*, and iso*propyl* esters of 6-hydroxyquinoline-4-carboxylic acid have m. p. 212°, 130°, and 157°, respectively. The *ethyl* ester, m. p. 185·5°, is converted in the usual way through the *hydrazide*, m. p. 244° (*hydrochloride*; *sulphate*; *nitrate*; iso*propylidene*, m. p. above 300°, and *methylbenzylidene*, m. p. 276°, derivatives), into the *azide*, decomp. 115°. The following compounds are prepared from the azide by the usual methods: 6-*hydroxyquinolyl*-4-*urethane*, m. p. 236° (decomp.), 6-*hydroxy*-4-*quinolylcarbimide*, m. p. 178° (hydrolysed by alcoholic potassium hydroxide to the amine described below), and NN′-*bis*-(6-*hydroxy*-4-*quinolyl*)*carbamide*, m. p. 253°. Acid hydrolysis of the urethane affords 4-*amino*-6-*hydroxyquinoline*, m. p. 264° (*hydrochloride*; *sulphate*).

XVI. 4-Amino-6-methoxyquinoline and 4-amino-6-hydroxyquinoline are converted by the usual diazo-reactions into 4-halogeno-compounds (cf. Hirsch, A., 1896, i, 626), of which the following are described: 4-*bromo*-6-*methoxyquinoline*, m. p. 106° (*picrate*, m. p. 180°), 4-*iodo*-6-*methoxyquinoline*, m. p. 85° (*picrate*, m. p. 254—255°), 4-*chloro*-, m. p. 210°, 4-*bromo*-, m. p. 253°, and 4-*iodo*-6-*hydroxyquinoline*, m. p. 283°. Many *salts* of all these bases are described without characterisation.

XVII. 4-Chloro-6-methoxyquinoline is converted into the following derivatives: 6-*methoxy*-4-*quinolylhydrazine*, m. p. 154° (*methyl*-p-*tolylidene* derivative, m. p. 105°) (interaction of hydrazine hydrate with 4-bromo-6-methoxyquinoline gives a less satisfactory yield); 6-*methoxy*-4-*thiolquinoline*, m. p. 139° (by the method of O. Fischer; A., 1899, i, 635); and 6-*methoxyquinoline*-4-*sulphonic acid*, m. p. 292° (by the hydrogen sulphite method of Besthorn and Geisselbrecht; A., 1920, i, 562) (*salts* described).

R. CHILD.

Doebner's reaction. X. L. MUSAJO (Gazzetta, 1930, **60**, 673—677; cf. A., 1930, 222).—The reaction between furfuraldehyde, β-naphthylamine, and pyruvic acid has been studied and the following secondary products have been isolated: 3-(2′-*furyl*)-1 : 2 : 3 : 4-*tetrahydro*-β-*naphthoquinoline*-1-*carboxylic acid*, m. p. 200°, and β-*naphthyl*-2-*furfurylamine*, $C_{10}H_7{\cdot}NH{\cdot}CH_2{\cdot}C_4H_3O$, b. p. 225—230°/17 mm. The *nitroso*-derivative, m. p. 98°, of the latter compound has been prepared.

O. J. WALKER.

Formation of aromatic thiosulphonic acids from disulphides. E. W. MCCLELLAND and L. A. WARREN (J.C.S., 1930, 2690—2693).—2 : 2′-*oo*′-Dithiodiphenyl-4 : 5-dihydroglyoxaline gives with sulphur dioxide in boiling alcoholic solution 2-*phenyl*-4 : 5-*dihydroglyoxaline*-o-*thiosulphonic acid*,

$SR{\cdot}C_6H_4{\cdot}C{<}{\genfrac{}{}{0pt}{}{N—CH_2}{N—CH_2}}$ (I) ($R{=}SO_3H$), m. p. 228° (decomp.), the constitution of which follows from its conversion by potassium cyanide into 2-*phenyl*-4 : 5-*dihydroglyoxaline* o-*thiocyanate*, m. p. 180° (I, R=CN).

The thiosulphonic acid is similarly obtained from the thiol (I, R=H), and also from the hydrobromide and perbromide of the tricyclic compound (cf. A., 1930, 95). The thiol is regarded as the intermediate in all these cases, and, in consequence of the non-occurrence of the reaction with a representative series of aryl disulphides, the reaction is ascribed to the betaine structure of the former. 2-*Phenyl*-4 : 5-*dihydroglyoxaline*-m-*thiosulphonic acid*, m. p. 246° (decomp.), -p-*thiosulphonic acid*, m. p. 248° (decomp.), and p-*thiocyanate*, m. p. above 265°, are prepared from the corresponding dithiodiphenyldihydroglyoxalines.

H. A. Piggott.

Synthesis of *l*-2-thiolhistidine. J. N. Ashley and C. R. Harington (J.C.S., 1930, 2586—2590).—*l*-Histidine methyl ester dihydrochloride in aqueous solution is converted by benzoyl chloride and powdered sodium carbonate at 0° into methyl $\alpha\gamma\delta$-tribenzamido-Δ^{γ}-pentenoate, hydrolysed by boiling 10% methyl-alcoholic hydrogen chloride to methyl $\alpha\delta$-dibenzamido-γ-ketovalerate (cf. Windaus, Dorries, and Jensen, A., 1922, i, 60). This is converted by further hydrolysis with 20% hydrochloric acid into the *dihydrochloride* of $\alpha\delta$-diamino-γ-ketovaleric acid, a concentrated aqueous solution of which with 1 mol. of sodium thiocyanate at 100° and subsequent treatment of the reaction mixture with sodium acetate, affords l-2-*thiolhistidine*, darkens about 290°, not melting at 310°, $[\alpha]_{5461}$ −9·5° in *N*-hydrochloric acid [*dihydrochloride*, m. p. 197—199° (decomp.); *monopicrate*, m. p. 156° (not analytically pure)]. The constitution and optical purity of the amino-acid were proved by its oxidation with ferric sulphate to *l*-histidine, $[\alpha]_{5461}$ −41·4°, identical with a genuine specimen and giving identical derivatives.

J. W. Baker.

Dioximes. LXXII. E. Durio and M. Bissi (Gazzetta, 1930, 60, 899—903).—Conditions are specified for obtaining an improved yield of dioxytetraphenylpyrazine, $O{:}N{<}\genfrac{}{}{0pt}{}{CPh{:}CPh}{CPh\cdot CPh}{>}N{:}O,2AcOH$, m. p. 322° (acetic acid free) (decomp.), which Auwers and Meyer (A., 1889, 403, 713) obtained in small amount, together with diphenylglyoxime peroxide, by oxidising α-benzildioxime (diphenylglyoxime) with potassium ferricyanide in basic solution. Two distinct reactions here occur: (1) a simple dehydrogenation, giving the peroxide, and (2) elimination, as nitrous acid, of two hydrogen atoms and two oximino-groups from two molecules of α-benzildioxime, the residues of which then unite to form dioxytetraphenylpyrazine. The latter, which is not formed by oxidation of β- or γ-benzildioxime under similar conditions, is deoxygenated, with formation of tetraphenylpyrazine, when treated with either nascent hydrogen or phosphorus pentachloride. Neither *p*-tolyldioxime nor anisyldioxime, although similar in many properties to α-benzildioxime, yields any trace of dioxypyrazine when oxidised by potassium ferricyanide.

T. H. Pope.

Conjugated double linkings. XV. Constitution of indolenine-yellow. R. Kuhn, A. Winterstein, and G. Balser (Ber., 1930, 63, [*B*], 3176—3184).—The constitution assigned hitherto to indolenine-yellow is not in harmony with the known effect of replacing the ·CH:CH· group by ·CH:N·. The mode of formulation is based on the analogy of O:N·OH to O:CH·OH, but the comparison is not valid in this case, since the condensation of 1 : 3 : 3-trimethyl-2-methyleneindoline salts with nitrous acid in presence of acetic anhydride differs from that with formic esters in that 1 mol. of hydrogen cyanide is lost in addition to 1 mol. of water. To indolenine-yellow the constitution $C_6H_4{<}\genfrac{}{}{0pt}{}{CMe_2}{\underset{X}{NMe}}{>}C\cdot CH{:}C{<}\genfrac{}{}{0pt}{}{CMe_2}{NMe}{>}C_6H_4$ is therefore ascribed; it thus becomes a lower vinylene homologue of indolenine-red,

$$C_6H_4{<}\genfrac{}{}{0pt}{}{CMe_2}{\underset{X}{NMe}}{>}C\cdot CH{:}CH\cdot CH{:}C{<}\genfrac{}{}{0pt}{}{CMe_2}{NMe}{>}C_6H_4.$$

Attempts to prepare indolenine-yellow by the condensation of 1 : 2 : 3 : 3-tetramethylindoleninium salts with 1 : 3 : 3-trimethylindolinone do not give the desired product. When, however, 1 : 3 : 3-trimethyl-2-methyleneindoline in glacial acetic acid is treated with sodium nitrite and then with perchloric acid 2-*formoximino*-1 : 3 : 3-*trimethylindoleninium perchlorate*, $C_6H_4{<}\genfrac{}{}{0pt}{}{CMe_2}{NMe(ClO_4)}{>}C\cdot CH{:}N\cdot OH$ m. p. 215° (decomp.), is almost quantitatively precipitated; it decomposes when heated in acetic anhydride into hydrocyanic acid and 1 : 3 : 3-trimethylindolinone. When warmed with 1 : 3 : 3-trimethyl-2-methyleneindoline in acetic anhydride at 80—90° it gives indolenine-yellow. 2-*Formoximino*-1 : 3 : 3 : 5 : 7-*pentamethylindoleninium perchlorate*, m. p. 210° (decomp.), and 1 : 3 : 3-trimethyl-2-methyleneindoline give 5 : 7-dimethylindolenine-yellow, isolated as the *perchlorate*, m. p. 250·5° (decomp.). This salt is also obtained from 2-formoximino-1 : 3 : 3-trimethylindoleninium perchlorate and 1 : 3 : 3 : 5 : 7-pentamethyl-2-methyleneindoline. The identity of the salts is explained on the basis of Konig's hypothesis that the anion in a dye of this type cannot be assigned to one or other nitrogen atom, but is attached to both, thus giving a system of "flowing heteropolar linkings."

H. Wren.

Oxidation. IV. Action of ferric chloride and hydrogen peroxide on *S*-alkylthiosemicarbazones. Formation of triazoles. S. C. De and T. K. Chakravorty (J. Indian Chem. Soc., 1930, 7, 875—878).—Oxidation of an aqueous-alcoholic solution of benzaldehyde-*S*-methyl- and -ethyl-thiosemicarbazone with hydrogen peroxide affords 3-*methylthiol*-, m. p. 164°, and 3-*ethylthiol*-5-*phenyl*-1 : 2 : 4-*triazoles*, m. p. 166°, respectively. 4-Phenylthiosemicarbazide and methyl iodide are allowed to react in boiling alcohol, the mixture is treated with benzaldehyde, whereby the *hydriodide*, m. p. 153°, of *benzaldehyde*-4-*phenyl*-S-*methylthiosemicarbazone*, m. p. 66—67° (*hydrochloride*), separates. The semicarbazone is oxidised as above to 3-*methylthiol*-4 : 5-*diphenyl*-1 : 2 : 4-*triazole*, m. p. 165—166°. Similarly, *benzaldehyde*-4-*phenyl*-S-*ethylthiosemicarbazone*, m. p. 78° [*hydriodide*, m. p. 118°; *hydrochloride*, m. p. 178° (decomp.)], gives 3-*ethylthiol*-4 : 5-*diphenyl*-1 : 2 : 4-*triazole*, m. p. 148°; *benzaldehyde*-4-o-*tolyl*-S-*methylthiosemicarbazone*, m. p. 62° [*hydriodide*, m. p. 189° (decomp.); *hydrochloride*, m. p. 194° (decomp.)], yields 3-*methylthiol*-5-*phenyl*-4-o-*tolyl*-1 : 2 : 4-*triazole*,

m. p. 130°; benzaldehyde-4-o-tolyl-*S*-ethylthiosemicarbazone (*hydriodide*, m. p. 123°; *hydrochloride*, m. p. 167°) affords 3-*ethylthiol-5-phenyl-4-o-tolyl-1 : 2 : 4-triazole*, m. p. 107°; *benzaldehyde-4-p-tolyl-S-methylthiosemicarbazone*, m. p. 71° [*hydriodide*, m. p. 180° (decomp.); *hydrochloride*, m. p. 130° (decomp.)], gives 3-*methylthiol-5-phenyl-4-p-tolyl-1 : 2 : 4-triazole*, m. p. 176°; benzaldehyde-4-*p*-tolyl-*S*-ethylthiosemicarbazone (*hydrochloride*, m. p. 158°; *hydriodide*, m. p. 165°) yields 3-*ethylthiol-5-phenyl-4-p-tolyl-1 : 2 : 4-triazole*, m. p. 148°. Ferric chloride may be used as the oxidising agent, but the products obtained are less pure. H. BURTON.

γ-Triazines : synthesis of thiolaminotriazines. A. OSTROGOVICH and V. GALEA (Atti R. Accad. Lincei, 1930, [vi], **11**, 1108—1116).—By the method previously described (A., 1912, i, 320; this vol., 101) the following compounds have been prepared. 2-*Amino-6-thiol-4-phenyl-1 : 3 : 5-triazine*, m. p. 281—282° (decomp.), forms *silver* and *copper* ($+0{\cdot}5H_2O$) salts, a *picrate*, m. p. 193—194° (decomp.), and a 5- or 6-*methyl* derivative, m. p. 170—171°. 2-*Amino-6-thiol-4-o-tolyl-1 : 3 : 5-triazine*, m. p. 243—244° (decomp.), forms a *silver* salt and a *picrate*, m. p. 224—225° (decomp.). 2-*Amino-6-thiol-4-m-tolyl-1 : 3 : 5-triazine*, m. p. 272—273° (decomp.), forms a *silver* salt and a *picrate*, m. p. 210—211° (decomp.). 2-*Amino-6-thiol-4-p-tolyl-1 : 3 : 5-triazine*, m. p. 279—280° (decomp.), forms a *silver* salt and a *picrate*, m. p. 191—192° (decomp.). 2-*Amino-6-thiol-4-p-anisyl-1 : 3 : 5-triazine*, m. p. 282—283°, forms a *silver* salt and a *picrate*, m. p. 198—199° (decomp.) T. H. POPE.

Triazole compounds. III. Alkylation of nitro-1 : 2 : 3-benztriazoles. O. L. BRADY and C. V. REYNOLDS (J.C.S., 1930, 2667—2673).—In agreement with Zincke and Helmert (A., 1896, i, 300), thermal decomposition of the methiodide obtained by the action of methyl iodide on 6-nitro-1 : 2 : 3-benztriazole affords only 6-nitro-3-methyl-1 : 2 : 3-benztriazole, which is converted by methyl sulphate into 6-*nitro-1 : 3-dimethyl-1 : 2 : 3-benztriazolinium methosulphate*, $\left[NO_2{\cdot}C_6H_3{<}^{NMe}_{NMe}{>}N\right]^{+}\overline{MeSO_4}$, m. p. 110° (decomp.) [*chloride*, m. p. 136° (decomp.)]. Thermal decomposition of either the methosulphate or the chloride affords only 6-nitro-3-methyl-1 : 2 : 3-benztriazole, identical with a specimen synthesised by the action of nitrous acid on 4-nitro-2-aminomethylaniline. Alkylation of 6-nitro-1 : 2 : 3-benztriazole with methyl sulphate and 2*N*-sodium hydroxide, however, affords the 3-methyl derivative together with a larger yield of 6-*nitro-1-methyl-1 : 2 : 3-benztriazole*, m. p. 187°, converted by methyl sulphate at 100° into 6-nitro-1 : 3-dimethyl-1 : 2 : 3-benztriazolinium methosulphate (above), and reduced by sodium hyposulphite to the 6-*amino*-compound, m. p. 201°, which affords 1-methyl-1 : 2 : 3-benztriazole by elimination of the amino-group in the usual manner. Similarly, methylation of 7-nitro-5-methyl-1 : 2 : 3-benztriazole with methyl sulphate and 2*N*-sodium hydroxide yields a mixture of 7-nitro-1 : 5-dimethyl- (Pinnow, A., 1901, i, 485) and a larger amount of 7-*nitro-3 : 5-dimethyl-*, m. p. 196°, -*1 : 2 : 3-benztriazole*. The latter is reduced to the corresponding 7-*amino*-compound, m. p. 190°, which by deamination affords 3 : 5-dimethyl-1 : 2 : 3-benztriazole. A mechanism for the formation of these derivatives, based on the assumption that the benztriazoles consist of an equilibrium mixture of two tautomeric forms, is suggested. In each case the methyl derivative in which the methyl group is attached to the nitrogen atom in the *m*-position to the nitro-group is converted, by heating with methyl sulphate alone, into the isomeride in which the methyl group is attached to the nitrogen in the *o*- or *p*-position to the nitro-group, the latter isomeride being the sole product of the action of methyl sulphate alone on the benztriazole. Thus 7-nitro-5-methyl-1 : 2 : 3-benztriazole is converted by methyl sulphate and subsequent thermal decomposition of the chloride obtained from the methosulphate so formed into 7-nitro-1 : 5-dimethyl-1 : 2 : 3-benztriazole, this product also being obtained by similar treatment of 7-nitro-3 : 5-dimethyl-1 : 2 : 3-benztriazole. J. W. BAKER.

2 : 5-Diphenyl-1 : 2 : 3-triazole-4-carboxylic acid. M. GALLOTTI [with G. BARRO and L. SALTO] (Gazzetta, 1930, **60**, 866—872; cf. A., 1925, i, 306).—*Phenyl oximinoethyl ketone phenylhydrazone*, NHPh·N:CPh·CMe:N·OH, m. p. 210°, forms an *acetyl* derivative, m. p. 137°, which, when boiled with aqueous sodium carbonate, gives 2 : 5-*diphenyl-4-methyl-1 : 2 : 3-triazole*. The latter, which was not purified, is oxidised by alkaline permanganate to 2 : 5-*diphenyl-1 : 2 : 3-triazole-4-carboxylic acid*, m. p. 208—209°. o-*Tolyl oximinoethyl ketone*, m. p. 114—115°, obtained by treating the parent ketone with *iso*amyl nitrite, gives a *phenylhydrazone*, m. p. 175—177°, which forms an *acetyl* compound, m. p. 140°, and this yields 2-*phenyl-5-o-tolyl-4-methyl-1 : 2 : 3-triazole* when boiled with aqueous sodium carbonate. T. H. POPE.

1-Hydroxy- and 1-amino-derivatives of theobromine. C. A. ROJAHN and H. FEGELER (Arch. Pharm., 1930, **268**, 567—572).—An attempt has been made to obtain derivatives of theobromine which are soluble in water and possess a narcotic action. Theobromine, glycol chlorohydrin, and 10% aqueous sodium hydroxide at 125° yield 1-β-*hydroxyethyltheobromine*, m. p. 193° (*acetate*, m. p. 139°; *benzoate*, m. p. 151°; *phenylurethane*, m. p. 125°), which with phosphorus pentachloride in boiling chloroform gives 1-β-*chloroethyltheobromine*, m. p. 152°. This with diethylamine at 100° yields 1-*diethylaminoethyltheobromine*, isolated as the *picrate*, m. p. 155—156°, with aniline, 1-β-*anilinoethyltheobromine*, m. p. 171°; and with *p*-phenetidine, 1-*p-phenetylaminoethyltheobromine*, m. p. 156°. Attempts to condense theobromine and ethyl β-bromoethyl ether yielded only hydroxyethyltheobromine. 1-β-*Hydroxypropyltheobromine*, m. p. 129° (*acetate*, m. p. 112°; *benzoate*, m. p. 162°; *phenylurethane*, m. p. 175—176°), formed in small yield from sodium theobromine and β-chloro-*n*-propyl alcohol in xylene at 110—120°, yields with phosphorus pentachloride 1-β-*chloropropyltheobromine*, m. p. 144°, from which 1-β-*anilinopropyltheobromine picrate*, m. p. 179—181°, and 1-β-*dimethylaminopropyltheobromine picrate*, m. p. 250° (decomp.), are obtained. H. E. F. NOTTON.

Porphyrin syntheses. XXXV. Hæmin, hæmatin, and protoporphyrin. H. Fischer, A. Treibs, and K. Zeile (Z. physiol. Chem., 1930, **193**, 138—166; cf. this vol., 101).—Synthetic hæmatoporphyrin was converted into tetramethylhæmatoporphyrin. The m. p. and mixed m. p. of the latter confirmed the identity of the synthetic hæmatoporphyrin with that obtained by analysis. The imides (α-methoxyethylcitraconimide) obtained on oxidation of the two specimens] were identical. Bromo- and iodo-hæmin were prepared from blood and also from protoporphyrin. Although the crystalline form varied according to the method of crystallisation there was little doubt of the identity of the respective products. Hæmin and protoporphyrin each crystallise in various forms which indicate varying degrees of purity rather than constitutional divergence. J. H. Birkinshaw.

Porphyrin synthesis. XXXVI. Conversion of mesoporphyrin IX into a porphyrinmonopropionic acid, and some porphyrin syntheses. H. Fischer and A. Rothaas (Annalen, 1930, **484**, 85—112).—The product obtained by reduction of mesochlorin with zinc dust and acetic acid is converted by oxidation and esterification into a *methyl* ester, m. p. 206—207°, not identical with the dimethyl ester of mesoporphyrin IX. Mesoporphyrin IX, when similarly treated, gives a mixture of three new porphyrins and a little ætioporphyrin (determined spectroscopically). The main *product* (isolated as methyl ester), m. p. indefinite (*copper* salt, m. p. 175°), is indicated by analysis to be derived by reduction of one of the propionic acid groups to propyl. It is not identical with either of the porphyrins derived by loss of a carboxyl group, nor with either of the expected propyl derivatives, the synthesis of which is described. Its conversion into an indifferent *rhodin*, m. p. 259—260°, confirms the constitution arrived at by analysis. As by-products are obtained an isomeric *mesoporphyrin* (as methyl ester), m. p. 197°, not identical with the known mesoporphyrins of similar m. p., or with those described below, and the *methyl* ester of a porphintripropionic acid, m. p. 257° (*copper* salt, m. p. 277°; *iron* salt), the constitution of the last being assumed from the formation of an acid *rhodin*, m. p. 205°. The hypothesis is advanced that these products are formed by decomposition followed by recombination, and is supported by the isolation of identical products from mesoporphyrin XI by similar treatment.

The following are described: ɔ-*bromo*-4 : 3′-*dimethyl*-3-*ethyl*-4′-*propyl*-5′-*bromomethylpyrromethene hydrobromide* (methene IV), decomp. 195° (from 2-aldehydo-4-methyl-3-ethylpyrrole-5-carboxylic acid and 2 : 4-dimethyl-3-propylpyrrole, followed by bromination); 3 : 5 : 3′-*trimethyl*-4′-*ethyl*-4-*propylpyrromethene hydrobromide* (methene VII), m. p. 211° (from 3 : 5-dimethyl-4-propylpyrrole-2-aldehyde and opsopyrrole); 3 : 5 : 4′ : 5′-*tetramethylpyrromethene*-4 : 3′-*dipropionic acid hydrobromide* (methene IX), m. p. 232° [*dimethyl* ester, m. p. 180° (decomp.)], *hydrochloride*, m. p. 173° (*dimethyl* ester, m. p. 169—170°) (from cryptopyrrolealdehydecarboxylic acid and hæmopyrrolecarboxylic acid: converted by bromination into the 5 : 5′-*dibromomethyl hydrobromide*, m. p. 191°, and a small quantity of an *isomeride*, decomp. 150°). *Mesoporphyrin XI* [*iron* salt; *copper* salt, m. p. above 299°; *dimethyl* ester, m. p. 174·5° (*iron* salt, m. p. 263°; *copper* salt, m. p. 189°)] is obtained by fusion of 4 : 3′-dimethyl-3 : 4′-diethyl-5 : 5′-dibromomethylpyrromethene and brominated 3 : 3′-dimethylpyrromethene-4 : 4′-dipropionate hydrobromides with succinic acid at 185—190°. 1 : 3 : 5 : 8-Tetramethyl-2 : 4-diethyl-6-propylporphin-7-propionic acid (*methyl* ester, m. p. 237°) is obtained, accompanied by mesoporphyrin V, by fusion of methenes III (cf. A., 1928, 902) and IV with methylsuccinic acid at 135—140°. Similar treatment of a mixture of methenes V (*loc. cit.*) and VII leads to 1 : 3 : 5 : 8-tetramethyl-2 : 4-diethyl-7-propylporphin-6-propionic acid (*methyl* ester, m. p. 215°) and mesoporphyrin II. *Mesoporphyrin VI* [*hydrochloride*; *iron* salt; *copper* salt, m. p. 314°; *dimethyl* ester, m. p. 199° (*iron* salt; *copper* salt, m. p. 210°)] may be obtained by fusion of a mixture of 5 : 5′-dibromo-4 : 4′-dimethyl-3 : 3′-diethylpyrromethene hydrobromide (A., 1926, 621) and methene IX with succinic acid at 180—190°, or by heating it with hydrogen bromide in acetic acid at 170—180°. *Mesoporphyrin VIII* [*iron* salt; *dimethyl* ester, m. p. 184—186° (*iron* salt, m. p. 223°; *copper* salt, m. p. 210°)] is the product of fusion of methene IX, 5 : 5′-dibromo-3 : 3′-dimethyl-4 : 4′-diethylpyrromethene hydrobromide, and succinic acid at 195°. Oxidation of mesorhodin with chromium trioxide in sulphuric acid gives methylethylmaleimide and hæmatic acid. H. A. Piggott.

Ring synthesis of porphyrins [with substituted and unsaturated side-chains]. IV. A bromovinylpyrrole and its transformations. H. Fischer and O. Süs (Annalen, 1930, **484**, 113—130).—Ethyl 2 : 4-dimethyl-3-β-carboxyvinylpyrrole-5-carboxylate and bromine in carbon disulphide give an impure *dibromide*, which when heated with aqueous alcohol at 100° passes into *ethyl* 2 : 4-*dimethyl*-3-β-*bromovinylpyrrole*-5-*carboxylate* (I), m. p. 158° (decomp.) (*dibromide*). Reduction of I with a solution (*d* 1·45) of hydrogen iodide in acetic acid at 100° causes elimination of the vinyl group (cf. A., 1926, 178) with the production of 2 : 4-dimethylpyrrole, whilst catalytic reduction (platinum-black) in ether affords *ethyl cryptopyrrolecarboxylate*, m. p. 94°. Treatment of I with silver cyanide, molecular silver, silver oxide, or copper powder in methyl alcohol at 90—95° gives *ethyl* 2 : 4-*dimethyl*-3-αβ-*dimethoxyethylpyrrole*-5-*carboxylate*, m. p. 112°; when the reaction is carried out in presence of alcohol, *ethyl* 2 : 4-*dimethyl*-3-β-*ethoxyvinylpyrrole*-5-*carboxylate*, m. p. 87°, results. Treatment of I with sulphuryl chloride (1 mol.) in ether gives a *chloro*-derivative, m. p. 168°; the dichloroderivative obtained by the action of 2 mols. of the chloride is hydrolysed by aqueous alcohol to *ethyl* 2-*aldehydo*-4-*methyl*-3-β-*bromovinylpyrrole*-5-*carboxylate*, m. p. 140° *azine*, m. p. 230° (decomp.); *phenylhydrazone*, m. [p. 142° (decomp.)]. This aldehyde condenses with cryptopyrrole in acetic and hydrobromic acids, forming 5-*carbethoxy*-4 : 3′ : 5′-*trimethyl*-4′-*ethyl*-3-β-*bromovinylpyrromethene hydrobromide*, not melted at 300° after darkening at 170° [the 5-*carboxy-methene*

hydrobromide is obtained similarly from 2-*aldehydo*-4-*methyl*-3-β-*bromovinylpyrrole*-5-*carboxylic acid*, m. p. 238° (decomp.)]. Treatment of I with 3 mols. of sulphuryl chloride in ether and decomposition of the resulting trichloro-compound with alcohol gives *ethyl* 4-*methyl*-3-β-*bromovinylpyrrole*-2 : 5-*dicarboxylate*, m. p. 115° (the 2-*methyl* 5-*ethyl* ester, m. p. 131°, is obtained similarly, using methyl alcohol). Catalytic reduction of the free *dicarboxylic acid*, chars from 230° without melting, furnishes 4-methyl-3-ethylpyrrole-2 : 5-dicarboxylic acid, which when heated at 240° yields opsopyrrole.

Ethyl 2 : 4-*dimethyl*-3-β-*carbethoxyvinylpyrrole*-5-*carboxylate*, m. p. 134°, prepared by esterification of the 3-β-carboxy-derivative or from ethyl 3-aldehydo-2 : 4-dimethylpyrrole-5-carboxylate and ethyl hydrogen malonate in presence of aniline at 100° (cf. A., 1926, 1261), is reduced catalytically (platinum-black) in ether to *ethyl* 2 : 4-*dimethyl*-3-β-*carbethoxyethylpyrrole*-5-*carboxylate*, m. p. 73°. When the *dibromide*, m. p. 121° (decomp.), of the above carbethoxyvinyl derivative is treated with alcoholic potassium hydroxide, a mixture of an unidentified bromine-containing *substance*, m. p. 196° (decomp.), and *ethyl* 2 : 4-*dimethyl*-3-β-*carbethoxy*-β-*ethoxyvinylpyrrole*-5-*carboxylate*, m. p. 163°, is produced; with methyl-alcoholic potassium hydroxide, *ethyl* 2 : 4-*dimethyl*-3-β-*carbethoxy*-αβ-*dimethoxyvinylpyrrole*-5-*carboxylate*, m. p. 178°, results. Oxidation of ethyl 2 : 4-dimethyl-3-β-carboxyvinylpyrrole-5-carboxylate with chromic oxide in acetic acid gives ethyl 3-carboxy-2 : 4-dimethylpyrrole-5-carboxylate. H. BURTON.

Amino-1-methylbenzoxazoles and their conversion into the arsinic acids of *o*-aminophenol. M. A. PHILLIPS (J.C.S., 1930, 2685—2690).—*o*-Acetamidophenol gives only a 15% yield of 1-methylbenzoxazole (*hydrochloride*) when treated with 5*N*-hydrochloric acid or 2*N*-sodium hydroxide at 90°, simple hydrolysis to *o*-aminophenol being the main reaction. The nitro-1-methylbenzoxazoles are best prepared by distillation of the corresponding nitro-acet- or -diacet-amidophenols at 10—20 mm., and thus are obtained: 3-, m. p. 125°, 4-, m. p. 154° (*hydrochloride*), and 6-, b. p. 240—250°/18 mm., m. p. 112°, -*nitro*-1-*methylbenzoxazole*. Dilute mineral acids or alkali hydroxides reconvert them into the nitroaminophenols, whilst reduction with iron powder and boiling 10% acetic acid affords the corresponding amino-derivatives and thus are obtained: 3-, m. p. 67° (*acetyl* derivative, m. p. 218°); 4-, b. p. 160—170°/20 mm., m. p. 77—78° (*dihydrochloride*; *acetyl* derivative, m. p. 205°); and 6-, m. p. 106° (*acetyl* derivative, m. p. 145—146°), -*amino*-1-*methylbenzoxazoles*, whilst acetylation of the 5-amino-compound (Newbery and Phillips, A., 1928, 311) gives the 5-*acetamido*-derivative, m. p. 120° (*dihydrate*, m. p. 83°). After reduction of the mixture of 4- and 5-nitro-compounds obtained by nitration of 1-methylbenzoxazole (Newbery and Phillips, *loc. cit.*) only the pure 5-amino-derivative separates (64% yield). Reduction of 5-nitro-2-acetamidophenol with boiling dilute acetic acid and iron powder affords the corresponding 5-amino-compound (*hydrochloride*), but fails with 2-nitro-4-acetamidophenol, whilst reduction of 3-nitro-4-acetamidophenol with activated aluminium and 90% alcohol gives a 30% yield of the 3-amino-compound, isolated as its *hydrochloride*. Ethyl chloroformate and sodium hydroxide convert 5-nitro-2-aminophenol into 5-*nitro*-2-*carbethoxylaminophenol*, m. p. 170°, reduced by alkaline sodium hyposulphite to the 5-*amino*-derivative, m. p. 129° (*acetyl* derivative, m. p. 233°). Application of the Bart reaction (action of copper arsenite on the diazotised amino-compound) to either the aminobenzoxazoles or the corresponding acetamidophenols affords the *o*-aminophenolarsinic acids, of which 4-*carbethoxylamino*-3-*hydroxyphenylarsinic acid* is new. J. W. BAKER.

Oxidation of leucomethylene-blue. A. REID (Biochem. Z., 1930, 228, 487—490; cf. A., 1930, 1381).—During the catalytic oxidation of leucomethylene-blue by copper, hydrogen peroxide is produced. It follows that the appearance of hydrogen peroxide during the oxidation of an organic substance gives no indication as to whether the process is a direct autoxidation or an oxidation in which a heavy metal is involved as oxygen carrier. The oxidation of leucomethylene-blue which takes place in the presence of proteins and is a surface phenomenon not appreciably influenced by the presence either of heavy metals or of substances such as carbon monoxide or hydrogen cyanide (which form complex compounds with heavy metals) also results in the production of hydrogen peroxide. W. MCCARTNEY.

Sparteine. P. KARRER, B. SHIBITA, A. WETTSTEIN, and L. JACUBOWICZ (Helv. Chim. Acta, 1930, 13, 1292—1308).—Sparteine methiodide when converted into the methohydroxide and distilled yields demethylsparteine, $C_{15}H_{25}N_2Me$, b. p. 170—172°/11 mm. (this and the compounds derived from it are probably mixtures of isomerides), reduced by hydrogen in presence of platinum and hydrochloric acid to *dihydromethylsparteine*, b. p. 176—181°/9 mm. This reacts with methyl iodide in benzene at 100° forming a *methiodide hydriodide* convertible into *dihydrodedimethylsparteine*, b. p. 174—182°/8·5 mm., and thence into tetrahydrodimethylsparteine. Four-fold repetition of the above process affords a *pentadecane*, b. p. 242°/729 mm., $d_4^{18.7}$ 0·7740, n_D^{20} 1·43304, which might be δ-methyl-ζ-propyl-*n*-undecane, ζ-propyl-*n*-dodecane, or ζ-methyl-η-ethyl-*n*-dodecane, assuming that one of the formulæ previously proposed for sparteine (A., 1929, 200) is correct. These hydrocarbons have been synthesised for comparison with the above pentadecane.

Ethyl *n*-amylmalonate is converted by the usual methods into *methyl*-n-*amylmalonic acid*, m. p. 104° (*ethyl* ester, b. p. 130—132°/12 mm.), and thence into α-*methylheptoic acid*, b. p. 121—122°/13 mm. Zinc diethyl and α-methylheptoyl chloride give *ethyl* α-*methylhexyl ketone*, b. p. 191—193°/728 mm., which with magnesium *n*-amyl bromide affords *ethyl*-n-*amyl*-α-*methylhexylcarbinol*, b. p. 140—141°/10 mm. Dehydration of this with oxalic acid furnishes an *olefine*, $C_{15}H_{30}$, b. p. 236—237°, $d_4^{22.6}$ 0·7889, $n_D^{23.6}$ 1·44195, reduced by hydrogen in presence of platinum and acetic acid to ζ-*methyl*-η-*ethyl*-n-*dodecane*, b. p. 240—242°/729 mm., $d_4^{21.9}$ 0·7769, n_D^{21} 1·43545. Oxidation of propyl-*n*-hexylcarbinol with chromic oxide in

acetic acid yields propyl *n*-hexyl ketone, b. p. 201—203°/726 mm., 87—89°/11 mm. (*semicarbazone*, m. p. 51—52°), which with an excess of magnesium *n*-amyl bromide affords mainly an *olefine*, $C_{15}H_{30}$, b. p. 239—241°, $d_4^{18.2}$ 0·7825, $n_D^{18.2}$ 1·44336. Catalytic reduction of this gives ζ-*propyl*-n-*dodecane*, b. p. 241—243°/730 mm., $d_4^{18.6}$ 0·7729, n_D^{20} 1·43277. β-Bromopentane and ethyl sodiomalonate furnish the *ethyl* ester, b. p. 120—121°/11 mm., of β-*methylpentane-αα-dicarboxylic acid*, m. p. 92—93°, which when heated passes into β-methylhexoic acid, b. p. 207—209°/728 mm. The chloride of this reacts with zinc propyl iodide in toluene, forming *propyl* β-*methylamyl ketone*, b. p. 192—193°/715 mm. The carbinol from this and magnesium *n*-amyl bromide is dehydrated by potassium hydrogen sulphate at 200° to an *olefine*, $C_{15}H_{30}$, b. p. 236°/725 mm., $d_4^{19.5}$ 0·7805, $n_D^{19.5}$ 1·44215, reduced catalytically to δ-*methyl*-ζ-*propyl*-n-*undecane*, b. p. 235—236°/727 mm., $d_4^{18.6}$ 0·7733, n_D^{20} 1·43262.
H. BURTON.

Alkaloid from *Anona reticulata*, Linn. A. C. SANTOS (Philippine J. Sci., 1930, **43**, 561).—Alcohol extraction of the trunk bark affords, after removal of phenolic bases, about 0·03—0·04% of an *alkaloid*, $C_{17}H_{16}O_3N$ (one methylenedioxy-group), m. p. 122—123°, $[\alpha]^{32.5}$ −83·01° in chloroform (*hydrochloride*; *chloroplatinate*). The name *anonaine* is suggested to distinguish the alkaloid from others occurring in *Anona* species (cf. Callan and Tutin, A., 1912, ii, 81; Trimurti, J. Ind. Inst. Sci., 1924, **7**, 232).
R. CHILD.

Alkaloids of *Berberis Thunbergii*, D.C. var. *Maximowiczii*, Franch. I. H. KONDO and M. TOMITA (Arch. Pharm., 1930, **268**, 549—559).—The acidified aqueous solution of the alcoholic extract of the root contains the following tertiary bases, which are precipitated by ammonia: (*a*) oxyacanthine (Späth, A., 1929, 1319; von Bruchhausen and Scholtze, A., 1930, 98) (*methyl ether hydrochloride*, m. p. 261°); (*b*) a *substance*, m. p. 207—209°, but identical in all other respects with oxyacanthine; (*c*) berbamine (Santos, Diss., Westfäl. Univ., Münster, 1929) (*methyl ether hydrochloride*, m. p. 264°), which has an absorption spectrum almost identical with that of oxyacanthine, and (*d*) oxyberberine, now found for the first time in nature. After removal of berberine as hydrochloride, the following quaternary bases were precipitated as iodides and separated after reduction to their tetrahydro-derivatives: *shobakunine* (*iodide*, m. p. 204—206°), isolated as *tetrahydroshobakunine*, $C_{16}H_{11}O(NMe)(OMe)_3$, m. p. 140° (*hydrochloride*, m. p. 242°; *methiodide*, m. p. 253°), jatrorrhizine, and a trace of columbamine.
H. E. F. NOTTON.

Resolution of tetrahydropalmatine and tetrahydroberberrubine into their optically active components. E. SPÄTH and W. LEITHE (Ber., 1930, **63**, [*B*], 3007—3012).—When treated with the equivalent amount of *d*-tartaric acid in alcohol, *dl*-tetrahydropalmatine yields d-*tetrahydropalmatine hydrogen* d-*tartrate*, from which *d*-tetrahydropalmatine, m. p. 141—142°, $[\alpha]_D^{20}$ +291° in alcohol, identical with the natural base, is readily obtained. The mixture of residual bases when treated with *l*-tartaric acid yields the *l*-base hydrogen *l*-tartrate, from which *l*-tetrahydropalmatine, m. p. 141—142°, $[\alpha]_D^{20}$ −294° in alcohol, is derived.

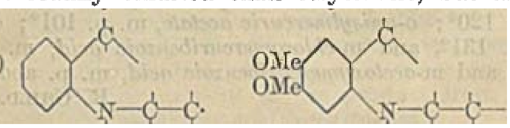
dl-Tetrahydroberberrubine, m. p. 187—188° (ethyl ether, m. p. 128°), is resolved into components by means of ammonium *d*-α-bromocamphor-π-sulphonate in alcohol and dilute acetic acid; the salt of the *d*-base separates more rapidly than that of the *l*-base. d-*Tetrahydroberberrubine* has m. p. 195—196°, $[\alpha]_D^{15}$ +303° in chloroform, +298° in ethyl alcohol, whereas the l-*base* has m. p. 195—196°, $[\alpha]_D^{15}$ −304° in chloroform. The mixture of equal amounts of the *d*- and *l*-base has m. p. 186°. These results are not in harmony with the observations of Kitasato (A., 1927, 1094).
H. WREN.

Quinoline derivatives. XVIII. Quitenine. H. JOHN [with E. ANDRASCHKO] (J. pr. Chem., 1930, [ii], **128**, 223—228).—The following derivatives of quitenine (Skraup, A., 1889, 626) are described: *quitenine chloride* (from quitenine and thionyl chloride), m. p. 206°; quitenine methyl ester, m. p. 217° (by esterification with methyl alcohol and sulphuric acid) (Goodson and others, A., 1930, 1310, give m. p. 170°); quitenine ethyl ester, m. p. 198° (Bucher, A., 1894, i, 152, gives m. p. 198°; Goodson, *loc. cit.*, gives m. p. 201°); and *quiteninehydrazide* (from the last-named and hydrazine hydrate), m. p. 236° (*benzylidene*, m. p. 179°, and *methylbenzylidene*, m. p. 223°, derivatives). Treatment of the hydrazide with cold aqueous sodium nitrite gives the azide (not isolable), which is transformed by water into NN′-*bis-quitenylcarbamide*, m. p. 154°.
R. CHILD.

***Strychnos* alkaloids. LVII. Oxidation of tetrahydrostrychnine and certain derivatives.** H. LEUCHS [with, in part, F. KROHNKE] (Ber., 1930, **63**, [*B*], 3184—3189).—Oxidation of tetrahydrostrychnine with chromic acid and dilute sulphuric acid at 20° affords a mixture of a *substance*, $C_{17}H_{20}O_4N_2$, m. p. 243—245° (decomp.) after softening at 230° (*perchlorate*, dihydrate and anhydrous, $[\alpha]_D^{15}$ +73·8°/*d* for the anhydrous salt), and an amino-acid, $C_{21}H_{22}O_4N_2,4H_2O$, not molten below 300° (*hydrochloride*, $[\alpha]_D^{15}$ −24·0°/*d*; *hydrobromide*). In the amino-acid the benzene nucleus of the base appears to persist unchanged. *ON*-Diacetyltetrahydrostrychnine, when similarly oxidised, loses the *O*-acetyl group and yields an *amino-acid*, $C_{23}H_{26}O_4N_2$, decomp. 305° after softening at 180—200° and foaming at 220° (*perchlorate*, $[\alpha]_D^{20}$ −118·5°/*d* in water). The amino-acid is obtained in better yield from the *N*-monoacetyl derivative. The following observations are incidental: *strychnidine hydroperchlorate*, $[\alpha]_D^{17}$ −10·1°/*d* in water, and *hydrochloride*, $[\alpha]_D^{15}$ −13·5°/*d* in 0·1*N*-hydrochloric acid; *tetrahydrostrychnine hydroperchlorate*, $[\alpha]_D^{15}$ −74·9°/*d*, and *hydrochloride*, $[\alpha]_D^{15}$ −86·6°/*d*; N-*monoacetyltetrahydrostrychnine*, m. p. 157—159°, or m. p. 197—199° after desiccation (*hydroperchlorate*, $[\alpha]_D^{15}$ +104°/*d*; *hydrochloride*, $[\alpha]_D^{16}$ +122·3°/*d*); *diacetyltetrahydrostrychnine*, as mixture of anhydrous and hydrated compounds (*hydroperchlorate*); *dibromotetrahydrostrychnine*, $C_{21}H_{24}O_2N_2Br_2$, m. p. 248—250° (decomp.) after softening at 238° (*hydrobromide*; *hydrochloride*, $[\alpha]_D^{15}$ −23·2°/*d*).
H. WREN.

Constitution of *Strychnos*, yohimbe, and quebracho alkaloids. E. SPÄTH and H. BRET-

SCHNEIDER (Ber., 1930, **63**, [*B*], 2997—3006).—Strychnine in alkaline solution is treated on the water-bath with potassium permanganate until the latter substance is only slowly consumed. The acids thus produced are separated by their differing acidity and from one fraction *N*-oxalylanthranilic acid, decomp. 202—203° (methyl ester, m. p. 152°), is obtained; thermal decomposition of the normal potassium salt affords anthranilic acid. Examination of the product obtained by Warnat (A., 1926, 1263) by the oxidation of yohimboaic acid proves its identity with *N*-oxalylanthranilic acid; Warnat's acid and its methyl ether have the compositions $C_9H_7O_5N$ and $C_{11}H_{11}O_5N$, instead of $C_8H_7O_4N$ and $C_{10}H_{11}O_4N$ as recorded. The products of the decomposition of yohimbine and the specific rotation of the base and of the acid derived therefrom coincide almost completely with Hahn's data (A., 1930, 1194) for quebrachin. Oxidation of the acid derived from quebrachin hydrochloride affords *N*-oxalylanthranilic acid. Great similarity is therefore observed at any rate in one portion of the molecular structure of strychnine and of the yohimbe and quebracho alkaloids with the ring system of yohimbol. In them the ring system I must be present in a quinoline or an indole ring. Brucine is more readily oxidised than strychnine, but affords

(I.)  (II.)

N-oxalyl-4 : 5-*dimethoxyanthranilic acid*; the alkaloid therefore contains the complex II.

Methyl hydrogen N-*oxalyl*-4 : 5-*dimethoxyanthranilic acid*, m. p. 230—232° (decomp.) after softening at 229°, is prepared by heating methyl 6-aminoveratrate with anhydrous oxalic acid in a vacuum at 110—140°; the *dimethyl* ester has m. p. 206—207°.

H. WREN.

Oxonitine. E. SPATH and F. GALINOVSKY (Ber., 1930, **63**, [*B*], 2994—2997).—Oxonitine, m. p. 277—278° (vac. decomp.), $[\alpha]_D$ —48° in chloroform, has the formula $C_{32}H_{43}O_{12}N$ and contains the four methoxyl groups present in aconitine. The composition is greatly confirmed by determination of the benzoyl groups in oxonitine and aconitine. This is effected by hydrolysis of the compounds followed by acidification and extraction of the liberated benzoic acid by ether. The acid is sublimed at 130—150°/10 mm. and weighed.

Reply is made to Akabori and Saito (A., 1930, 1445).

H. WREN.

M. p. of pure yohimbine. K. WARNAT (Ber., 1930, **63**, [*B*], 2959—2961).—Contrary to Hahn and Schuch (A., 1930, 1194), pure yohimbine has m. p. 234—235°; the preparation of Hahn and Schuch was probably contaminated with α-yohimbine, from which it is not readily separated by fractional crystallisation.

H. WREN.

Identity of α-yohimbine with *iso*yohimbine. G. HAHN and W. SCHUCH (Ber., 1930, **63**, [*B*], 2961—2962; cf. Warnat, preceding abstract).—The α-yohimbin of Lillig and Kreitmair (Merck's Jahresber., 1928, 20) and Hahn and Schuch (A., 1930, 1194) is not identical with the *iso*yohimbine of Hahn and Schuch (*loc. cit.*).

H. WREN.

Alkaloids of *Sinomenium* and *Cocculus*. XXIX. Dauricine. H. KONDO and Z. NARITA. **XXX. Alkaloids of *Cocculus sarmentosus*, Diels.** H. KONDO and M. TOMITA (J. Pharm. Soc. Japan, 1930, **50**, 589—593, 633—644).—XXIX. Treatment of dauricine with methyl-alcoholic alkali and ethyl bromide affords *ethyldauricine ethobromide*, decomp. 136—139° (*platinum* salt, decomp. 215—218°), which, with 20% potassium hydroxide solution, gives α-*ethyldauricinethylmethine* (*methiodide*, decomp. 162—165°). The methiodide, when treated with potassium hydroxide, afforded a substance oxidisable to an acid, m. p. 276—279°, not identical with 4-methoxy-3 : 4′-diphenyl ether 1 : 1′-dicarboxylic acid, m. p. 312°. The corresponding ethoxy-acid has m. p. 276—279°. The formula

$OMe{\cdot}C{:}CH{\cdot}C{\cdot}CH_2{\cdot}CH_2{\cdot}NMe$

$OH{\cdot}C{:}CH{\cdot}C$——————$CH{\cdot}CH_2{\cdot}C_6H_4{\cdot}OMe$ is proposed for dauricine.

XXX. *Menisarine*; m. p. 203° [*gold* salt, decomp.; *platinum* salt, decomp. 304°; *hydrochloride*, decomp. 279°; *hydrobromide*, $C_{37}H_{38(36)}O_6N_2,2HBr,2H_2O$, decomp. 285°; *methiodide*, decomp. 269—270°; *acetyl* derivatives: $OAc{\cdot}C_{37}H_{37(35)}O_5N_2$, m. p. 141°; $(OAc)_3C_{37}H_{35(33)}O_3(.NAc_3)_2(OAc)_2$, m. p. 105], when reduced by zinc in acid solution gave a *compound* $C_{37}H_{40(42)}O_6N_2$, m. p. 162°, and when treated with methyl sulphate followed by potassium iodide afforded the *compound* $C_{34}H_{28(26)}O_2N_2(OMe)_4,2MeI$ m. p. 252—263°. The structure of menisarine is discussed.

CHEMICAL ABSTRACTS.

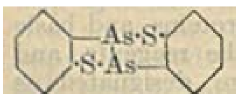
Identification of alkaloids by precipitation. I. Natural classification of alkaloids based on precipitation. C. C. FULTON (J. Assoc. Off. Agric. Chem., 1930, **13**, 491—497).—The usual reagents are compared with phosphomolybdic acid as a standard precipitant and are classified according as their sensitivities with a particular alkaloid are equal to, or less than, that of phosphomolybdic acid. The alkaloids may be arranged similarly, according to their sensitivity towards precipitating agents, but to avoid inconsistencies they are classified in groups. The nine groups embrace amines, proteins, and basic dyes, which are precipitable by the reagents, and the remaining alkaloid classes are designated as the caffeine, aniline-pyridine, atropine, cotarnine, quinine, and narcotine classes. The classification corresponds with the data of precipitation from 2% solutions and with the solubility in water and the basic strength of the free alkaloids. The concentrations of the solutions never exceed 1 : 1000, and a few mg. of the alkaloid suffice for the classification and tentative identification.

H. J. DOWDEN.

Microchemical detection of alkaloids in plants. XIV. Cytisine. G. KLEIN and E. FARKASS (Oesterr. Bot. Z., 1930, **79**, 107—124; Chem. Zentr., 1930, ii, 1257—1258).—The most sensitive and characteristic reaction for cytisine is that of Bertheaumé employing potassium tri-iodide which gives rosettes of dark brown prisms. The distribution of cytisine in *Laburnum anagyroides* and its presence in 15 *Papilionaceæ* is recorded. Cytisine does not appear to be identical with ulexine. Laburnum contains thiocarbamide.

A. A. ELDRIDGE.

Aromatic arsenic compounds containing sulphur groups attached to the nucleus. II. Thiocyano- and disulphido-groups. H. J. Barber (J.C.S., 1930, 2725—2729).—Diazotisation of 4-aminophenylarsinic acid and subsequent treatment with a solution of cuprous thiocyanate containing potassium thiocyanate gives a 30% yield of 4-*thiocyanophenylarsinic acid*, converted by boiling 2*N*-sodium hydroxide into an amorphous substance which when oxidised in sodium hydrogen carbonate suspension with iodine in potassium iodide gives diphenyl disulphide-4 : 4′-diarsinic acid (King and others, A., 1926, 851). 2-*Thiocyanophenylarsinic acid* is similarly prepared and converted into *diphenyl disulphide*-2 : 2-*diarsinic acid*, which is also obtained, contaminated somewhat with the disulphoxide from 2-sulphinophenylarsenious oxide (A., 1930, 1456), by mild reduction with boiling alcoholic sulphur dioxide containing a little hydrogen iodide, or with very dilute sulphuric-hydriodic acid solution at 95°, followed by oxidation of the arsinoxide to the arsinic acid. It is suggested that the thiol group formed by hydrolysis of either the thiocyano- or disulphido-group reacts with the arsinic acid group as follows : $R{\cdot}AsO_3H_2+4R'SH=RAs(SR')_2+R'{\cdot}S{\cdot}S{\cdot}R'+3H_2O$, thus giving a complex intramolecular thioarsinite of the type $[{-}S{\cdot}C_6H_4{\cdot}As(S{\cdot}C_6H_4{\cdot}As{<})_2]_n$, which regenerates the disulphide arsinic acid on oxidation. It is considered very improbable that the thiol group would remain intact under the conditions used by Krishna and Krishna (A., 1929, 1320) for the supposed preparation of 4-thiolphenylarsinic acid. 3-Nitro-4-aminophenylarsinic acid is similarly converted by diazotisation and potassium cuprothiocyanate into 3-*nitro*-4-*thiocyanophenylarsinic acid*, which loses its sulphur group when hydrolysed with 2*N*-sodium hydroxide, yielding only tarry material. Reduction of 2-sulphinophenylarsenious oxide in hot glacial acetic acid with hypophosphorous acid (*d* 1·14) and potassium iodide, with sodium hyposulphite, or with zinc and hydrochloric acid gives a *substance*, m. p. 177—178°, to which the annexed structure is assigned; it is



also obtained by similar reduction of the 2 : 2′-disulphide- or 2-thiocyanophenyl-arsinic acid. It is stable to boiling alkali, is slowly oxidised by iodine in sodium hydrogen carbonate suspension to the disulphide-arsinic acid, and rapidly to 2-sulphophenylarsinic acid by concentrated nitric acid. J. W. Baker.

Aromatic boron compounds and arylmercuric salts derived therefrom. W. König and W. Scharrnbeck (J. pr. Chem., 1930, [ii], 128, 153—170).—A series of arylboric acids has been prepared by the interaction of *iso*butyl borate and the appropriate Grignard reagent (cf. Khotinsky and Melamed, A., 1909, i, 864) for investigation of their trypanocidal activity; certain of the acids have considerable activity *in vitro*, but are unsuitable for chemotherapeutic application owing to the ease of hydrolytic fission of the boric acid residue from the aromatic nucleus. The following new acids are described and revised m. p. recorded : p-*bromophenyl*-, m. p. 266° (*oxide*, m. p. 280°), o-*chlorophenyl*-, m. p. 149°, o-anisyl-, m. p. 105° (Michaelis and others, A., 1894, i, 190, give 165°), m-*anisyl*-, m. p. 147° (*oxide*, m. p. 159°), *o*-tolyl-, m. p. 168° (*loc. cit.*, 161°), m-*tolyl*-, m. p. 157° (Khotinsky, *loc. cit.*, 137—140°), and α-naphthyl-boric acid, two modifications, m. p. 248° and 266°, respectively (Michaelis, *loc. cit.*, 259°). The borobenzoic acids, $CO_2H{\cdot}C_6H_4{\cdot}B(OH)_2$, are obtained by oxidation of the corresponding tolylboric acids (Michaelis and Richter, A., 1901, i, 355) : o-*borobenzoic acid*, m. p. 152°, and m-*borobenzoic acid*, m. p. 240° (basic *lead* salt, $C_{14}H_{12}O_{10}B_2Pb_3$; normal *barium* salt; *silver* salt of "pyro"-acid, $C_{14}H_8O_7Ag_4B_2$). Diarylboric acids, $Ar_2B{\cdot}OH$, are formed as by-products in the preparation of the arylboric acids, or, better, by the use of 2 mols. of the Grignard reagent; diphenylboric acid, b. p. 150—155°/20 mm., m. p. 57·5° (Michaelis, *loc. cit.*, gives b. p. 215—235°/17 mm.), *di*-p-*anisyl*-, m. p. 107°, *di*-p-*bromophenyl*-, m. p. 113°, and *di*-β-*naphthyl-boric acid*, b. p. 135—138°/14 mm., m. p. 172°.

Mercuric salts readily displace the boric acid residue with formation of corresponding arylmercuric salts, of which the following are new : p-*bromophenylmercuric chloride*, m. p. 235°, and *acetate*, m. p. 188°; o-*chlorophenylmercuric chloride*, m. p. 133°; m-*anisylmercuric chloride*, m. p. 158°, and *acetate*, m. p. 120°; o-*anisylmercuric acetate*, m. p. 101°; o-, m. p. 131°, and m-*chloromercuribenzoic acid*, m. p. 258°, and m-*acetoxymercuribenzoic acid*, m. p. above 310°. R. Child.

Formation of a heterocyclic ring closed through mercury atoms. II. L. Vecchiotti and M. Panciera (Gazzetta, 1930, 60, 904—909; cf. A., 1929, 203).—By heating *o*-dibromobenzene at 120° with 2% sodium amalgam in petroleum solution a *substance*, C_6H_4Hg, which does not melt even at 300°, was obtained. From its chemical behaviour it probably has the structure $C_6H_4{<}{}^{Hg}_{Hg}{>}C_6H_4$. O. J. Walker.

Bis-*p*-phenetyl telluride and its derivatives. G. T. Morgan and F. H. Burstall (J.C.S., 1930, 2599—2601).—By the action of magnesium *p*-ethoxyphenyl bromide on tellurium dibromide in ether is obtained *bis*-p-*phenetyl telluride*, R_2Te ($R=p\text{-}EtO{\cdot}C_6H_4{\cdot}$), m. p. 64°, converted by chlorine in carbon tetrachloride into the corresponding telluridichloride, R_2TeCl_2, identical with the specimen previously obtained by Morgan and Drew (A., 1926, 83). The original constitution assigned to the dichloride is thus confirmed, despite the contrary evidence of parachor measurements (Burstall and Sugden, A., 1930, 399), which suggested that it was a nuclear-substituted telluride. The telluridichloride is converted by boiling water into the corresponding *tellurioxychloride*, $(R_2TeCl)_2O$, decomp. 193°, and by boiling 2*N*-aqueous alkali into the *telluroxide*, R_2TeO. *Bis*-p-*phenetyl telluri-dibromide*, m. p. 127°, and -*di-iodide*, m. p. 144°, are obtained similarly. Concentrated nitric acid converts these three tellurihalides into *o*-halogenated-*p*-nitrophenetoles, the yield being greatest with the di-iodide. p-*Anisyl*-p-*phenetyl telluridichloride*, m. p. 165—166°, prepared by heating *p*-phenetyl telluritrichloride with 4 mols. of anisole

at 100°, is reduced by zinc dust and glacial acetic acid to p-*anisyl* p-*phenetyl telluride*, m. p. 45°.

J. W. BAKER.

Clupein. II. K. FELIX and A. LANG (Z. physiol. Chem., 1930, **193**, 1—14; cf. A., 1929, 1322).—Trypsin-kinase was allowed to act on clupein hydrochloride *B* at p_H 8·4 until no further action occurred. The enzyme was then destroyed and the solution hydrolysed with intestinal erepsin at 7·8. The trysin-kinase hydrolysis liberated 4 mols. of arginine, 6 amino-groups, and 6 acid equivalents; the erepsin set free 4 arginine mols., 4 amino-groups, and 5 acid equivalents. Four of the amino-groups and four acid equivalents in the first hydrolysis belong to the arginine. The two remaining amino- and acid groups may belong to the unhydrolysed portion, or to monoamino-acids. The clupein molecule appears to be built symmetrically from two similar halves, one of these being hydrolysed by trypsin-kinase.

J. H. BIRKINSHAW.

Sphingomyelin. W. MERZ (Z. physiol. Chem., 1930, **193**, 59—87).—Cerebroside-free sphingomyelin preparations with P : N ratio of 2 : 1 were obtained from human brain. Sphingomyelin on catalytic hydrogenation furnishes *hydrosphingomyelin*, $[\alpha]^{20}$ +12·85°; the latter on acetylation forms *monoacetylhydrosphingomyelin*, various fractions of which were hydrolysed. Stearic, lignoceric, and nervonic acids were obtained, showing that there are three sphingomyelins present in the product from brain, differing in their fatty acid constituents.

J. H. BIRKINSHAW.

***d*-α-Aminonorvaleric acid (norvaline) as a constituent of proteins.** E. ABDERHALDEN and F. REICH (Z. physiol. Chem., 1930, **193**, 198—200).—*d*-Norvaline was obtained from the products of acid hydrolysis of caseinogen. J. H. BIRKINSHAW.

"Acetyl bases" from proteins. N. TROENSEGAARD, F. WREDE, and H. G. MYGIND (Z. physiol. Chem., 1930, **193**, 49—55).—Two crystalline acetyl bases were obtained from the syrupy mixture formed by the acetolysis of proteins (cf. A., 1926, 634); *base A*, $C_{10}H_{14}O_2N_2$, isolated as the *chloroaurate*, m. p. 193° (darkens at 175°), and *base B*, $C_9H_{11}ON_3$ (*chloroaurate*, m. p. 184° (decomp.); *chloroplatinate*, blackens at 260°; m-*nitrobenzoyl* derivative, m. p. 185°). The bases were obtained from serum-globulin, serum-albumin, globin, fibrin, and caseinogen. Gliadin yielded only base B, silk-fibroin neither base. J. H. BIRKINSHAW.

Fission products of hydrogenated proteins. I. N. TROENSEGAARD and H. G. MYGIND (Z. physiol. Chem., 1930, **193**, 171—180).—In addition to the bases described above, there were isolated piperidine, *iso*amylamine, and two bases yielding crystalline derivatives from the acetolysis of proteins and reduction of the acetyl products: *base*, $C\ H_{22}N_2$: *picrate* (A_2B), decomp. 231°; *chloroaurate*, m. p. 197° (decomp.); *reineckate*, m. p. 185°; *base*, $C_{14}H_{22}N_2$: *styphnate* (A_2B), m. p. 234° (decomp.); *chloroaurate*, m. p. 197° (decomp.); *chloroplatinate*, m. p. 257° (decomp.); *picrate*, m. p. 242° (decomp.). All m. p. are uncorr. Both new bases were obtained from gliadin and caseinogen, and $C_{14}H_{22}N_2$ from globin in addition. J. H. BIRKINSHAW.

Constitution of soluble proteins. (Reversibly dissociable component systems.) S. P. L. SORENSEN (Compt. rend. Trav. Lab. Carlsberg, 1930, **18**, No. 5, 1—124, and Kolloid-Z., 1930, **53**, 306—318; cf. this vol., 38).—The conception of proteins as reversibly dissociable component systems is discussed with reference to experimental data on the fractionation and solubility of egg-albumin, horse-serum-albumin, horse-serum-globulin, casein, and wheat gliadin (published by the author and his colleagues during the past 13 years) and to modern views (Meyer, Staudinger) on the structure of high-molecular substances. Svedberg's work on the determination of mol. wt. of proteins is discussed. The necessity of discriminating between reversible dissociation and true protein scission is emphasised. H. BURTON.

Glutelins. VI. Optical rotations of glutelins from wheat, rye, barley, maize, and rice. F. A. CSONKA, M. J. HORN, and D. B. JONES (J. Biol. Chem., 1930, **89**, 267—273).—The following values for $[\alpha]^{20}$ in 0·5*M*-sodium hydroxide solution were obtained: wheat α-glutelin −85·1°, wheat β-glutelin −76·6°, rye glutelin −81·2°, barley α-glutelin −111·1°, maize α-glutelin −72·6°, rice glutelin −65·1°. The curves representing the course of racemisation of gliadin and of the glutelins of wheat in 0·5*M*-sodium hydroxide solution at 38° are hyperbolic.

C. R. HARINGTON.

Structure of the polypeptide associates obtained from gelatin and gelatin-peptone by means of acetic anhydride. VII, VIII. A. FODOR and C. EPSTEIN (Biochem. Z., 1930, **228**, 310—314, 315—326).—VII. Results obtained from the examination of other fractions confirm in the main the conclusions formerly reached (A., 1930, 1197). The procedure of Frankel and Kuk (*ibid.*, 1198) has been adopted.

VIII. The glycerol-soluble product obtained when gelatin is heated with glycerol (cf. A., 1928, 1387) has been treated with acetic anhydride and the products formed have been separated by fractional precipitation. Consideration of the mol. wt. of the purified materials and of their other properties leads to the conclusion that the gelatin molecule consists of associations of comparatively simple polypeptides. Peptides formed from more than six amino-acids are probably not present in the molecule. W. McCARTNEY.

Fine structure of gelatin micelle. O. GERNGROSS, K. KERRMANN, and W. ABITZ (Biochem. Z., 1930, **228**, 409—425).—From the examination of Röntgen diagrams of unstretched, stretched, and swollen gelatin and collagen, conclusions which satisfactorily explain the properties of the substances are reached regarding the ways in which the constituent amino-acids of the proteins are combined and grouped. The so-called crystalline and amorphous constituents of the substances probably differ only in the way in which they are arranged and not in their forms. The structure of collagen is very similar to that of gelatin.

W. McCARTNEY.

Determination of amino-acids formed by hydrolysis of proteins. III. Application of the processes of esterification and acetylation to the

hydrolysis products of proteins. E. CHERBULIEZ, P. PLATTNER, and S. ARIEL (Helv. Chim. Acta, 1930, **13**, 1390—1402).—The protein is hydrolysed by hydrochloric (or sulphuric) acid, the hydrolysate neutralised with sodium (or barium) hydroxide, and cystine and tyrosine are allowed to crystallise. The filtrate is made alkaline, evaporated in a vacuum to remove ammonia, the residue acidified, the residual amino-acids are esterified by Fischer's method, and the esters acetylated by the method previously described (A., 1929, 685). The acetylated esters are extracted with chloroform and freed from resinous material by adding the concentrated extract to much ether; the resins are thereby precipitated, and this material is subjected to the esterification–acetylation process and again separated into esters and resin. The residue from the ethereal extract is then fractionally distilled and the various esters are hydrolysed by 20% hydrochloric acid. When an appreciable residue remains after distillation, it is subjected to the above process and redistilled. The esters of acetylated diamino-acids do not distil; in some cases the diamino-acids are removed from the hydrolysate first. The above method, with slight modifications, is illustrated by analyses of serum-albumin, casein, and silk fibroin. The results indicate that it is the best method of analysis. H. BURTON.

Micro-sublimation. A. CHALMETA (Anal. Fís. Quím., 1930, **28**, 1407—1419).—An account is given of the application of micro-sublimation methods to the identification of small quantities of material, and especially of caffeine and theobromine in pharmaceutical and other products. The sensitivity of the method is dependent on the content in the mixture under examination, but quantities of 7×10^{-6} g. may be detected with certainty. Precipitation reactions suitable for the identification of sublimates of caffeine and theobromine which are too small for their recognition under the microscope are described. In certain cases glucosides may be identified by examination of the sublimates obtained after hydrolysis. H. F. GILLBE.

Volumetric determination of methoxyl and ethoxyl groups. F. VIEBOCK and C. BRECHER (Ber., 1930, **63**, [*B*], 3207—3210).—The method described previously (this vol., 107) is adapted to microchemical analysis. H. WREN.

Determination of alanine. A. I. KENDALL and T. E. FRIEDEMANN (J. Infect. Dis., 1930, **47**, 171—175).—Lactic acid resulting from interaction of alanine and nitric acid is determined after interfering substances have been removed with copper sulphate and calcium hydroxide. CHEMICAL ABSTRACTS.

New reactions of creatine and creatinine. J. A. SANCHEZ (Semana Méd., 1930, II, 616—617).—(1) The solution (1 c.c.) of creatinine (1 in 10^4) is treated with 1 drop of silver nitrate solution and 1 drop of sodium hydroxide solution and is heated at 100°; the unreduced silver oxide is dissolved in a drop of acetic acid, and a drop of ammonia solution is added, a comparison of the volume of the silver being employed to determine the creatinine. (2) Creatinine (0·02—0·03 g.) is boiled with water (2 c.c.) and mercuric oxide (0·05 g.); resorcinol (0·05 g.) is dissolved in the decanted liquid, 2 c.c. of sulphuric acid then being added without mixing. A blue colour, dependent on the formation of oxalic acid, is formed at the interface. (3) Creatinine forms cinnamon-red crystals with Dragendorff's reagent. CHEMICAL ABSTRACTS.

Determination of quinine, cinchonine, and cinchonidine with the quinhydrone electrode, and the choice of end-points in alkaloid titrations. E. B. R. PRIDEAUX and F. T. WINFIELD (Analyst, 1930, **55**, 561—565).—Since the changes in p_H during neutralisation of the alkaloid bases have been determined either colorimetrically or by the hydrogen electrode, the dissociation constants may be calculated and the values of p_H at the end-point (the titration exponent p_T) deduced. The p_T of the chosen indicator should be as near as possible to that of the base hydrochlorides etc. For strong monoacid bases (k—1×10^{-3} to 10^{-4}), *e.g.*, piperidine, coniine, berberine, hydrastine, any ordinary indicator changing at p_H 7·0—5·0 may be used. For weaker monoacid bases ($k=1\times10^{-5}$ to 10^{-6}) methyl-red is best (excepting atropine, cocaine, tropacocine). Diacid alkaloids having k_1 about 1×10^{-6} and k_2 1×10^{-8} or less have their titration exponents calculated differently and show important differences to the monoacid bases. Bromocresol-purple is a suitable indicator, or if an alcoholic solution is necessary bromophenol-blue gives good results for brucine or strychnine. Nicotine and quinine belong to this class. The quinhydrone electrode offers many advantages and the titration is best carried out by dissolving the base in a known excess of standard acid and titrating back. Details are given for titration of quinine (0·05, 0·01, and 0·005*M* solutions), cinchonine (0·002), and cinchonidine (0·100 and 0·002-*M* solutions). Dilute conchonine and cinchonidine (0·002*M* solutions) should be titrated with ethyl-red as well as methyl-red. D. G. HEWER.

Biochemistry.

Determination of oxygen and carbon monoxide in blood. J. SENDROY, jun., and S. H. LIU (J. Biol. Chem., 1930, **89**, 133—152).—The gases are completely extracted from blood in the apparatus of Van Slyke and Neill (A., 1924, ii, 872) and after absorption of carbon dioxide with sodium hydroxide are transferred to a special absorption pipette containing alkaline pyrogallol to remove the oxygen; the residual mixture of carbon monoxide and nitrogen is returned to the apparatus (in which the blood has in the meantime been replaced by a mixture of glycerol and sodium chloride solution) and the carbon monoxide is determined by absorption with cuprous chloride. The method gives results in good agreement with those obtained by the more complex technique of Van Slyke and Robscheit-Robbins (A., 1927, 475). C. R. HARINGTON.

Origin of chlorophyll and its relation to blood-pigments. II. K. Noack and W. Kiessling (Z. physiol. Chem., 1930, **193**, 97—137; cf. A., 1929, 727).—On reduction with iron and formic acid, methylphæophorbide *a* yields *methylprotophæophorbide*, m. p. 264—265°. Reduction of phæophytin by the same method at 0—5° gives an impure protophæophytin similar to that prepared from pumpkin seeds. The crude product forms *protophytochlorin trimethyl ester*, m. p. 234—235°, on esterification with methyl-alcoholic hydrogen chloride. The same substance is obtained direct from phæophytin by reduction, hydrolysis, and esterification, also from methyl protophæophorbide. The hydrolysis of the trimethyl ester yields pure protophæophorbide.

Phylloerythrin, prepared from ox-bile, on hydrolysis gives phylloerythrincarboxylic acid. The latter with diazomethane yields *phylloerythrin trimethyl ester*, m. p. 230—232°, and with methyl-alcoholic hydrogen chloride the monomethyl ester. Hydrolysis with methyl-alcoholic potassium hydroxide furnishes a *dicarboxylic acid monoester*, which swells at 250—270°. Esterification of the latter gives a *trimethyl* ester, m. p. 210—212°. A *dicarboxylic acid diester* was also obtained. Certain phylloerythrin-like substances were prepared from the protophæophytin series. A reduction product of methylphæophorbide *a* yields a *monomethyl* ester, m. p. 296—298°. A *monomethyl* ester, m. p. 272—274°, was obtained in one case from the preparation of protophæophorbide.

J. H. Birkinshaw.

Maintenance and production of hæmoglobin on synthetic diets. Determination of copper. D. L. Drabkin and C. S. Waggoner (J. Biol. Chem., 1930, **89**, 51—75; cf. A., 1929, 1476).—Rats suffering from nutritional anæmia on a milk diet recovered when transferred to a synthetic diet containing iron but lower in copper content than the milk diet. Nevertheless addition of iron to the latter diet did not prevent the development of anæmia. Previous administration of copper failed to increase the resistance of rats to nutritional anæmia. It is therefore doubted whether copper has any connexion with this type of anæmia.

In using the method of Biazzo (B., 1926, 383) for the determination of copper it is important to remove iron before the stage of development of colour; this is best achieved by addition of sodium pyrophosphate solution. In the potassium ethyl xanthate method (Scott, "Standard Methods of Chemical Analysis," New York, 1917) control of the p_H, which should be maintained near 3·8, is essential.

C. R. Harington.

Crystalline methæmoglobin from horse-blood. M. Levy (J. Biol. Chem., 1930, **89**, 173—183).—The paste of oxyhæmoglobin crystals prepared from horse-blood by the method of Ferry and Green (A., 1929, 338) is diluted with water and either reduced by evacuation and agitation or brought into solution by means of potassium hydroxide, and then oxidised with potassium ferricyanide in 10% excess, when the methæmoglobin crystallises. Alternatively, the oxyhæmoglobin paste is diluted, treated with 10% of alcohol, and kept at 37—38° for 70—80 hrs. Figures are given for the solubilities of the preparations thus obtained in phosphate buffers of varying p_H and ionic strength. Minimum solubility occurs at p_H 6·8. Solutions of methæmoglobin are stable for several weeks at 2—4°, and thermodynamical arguments show that the formation of oxyhæmoglobin in such solutions in presence of oxygen is possible only to a minute extent.

C. R. Harington.

Constitution of proteins of serum and of organs. III. A. Blankenstein and A. Fischer (Biochem. Z., 1930, **228**, 437—442; cf. A., 1930, 1305).—When the proteins in various samples of human, ox-, and horse-serum are separated by fractional precipitation with ammonium sulphate solution it is necessary that this be exactly neutral if comparable results are to be obtained in the analysis of the fractions. The proteins obtained thus from kidneys, liver, and lungs are chemically different from each other and from those derived from serum or musculature.

W. McCartney.

Protein-carbohydrate groupings in plasma of animals. H. Bierry (Compt. rend., 1930, **191**, 1381—1382).—Plasma-proteins are autoclaved with dilute potassium hydroxide solution ($N/3$ or $N/6$) at 120° for ½ hr. and the polysaccharide is precipitated with 8 vols. of spirit. Acid hydrolysis of this material gives *d*-mannose and *d*-galactose.

P. G. Marshall.

Determination of carbon and nitrogen in the total crystalloid substances in blood-serum. A. Boivin (Compt. rend. Soc. Biol., 1930, **103**, 153—155; Chem. Zentr., 1930, ii, 260).—The values obtained with the filtrate from precipitation with sodium tungstate (Folin and Wu) do not differ from those obtained with the ultra-filtrate of the tenfold diluted serum by more than 5%. Increase or decrease of the concentration of sulphuric acid (0·67N) leads to incorrect results.

A. A. Eldridge.

Blood-creatinine. O. H. Gaebler (J. Biol. Chem., 1930, **89**, 451—466).—The previous work (A., 1928, 437) on the isolation of creatinine from protein-free blood-filtrates has been repeated, using, however, magnesium oxide instead of lead hydroxide for the decomposition of the precipitate with Lloyd's reagent. Preliminary treatment of the blood-filtrates with kaolin renders the isolation of creatinine impossible whilst leaving the chromogenic value of these filtrates for Jaffe's reaction unaffected. It therefore appears that blood contains a substance other than creatine or creatinine which yields the latter when the above-mentioned isolation procedure is employed.

C. R. Harington.

Folin's method for determining blood-amino-acids. P. M. Re and D. Potick (Compt. rend. Soc. Biol., 1930, **103**, 1283—1285; Chem. Zentr., 1930, ii, 592).—Folin's method gives accurate results only when the amino-acid does not exceed 5 mg. per 100 c.c. Trichloroacetic acid is preferred to tungstic or phosphotungstic acid as protein precipitant for blood.

A. A. Eldridge.

Colorimetric determination of blood-nitrogen. A. Cassuto (Presse méd., 1930, **38**, 1155—1157).—Blood-filtrate (after use of trichloroacetic acid) is digested with sulphuric acid and copper sulphate; nesslerisation follows.

Chemical Abstracts.

Deproteinising blood-serum. G. TURNER (J. Lab. Clin. Med., 1930, **15**, 720—723).—A method for the electrolytic precipitation of protein from antitoxic sera is described. CHEMICAL ABSTRACTS.

Analysis of the osmotic pressures of serum-proteins, and mol. wt. of albumin and globulins. G. S. ADAIR and M. E. ROBINSON (Biochem. J., 1930, **24**, 1864—1889).—Serum-albumin can be recrystallised four times without change in the mol. wt. (cf. Svedberg and Sjogren, A., 1929, 203). Adair's methods for the determination of mol. wt. of proteins in non-ideal solutions have been developed with the special purpose of determining the mol. wt. of serum-proteins in the physiological range of hydrogen-ion and salt concentrations. The mean value of the mol. wt. of horse-serum albumin in 27 experiments was 72,000±3000. One preparation gave a value of 67,000. Sorensen's provisional estimate of 45,000 when corrected for deviation from the ideal solution laws is 74,000. Preliminary determinations indicate that the serum-albumins of the ox and sheep have mol. wt. about 70,000. The mean value of the mol. wt. of the unfractionated globulin of the horse is 175,000 (maximum and minimum 182,000 and 154,000 in 17 experiments). The unfractionated globulins of the ox and the sheep gave similar results. Euglobulin prepared by a rapid method resembles total globulin, and the mol. wt. obtained by the authors is, therefore, higher than the value obtained by Svedberg, namely, 103,800. The osmotic pressure of the total serum-protein before fractionation has been studied from the point of view of Dalton's law of partial pressures and it appears that serum-protein is not a compound of albumins and globulins. The state of aggregation of the proteins in the untreated serum appears to be the same as their state of aggregation in the purified proteins prepared by the methods used in this work. The protein solutions which have been examined are beyond the range of application of Donnan's formulæ for osmotic pressure. Methods for determining p_i, the pressure due to the excess of diffusible ions inside the membrane, in non-ideal solutions are described and calculations of p_i and of p_p, the partial pressure of the protein ions, have been made. A method is suggested for ascertaining the valency of the protein ions in non-ideal solutions. S. S. ZILVA.

Comparison of colorimetric and electrometric methods for determination of the p_H of serum or plasma. R. J. FOSBINDER and J. W. SCHOONOVER (Biochem. J., 1930, **24**, 1805—1810).—The colorimetric method of Hastings and Sendroy (A., 1924, ii, 869) may be used with accuracy for the determination of the p_H of blood or plasma at 38°. Determinations carried out at 38° on 28 samples of diluted plasma from cancerous and normal subjects reveal no discrepancy between the colorimetric and glass electrode methods. The p_H of normal plasma or blood lies between 7·35 and 7·38. S. S. ZILVA.

Determination of alcohol in blood. T. HIRAMATSU (Sei-i-kwai Med. J., 1929, **48**, No. 12, 21—31).—The method depends on the proportionality between the intensity of the black colour produced by interaction between osmic acid and alcohol with the concentration of the alcohol. For 0·02% 30 hrs.' development is required. The alcohol should be removed from the blood by distillation. Alcohols other than ethyl give the reaction, but ketonic substances do not interfere. CHEMICAL ABSTRACTS.

A volatile organic chlorine compound in blood. N. MORRIS and S. MORRIS (Biochem. J., 1930, **24**, 1716—1722).—After preliminary drying of serum the amount of chlorine recovered is less than when no drying is employed. This is due to the loss of chlorine in the form of a volatile organic chlorine compound. The corpuscles of the blood contain a much greater amount of this volatile compound. The maximum of volatilisation takes places when the drying has proceeded for at least 400 hrs. The amount of chlorine lost by distillation can be accounted for in the distillate. When compounds such as urea, histamine, glycine, and primary and secondary amines are added to the blood in progressively increasing amounts, the curve showing the effect of concentration of the added substance on volatile chlorine resembles the coagulator concentration curves. The addition of ammonium sulphate yields a similar curve, although the maximum and minimum values are lower than those found with urea. When a chloride or a very dilute acid is added the results obtained are the inverse of those obtained with NH_2 or NH_4 groups, producing an increase in the amount of volatile chlorine. There is a gradual decrease in the volatile organic chlorine to a value which remains steady at about 5 milliequiv. below the original, when mixtures of blood and coagulator are kept before drying. Thereafter prolonged keeping does not appreciably alter the amount of volatile chlorine. S. S. ZILVA.

Blood-cholesterol balance. L. BUGNARD and C. SOULA (Compt. rend., 1930, **191**, 1382—1384).—The cholesterol content of venous plasma is higher than that of arterial plasma by 0·13 g. per litre. Lowering the p_H of blood increases the cholesterol content of plasma and *vice versa*, although with separated plasma such variations do not occur. The partition between plasma and corpuscles is controlled by the reaction of the medium. P. G. MARSHALL.

Blood-calcium and oxalate precipitation. Partition of calcium between corpuscles and serum or plasma. C. O. GUILLAUMIN (Bull. Soc. Chim. biol., 1930, **12**, 1269—1297).—The methods of blood-calcium determination are investigated. Precipitation by ammonium oxalate is shown to be incomplete; the method finally adopted is a modified combination of those of Kramer and Tisdall (A., 1921, ii, 595, 655) and of Hirth (A., 1923, ii, 698). The blood is deproteinised by trichloroacetic acid, the filtrate digested with nitroperchloric acid, taken to dryness, and the calcium in the residue determined. The total plasma- and serum-calcium are equal, whilst the erythrocytes contain a small but varying amount of calcium. F. O. HOWITT.

Fission of tributyrin in the blood and serum of various animals. W. TAKAHASHI (Pflüger's Archiv, 1930, **225**, 42—48; Chem. Zentr., 1930, ii, 1243).—The order of diminishing ability of blood to cause fission of tributyrin is: rabbit, cat, horse, man,

dog, ox. In cat's and horse's blood the serum contains the active agent. A. A. ELDRIDGE.

Physiological blood coagulant. O. BEYER (Chem.-Ztg., 1930, **54**, 1007).—A solution containing the substance which causes formation of thrombin with subsequent stasis and coagulation of the blood is obtained by extracting ox-liver with alcohol, precipitating the extract with ether, and dissolving the wax-like precipitate in water. The solution can be sterilised in steam at 95° for ½ hr. without decrease in activity. F. O. HOWITT.

Blood coagulation. H. J. FUCHS (Klin. Woch., 1930, **9**, 243—245; Chem. Zentr., 1930, i, 3804—3805).—Blood coagulation is regarded as consisting of two simultaneous processes: (1) The blood-corpuscles contain prothrombin-cytozyme, which forms thrombin with the plasma-calcium ions. In hæmophilia or after injection of peptone the excess of antiprothrombin is so great that the formation of thrombin is arrested and the conversion of fibrinogen into fibrin is retarded. (2) Prothrombin is present in plasma only as antiprothrombin, a carbohydrate-like substance which passes from the liver into the blood, and is thereby inactivated for plasma coagulation. If sufficient free prothrombin is not present, but enough cytozyme is available, thrombin is formed in presence of calcium ions. Cytozyme phosphatides, but not prothrombin or antiprothrombin, possess species specificity. A. A. ELDRIDGE.

Mechanism of passage of clot-arresting substances (antiprothrombin) into the blood after injection of Witte's peptone. M. VON FALKENHAUSEN (Z. ges. exp. Med., 1930, **70**, 535—542; Chem. Zentr., 1930, i, 3805).—Intravascular injection of Witte's peptone into the goose, as into the dog, leads to uncoagulability of the blood. If the liver is removed, acceleration of blood coagulation is observed. Hence the antiprothrombin arises chiefly from the liver. The action of the peptone is attributed to that of a phosphatide. A. A. ELDRIDGE.

Specific agglutination and precipitation. I. Mechanism of the reactions. H. EAGLE (J. Immunol., 1930, **18**, 393—417).—Agglutinating and precipitating antibodies are a specifically altered fraction of the serum-globulin. The antigen–antibody complex, regardless of its type, contains this antibody-globulin. The factors determining specific flocculation are discussed. The hydrophilic antigen is covered with a film of immune globulin, denatured by its combination with antigen. In the absence of electrolytes the charge due to the ionisation of this protein is sufficient to prevent aggregation; minute concentrations of electrolyte, however, depress this surface charge below the critical value necessary for stability. The optimum hydrogen-ion concentration for flocculation is intermediate between that of the original cell and that of the antibody-globulin.
CHEMICAL ABSTRACTS.

Antigenic properties of yeast-invertase. K. MATSUOKA (Z. physiol. Chem., 1930, **193**, 167—170).—Intravenous injection of invertase from beer-yeast autolysate into rabbits yielded a serum which inhibited the inverting capacity of the enzyme (cf. Knaffl-Lenz, A., 1922, i, 694). Addition of pig's serum as activator to the invertase preparation increased the production of the inhibitor. Injection of sucrose did not produce a serum capable of inverting this sugar unless pig's serum was added as activator.
J. H. BIRKINSHAW.

Highly unsaturated fatty acids of the brains of the ox, pig, and sheep. J. B. BROWN and W. C. AULT (J. Biol. Chem., 1930, **89**, 167—171).—The brain-tissue was hydrolysed with sodium hydroxide; the soaps were extracted with butyl alcohol, and the fatty acids liberated by treatment of the extract with hydrochloric acid. The acids were brominated in ethereal solution and the insoluble bromides converted into the methyl esters of the corresponding unsaturated acids. The high iodine values (340—350) of this material from the brains of the ox and sheep confirm the previous suggestion of the occurrence of tetracosapentenoic acid (A., 1929, 1329). Pig's brain yielded a preparation with iodine value corresponding with that of methyl arachidonate, the presence of which was, however, excluded by the fact that the bromide did not melt below 250°; the presence of an isomeride of arachidonic acid is suggested.
C. R. HARINGTON.

Cephalin from human brain. H. RUDY and I. H. PAGE (Z. physiol. Chem., 1930, **193**, 251—268).—In the characterisation of cephalin the titration value, which corresponds with the amino-nitrogen value, is employed. It may also be used to determine the cephalin content of lecithin–cephalin mixtures. Unhydrolysed cephalin gives, in water, amino-nitrogen values about 10% too high. In human brain, besides the cephalins of low carbon content, there are cephalins present of high carbon content, corresponding fairly well with the theoretical value. Barium salts of cephalin were obtained and used in separating cephalin from mixtures of cephalin and lecithin. J. H. BIRKINSHAW.

Placental enzymes. WEHEFRITZ and E. GIERHAKE (Arch. Gynakol., 1928, **135**, 212—222; Chem. Zentr., 1930, ii, 252).—The placenta, of whatever age, contains arginase in quantity unrelated to the age. Preformed urea or urease could not be detected in the placenta. A. A. ELDRIDGE.

Glycogen of rabbit's liver. M. SAHYUN and C. L. ALSBERG (J. Biol. Chem., 1930, **89**, 33—39).—Fresh rabbit's liver was extracted by grinding with two successive portions of 3% aqueous trichloroacetic acid; the extracts, after clearing on the centrifuge, were treated with 2 vols. of 95% alcohol. The precipitated glycogen was dissolved in 3% trichloroacetic acid, again precipitated with alcohol, and then repeatedly dissolved in water and precipitated with alcohol, if necessary with addition of a little ammonium acetate. After dehydration with alcohol and ether followed by drying over calcium chloride, the glycogen had 0·2% of ash (including traces of calcium and iron) and 0·032% of phosphorus; when hydrolysed it yielded more than 95% of the theoretical amount of reducing sugar. When heated to 105° the glycogen became less soluble. C. R. HARINGTON.

Change in the colloidal condition of the muscle-proteins in mortification and in fatigue. H. J.

DEUTICKE (Pflüger's Archiv, 1930, **224**, 1—43; Chem. Zentr., 1930, i, 3808).—On long preservation, minced muscle loses the property of forming hexosediphosphoric acid from phosphoric acid and carbohydrate in presence of fluoride. Physico-chemical changes in the muscle-protein take place, the solubility in various salt solutions diminishing. The same changes were observed in isolated and in minced frog's muscle during rigor. The protein of fatigued isolated frog's muscle also is less soluble. Both changes were observed in living muscle after severe insulin convulsions. A. A. ELDRIDGE.

Effect of various buffer mixtures on the solubility of protein of active, fatigued, dying, and rigid muscle. J. HENSAY (Pflüger's Archiv, 1930, **224**, 44—61; Chem. Zentr., 1930, i, 3088; cf. preceding abstract).—Under otherwise similar conditions the solubility of muscle-proteins in potassium salt solutions is greater than that in sodium salt solutions, and in phosphate mixtures greater than in acetate mixtures. The solubility in buffer mixtures is least at p_H 5. With increase in the salt content of the extractive medium the absolute quantity of protein dissolved increases. The "ageing" of muscle-protein was shown by increase in solubility (at p_H 4 in an acetate mixture); with a phosphate mixture the solubility always diminished for given and concentration values. Similar solubility changes were exhibited by fatigued muscle; in rigor the solubility in phosphate diminished and in strongly acid acetate either diminished or was unchanged. A. A. ELDRIDGE.

Muscle-globulin (myosin). II. Properties. J. T. EDSALL. **III. Anisotropy and vortex angle. IV. Streaming anisotropy.** A. L. VON MURALT and J. T. EDSALL (J. Biol. Chem., 1930, **89**, 289—313, 315—350, 351—386).—II. Fresh muscle is minced and extracted at a low temperature with dilute potassium chloride solution buffered with phosphate at p_H 7·0—8·5; the globulin is precipitated from the extract by dilution with water. After purification by repeated re-dissolution in dilute salt solution and precipitation by dilution or by salting out it forms a viscous fluid which cannot be crystallised. The acid- and base-binding capacity of the protein is at a minimum over the range p_H 6·2—6·6. At p_H 5—6 the globulin is insoluble in all concentrations of salt; at reactions more acid than p_H 5·0 or more alkaline than p_H 10·0 no salt is required for its dissolution. In potassium phosphate solution at p_H 7·4 the protein is almost insoluble at ionic strengths up to 0·25; as the ionic strength increases to 0·4 the solubility shows a sudden large increase, followed by a decrease, until at ionic strength 3·5 solubility has again become very low. Myosin is also precipitated at 0° and p_H 7·0 by 4·4—4·6*M*-sodium chloride and by one third saturation with neutralised ammonium sulphate. Associated with its high degree of hydration it exhibits a high degree of viscosity. In the almost complete absence of salt at the isoelectric point myosin forms gels the rigidity of which is much increased by addition of small amounts of alkali.

III. Solutions of myosin exhibit streaming anisotropy. The concentric cylinder apparatus and technique employed for the investigation of this phenomenon are described. The vortex angle of all preparations ranged from 65° to 78°, the precise value being determined by concentration and by the angular velocity of the rotating cylinder; it was independent of the age of the solutions, which differed in this respect from the vanadium pentoxide sols examined by Freundlich and others (A., 1925, ii, 199, 200; 1926, 241). Rise of temperature decreased the vortex angle, this effect being correlated with coincident changes in the viscosity of the solution. Gels of myosin showed abnormal behaviour, there being observed two vortex crosses, one at an angle of 63° for the part of the solution in opposition to the fixed cylinder, and one at 45° in the part near the rotating cylinder, the intermediate part of the solution appearing as an isotropic ring. This phenomenon is ascribed to the thixotropic character of the gel, which becomes liquefied in the region near the fixed cylinder where the shearing stresses are greatest; the vortex angle of 45° in the rigid part of the gel is due to elastic deformation. The constancy of the vortex angle (77·5—78·5° for solutions of moderate or high concentration at 2—4°) is taken to indicate that the anisotropic myosin is present in solution in particles of uniform and constant shape. The mechanism of the formation of the vortex cross is discussed.

IV. The streaming double refraction of myosin solutions has been quantitatively measured with the aid of a Senarmont compensator, and it is found that double refraction and angular velocity are related, at constant temperature and p_H, in a manner which is characteristic for a given concentration of protein and is independent of the age of the solution. Denaturation of the protein by any means abolishes the phenomenon of streaming anisotropy altogether. The latter is therefore a characteristic property of myosin, and the fact that different preparations fail to exhibit entirely identical relationships is due to the incomplete removal of contaminating isotropic proteins. The results are discussed in their relation to the anisotropy of muscle fibres. C. R. HARINGTON.

Biose of chitin. M. BERGMANN, L. ZERVAS, and E. SILBERKWEIT (Naturwiss., 1931, **19**, 20).—Hydrolysis by acetylation of the chitin of crab results in the separation of the *octa-acetyl* derivative, m. p. 289°, [α] +50° in acetic acid, iodine value 31·3, of a disaccharide, *chitobiose*. F. O. HOWITT.

Zinc content of rat's liver at various ages. G. BERTRAND and (MME.) Y. BRANDT-BEAUZEMONT (Compt. rend., 1930, **191**, 1410—1411).—The zinc content of the livers of white rats has been determined at the ages of 1, 15, and 30 days, and at 7 months, the mean values being, respectively, 114·31, 51·31, 36·84, and 32·42 mg. of zinc per 100 g. of dried liver. Thus in agreement with previous results relating to the whole rat (A., 1930, 953) the quantity of zinc present decreases progressively with increase in age. J. W. BAKER.

Microchemical detection of urease in tissue. P. B. SEN (Indian J. Med. Res., 1930, **18**, 79—82).—Use is made of the interaction of urease with urea to form

ammonium carbonate, which then affords insoluble heavy-metal carbonates. CHEMICAL ABSTRACTS.

Rapid method for tissue diagnosis. C. F. GESCHICKTER, E. P. WALKER, A. M. HJORT, and C. H. MOULTON (Stain Tech., 1931, **6**, 3—12).—The following procedure is suitable for either fresh or formalin-fixed frozen sections. The sections are collected from the microtome in a solution containing potassium dihydrogen phosphate (6·75 g.), *N*-sodium hydroxide (30 c.c.), distilled water (570 c.c.), glycerol (200 c.c.), 95% alcohol (200 c.c.). They are then stained for 20—30 sec. in a bath containing thionine eosinate (0·75 g.), barium eosinate (0·25 g.), azure-A (0·25 g.), dissolved in 100 c.c. of a mixture of ethylene glycol (4 parts) and 95% alcohol (1 part) with 0·2% of glacial acetic acid. The excess of stain is then removed in two successive changes of 20% glycerol in 95% alcohol. The sections are then dehydrated for 10—15 sec. in diethylene glycol monobutyl ether and finally cleared in *n*-butyl phthalate for 20 sec., when they are ready for mounting. H. W. DUDLEY.

Glycogen. III. Glycogen in pigeon's lenses. S. HARADA (Sei-i-kwai Med. J., 1929, **48**, No. 12, 1—20).—The lenses of pigeons, but not of dogs or rabbits, contain glycogen; in polyneuritic pigeons the amount is often subnormal.

CHEMICAL ABSTRACTS.

Phosphatides. II. Highly unsaturated fatty acids in the phosphatide from different organs. E. KLENK and O. VON SCHOENEBECK (Z. physiol. Chem., 1931, **194**, 191—192; cf. this vol., 112).—The unsaturated acids are separated from the total fatty acids of the phosphatide from ox-liver by Tsujimoto's method (A., 1921, i, 78), converted into their methyl esters, and fractionated. Hydrolysis of the high-boiling fraction (iodine value 249) after reduction, gives erucic acid, also obtained similarly from brain-lecithin. Bromination of the unsaturated acids from the liver-phosphatide affords, in addition to ether-soluble products, some insoluble arachidonic acid octabromide. H. BURTON.

Mucin of articular liquids. C. ACHARD and M. PIETTRE (Compt. rend., 1930, **191**, 1412—1414).—After separation of fibrinous clots by centrifuging, precipitation of articular liquid with an equal volume of acetone causes separation of a synovial mucin (larger volumes of acetone are necessary to cause flocculation of the proteins), purified by repeated precipitation from its aqueous solution with acetone and washing with dry ether. The sulphur content of the powder, dried in a vacuum over sulphuric acid, is 0·70%, that is, only half that normally present in serum-proteins. Also the viscosity of a 0·8% aqueous solution (η^{20} 5·389) is much greater than that of a solution of serum-proteins of the same concentration (η^{20} 1·090). J. W. BAKER.

Determination of protein in cerebrospinal fluid and other body-fluids. I. BERGER (Klin. Woch., 1930, **9**, 888—889; Chem. Zentr., 1930, ii, 592—593).—The turbidity caused by the addition of sulphosalicylic acid is compared (apparatus described) with that produced in a standard solution of protein. A. A. ELDRIDGE.

Extra-hepatic production of bile-pigments in surviving organs. V. Z. ERNST and E. HALLAY (Biochem. Z., 1930, **228**, 354—365; A., 1925, i, 732).—No relation could be found between the amount of bile-pigment in the parenchyma of the surviving spleen of the dog and the number of red blood-corpuscles which are decomposed there during perfusion. W. MCCARTNEY.

Polarimetric determination of bile acids in body-fluids and organs. F. ROSENTHAL (Arch. exp. Path. Pharm., 1930, **157**, 165—177).—The method given by Hoppe-Seyler ("Handb. Chem. Analyse," 1893, p. 451) has been modified. Thus for liver tissue etc. optically active sterols are removed by ether after saponification by potassium hydroxide, and the acidified aqueous layer is concentrated and treated with magnesium sulphate. The bile acids are extracted from the precipitate with alcohol, the extract is evaporated to dryness, treated with potassium hydroxide and hydrogen peroxide, made up to a known volume in 65% alcohol, and the rotation determined. F. O. HOWITT.

Determination of bile salts in bile; gasometric determination, formol titration, and biliary sulphur determination. L. CUNY (J. Pharm. Chim., 1930, [viii], **12**, 485—498, and Bull. Soc. Chim. biol., 1930, **12**, 1298—1318; cf. A., 1929, 592).—The gasometric determination of bile salts, depending on the determination of amino-nitrogen before and after alkaline hydrolysis, is affected by the interval necessary between the two determinations, and a modified process is described in which free amino-acids, urea, and ammoniacal nitrogen are oxidised with sodium hypobromite previous to hydrolysis of the bile salts, which are unaffected by the hypobromite. As a control method the bile, after treatment with alcohol and subsequent filtration, is treated with sodium hypobromite and hydrolysed, and, after elimination of cholalic acid and carbonates, neutral formaldehyde is added and the liquid titrated with baryta solution. A modification of the benzidine method for the volumetric determination of sulphur in body-fluids is adapted to the determination of biliary sulphur. E. H. SHARPLES.

Human milk: (*a*) carbohydrates; (*b*) analysis. M. POLONOVSKI and A. LESPAGNOL (Bull. Soc. Chim. biol., 1930, **12**, 1170—1194, 1195—1211).—(*a*) The disagreement in lactose content of human milk as determined by rotation and reducing power is explained by the presence of other carbohydrates. The residue from alcohol precipitation and ether extraction of fat on fractional crystallisation from methyl alcohol yields "*gynolactose*," m. p. about 205°, $[\alpha]_D$ —12°. In addition, a third carbohydrate occurs which has a low dextrorotatory power and yields galactose on acid hydrolysis. Some physical properties of these new sugars are described.

(*b*) The carbohydrates are determined by precipitation with silicotungstic acid, oxidation of the filtrate with dichromate, and iodometric titration of excess of dichromate, lipins by extraction of the silicotungstic acid precipitate by ether, and caseinogen by the volumetric method of Baudouin and Lewin (A., 1927, 476). F. O. HOWITT.

Does the antirachitic vitamin exist in human milk? A. MACCHI and P. SCALFATI (Arch. Ist. Biochem. Ital., 1930, **2**, 625—638).—Human milk contains varying amounts of the antirachitic vitamin.
T. H. POPE.

Lactenin. F. S. JONES and H. S. SIMMS (Science, 1930, **72**, 456—457).—The properties and possible uses of the substance in milk named lactenin, which inhibits the growth of certain bacteria, are summarised.
L. S. THEOBALD.

Phrynolysin. L. GÓZONY and F. HOFFENREICH (Zentr. Bakt. Par., 1930, **115**, 377—383; Chem. Zentr., 1930, i, 3068).—Phrynolysin, the cutaneous gland fluid of *Bombinator igneus*, possesses agglutinating and hæmolytic properties, the latter being difficult to conserve, as it is much weakened by alcohol, chloroform, or ether. The toxin acts differently at different times and on different animals. An acid reaction inhibits toxicity, but an alkaline reaction promotes it; with phosphate buffer mixture it is first noticeable at p_H 7·4. Phrynolysin contains lipase as well as a diastatic enzyme, but a proteolytic enzyme could not be detected. It agglutinates leucocytes, liver cells, and semen. Attempts to prepare the pure toxin failed. It contains albumin, however, and the ninhydrin reaction is strongly positive. Bile acid could not be detected.
L. S. THEOBALD.

Clinical test for urinary acetone and acetoacetic acid. J. A. BEHRE (J. Lab. Clin. Med., 1928, **13**, 770—772).—The pink colour produced when salicylaldehyde is heated with acetone is employed to detect acetone and acetoacetic acid in urine; 1 mg. of acetone, or the equivalent amount of acetoacetic acid, in 100 c.c. can be detected. Addition of a drop of dilute aqueous potassium dichromate before the urine is heated partly overcomes the inhibiting effect of formaldehyde.
CHEMICAL ABSTRACTS.

Determination of urinary sugar by Bertrand's method. F. JÜSTEN (Arch. Pharm., 1930, **268**, 559—565).—A modification of Bertrand's method is described in which the standard solutions of the D. A. B. VI are used. The dextrose content may then be obtained from Allihn's tables, but it is given with sufficient accuracy, when the urine is diluted to contain 0·1—0·75% of dextrose, by the expression 3·30n mg., where n c.c. of 0·1N-permanganate are required to reoxidise the ferric sulphate reduced by the cuprous oxide formed. A further check is given by the iodometric determination of the excess of Fehling's solution (cf. A., 1929, 1099).
H. E. F. NOTTON.

Determination of sulphide-sulphur in fæces. J. S. LORANT and F. REIMANN (Biochem. Z., 1930, **228**, 300—309).—Air, freed from oxygen and sulphur dioxide, is drawn through an acidified suspension of fresh fæces in sodium borate solution, hydrogen sulphide being collected in zinc acetate solution. The sulphide content of this solution is then determined by the method of Lorant (A., 1930, 181). Hydrogen sulphide produced during digestion but ordinarily lost from the fæces can be fixed, possibly completely, in the fæces by administration of reduced iron or ferrous chloride.
W. MCCARTNEY.

Trypsin preparations suitable for the prevention of adhesions. R. P. WALTON (J. Pharm. Exp. Ther., 1930, **40**, 403—411).—Relatively stable active preparations of trypsin are obtained by extracting a dried trypsin powder with 75% glycerol in water and filtering the extract through a Chamberland filter under pressure, rejecting the first portion of the filtrate. The glycerol extracts are effective in preventing peritoneal adhesions when introduced into the peritoneal cavity (cf., Ochsner and Mason, Proc. Soc. Exp. Biol. Med., 1928, **25**, 524).
W. O. KERMACK.

Tryptophan and histidine lack in pernicious anæmia. Hæmatogenic amino-acid therapy. G. FONTÈS and L. THIVOLLE (Compt. rend., 1930, **191**, 1395—1397).—Liver extracts are effective in the cure of pernicious anæmia only in so far as they contain tryptophan and histidine. Daily subcutaneous injection of 100 mg. of tryptophan and 200 mg. of histidine rapidly gives rise to a normal blood count, increase in hæmoglobin content, and increase in weight, all of which are maintained for at least 6 months without further treatment.
P. G. MARSHALL.

Glutathione in pathological blood. K. VARELA, E. APOLO, and A. VILAR (Klin. Woch., 1930, **9**, 1029—1030; Chem. Zentr., 1930, ii, 937).—The normal glutathione content of human blood is 47 mg. per 100 c.c.; in pathological conditions variations between the limits 28 and 66 mg. were observed. Low values are always observed in anæmia, and usually in diabetes.
A. A. ELDRIDGE.

Carcinogenic substances and their fluorescence spectra. E. L. KENNAWAY and I. HIEGER (Brit. Med. J., 1930, i, 1044—1046).—An attempt has been made to correlate fluorescence and carcinogenesis. The carcinogenic material formed by the action of aluminium chloride on tetrahydronaphthalene shows a bluish-violet fluorescence and gives a spectrum consisting of three bands at 4000, 4180, 4400 Å. The 1 : 2 : 7 : 8- and the 1 : 2 : 5 : 6-dibenzanthracenes give spectra of a similar type and produce cancerous tumours in mice. Other carcinogenic materials such as gas-works tar and its products, tars from yeast, muscle, and hair also show bands at the wave-lengths quoted above, but, on the other hand, certain materials such as crude oleic acid and benzyl oleate show the same spectrum but have not produced cancer. Further, non-fluorescent commercial tetralin has produced cancer in mice. The results suggest, however, the possibility of using fluorescence for a preliminary examination of materials suspected of carcinogenic properties.
L. S. THEOBALD.

Formation of phospholipins during autolysis of normal and neoplastic tissue. A. H. ROFFO and L. M. CORREA (Bull. Soc. Chim. biol., 1930, **12**, 1247—1254).—The phospholipin contents of the spleen and liver, both normal and in varying stages of tumour growth, were followed by the technique of Artom (A., 1926, 201). Liver tissue contains almost twice as much phospholipin as does tumour tissue, in both cases the amount being reduced by autolysis at 38° in presence of sodium fluoride. With tumour growth the phospholipin contents of fresh and autolysed tissue diminish and then remain constant,

whilst the non-phosphorus lipins have a higher value and run a somewhat parallel course.

F. O. Howitt.

Metabolism of tumours. O. Warburg (Biochem. Z., 1930, **228**, 257—258).—In tumour tissues the injury to respiration is transmitted in cell division.

P. W. Clutterbuck.

Correlation between arginine and vitamin-*B* content of diets and effect of thyroxine on tumour growth. G. Gilroy (Biochem. J., 1930, **24**, 1659—1665; cf. A., 1930, 948, 1309, 1468).—Tumour growth is inhibited in implanted male mice kept on a diet deficient in arginine to an extent similar to that induced by a diet deficient in vitamin-*B*. When thyroxine is also injected there is a steady loss of weight and a high mortality in the animals. The addition of gelatin to the above diet and to a diet deficient in vitamin-*B* causes only a temporary recovery, whilst wheat germ induces a permanent increase in weight in unimplanted mice. Injection of arginine increases the loss of weight. Injections of thyroxine had a slight but definite inhibitory effect on tumour growth in spite of an increase in weight; the less marked effect in this second experiment is due to the larger quantity of food consumed by mice receiving thyroxine as compared with untreated controls.

S. S. Zilva.

Vitamins and tumour growth. IV. Vitamin-*B* consumption by growing rat-tumour. W. Nakahara and E. Somekawa (Proc. Imp. Acad. Tokyo, 1930, **6**, 345—347; cf. A., 1929, 718).—The vitamin-*B* content of the liver of rats fed on a diet deficient in vitamin-*B* is not reduced by inoculation of the animal with rapidly growing Fujinawa rat-sarcoma. It is concluded that vitamin-*B* consumption by the tumour is negligibly small.

A. Cohen.

Colloidal osmotic pressure of the blood in diabetes mellitus. I. M. Rabinovitch (Arch. Int. Med., 1930, **46**, 752—767).—The colloidal osmotic pressure was frequently higher than the value expected from the protein content. This phenomenon was associated with hypercholesterolæmia, to which it is considered to be due. High blood-pressures were shown by diabetics with hypercholesterolæmia and œdema. It is suggested that the hypertension is necessary to overcome the increased colloidal osmotic pressure of the blood for urinary secretion.

G. F. Marrian.

Lipæmia. Effect of insulin on blood-fat and on alimentary lipæmia in normal and diabetic man. N. I. Nissen (Acta med. Scand., 1930, **73**, 99—124; Chem. Zentr., 1930, ii, 259).—The neutral fat–cholesterol values in normal fasting persons varied during 6 hrs. from 0·081 to 0·088 mg. per 100 c.c.; after oral administration of dextrose (100 g.) 0·058—0·071; in obesity 0·082—0·094. After intravenous injection of dextrose, or in diabetes, similar values were observed. Values after subcutaneous injection of dextrose were: normal, 0·067—0·77, diabetic 0·082—0·100. The blood-fat after administration of 60 g. of fat reached 0·100 mg. per 100 c.c. (normal), 0·146 mg. (obese). Administration of insulin in either case did not affect the lipæmic curves.

A. A. Eldridge.

Relation of the plasma-sugar to the corpuscle-sugar in normal and diabetic individuals. H. J. John (J. Lab. Clin. Med., 1930, **15**, 713—719).—The red corpuscles of diabetic individuals are less capable of absorbing and retaining sugar than those of normal individuals; normally the corpuscular sugar is slightly lower than the plasma-sugar.

Chemical Abstracts.

Favus. R. Binaghi and G. Falconi (Annali Chim. Appl., 1930, **20**, 547—558).—The pungent perfume of the flowers and fresh seeds of *Vicia faba*, or ingestion of the raw or cooked seeds, is regarded as the cause of favus, which occurs more especially in Sardinia, where beans are eaten in large quantities. A glucosidic compound, vicin, which is not cyanogenetic, a phytosterol (viciosterol), and a sugar not yet identified have been isolated from the beans.

T. H. Pope.

Goitre survey in albino rats. R. McCarrison (Brit. Med. J., 1930, i, 989—992).—Vitamin-deficiency is the direct or indirect cause of goitre. Iodine has an effect only when administered to deficiently fed rats, and in these cases goitre formation is favoured.

L. S. Theobald.

Nutrition and the action of the thyroid gland. I. Influence of caseinogen on the metabolism of hyperthyroidism. II. Significance of vitamins on the course of experimental thyroidism [with M. Knuchel and W. Spichtin]. **III. Influence of nutritive mixtures on the metabolic disturbances of hyperthyroidism.** I. Abelin (Biochem. Z., 1930, **228**, 165—188, 189—210, 211—232).—I. Various glandular organs, especially the liver, form a means of protection against the flooding of the organism with thyroid hormone. When thyroid is first administered, the liver retains large amounts and converts it into products which are excreted in the bile. With further administration, the liver gradually loses the power of storing glycogen, of metabolising fat, and of forming creatine and creatinine. The excess of hormone is also used by muscle, heart, respiratory organs, and intestine, and these also lose their glycogen-storing power. Accompanying changes of metabolism occur also in the nervous system, especially the central nervous system. The livers of rats fed with caseinogen and excess of thyroid do not lose their glycogen-storing power as quickly as when thyroid alone is administered, caseinogen having a protective action on the liver.

II. The disturbances due to administration of thyroid are also alleviated by feeding vitamin-rich products (cod-liver oil, egg-yolk, yeast, tomato, carrots, spinach), the presence of vitamins-*A* and -*B* being especially important; administration of bone marrow is especially beneficial.

III. Tables summarise the results of metabolism experiments with rats, showing experimental hyperthyroidism, on a number of diets containing caseinogen, fats, vitamins, etc., and confirm the conclusions of the previous papers.

P. W. Clutterbuck.

Inflammation. III. Fixation of a metal in inflamed areas. IV. Fixation of foreign protein at site of inflammation. V. Menkin (J. Exp. Med., 1930, **51**, 879—887; **52**, 201—213).—The

fixation of iron, injected as colloidal iron or ferric chloride, in inflamed tissue is described; foreign protein, when injected, likewise accumulates in inflamed tissue. CHEMICAL ABSTRACTS.

Non-sugar reducing substances of human blood in pathological conditions. F. K. HERBERT and M. C. BOURNE (Biochem. J., 1930, **24**, 1787—1793).—The concentration of the non-diffusible reducing substance, which is most probably glutathione, in whole blood varies with the hæmatocrit reading for the corpuscle volume. The results in one case of myelogenous leucæmia suggest that the concentration of non-diffusible reducing substance in leucocytes and erythrocytes is of the same order. The concentration of the non-diffusible reducing substance in corpuscles varies, but in the majority of cases the variation from the normal average is within experimental error. In two cases of marked secondary polycythæmia the non-diffusible substance is above the normal average. S. S. ZILVA.

Lipoid nephrosis. H. MOORE and W. R. O'FARRELL (Brit. Med. J., 1930, ii, 242—243, 243—244).—The condition, which included reversal of the blood-albumin : globulin ratio with marked diminution of total protein, was ameliorated, with rise in serum-protein, by treatment which included administration of thyroxine, hydrochloric acid, and iron. CHEMICAL ABSTRACTS.

Boltz test in urine analysis. A. T. BRICE (Arch. Int. Med., 1930, **46**, 778—781).—The Boltz test with acetic anhydride and sulphuric acid (Amer. J. Psychiat., 1923—1924, **3**, 111) was used to examine urines from different types of medical and surgical cases. Negative reactions were given by urines from normal males on an average diet. A high percentage of positive reactions was given by urines from cases of degenerative diseases of the kidneys, acute infections, and appendicitis. Many of the positive reactions were obtained with protein-free urines. The reaction is believed to be due to the presence of an amino-acid. It may prove to be of value for the early diagnosis of kidney disease. G. F. MARRIAN.

Nature of the sugar in pentosuria. A correction. I. GREENWALD (J. Biol. Chem., 1930, **89**, 501).—The sugar isolated from the urine (A., 1930, 1311) should be described as *l*-xyloketose. C. R. HARINGTON.

Rickets. IV. Concentration of inorganic phosphorus in the blood in rickets. G. A. CHAIN (Zhur. exp. Biol. Med., 1929, **13**, 56—59).—The blood-phosphorus [inorganic] increases when the blood is kept; the increase takes place more slowly in serum. The blood-phosphorus in rachitic children is 2·9 mg. per 100 c.c. (normally 5·1 mg.). In rats with experimental rickets the blood-phosphorus falls from 11·4 to 4·4 mg. per 100 c.c., but the fall can be prevented by the administration of fish oils. CHEMICAL ABSTRACTS.

Calcium content of striated muscle of rachitic animals. V. G. HAURY (J. Biol. Chem., 1930, **89**, 467—469).—Striated muscle of normal rats contains on the average 74·0 mg. of calcium per 100 g., that of rachitic rats 41·6 mg. per 100 g. C. R. HARINGTON.

Serum-chlorides and chloride excretion in experimental scurvy. L. RANDOIN and A. MICHAUX (Compt rend., 1930, **191**, 1378—1380).—Chloride retention is found in guinea-pigs kept on a vitamin-*C*-deficient diet, a further proof of the development of nephritis on such a diet. P. G. MARSHALL.

Hypertrophy and atrophy of muscular organs. IV. Right ventricle in tricuspid insufficiency. J. JACOBI and H. WASSERMEYER. **V. Heart-muscle in experimental beri-beri.** H. WASSERMEYER (Arch. exp. Path. Pharm., 1930, **157**, 234—243, 244—250).—IV. Extirpation of the tricuspid valve in the rabbit heart results in a primary increase in the ammonia content of the right ventricle muscle, and, 25—31 days after the operation, in a secondary phase with further increase of ammonia and reduction of glycogen contents which in the normal right ventricle are 0·00133±0·00014% of ammonia and 0·43±0·03% of glycogen.

V. In the normal pigeon's heart, the ammonia content (2—4 mg. per 100 g.), the *post-mortem* ammonia formation, and that on incubation at 38° in 2% sodium hydrogen carbonate solution show no difference from those of pigeons suffering from beri-beri. In the latter, however, the glycogen and the lipoidal phosphoric acid contents are higher than the normal (0·30±0·08% for glycogen). F. O. HOWITT.

Content of fibrinogen, albumin, and globulin in the plasma of tubercular guinea-pigs. C. VIDAL (Compt. rend. Soc. Biol., 1930, **103**, 347—349; Chem. Zentr., 1930, i, 3069).—In the first stages of infection the ratio albumin : globulin in the blood-plasma is less than normal; the lowering increases during the first three months after infection, but the ratio increases again during the final stages. The total protein content and the fibrinogen content are diminished at first, but are increased in the last stages. L. S. THEOBALD.

Copper and tuberculosis. P. SEABRA (Arch. Pharm., 1930, **268**, 565—567).—The mean copper content, determined after incineration, by the method of Dick and Spacu (A., 1927, 746), of the lungs of three persons dying of tuberculosis was 0·1 mg., and that of three persons dying of other diseases, 0·9 mg. after making allowance for the copper content of the retained blood. The decrease in copper content appears to run parallel with the increasing extent of the lesions. H. E. F. NOTTON.

Metabolism of the albino rat during prolonged fasting at two different environmental temperatures. K. HORST, L. B. MENDEL, and F. G. BENEDICT (J. Nutrition, 1930, **3**, 177—200).—The total metabolism of rats fasting at 26° was at a lower level than that of the group fasting at 16°, but the decrease in the total metabolism as the fast progressed was greater. The basal metabolism of adult female rats fasting at 26° and about 24 hrs. after food was 600—700 g.-cal. per m.^{2} of body surface per 24 hrs. CHEMICAL ABSTRACTS.

Metabolism of nerves on stimulation. O. MEYERHOF and W. SCHULZE (Biochem. Z., 1930, **228**. 1—5).—The criticisms of Winterstein (Pflüger's Archiv, 1930, **224**, 749) of the work of Gerard, Meyerhof, *et al.*

(A., 1928, 198, 910) on the metabolism of nerves in which the increased utilisation of oxygen and output of carbon dioxide of nerves during stimulation is shown to correspond closely with that required by the heat changes, are controverted. The close agreement relates to stimulation of the whole nerve and not to a local stimulation and to stimulation of peripheral nerves under the conditions laid down.

P. W. CLUTTERBUCK.

Effect of glycine on the oxygen demand of surviving organs. A. BORNSTEIN and H. F. ROESE (Pflüger's Archiv, 1929, **223**, 498—508; Chem. Zentr., 1930, i, 3078).

Proliferation of rat and mouse epithelium and the thiol group. S. P. REIMANN (Protoplasma, 1930, **10**, 82—83).—Comparison of the effects of cresol and of thiocresol on rat and mouse skin shows that the thiol group has a stimulative effect on cell division.

A. G. POLLARD.

Nuclein synthesis in the development of eggs. J. NEEDHAM and D. NEEDHAM (Compt. rend. Soc. Biol., 1930, **104**, 671—674; Chem. Zentr., 1930, ii, 938).—There is practically no change in the extractable nucleoprotein-phosphorus during the development of eggs of marine animals. A. A. ELDRIDGE.

Colorimetric determination of the tyrosine and tryptophan content of various crude protein concentrates. W. D. MCFARLANE and H. L. FULMER (Biochem. J., 1930, **24**, 1601—1610).—The tyrosine and tryptophan content of the proteins of butter-milk powder is much higher than that of the other crude protein materials examined. There is no appreciable difference in the tyrosine content of fish meal, cod-liver meal, meat meal, and tankage. In general the tryptophan content of fish meal is higher than that of meat meal, although conflicting results were obtained according to the methods used. The alkali digest of the crude protein materials contains a substance or substances (not indole), precipitable by mercuric sulphate and giving a blue colour with the phenol reagent, which, unlike tryptophan, is soluble in toluene. The results obtained after extraction of the alkali hydrolysates with toluene appear to represent the true tyrosine and tryptophan content of these protein concentrates.

S. S. ZILVA.

Embryonic mortality in the chick. I. Effect of diet on the nitrogen, amino-nitrogen, tyrosine, tryptophan, cystine, and iron content of the proteins and on the total copper of the hen's egg. W. D. MCFARLANE, H. L. FULMER, and T. H. JUKES (Biochem. J., 1930, **24**, 1611—1631).—The source of protein in the diet of the hen has a marked influence on the mortality of the embryos during incubation. There is, however, no significant difference in the total nitrogen, total amino-nitrogen, tyrosine, tryptophan, and cystine content of the proteins of eggs of poor hatchability. The diet of the hen has no influence on these values nor on the total ash and iron content of the egg-yolk proteins. The copper content of the hen's egg varies considerably. S. S. ZILVA.

Arginine metabolism. I. Relation of arginine content of diet to increments in tissue-arginine during growth. C. W. SCULL and W. C. ROSE (J. Biol. Chem., 1930, **89**, 109—123).—The increase in the total arginine content of the growing rat on diets low in this amino-acid greatly exceeds the arginine ingested with the food, from which it is concluded that, for the rat at least, arginine is not an essential constituent of the diet. C. R. HARINGTON.

Proteopexic function of the liver. R. MARTENS (Bull. Soc. Chim. biol., 1930, **12**, 1212—1246).—Variations in amino- and polypeptide-nitrogen of the blood entering or leaving the liver as determined by the amino-nitrogen in the filtrate from a trichloroacetic acid precipitation before and after acid hydrolysis were followed in normal and diseased animals and also after ingestion of gelatin, amino-acids, and meat. The normal liver is able to synthesise polypeptides (cf. Abderhalden and London, A., 1908, ii, 51), whilst the diseased liver has an efferent blood-stream with a content of amino-nitrogen much higher and of polypeptide-nitrogen only slightly higher than the normal.

F. O. HOWITT.

Excretion of creatine-like substances as a function of the magnitude of the endogenous expenditure of nitrogen. E. F. TERROINE, R. BONNET, P. DANMANVILLE, and (MLLE.) G. MOUROT (Compt. rend., 1930, **191**, 1473—1475).—The total nitrogen, creatine, and creatinine content of the excreta of rats and guinea-pigs has been determined under conditions of inanition produced by feeding on a protein-free diet, preceded in some cases by administration of benzoic acid, phloridzin, or phosphorus as a toxic substance. Under such conditions when the endogenous nitrogen metabolism is reduced to a minimum the amount of creatinine remains constant, whilst the creatine follows the total nitrogen content, increasing when the latter is increased either by dieting or a specific reagent. J. W. BAKER.

Nitrogenous metabolism of the sucking calf on a milk diet. (Determination of total nitrogen, carbamide, uric acid, creatinine, creatine, hippuric acid, and ammonia.) S. J. ERLER and K. J. PAVLOVSKY (Biochem. Z., 1930, **228**, 89—100).—The urine of a sucking calf on a milk diet is alkaline, contains creatine, uric acid, considerable amounts of hippuric acid, is deficient in ammonia, has a creatinine coefficient of 20·33 and a percentage of carbamide-nitrogen smaller than in the adult animal. The curves for the daily excretion of all the above nitrogenous substances show small wave-like variations.

P. W. CLUTTERBUCK.

Production of ammonia in, and ammonia content of, frog muscle. VII. J. K. PARNAS, W. LEWINSKI, J. JAWORSKA, and B. UMSCHWEIF (Biochem. Z., 1930, **228**, 366—400; cf. A., 1929, 598).—Embden and his co-workers employ methods leading to results and conclusions which differ greatly from those of the authors. Since the methods of the former workers are unsatisfactory and the errors in their results great and variable their conclusions cannot be accepted. W. MCCARTNEY.

Ammonia production in the frog heart. I. P. OSTERN (Biochem. Z., 1930, **228**, 401—406).—Ammonia, in amounts probably proportional to the work done, is produced by the beating frog heart. Traumatic production of ammonia occurs in the

heart muscle but proceeds more slowly than in skeletal muscle. W. McCartney.

Ammonia formation in the kidney. G. Embden and H. Schumacher (Pflüger's Archiv, 1929, **223**, 487—495; Chem. Zentr., 1930, i, 3077—3078).—The ammonia formed during 3·5 hrs.' treatment with 2% sodium hydrogen carbonate solution at 37° from pulverised kidney which had been frozen in liquid air has been determined; 100 g. of kidney formed 12—16 mg. of ammonia. After destruction of the deaminising enzyme, about 60% of the ammonia formed is liberated by the addition of an enzyme which eliminates ammonia only from muscle-adenylic acid. Caffeine diuresis diminishes the content of substances yielding ammonia. L. S. Theobald.

Biological values of proteins. I. Measurement of the nitrogenous exchange of rats for determining biological value of proteins. H. Chick and M. H. Roscoe. **II. Biological value of purified caseinogen and influence of vitamin-B_2 on biological values determined by the balance-sheet method.** M. A. B. Fixsen (Biochem. J., 1930, **24**, 1780—1782, 1794—1804).—I. The method consists in the determination of the average daily nitrogenous balance-sheet on a diet containing a definite proportion of the protein under investigation. The provision of vitamins-B was ensured by the administration of purified concentrates from yeast which contained very small quantities of nitrogen.

II. The biological value of purified caseinogen as determined by means of 12 metabolism experiments on adult male rats is 45, a figure considerably lower than that found by previous workers. In experiments in which the intake of calories from fat and carbohydrate combined fell below a certain value, the use of ingested protein for fuel is at once indicated by the underestimation of the biological value. The absence of either vitamin-B_1 or -B_2 from the diet caused a decline in appetite within 48 hrs. So great was this decline in absence of vitamin-B_1 that the intake of calories was too low to allow trustworthy figures to be obtained for the calculation of biological values. The absence of vitamin-B_2 from the diet does not appear to prevent the economical use of ingested nitrogen, provided the caloric intake from fat and carbohydrate is adequate. There was no evidence either of variations in biological value at different levels of intake or of the existence of different biological values for growth and maintenance. S. S. Zilva.

Influence of high- and low-protein diet on the basal metabolism and the chemistry of blood and urine in normal women. C. C. Wang and others (J. Nutrition, 1930, **3**, 79—98).—A high-protein diet for 5 weeks was followed by reduction (with constant caloric value) during 3 weeks to a low-protein diet for 4 weeks and then, a month later, by a normal diet for 2 weeks. There was no marked difference in basal metabolic rate. During the high-protein period the blood-non-protein-nitrogen, -urea-nitrogen, and -creatine, but not the -uric acid, -creatinine, or -calcium, were increased. During the low-protein period the blood-sugar was slightly and -lactic acid markedly increased. The total urinary nitrogen, urea-nitrogen, ammonia-nitrogen, uric acid, and creatine varied directly with the protein intake, whilst the creatinine and lactic acid remained constant. Chemical Abstracts.

Comparative values of different food proteins for reproduction and lactation in the rat. II. Milk, egg, and meats. M. M. Clayton and M. J. Cummings (J. Nutrition, 1930, **3**, 23—38).—Egg is superior to milk for both reproduction and lactation. The difference in results on egg and milk rations containing Osborne and Mendel's salt mixture is due partly to a difference in ash content. Muscle-protein is of lower value than that of milk, egg, or the glandular meats. The vitamin-E content of dried products decreases in the order: egg, milk, beef round, liver, kidney. More vitamin-E is needed for lactation than for reproduction. Vitamin-B_1 is of special significance in lactation. Chemical Abstracts.

Nutritional potency of fresh, cooked, dry, and alcohol-extracted liver. J. S. McHargue, W. R. Roy, and F. E. Hull (J. Nutrition, 1930, **3**, 49—60).—Raw liver, but not liver dried at 100°, was an adequate growth supplement to a synthetic diet in rats. Chemical Abstracts.

Nutritive value of cereal breakfast foods. IV. Response of the human stomach. H. D. Blough, J. S. Carman, and E. M. Austin (J. Nutrition, 1930, **3**, 1—16). Chemical Abstracts.

Nutritive value of cereal breakfast foods. V. Biological value of some cereal proteins as determined on rats. H. A. Mattill and M. M. Clayton (J. Nutrition, 1930, **3**, 17—22).—Average biological values were: milk 89, " precooked oats " 82, wheat preparations 73, 72. Chemical Abstracts.

Effect of cooking on the digestibility of meat. W. M. Clifford (Biochem. J., 1930, **24**, 1728—1733).—Raw meat is digested *in vitro* much more slowly than cooked meat. Over-cooked meat is very slowly digested as compared with under-cooked meat. The maximum rate of digestion is obtained with under-cooked roast meat. Rewarming under-cooked meat does not diminish its digestive rate. Reheating, with consequent over-cooking, diminishes the rate of digestion. The rate of digestion of meat (raw or cooked) is the same whether trypsin alone be used or pepsin followed by trypsin. S. S. Zilva.

Nutritive equilibrium and synthetic milk. L. Randoin and R. Lecoq (Compt. rend. Soc. Biol., 1929, **102**, 371—373; Chem. Zentr., 1930, ii, 261).—With mixtures similar in composition to dried milk nutritive equilibrium is reached with pigeons only within narrow limits; in particular there is an optimum as regards vitamin-B. A. A. Eldridge.

Deficiencies of synthetic diets in chick nutrition. A. G. Hogan and C. L. Shrewsbury (J. Nutrition, 1930, **3**, 39—48).—Dried yeast (40%) must be included in simplified rations. Chemical Abstracts.

Influence of salted yeast on the growth of young rats. L. Rosenov and M. Rosenov (Biochem. Z., 1930, **228**, 163—164).—Salting forms a good method of preserving fodder yeast. Addition of salted

yeast to bread as fodder gives an acceleration of the growth of rats by 36—60% in 24 days.

P. W. CLUTTERBUCK.

Effect of yeast administration on the chemical condition of muscle and liver in chronic training and in isolated muscular effort. C. PI-SUNER BAYO and G. LISS (Z. physiol. Chem., 1930, **193**, 193—197).—Addition of yeast to dogs' diet normally produces no increase in liver-glycogen. In dogs performing regular exercise (chronic experiment), the liver showed a very high fat content after administration of yeast. Yeast seems also to increase the lactic acid. In the acute experiment, yeast administration prior to the exercise causes a very large increase in liver-glycogen.

J. H. BIRKINSHAW.

Influence of food-stuffs on the acid-base balance of cattle urine. F. J. WARTH and N. K. AYYAR (Biochem. J., 1930, **24**, 1595—1600).—The urines from green fodders and cereal straws contain excess of alkali and large amounts of carbon dioxide. Those from over-ripe hays contain little carbon dioxide and are neutral or acid. The urine from wheat straw is acid. Progressive ripening of a fodder tends to increase the acidity of the urine; climatic conditions may modify the effect of ripening. The urines examined contain only traces of phosphoric acid. The buffering is effected by organic acids of which hippuric acid forms nearly two thirds. S. S. ZILVA.

Soft pork. IV. Influence of diet low in fat on composition of body-fat of pigs. N. R. ELLIS and J. H. ZELLER (J. Biol. Chem., 1930, **89**, 185—197). —Pigs reared on a diet of low fat content stored fat at a normal rate. The degree of saturation of the fat increased with the size of the animal, this phenomenon being principally due to a continuous diminution in the proportion of linoleic acid. C. R. HARINGTON.

Behaviour of δ-keto-*n*-hexoic acid in the perfused liver. W. L. DULIÈRE and H. S. RAPER (Biochem. J., 1930, **24**, 1672—1677).—The sodium salt of δ-ketohexoic acid on perfusion through the liver yields a considerable amount of acetone substances which indicates that it undergoes β-oxidation and not further γ- or δ-oxidation in the animal body. Succinic acid is normally found in the liver in small amount and is not influenced by the perfusion of blood.

S. S. ZILVA.

Carbohydrate content of foods. I. Plant foods. II. Food value of vegetable carbohydrates. R. A. MCCANCE and R. D. LAWRENCE (Med. Res. Council Spec. Rep., 1929, No. 135, 73 pp.).

Data concerning the carbohydrate content of various fruits, nuts, and vegetables are recorded. The food value of vegetable carbohydrates other than starch and sugars is discussed.

CHEMICAL ABSTRACTS.

Effects of high-sugar diets on the growth and structure of the rat. C. M. JACKSON (J. Nutrition, 1930, **3**, 61—75).—Little difference was observed between starch-fed and sugar-fed rats.

CHEMICAL ABSTRACTS.

Effect of oats on carbohydrate metabolism. I. A. PARTOS (Z. ges. exp. Med., 1930, **71**, 538—542; Chem. Zentr., 1930, ii, 939).—Oat husk, fed to fasting rabbits, caused a fall in blood-sugar, whilst ingestion of grain resulted in hyperglycæmia.

A. A. ELDRIDGE.

Carbohydrate metabolism of washed muscle. A. UTEVSKI (Biochem. Z., 1930, **228**, 135—145).—The formation of acetaldehyde from pyruvic, fumaric, and malic acids in presence of normal and washed muscle, and washed muscle to which boiled muscle extract had been added, is investigated. The formation of aldehyde is scarcely detectable in autolysing washed muscle or after addition of glycogen, dextrose, lævulose, and glycerol. Traces of aldehyde are obtained with addition of ethyl alcohol and lactates but with pyruvates almost the normal amount is obtained. Washing of muscle causes the loss of oxidative but not of carboxylase power, and addition of boiled muscle extract leads to a return of oxidative power. The conversion of fumaric into malic acid proceeds as readily with washed as with unwashed muscle. The further attack on the malic acid is greatly decreased with washed muscle, but becomes normal on addition of boiled muscle extract. P. W. CLUTTERBUCK.

Methods of sugar degradation in the animal organism. E. BUMM and K. FEHRENBACH (Z. physiol. Chem., 1930, **193**, 238—250).—Red muscle alone hydrolyses glycogen, dextrose only in presence of hexokinase. Addition of co-enzyme-*T* does not promote dextrose hydrolysis. White muscle hydrolyses both carbohydrates; addition of co-enzyme-*T* accelerates the action on dextrose, but does not affect hydrolysis of the polysaccharide. Inversely, co-zymase stimulates the hydrolysis of glycogen only by white muscle. The total glycolysis in presence of all four components dextrose, glycogen, co-enzyme-*T*, and co-zymase is the sum of the glycolysis due to the two reactions.

Kidney hydrolyses dextrose rapidly and glycogen slowly, but hexosephosphoric acid, the intermediate product of glycogen hydrolysis, is very rapidly attacked. Glycolysis of dextrose by kidney is stimulated by yeast co-zymase and also by co-enzyme-*T*, but the course of the reaction appears to be different in the two cases. J. H. BIRKINSHAW.

Metabolism of monohexoses intravenously infused at a constant rate. Dextrose, lævulose, and galactose in blood. W. PIESKOW and M. WIERZUCHOWSKI (Compt. rend. Soc. Biol., 1930, **103**, 415—416; Chem. Zentr., 1930, i, 3076).—The infusion of these sugars in the dog at the rate of 2 g. per kg. per hr. during 3 hrs. has been followed. The dextrose in the blood is unchanged by the addition of lævulose or galactose. The form of the curves correlating the blood-sugar with the amount of sugar added and the effect of insulin thereon is described.

L. S. THEOBALD.

Assimilation of intravenously injected monohexoses. Phosphorus and water metabolisms. E. OWSIANY and M. WIERZUCHOWSKI (Compt. rend. Soc. Biol., 1930, 416—418; Chem. Zentr., 1930, i, 3076—3077; cf. preceding abstract).—Dextrose and lævulose are assimilated to the same extent (90—100%), but galactose to about 30%. During the sugar infusion the blood-phosphorus falls to 2 mg. per 100 c.c. and in the urine to less than 1 mg. per hr.

Insulin increases both diminutions and lengthens the time of the lowered phosphorus content, but does not hinder the return of the latter to the normal.

L. S. THEOBALD.

Production of lactic acid after intravenous injection of monohexoses. M. LANIEWSKI and M. WIERZUCHOWSKI (Compt. rend. Soc. Biol., 1930, **103**, 419—420; Chem. Zentr., 1930, i, 3077; cf. preceding abstract).—Infusion of dextrose at first increases the lactic acid of the blood and urine, the value falling only when infusion has ended. Lævulose produces an even stronger effect, and in both cases the effect of insulin is still more pronounced. The action of galactose is slower. L. S. THEOBALD.

Specific dynamic effect and the oxidation of dextrose, lævulose, and galactose. M. WIERZUCHOWSKI (Compt. rend. Soc. Biol., 1930, **103**, 420—422; Chem. Zentr., 1930, i, 3077).—In the previous investigations (cf. preceding abstracts) 0·5 g. of sugar per kg. per hr. was oxidised; 34% of dextrose, 41% of lævulose, and 56% of galactose were assimilated. Insulin increased oxidation in those cases, *e.g.*, lævulose, in which assimilation was unaffected. The relationship between lactic acid formation and the specific dynamic effect is discussed.

L. S. THEOBALD.

Influence of oxygen on lactic acid formation in muscle. A. HAHN, E. FISCHBACH, and H. NIEMER (Z. Biol., 1930, **91**, 53—62).—The lactic acid content of freshly-pulped muscle shaken with oxygen is constant. Under the same conditions, the carbohydrate content is also constant, or shows a slight decrease. In a vacuum lactic acid increases, but becomes stationary when the carbohydrate content has fallen to a value equivalent to 18—21 mg. of dextrose per 10 g. of muscle. These results are regarded as incapable of explanation by Meyerhof's view that identical phenomena are observed in pulped muscle and in the recovery of intact muscle. A. COHEN.

Metabolism of acetaldehyde. I. Assimilation limits in normal dogs. R. MANCKE (Arch. exp. Path. Pharm., 1930, **157**, 372—380).—During 30 and 98 hrs., respectively, 55 and 85 g. of acetaldehyde were absorbed without toxic effects being observed. F. O. HOWITT.

Intermediary iron metabolism. E. STARKENSTEIN (Z. ges. exp. Med., 1929, **68**, 425—440; Chem. Zentr., 1930, ii, 262).—A complex ferric–protein compound is formed from simple inorganic ferrous compounds and circulates in the blood as an intermediary metabolic product; it differs from ferric chloride–protein precipitates. Complex formation is assisted by carboxyl groups (monocarboxylic acids and amino-acids) and hydroxyl groups (polyalcohols, glycerol, and sugar). On injection of iron tartrate, malate, or citrate, but not on that of gluconate, an iron–sodium complex is formed; injected ferric sodium lactate or gluconate remains in the organism as a complex. Simple amino-acids of the protein molecule do not produce the ferric–protein complex, in which the iron is anionic. Only anionic iron is physiologically active. Simple inorganic ferrous compounds are biologically important as sources of the necessary iron.

A. A. ELDRIDGE.

Effect of crude fibre on retention of calcium and phosphorus. M. A. BLOOM (J. Biol. Chem., 1930, **89**, 221—233).—The retention of calcium and phosphorus by young rats on a basal diet containing 0·9% of spinach ash and only a small amount of fibre was reduced by the substitution of 5% of dried spinach (raw or cooked) for the spinach ash and was not significantly affected by the addition of crude fibre (filter-paper) in amounts up to 8% of the diet.

C. R. HARINGTON.

Possible significance of hexosephosphoric esters in ossification. Calcification *in vitro*. VIII. R. ROBISON and K. M. SOAMES. **IX.** R. ROBISON, M. MACLEOD, and A. H. ROSENHEIM (Biochem. J., 1930, **24**, 1922—1926, 1927—1941).—VIII. Whilst calcification *in vitro* may occur in solutions of inorganic salts supersaturated with respect to the bone salt, calcification will take place with lower concentrations of calcium and inorganic phosphates, if phosphoric ester is also present, even in very small amount.

IX. In inorganic solutions with salt concentrations approximating to those in plasma, calcification was obtained with concentrations of calcium varying from 2·5 to 50 mg. per 100 c.c. and of inorganic phosphate varying from 1 to 20 mg. per 100 c.c. Calcification was observed at somewhat lower levels of the product [Ca]×[P] when the concentration of calcium was high and that of phosphate low than under the reverse conditions. With concentrations of calcium around 10 mg. per 100 c.c. some degree of calcification was usually obtained in 16 hrs. when the concentration of inorganic phosphate was such that the product [Ca]×[P] was equal to 30. Variations were, however, observed in the minimum level required with bones from different rats. This variability in response was apparent also in the extent of the deposit obtained at higher [Ca]×[P] levels. Definitely higher [Ca]×[P] levels were necessary for calcification when the concentration of sodium hydrogen carbonate was reduced from 0·2% to 0·03%, and still higher levels were required when the salt was entirely omitted. This suggests that the compound normally deposited in calcifying cartilage is a complex carbonato-phosphate (carbonato-apatite) rather than a mixture of basic phosphate and carbonate. It is confirmed that sodium chloride in concentrations as low as 0·034*M* (0·2%) has an inhibitory effect on calcification in inorganic solutions. Potassium chloride in concentrations up to 0·01*M* (twice the concentration in plasma) had no appreciable inhibitory effect. Magnesium in concentration 0·0008*M* (slightly lower than that in plasma) affected adversely calcification and with higher concentrations the inhibitory effect was pronounced. The inorganic solutions in which calcification occurred were all supersaturated with respect to the calcium salt deposited. In presence of phosphoric ester, however, calcification occurred at [Ca]×[P] levels much lower than 30, whilst at higher levels the effect of the ester was seen in the greatly increased extent and density of the deposit. The increased calcification which occurred in presence of phosphoric ester tended to mask the favourable effect of sodium hydrogen carbonate and the inhibitory effects of sodium chloride and magnesium. There was

no evidence that any of the inorganic radicals directly influenced the enzyme mechanism. Between p_H 7·2 and 7·8 no marked optimum was found for calcification in presence or absence of ester. Calcification was obtained at p_H 6·5 with very high [Ca]×[P] levels (60—80) in inorganic solutions, and at the low level 24 in presence of phosphoric ester. Formaldehyde completely inhibited calcification in inorganic solutions and almost completely inactivated the phosphatase mechanism. The presence of chloroform or potassium cyanide strongly inhibited calcification in inorganic solutions, but had no appreciably effect in solutions containing phosphoric ester. Bone slices after being soaked for 24 hrs. in chloroform, acetone, or alcohol, or desiccated in a vacuum over sulphuric acid failed to calcify on subsequent immersion in inorganic solutions of high [Ca]×[P] levels. In solutions containing phosphoric ester, however, extensive calcification occurred and the deposits were normal in appearance. In normal calcification of the skeleton there are two mechanisms, the first the bone phosphatase which produces the necessary degree of supersaturation in the matrix, and the second which assists in the deposition of the bone salt from this supersaturated solution.

S. S. Zilva.

Development and phosphatase activity *in vivo* and *in vitro* of the mandibular skeletal tissue of embryonic fowl. H. B. Fell and R. Robison (Biochem. J., 1930, **24**, 1905—1921).—The embryonic mandibular skeleton of the fowl consists of a rod of cartilage (Meckel's cartilage) surrounded by a sheath of membrane bone. The distal part of this cartilage does not ossify and synthesises no phosphatase. The membrane bone surrounding Meckel's cartilage develops high phosphatase activity. Explants of Meckel's cartilage from 6-day embryos neither ossified nor synthesised phosphatase *in vitro*. Explants of the mandibular mesoderm (pre-membrane bone) during growth *in vitro* developed ossification centres and synthesised phosphatase. S. S. Zilva.

Measurements of the acid taste and their bearing on the nature of the nerve receptor. N. W. Taylor, F. R. Farthing, and R. Berman (Protoplasma, 1930, **10**, 84—97).—Determinations of the "threshold concentration" for sourness of numerous organic acids by Taylor's method (A., 1929, 347) are described and the relative concentration gradients of the non-ionised acids calculated. The addition of polar groupings, ·OH, >C:C<, >C:O, $\cdot CO_2H$, $\cdot NH_2$, to organic acids renders the penetration of the acid to the nerve receptor 20—500 times as difficult. Lengthening the carbon chain by addition of CH_2 groups makes penetration easier. It is concluded that the organic acids are absorbed by a tissue which resembles fat rather than protein. A. G. Pollard.

Nature of the nerve receptor for the acid taste as indicated by the absorption of organic acids by fats and proteins. N. W. Taylor (Protoplasma, 1930, **10**, 98—105).—Distribution coefficients of a number of organic acids between olive oil and water were determined. The relative effects of the groups ·OH, :CO, $\cdot SO_3H$, $\cdot NH_2$, and :C:C: on the coefficients are of the same nature and order of magnitude as their effects on the concentration gradients of the undissociated acids between water and the nerve receptor (cf. preceding abstract). Specific effects of the amino- and phenyl groups are recorded. Changes in the p_H of gelatin to which increasing proportions of the acids were added are represented by a series of curves the relative positions of which are determined by their dissociation constants. The various polar groups affect the position of the curves only in so far as they affect dissociation constants and the results are not paralleled by the taste experiments. The nerve-ending which the acid penetrates and stimulates to give the sensation of sourness is concluded to have the characteristics of fat and not of protein. A. G. Pollard.

Alkali deficit and dextrose tolerance in the dog. H. J. Deuel, jun., and M. Gulick (J. Biol. Chem., 1930, **89**, 93—95).—Dextrose tolerance in dogs is not impaired by the acidosis which results from administration of ammonium chloride. C. R. Harington.

Toxicity of ethylene chlorohydrin. J. D. Pratt (Nature, 1930, **126**, 995).—Attention is directed to fatalities which have occurred from inhaling the vapour of ethylene chlorohydrin, which appears to act as a metabolic poison. L. S. Theobald.

Carbohydrate metabolism following guanidine deglycogenation. F. Bischoff and M. L. Long (J. Nutrition, 1930, **3**, 201—216).—Insulin increases the utilisation of dextrose at normal or hyperglycæmic levels by guanidine-deglycogenated rabbits with or without storing glycogen. Adrenaline decreases the utilisation of injected dextrose in animals in which the liver has been depleted of glycogen and has been deprived (by means of guanidine derivatives) of the power of storing glycogen; hence normal adrenaline hyperglycæmia is not entirely due to an increased output of dextrose by the liver. Adrenaline increases the blood-lactic acid and insulin does not affect it in rabbits suffering from guanidine-deglycogenation. Chemical Abstracts.

Chemical constitution and pharmacological properties of methylglyoxaline derivatives. J. V. Supniewski (Compt. rend. Soc. Biol., 1928, **98**, 1229—1230; Chem. Zentr., 1930, i, 3809).—Glyoxaline, 4-hydroxymethylglyoxaline and glyoxaline-4-aldehyde cause increased blood-pressure in cats, and contract the isolated guinea-pig uterus. 4-Methylglyoxaline or 5-methyl-4-hydroxymethylglyoxaline when injected intravenously into cats causes a diminution in blood-pressure, and with rabbits produces increased peristaltic contractions. 4-Chloromethylglyoxaline reduces the blood-pressure; 4-aminomethylglyoxaline causes first a rise and then a fall in blood-pressure, uterine contraction in guinea-pigs, and intestinal contraction in rabbits. 2-Thio-4-methylglyoxaline [?] causes with cats a fall in blood-pressure, and increase of respiratory movement. 4-Diethylaminomethylglyoxaline causes a fall in blood-pressure in cats, and uterine contraction in guinea-pigs. 4-Piperidylmethylglyoxaline causes in cats a marked fall in blood-pressure, contracts the isolated guinea-pig uterus, and is diuretic. Glyoxaline-4-carboxylic acid, -4:5-dicarboxylic acid, and 2-thio-4-methylglyoxaline [?] have no particular pharmacological properties. A. A. Eldridge.

Antipyretic action of 3-aminohydrocarbostyril, its isomerides and derivatives. K. WATANABE (J. Biochem., Japan, 1930, **12**, 71—81).—1-, 3-, and 7-Aminohydrocarbostyril are strongly antipyretic, but the 1- and 3-derivatives are toxic; diacetyl-3-aminohydrocarbostyril is antipyretic and less toxic. *m*-Aminophenylalanine, but not *p*-compound, exhibits some antipyretic action.

CHEMICAL ABSTRACTS.

Isotonic soap solution for injection. PICON (J. Pharm. Chim., 1930, [viii], **12**, 481—484).—A stable, neutral soap solution, miscible with water and salt solution, is prepared by dissolving 100 g. of ricinoleic acid in 700 c.c. of warm 10% alcoholic sodium hydroxide solution followed by removal of the alcohol. A 1% solution (wt./vol.) of the soap thus obtained in 0·7% sodium chloride solution forms an isotonic solution which is not changed by sterilisation, produces only feeble hæmolysis, does not coagulate the blood, and has given satisfactory results when injected into human beings. E. H. SHARPLES.

Toxicity of rotenone, *iso*rotenone, and dihydrorotenone to goldfish. W. A. GERSDORFF (J. Amer. Chem. Soc., 1930, **52**, 5051—5056).—The minimum toxic concentrations of rotenone, *iso*rotenone, and dihydrorotenone are determined by the method previously described (A., 1930, 1316) to be 0·0125, 0·055, and 0·005 mg. per litre, respectively.

H. BURTON.

Heart tonics. IV. Digitalis standardisation; a new assay method. W. NYIRI and L. DUBOIS (J. Pharm. Exp. Ther., 1930, **40**, 373—401).—The factors affecting the pharmacological assay of digitalis preparations have been investigated and a method in which the rabbit is used as test animal is recommended. W. O. KERMACK.

Phloridzin diabetes. II. Relationship between state of nutrition and dextrose tolerance. H. J. DEUEL, jun. (J. Biol. Chem., 1930, **89**, 77—91).—Although in the fasting condition the phloridzinised dog exhibits a dextrose tolerance curve similar to that of a diabetic animal, if the sugar tolerance be observed 14 hrs. after a heavy dose of carbohydrate the responses of phloridzinised and normal animals are closely similar. This affords additional evidence (cf. A., 1927, 987) that the action of phloridzin is exclusively renal and does not affect the normal processes of oxidation of carbohydrate. C. R. HARINGTON.

Action of "trional" on normal blood constituents. F. G. GERMUTH (Amer. J. Pharm., 1930, **102**, 653—658).—Subcutaneous or intravenous injection daily for 10 days of an aqueous-alcoholic solution of trional causes a decrease in the body-weight of rabbits with an increase in the uric acid, sulphate, sugar, and creatinine content, and a decrease in the iron, calcium, magnesium, chlorine, total phosphorus, acid-soluble phosphorus, protein-combined phosphorus, and total solid content, and in the *d* and *n* of the blood. H. E. F. NOTTON.

Pharmacology of local anæsthetics. III. Comparison of γ-2-methylpiperidinopropyl benzoate hydrochloride with cocaine and procaine on experimental animals. C. L. ROSE, H. W. COLES, and H. E. THOMPSON (J. Lab. Clin. Med., 1930, **15**, 731—735).—γ-2-Methylpiperidinopropyl benzoate hydrochloride is intermediate in toxicity between cocaine and procaine.

CHEMICAL ABSTRACTS.

Disturbance of carbohydrate economy in ether narcosis. H. FUSS (Klin. Woch., 1930, **9**, 410; Chem. Zentr., 1930, ii, 265).—In normal dogs the blood-lactic acid was markedly raised unless oxygen was freely administered. With phloridzinised or fasting dogs only a slight rise was observed; hence in normal animals the excess of lactic acid appears to originate from the reserve carbohydrate. The hyperglycæmia is not, however, repressed by administration of oxygen; hyperglycæmia and excessive urinary excretion of sugar were not observed with dogs poor in glycogen. Ether-narcotised dogs showed no increase of blood-acetone and -acetoacetic acid, whilst the β-hydroxybutyric acid was only slightly and irregularly increased. Acetone and acetoacetic acid were not found in the urine. In glycogen-impoverished dogs the blood-ketone substances increased 24 hrs. after narcosis. The alkali reserve always diminished during ether narcosis; ketonic substances are not the cause of the acidosis. In ether–oxygen narcosis there was a slight fall in the alkali reserve.

A. A. ELDRIDGE.

[Pharmacological] action of nitrogen oxides–carbon monoxide mixtures. W. WIRTH (Arch. exp. Path. Pharm., 1930, **157**, 264—285).—A mixture of the two gases in definite proportions and air causes death in cats, whereas an equal concentration of either constituent results only in slight illness.

F. O. HOWITT.

Action of arsenite on tissue respiration. A. SZENT-GYORGYI (Biochem. J., 1930, **24**, 1723—1727).—Arsenite strongly inhibits the respiration of minced liver tissue, but has no effect on oxygen activation and little effect on hydrogen activation. In yeast arsenite in higher concentrations inhibits respiration, but has no effect on alcoholic fermentation.

S. S. ZILVA.

Relation between trypanocidal and spirochæticidal activities of neosalvarsan. T. F. PROBEY and G. W. MCCOY (U.S. Pub. Health Repts., 1930, **45**, 1716—1728).—Two brands of neosalvarsan of widely different trypanocidal activity are approximately equally effective (*a*) in clearing the chancre of spirochætes, (*b*) in healing the lesion without clinical relapse, and (*c*) in influencing the Kahn reaction in experimental rabbit syphilis over periods of 67—88 days. A. COHEN.

Circulation of bismuth in the organism. C. LEVADITI, Y. MANIN, and A. HOWARD (Compt. rend. Soc. Biol., 1929, **102**, 813—816; Chem. Zentr., 1930, ii, 264).—A few hours after intramuscular injection of "lipoid-soluble bismuth" bismuth can be detected in the kidneys. The excretion does not parallel the bismuth content of the kidneys.

A. A. ELDRIDGE.

Biological effect of bromine. I. Gaseous metabolism of the blood and of the whole organism. II. Oxygen and carbon dioxide dissociation curves of the blood. III. Circulation in

rabbits. S. TADA (Tohoku J. Exp. Med., 1930, **15**, 236—248, 249—258, 259—266).—The oxygen consumption of rabbit's blood-corpuscles when washed in isotonic sodium bromide solution is less than when sodium chloride is used; the oxygen and carbon dioxide dissociation curves also are below those of unwashed cells or of cells washed in sodium chloride solution. Intravenous injection of sodium bromide reduces the oxygen consumption of the rabbit more than does that of sodium chloride, but the effect is not immediate. CHEMICAL ABSTRACTS,

Fluoride intoxication in white rats. J. CHANELES (Rev. soc. Argentina biol., 1929, **5**, 317, 336, 340, 352, 376).—The physiological effects of feeding 50 mg. of fluoride per kg. to young rats are described. The calcium contents of the bones and teeth were diminished; the incisors contained less phosphorus and magnesium than normally. Irradiation with ultra-violet light, however, led to increased values in each case. The bone of treated rats, whether irradiated or not, contained more phosphorus and magnesium than normally.

CHEMICAL ABSTRACTS.

Urinary sulphur and thiocyanate excretion in cyanide poisoning. R. G. SMITH and R. L. MALCOLM (J. Pharm. Exp. Ther., 1930, **40**, 457—471).—The increase of neutral sulphur in the urine of rabbits subjected to hydrogen cyanide vapour for several weeks is practically all accounted for by the thiocyanate excreted in the urine. A fall in inorganic sulphur usually occurs which equals or exceeds the rise in neutral sulphur. An increase in the total nitrogen and in the N : S ratio of the urine is also observed. Cyanide solution ($0{\cdot}01N$) administered to rabbits appears in the urine as thiocyanate, about 72% being accounted for in this way, and when thiocyanate is administered as such an average of 80% is found in the urine. The formation of thiocyanate appears to be the chief method of detoxication of cyanide in the body. W. O. KERMACK.

Reaction of iodates *in vivo*. L. C. MAXWELL (J. Pharm. Exp. Ther., 1930, **40**, 451—455).—Sodium iodate administered intravenously into rabbits has a toxic action in doses of approximately 75 mg. per kg. body-weight. The effect is apparently not due to the liberation of iodine in the tissues. The toxic action of iodate is much increased by iodide.

W. O. KERMACK.

Action and excretion of nitrates. N. M. KEITH, M. WHELAN, and E. G. BANNICK (Arch. Int. Med., 1930, **46**, 797—832; cf. A., 1930, 639).—The diuretic action of ammonium nitrate is confirmed. Data showing its action on normal dogs and normal and œdematous humans are given. G. F. MARRIAN.

Biological action of rays of short wave-length on the metabolism of the cell. K. ADLER (Strahlenther., 1930, **36**, 1—31; Chem. Zentr., 1930, i, 3078).—The point of attack of *X*- and radium rays is not to be sought in the metabolism of the cell. The first changes in cell metabolism appear 24 hrs. after irradiation and increase to a maximum after 34—36 days. The respiration of the tissue diminishes, whilst aerobic and anaerobic glycolysis is doubled; an approximation to the type of metabolism of malignant tumours takes place. After 40 days glycolysis falls below normal. Histological investigations showed degenerative changes in the nuclei of the spermatic cells. L. S. THEOBALD.

Hydrogen acceptors and catalase. I. Influence of hydrogen acceptors on human blood catalase *in vitro*. A. I. ALEXEEV and K. I. RUSINOVA (Bull. inst. recherches biol., Perm, 1929, **6**, 425—461).—The activity of catalase is inhibited by aqueous solutions of methylene-blue, 2 : 4-dinitrophenol, and benzoquinone in proportion to the concentration; the inhibition is maximal at p_H 4·7 and vanishes at p_H 7·27. Trinitrophenol inactivates catalase in neutral solution. Salts in dilute solution activate catalase and destroy the inhibiting action of the hydrogen acceptors. CHEMICAL ABSTRACTS.

Irradiation of *Dolichos* tyrosinase. D. NARAYANAMURTI and C. V. RAMASWAMI (Biochem. J., 1930, **24**, 1655—1658).—The enzyme obtained from *Dolichos lab lab* is activated by irradiation. Addition of irradiated water causes less marked acceleration than irradiation in glass vessels. The increase in activity diminishes with longer exposure in the case of old solutions. The irradiated enzyme decreases in activity on keeping, and is most active when it is least charged. On longer exposure the positive charge on the enzyme particle is increased, thus causing a slight diminution in activity. S. S. ZILVA.

Detection of methylglyoxal formed by the biochemical fission of sugar. C. NEUBERG and M. SCHEUER (Ber., 1930, **63**, [*B*], 3068—3072).—An alcohol–ether preparation of *B. lactis aerogenes* is allowed to act on a 4% solution of magnesium hexosediphosphate, which is then centrifuged after addition of fuller's earth and filtered. After addition of 1 : 2-naphthylenediamine hydrochloride, the mixture is agitated for 2 hrs. and subsequently evaporated to dryness at the ordinary temperature. The residue is triturated with alcohol and the extract evaporated in a vacuum at 37°. The residue is mixed with sodium oxalate and oxalic acid solution and extracted with ether. The ethereal solution is shaken with sodium carbonate, dried, and the ether is removed. The residue is treated with cold 20% sulphuric acid, the solution is filtered and poured into about 8% sodium hydroxide, whereby 3-*methylnaphthopyrazine*, m. p. 95°, is obtained. H. WREN.

Inhibition of esterases by excess of substrate. D. R. P. MURRAY (Biochem. J., 1930, **24**, 1890—1896).—From the observed velocities of the action of the esterase from sheep-liver on different concentrations of ethyl butyrate it is deduced that the inhibition of certain enzymes by excess of substrate is due to the formation of a non-hydrolysable complex of the enzyme with 2 mols. of the substrate. By extending the equation it is possible to predict correctly the effect of competitive inhibitors. S. S. ZILVA.

Kinetics of the stereochemical specificity of human liver-esterase. P. RONA, H. FISCHGOLD, and R. AMMON (Biochem. Z., 1930, **228**, 77—88).—Bamann's result (A., 1929, 957) that when human liver-esterase acts on ethyl *dl*-mandelate, the rotation of the acid liberated may be either *d* or *l*, according to

the concentration of the substrate, is confirmed with the methyl ester. The rotation obtained does not depend on the ratio of the amounts of enzyme and substrate, but only on the concentration of the latter. The activity–p_s curves are obtained for both *d*- and *l*-modifications of the methyl ester. No satisfactory explanation for the cause of inversion is available.

P. W. Clutterbuck.

Asymmetric hydrolysis of esters by enzymes. IV. Influence of optically active foreign substances on the configuration specificity of liver-esterase of various degrees of purity. E. Bamann and P. Laeverenz (Z. physiol. Chem., 1930, **193**, 201—214; cf. A., 1930, 499).—The age of the enzyme preparation affects the optically selective hydrolysis of *dl*-ethyl mandelate by human liver-esterase in presence of strychnine. The effect of strychnine on stereochemical specificity is also influenced by the pre-treatment of the enzyme. When the strychnine concentration is maintained constant, a change in the enzyme concentration does not affect the result, but a variation of strychnine concentration coupled with constant enzyme concentration produces varying rotation of the products. The enzyme–strychnine mixture, after long dialysis, has the same effect as the enzyme alone, which indicates that the enzyme–strychnine complex is dissociable.

J. H. Birkinshaw.

Asymmetric hydrolysis of esters by enzymes. V. Configuration-specificity of liver-esterase in its dependence on alterations in enzyme complex. E. Bamann and P. Laeverenz (Ber., 1930, **63**, [*B*], 2939—2948; cf. Willstatter, Kuhn, and Bamann; A., 1930, 499).—It has not been found possible to influence the optical selectivity of the liver-esterase of man by exhaustive purification by the adsorption method. Such influence, previously noted only after addition of suitable optically active material, can be caused by pre-treatment of the enzymic preparations. The enzyme from the untreated dry preparations of the liver of man or rabbit hydrolyses the two components of ethyl *dl*-mandelate at almost equal rates, whereas an extract from the same dry preparations which has been preserved for some days at 60—65° favours the *d*-ester, and that derived by submitting the extract to proteolytic degradation in faintly acid solution for about a week favours the *l*-ester.

H. Wren.

Nature of enzyme action. A. Fodor and L. Frankenthal (Biochem. Z., 1930, **228**, 101—122).—When dried pancreatic preparations are treated with water, the insoluble residue hydrolyses glycylglycine readily, but glycylglycyl-*l*-leucine only with difficulty. The filtrate, on the other hand, when incubated for 24 hrs. with glycylglycine initially does not attack, but later shows a strongly autocatalysed hydrolysis of the dipeptide. This period of induction is not obtained either with the tripeptide or with peptone, and is regarded as due to changes in the nature of the enzyme carrier during autolysis of the extract. When amounts of glycyl-*l*-leucine and glycyl-*dl*-leucine such that both contain the same amount of glycyl-*l*-leucine are incubated with yeast macerates, both fresh and 3 days old, the presence of the *d*-isomerides causes acceleration of hydrolysis. The bearing of these results on the general nature of enzyme reaction is discussed.

P. W. Clutterbuck

Action of degradation products on enzymic proteolysis. P. Rona, H. Kleinmann, and E. Dressler (Biochem. Z., 1930, **228**, 6—76).—The contradictory results of Weber and Gesenius (A., 1927, 992), who showed that the solution obtained by digestion of caseinogen with trypsin and pepsin retarded proteolysis of further amounts of caseinogen, and of the authors (A., 1925, i, 473; 1926, 543), who did not obtain inhibition, are shown to depend on the different concentrations of reactants and on the different methods of analysis used by the two sets of investigators. A solution containing only a small amount of protein and enzyme (micro-determination) showed no inhibition of proteolysis (as determined by the nephelometric method) even when 100% of degradation products are added. On the other hand, a solution containing 50 times the amount of substrate and 20 times the amount of enzyme (macro-determination) showed considerable inhibition (as determined by titration of the liberated carboxyl groups) on addition of degradation products. With tryptic hydrolysis, the difference of results depends entirely on the concentration of reactants. When the concentration of enzyme is sufficiently small, the enzyme–inhibitor complex is completely dissociated and no inhibition is recorded. With peptic hydrolysis, although inhibition was again obtained using the macro-method and was not obtained using the micro-method, yet the inhibition was dependent only on the method of analysis. When the reaction was followed on the macro-scale by the titration method an inhibition was recorded on adding degradation products, whereas when followed by the nephelometric method (*i.e.*, in terms of unused protein) inhibition was not obtained. These results are reproduced on the same solution, and it seems certain that the two determinations, with peptic digestion, measure different processes.

P. W. Clutterbuck.

Formation of diketopiperazine in the enzymolysis of gelatin. A. Blanchetiere (Compt. rend., 1930, **191**, 1479—1481).—Unlike the results obtained with gliadin and ovalbumin (A., 1930, 100) hydrolysis of gelatin occurs less regularly with trypsin than with pepsin and the amount of diketopiperazine formed is only about 66% of that expected from the amino-acids constituting this protein.

J. W. Baker.

Analysis of proteolytic enzyme of *Maja squinado* by the adsorption method. J. J. Mansour-Bek (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 858—870).—Adsorption measurements have shown that the gastric juice of *Maja squinado* contains several proteolytic enzymes, including a proteinase, a carboxypolypeptidase, an aminopolypeptidase, and a dipeptidase. The proteinase can be purified and is then most active at p_H 7·4—8·1, whilst the activity of the crude extract is greatest at p_H 6·0—6·1. The proteinase is of a trypsin-like character, degrades peptone and clupeine sulphate, and is activated by enterokinase, but not by hydrocyanic acid, hydrogen sulphide, or zookinase.

E. S. Hedges.

Pathological decomposition of protein. III. Hexone bases and monoaminodicarboxylic acids

liberated from caseinogen by the action of coli-protease. M. Schierge (Z. ges. exp. Med., 1929, **62**, 141—146; Chem. Zentr., 1930, ii, 756).—In addition to tyrosine, leucine, tryptophan, and phenylalanine, there were also found histidine and lysine; glutamic and aspartic acid were not detected.

A. A. Eldridge.

Purinolytic enzymes of the human organism. R. Truszkowski (Biochem. J., 1930, **24**, 1681—1686).—Uricase was absent from the livers of a new-born child and of two adults and from the livers and kidneys of six fœtuses from the 12th to the 40th week of pregnancy. Xanthine oxidase was absent from the extracts of the kidneys of the above fœtuses but present in all their liver extracts. S. S. Zilva.

Plasma-phosphatase. I. Determination and properties. II. The enzyme in disease, particularly of bone. H. D. Kay (J. Biol. Chem., 1930, **89**, 235—247, 249—266).—I. Blood-plasma is added to excess of a solution of sodium β-glycerophosphate at p_H 7·6 and the mixture is kept at 38° for 48 hrs. The difference between the inorganic phosphate content of such a mixture and that of a similar mixture treated at the beginning of the experiment with trichloroacetic acid to remove the enzyme represents the liberation of phosphoric acid brought about by the phosphatase. The optimum p_H for the enzyme is 8·8—9·1; its action is inhibited by calcium ions and by high concentrations of magnesium ions, although low concentrations of the latter have a stimulating effect. Plasma-phosphatase liberates phosphoric acid from sodium hexosediphosphate, α- and β-glycerophosphate, pyrophosphate, glycophosphate, and guanine nucleotidate at descending rates in the order mentioned. The phosphatase concentration in the blood decreases with the age of the animal.

II. The phosphatase content of the blood-plasma is largely and specifically increased in patients suffering from generalised disease of the bones. The possible role of the enzyme in normal bone-formation is discussed. C. R. Harington.

Selective fermentation. II. Fermentation of sugar mixtures by Sauterne yeast. H. Sobotka and M. Reiner (Biochem. J., 1930, **24**, 1783—1786).—This yeast ferments lævulose preferably to dextrose in a mixture, the ratio of the rate of fermentation of lævulose to that of dextrose, which depends on adaptation phenomena, varying from 1·2 to values above 10. It ferments lævulose alone 50—100% faster than dextrose alone. S. S. Zilva.

Zymatic system of *Saccharomyces Johannesberg*. I. Yamasaki (Biochem. Z., 1930, **228**, 127—134).—*S. Johannesberg*, II, either the alcohol–ether or the dried preparation, is able to convert magnesium hexosediphosphate into methylglyoxal and pyruvic acid. The dry preparation ferments pyruvic acid readily. Both the fresh and dry yeast, in presence of toluene, cause phosphorylation of sugar as soon as co-enzyme is added, at least two phosphoric esters being formed, of which one yields a sparingly and the other a readily soluble barium salt.

P. W. Clutterbuck.

Growth of yeast by the aeration method and the increase in its constituents. H. Claassen (Biochem. Z., 1930, **228**, 154—162).—In two fermentations, the hourly increase of yeast in dry weight, protein, nitrogen-free substances, and ash is determined. Formation of protein is greatest when the wort contains sugar and readily assimilable nitrogen, especially ammonia, whereas nitrogen-free constituents are predominantly formed in the later stages of fermentation, *i.e.*, when the wort contains no sugar but still contains amino-acids, alcohol, and nitrogen-free organic acids. Addition of limited amounts of ammonia to a wort containing sufficient assimilable organic nitrogenous material for normal growth does not increase the dry weight of yeast but only causes an increase of the protein fraction and a corresponding decrease of the nitrogen-free substances.

P. W. Clutterbuck.

Conditions of activation of washed zymin. II. A. A. Stheeman (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 889—897; cf. A., 1929, 1107).—When zymin has been exhaustively washed with water it cannot be reactivated without the addition of the co-enzyme of alcoholic fermentation isolated by von Euler. With less washing the inactive preparation may be activated by adding methylene-blue or a mixture of methylene-blue and hexosediphosphate. Von Euler's principle is able to replace hexosediphosphate, although the substitution is not mutual; the principle contains esterified phosphoric acid groups, but also has a specific action of an unknown character.

E. S. Hedges.

Action of sodium monoiodoacetate on the enzymes of zymase and on the fermentation of hexosediphosphate. I. Yamasaki (Biochem. Z., 1930, **228**, 123—126).—Iodoacetic acid, although inhibiting the action of whole zymase, has little effect on the action of glycollase and causes only a 30% inhibition of carboxylase, the chief effect being on the phosphatese. P. W. Clutterbuck.

Activator *Z*. VI. T. Philipson (Z. physiol. Chem., 1930, **193**, 181—192; cf. this vol., 128).—Methods of purification of the *Z* factor were examined. Dialysis of boiled yeast-juice followed by precipitation with lead and mercury salts increased the activity. By autolysis of bottom yeast, preparations with two to three times the activity of the original material were obtained. The bottom yeast employed contained twice as much *Z* activator as top yeast. The activator is very stable to acids and alkalis before the mercury treatment, but becomes somewhat sensitive to alkali after the treatment. J. H. Birkinshaw.

Bios. VI, VII. B. Suzuki, K. Matsusita, and K. Aoki. **VIII.** B. Suzuki and Y. Hamamura (Proc. Imp. Acad. Tokyo, 1930, 6, 334—340).—VI, VII. *Saccharomyces saké*, which ferments sugar in the absence of rice-bran bios, *S. cerevisiæ*, which is active in bios-free media, and several species of yeast of intermediate activity are all incapable of synthesising bios, although propagation is possible in its absence. *Aspergillus oryzæ*, however, is able to synthesise bios.

VIII. The purification of bios is described, giving a 10% yield having ten times the activity of the starting material. Purified bios appears to be a non-nitrogenous substance containing three hydroxyl groups. The *benzoate* (highest m. p. 116—118°) is not

fractionated by decalin or carbon tetrachloride, and is inactive. Activity reappears on hydrolysis with 0·1*N*-sodium hydroxide. A. COHEN.

Influence of hydrogen sulphide on reproduction rate in *Paramecium caudatum*. M. J. SHARPE (Protoplasma, 1930, **10**, 251—252).—Hydrogen sulphide and also sodium sulphide in equivalent sulphur concentration increased the rate of reproduction of *P. caudatum* (cf. Hammett, *ibid.*, 1929, 297; Reimann, this vol., 255). A. G. POLLARD.

Growth of *Aspergillus niger* and copper content of the nutrient medium. L. K. WOLFF and A. EMMERIE (Biochem. Z., 1930, **228**, 443—450). —*A. niger* absorbs copper from the medium in which it grows, the depth of the colour of the spores being proportional to the amount of copper taken up. For the growth of the organism the presence of at least 0·0002 mg. of copper in 250 c.c. of medium is necessary and for the production of spores at least 0·0003 mg. No degeneration takes place when the organism is propagated in media too poor in copper to promote the production of spores, and this production can at once be initiated in such media by the addition of sufficient copper. W. McCARTNEY.

Colouring matter of *Aspergillus* and *Mucor*. A. BLOCHWITZ (Zentr. Bakt. Par., 1930, II, **80**, 201—202; Chem. Zentr., 1930, i, 3066).—Potassium hydroxide extracts from all green conidia of *Aspergillus*, *Penicillium*, and *Citromyces* a characteristic reddish-brown colouring matter which with hydrochloric acid becomes yellow or yellowish-brown according to the concentration. The deep violet conidia of *A. purpurea*, *A. japonicus*, and *A. violata* immediately become deep brown in potassium hydroxide. This brown colour is already present in the conidia. Intense sunlight and high temperature also bring about the change in colour. Young sporangia of *Phycomyces*, *Pilobolus*, *Pilaira*, and *Mucor mucedo* contain a yellow, oily substance soluble in ether, benzene, and chloroform, but unchanged by potassium hydroxide and hydrochloric acid. L. S. THEOBALD.

Lipase of *Aspergillus niger* (Van Tiegh). I, II. Optimum p_H for glycerides of fatty acids. A. JURACEC (Bull. Acad. Sci. Roumaine, 1930, **13**, 103—110, 169—176).—The optimum p_H for the action of the lipase on triacetin, monobutyrin, and triolein is 7·8. A more potent enzyme preparation is obtained by extraction of dried mycelium with disodium hydrogen phosphate than by glycerol extraction of fresh mycelium. P. G. MARSHALL.

Citric fermentation caused by *Aspergillus niger*. L. V. KOTOVSKI (Arkh. Biol. Nauk, 1930, **30**, 303—308).—Currie's medium contains too little nitrogen; for cultures 3 cm. deep 5 g. of ammonium nitrate per litre is recommended. Prolonged cultivation produces strains which operate well at the ordinary temperature. CHEMICAL ABSTRACTS.

Variations in the unsaponifiable matter and lipoidal phosphorus of *Aspergillus niger* as a function of the mineral composition of the culture medium. C. PONTILLON (Compt. rend., 1930, **191**, 1367—1369).—The lipoidal phosphorus content reaches a maximum after 48 hrs. in a normal medium, somewhat later in acid or alkaline media, the formation being greatest as the mineral composition approaches that of Molliard's fluid. Disappearance of lipoidal phosphorus does not run parallel with loss of weight in the mycelium. Sterols are utilised during spore formation. P. G. MARSHALL.

Esterase and protease of *Penicillium Roqueforti*. N. M. NAYLOR, L. W. SMITH, and H. J. COLLINS (Iowa State Coll. J. Sci., 1930, **4**, 465—471).—Optimal conditions for growth, corresponding with increased production of protease and esterase, are recorded. CHEMICAL ABSTRACTS.

Bacterial metabolism. LXXXVIII. Methods for study of "resting" bacteria. LXXXIX. Chemical activity of "resting" *Bacillus coli*. XC. *B. alcaligenes*. XCI. *B. pyogenes-fœtidus*. XCII. *Vibrio* H/61. XCIII. *Staphylococcus aureus*. XCIV. *B. pyocyaneus*. XCV. Glyoxalase-like action of certain "resting" bacteria. A. I. KENDALL, T. E. FRIEDMANN, and M. ISHIKAWA. **XCVI. Utilisation of certain substituted carbohydrates by bacteria.** A. I. KENDALL and C. E. GROSS. **XCVII. Production of histamine by certain strains of the gas bacillus.** A. I. KENDALL and E. GEBAUER-FÜLNEGG. **XCVIII. Quantitative response of intestine from sensitised guinea-pigs to homologous protein and to histamine.** A. I. KENDALL and F. O. SHUMATE. **XCIX. Anaphylactic reaction in smooth muscle.** A. I. KENDALL (J. Infect. Dis., 1930, **47**, 186—193, 194—205, 206—212, 213—218, 219—222, 223—228, 229—236, 237—248, 249—260, 261—266, 267—283, 284—291).—LXXXVIII. Methods for the determination of carbon dioxide, alanine, pyruvic acid, lactic acid, methylglyoxal, dextrose, and volatile acids are described.

LXXXIX. Lactic and pyruvic acids are transformed; the fate of the former is not known, but about 25% of the latter is converted into lactic acid. Alanine is affected only slightly. Dextrose is a good substrate.

XC. Lactic acid is converted into pyruvic acid under aerobic conditions; alanine is readily converted into unknown products. Dextrose is not attacked.

XCI. Dextrose and lactic acid are attacked, particularly under aerobic conditions.

XCII. Lactic acid, but not dextrose or alanine, is utilised.

XCIII. Dextrose, pyruvic acid, and lactic acid are utilised. The action on alanine is pronounced only in presence of oxygen.

XCIV. Pyruvic acid is attacked with production of volatile acids. Alanine and dextrose are attacked in presence of oxygen. Lactic acid is not a favourable substrate.

XCV. Certain "resting" bacteria which ferment dextrose have a glyoxalase-like action.

XCVI. Of carbohydrates dextrose is most readily utilised by bacteria; oxidation to gluconic acid alters the utilisability less than that of the other dextrose derivatives examined. Sorbitol is less readily fer-

mented than mannitol; dulcitol is very resistant. Methyl derivatives of dextrose are refractory to fermentation. *iso*Propylideneglucose is decomposed by the more vigorous types of bacteria; β-methylglucoside is more readily utilised than α-methylglucoside. Mannose is less readily utilised than dextrose; whereas gluconic acid is nearly as readily utilised as dextrose, the utilisability of mannonic acid is restricted. On the other hand, reduction to mannitol does not greatly reduce utilisability as is the case when dextrose is reduced to sorbitol. Tetramethylmannose and α-methylmannoside are refractory. Lævulose is utilised less readily than dextrose. Methyl and *iso*propylidene derivatives of lævulose are unfermentable. Galactose is utilised more frequently than mannose or lævulose, but 6-methyl- and *iso*propylidene-galactose are not fermented. Xylose is fairly readily fermented, whilst γ-trimethylxylose is refractory; *d*-arabinose is fermented by various bacteria that also ferment *l*-arabinose.

XCVII. Some strains of *B. welchii* produce histamine in milk. CHEMICAL ABSTRACTS.

Relation of the quantity of cystine in bacterial protein and anaerobiosis. S. KISHINO (Japan. J. Exp. Med., 1929, **7**, 575—577).—Cystine could not be found in *B. coli*; *V. choleræ*, *M. tuberculosis*, *C. welchii*, and *C. sporogenes* contained 0·144, 0·105, 0·872, and 0·896%, respectively. Sulphur is considered to be essential for the synthesis of bacterial protein of anaerobes. CHEMICAL ABSTRACTS.

Correlation of the oxidation of certain phenols and dimethyl-*p*-phenylenediamine by bacterial suspensions. F. C. HAPPOLD (Biochem. J., 1930, **24**, 1737—1743).—The capacity of bacterial suspension to catalyse the oxidation of pyrocatechol, guaiacol, orcinol, phenol, *p*-cresol, and tyrosine has been studied. Oxidation of pyrocatechol with the formation of *o*-benzoquinone is catalysed only by those organisms which give the dimethyl-*p*-phenylenediamine reaction (cf. Gordon and McLeod, J. Path. Bact., 1928, **31**, 185). The suspensions of staphylococcus used gave a typical although weak colour change with pyrocatechol and did not deaminate in the system bacterial suspension–alanine–pyrocatechol. The anthracoids, unlike the other oxidase-containing bacteria, catalysed the oxidation of guaiacol to a maroon-coloured compound of unknown type, whilst *V. tyrosinatica* catalysed the oxidation of phenol and *p*-cresol; pyrocatechol, which is not appreciably autoxidised at slightly acid reactions, is markedly oxidised at p_H 9·0, and when the oxidation is carried out in the presence of aniline two distinct crystalline substances, of which one appears to be the anilino-*o*-quinone, can be isolated. Anilinobenzoquinone is also obtained by the action of washed bacterial suspensions of anthracoid or of *V. choleræ* on pyrocatechol in the presence of aniline. S. S. ZILVA.

Bacillus thermofibrincolus. **III.** A. ITANO and S. ARAKAWA (Ber. Ohara Inst. Landw. Forsch., 1930, **4**, 457—469).—The influence of several factors on the fermentation of cellulose by *B. thermofibrincolus* has been studied. Cellulose is best decomposed (88%) at 65° by a 7-day aerobic test-tube culture containing —2·20% of cellulose, 0·5% of peptone, and calcium carbonate. Anaerobic flask culture at 50° containing 0·75—3·75% of cellulose, meat extract, and calcium carbonate is most favourable for the production of alcohol and volatile acids. Slight acidity developed in the absence of calcium carbonate greatly impairs the activity of the organism. The organism produces a proteolytic enzyme. Bacterial growth and production of amino-nitrogen are dependent on the supply of cellulose. A. COHEN.

Aerobic soil bacteria which decompose cellulose. A. KALNINS (Latvij. Univ. Raksti, 1930, **1**, 11; Proc. Internat. Soc. Soil Sci., 1930, **5**, 216—217).—The isolation and morphology of aerobic cellulose-splitting organisms are described. Ammonium salts and nitrates proved the best sources of nitrogen for the bacteria, although organic materials could be utilised. Cellulose, starch, or sugars served as energy sources, but glycerol, mannitol, and calcium salts of organic acids were not utilisable. Acid was produced during the decomposition by the organisms of starch or sugars, but not from cellulose. Among the products of decomposition of cellulose was a reducing, osazone-forming substance the formation of which was favoured by limitation of the oxygen supply. The products of cellulose decomposition served as an energy source for *Azotobacter chroococcum*. Starch and dextrose, in concentrations up to 1% in the medium, retard cellulose decomposition. The optimum temperature for the majority of the organisms is 25—27° with p_H 7·5 approx.

A. G. POLLARD.

Decomposition of peat. II. Symbiosis of cellulose-decomposing and nitrogen-fixing bacteria in the anaerobic decomposition of peat. I. A. MAKRINOV and M. L. STEPANOVA (Arkh. Biol. Nauk, 1930, **30**, 293—302).—The two groups of bacteria were grown together on aerobically fermenting peat, and their natural symbiosis is postulated.

CHEMICAL ABSTRACTS.

Influence of caffeine on the fixation of free nitrogen by nodule bacteria. S. BAZAREWSKI (Rocz. Nauk Roln. Les., 1929, **21**, 473—484).—Caffeine contributes to the transformation of nodules into bacteroids, but does not increase their capacity to fix free nitrogen; there is no correlation between the two processes. CHEMICAL ABSTRACTS.

Influence of silica gel on the assimilation of phosphorus by *Azotobacter*. J. ZIEMIECKA (Rocz. Nauk Roln. Les., 1929, **22**, 343—349).—A discussion of the favourable influence of silica gel on the assimilation of phosphorus by plants and micro-organisms of the *Azotobacter* group. CHEMICAL ABSTRACTS.

Biological determination of dextrose. II. Relation between dextrose concentration and p_H change in media. A. LE VESCONTE, J. H. BUCHANAN, and M. LEVINE (Iowa State Coll. J. Sci., 1930, **4**, 451—457).—*Azotobacter levans* acting on replicate media for periods up to 60 hrs. produces uniform p_H values when the media are dextrose (0·01—0·40%) solutions. The most accurate determinations are made by recording data at the minimum p_H value.

CHEMICAL ABSTRACTS.

Reduction of nitrates by bacteria. M. P. KORSAKOV (Russ. Microbiol. J., 1929, **9**, 108—113).—

The reduction of nitrates by bacteria is discussed from the point of view of the theory of oxidation–reduction potential. The oxidation–reduction process can take place only if the compounds in the medium can be activated by the bacteria so that one becomes the donator and another the acceptor of hydrogen, but whether the reduction of nitrates by bacteria in one medium and not in another depends solely on change of the oxidation–reduction potential is an open question. Aerobic bacteria are able to activate, not only the system donator of hydrogen (organic substance)+acceptor (oxygen), but also other systems in which the oxygen is replaced by other acceptors, *e.g.*, nitrates. Thus, *B. pyocyaneus*, incapable of fermentation when the source of oxygen is citric acid, is able to develop under aerobic conditions at the expense of the system citric acid+nitrate, the acid being oxidised completely to carbon dioxide.

The products formed under aerobic conditions are the final products, these being, for *B. coli*, lactic, acetic, and formic acids, which cannot be fermented further, as they cannot be activated. Under aerobic conditions, however, lactic and acetic acids form, with the oxygen, systems which *B. coli* is able to activate, lactic acid being then oxidised to pyrotartaric acid. When nitrates are present in addition to lactic or acetic acid, *B. coli* oxidises these acids also under anaerobic conditions, since systems of donator and acceptor, capable of activation, are then formed (cf. Quastel and Wooldridge, A., 1929, 355). The general conclusion reached from the available data is that the reduction of nitrates by bacteria represents an oxidation–reduction process, conditioned by the differences of potential which depend on the mutual relationships between the bacteria and the medium and may change with alteration of such relationships.

T. H. Pope.

Biological reduction of mineral phosphates. K. I. Rudakov (Zentr. Bakt. Par., 1929, II, **79**, 229; Bied. Zentr., 1930, **59**, 543—544; cf. A., 1928, 447).—Phosphate-reducing organisms develop in cultures with p_H range 4·6—7·7, with an optimum reducing power at p_H 7·1. Maximum reduction is reached after 2 days. The short period of the reduction process has no relationship to the accumulation of acid in the cultures. The development of the organisms is proportional to the phosphate concentration of the substrate. Simple organic acids and alcohols as well as reduced phosphate compounds are among the products of metabolism of the organisms. The colorimetric method, using quinine sulphomolybdate, serves for the determination of phosphates in the presence of phosphites and hypophosphites.

A. G. Pollard.

Cholesterol in bacteria. K. Miyoshi (Sei-i-kwai Med. J., 1930, **49**, No. 6, 47—49).—No measurable amount of cholesterol is present in *B. coli communis*, *S. pyogenes aureus*, *V. choleræ*, *B. pyocyaneus*, or *B. dysenteriæ*. Chemical Abstracts.

Phosphoric esters produced during lactic fermentation. A. I. Virtanen and J. Tikka (Biochem. Z., 1930, **228**, 407—408).—By the action of dried *B. casei* ε on dextrose about half of this is converted into lactic acid and half into a mixture of equal amounts of two phosphoric esters which are formed by the decomposition of Robison's hexosemonophosphoric ester first produced. Neither of the new esters reduces Fehling's solution. One forms a water-soluble *barium* salt, $C_{12}H_{19}O_6PBa_2$, $[\alpha]_D$ −8°, and a crystalline strychnine salt. When boiled with mineral acid this ester loses phosphoric acid only with difficulty and yields a solution which does not reduce Fehling's solution. The other ester forms a barium salt which is sparingly soluble in water and when boiled with dilute mineral acid it also yields a solution which does not reduce Fehling's solution. This ester probably contains a hydroxyl group in place of the aldehyde group of the dextrose molecule. It seems that one ester is an oxidation product, the other a reduction product of dextrose and hence that they are formed by oxido-reduction from Robison's ester (cf. A., 1928, 797). W. McCartney.

Biochemical preparation of optically active glyceraldehyde. C. Neuberg (Biochem. Z., 1930, **228**, 259—261).—*d*-Glyceraldehyde is obtained from the racemic aldehyde by the action of *B. lactis aerogenes* and *B. coli*. P. W. Clutterbuck.

Influence of hydrogen-ion concentration on the growth of tubercle bacilli. II. Biochemistry of the acid-resistant bacilli. L. M. Model (Zhur. exp. Biol. Med., 1929, **13**, 103—107).—Growth is possible within a wide range of p_H values; the optimal value is 7·2—7·5. In a medium poor in nitrogen the p_H shifts to the acid side, but in one rich in nitrogen and poor in phosphorus it shifts to the alkaline side. Autolysis causes a shift to the alkaline side.

Chemical Abstracts.

Purification of tuberculin. I. E. Maschmann and E. Küster (Z. physiol. Chem., 1930, **193**, 215—237).—Tuberculin obtained from cultures on Sauton nutrient solution is purified by 3 days' dialysis (during which there is about 30% loss) and precipitation of proteins by addition of acetic acid to p_H 3·8. The specific substance is then adsorbed on electro-osmotically purified kaolin, the associated carbohydrates remaining in solution. Elution with dilute ammonia solution regenerates the specific substance, which now shows about twenty times its original activity. It gives the biuret, ninhydrin, sometimes Millon, but no tryptophan or Molisch reaction. A preliminary investigation of the carbohydrate fraction yielded a substance resembling glycogen.

J. H. Birkinshaw.

Lipins of tubercle bacilli. XXI. Polysaccharide occurring in the phosphatide from human tubercle bacilli. R. J. Anderson and E. G. Roberts (J. Amer. Chem. Soc., 1930, **52**, 5023—5029).—Hydrolysis of the phosphatide (A., 1927, 1114) with 1% alcoholic potassium hydroxide solution gives an alcohol-insoluble mixture of the potassium salt of an *acid* (*barium* salt) which contains phosphorus, and a polysaccharide termed *maninositose*, $[\alpha]^{23}$ +57° in water, which when heated sinters at 100°, froths at 150°, and darkens slowly above 250°. Hydrolysis of the acid with 5% sulphuric acid affords a reducing sugar, whilst maninositose yields mannose and *i*-inositol (cf. A., 1930, 819). H. Burton.

Reactions relating to carbohydrates and polysaccharides. XXXIII. Synthesis of polysaccharides by bacteria and enzymes. C. F. HARRISON, H. L. A. TARR, and H. HIBBERT (Canad. J. Res., 1930, 3, 449—463).—The formation of polysaccharides from simple sugars by microbiological agents is reviewed.

The production of "gum levan" from sucrose by the *subtilis–mesentericus* group is confirmed; of these the most active agent is *B. mesentericus*, Trevisan. A nutrient 20% sucrose broth is inoculated with a culture of this organism and incubated at 37·5° for 6 days. The crude product, obtained by precipitation with alcohol, is purified by electrodialysis and further precipitations from aqueous solution by alcohol; the yield of levan is 55% of the theoretical quantity. Levan is produced both by *B. mesentericus* and *B. subtilis*, Cohn, in nutrient media containing sucrose and raffinose, but not from those containing melezitose, maltose, lactose, dextrose, xylose, or lævulose. The production of levan, which is formulated as a polymeric 2 : 6-anhydrofructofuranose (cf. Hibbert and Tipson, A., 1930, 1024), is assigned to a specific enzyme, capable of converting the terminal fructofuranose group of sucrose and raffinose, but not the central fructofuranose residue of melezitose, since the production of some polysaccharide is observed in sucrose solutions to which a sterile ultrafiltrate of an active culture has been added. In addition, levan is formed in sucrose solution containing *B. mesentericus* in the presence of toluene at a time when the concentration of viable cells is rapidly diminishing.

T. H. MORTON.

Molecular size of type III specific polysaccharide of pneumococcus. F. H. BABERS and W. F. GOEBEL (J. Biol. Chem., 1930, 89, 387—394).—Determinations of the diffusion coefficient of the specific polysaccharide from type III pneumococcus lead to the value 118,000 for the mol. wt. C. R. HARINGTON.

Preparation of type-specific polysaccharides of pneumococcus. W. F. GOEBEL (J. Biol. Chem., 1930, 89, 395—398).—Cultures of pneumococcus were concentrated and precipitated with alcohol; the precipitate was extracted with water and the filtered solution again precipitated with alcohol. The aqueous solution of the precipitate was freed from protein with trichloroacetic acid, neutralised, and treated with alcohol; after one more separation from aqueous solution by addition of alcohol the carbohydrate was dissolved in water and precipitated at 0° by addition of hydrochloric acid (in the case of type III pneumococcus) or of alcohol (type I). The yield was 0·197 g. per 1000 c.c. (type III) and 0·053 g. per 1000 c.c. (type I). C. R. HARINGTON.

Chemical alteration of purified antibody proteins. L. REINER (Science, 1930, 72, 483—484).—Diazo-coupling of atoxyl with a type I and II pneumococcus antibody gives a product practically insoluble at the isoelectric point p_H 6 and soluble on the acid or alkaline side. Mice infected with 10^5 lethal doses of virulent pneumococci could be fully protected with the preparation. Normal horse serum-globulin coupled with atoxyl had practically no effect.

L. S. THEOBALD.

(a) **Purification and concentration of diphtheria toxin and anatoxin with special reference to active immunisation of man.** S. SCHMIDT and A. HANSEN. (b) **Purification and concentration of diphtheria toxin and anatoxin by precipitation with acid.** S. SCHMIDT and K. A. KJAER (Biochem. Z., 1930, 228, 263—290, 291—299).—(*a*) Highly concentrated colourless and odourless solutions of diphtheria toxin and anatoxin can be prepared from the original impure materials by adsorption on a mixture of aluminium hydroxide and charcoal. The purified toxin and anatoxin solutions retain the specific immunological properties of the crude materials, contain 500—1000 units per c.c., and have protein contents which do not exceed those of the original solutions.

(*b*) For practical purposes diphtheria toxin and anatoxin are best purified by precipitation with hydrochloric acid at p_H 3·5—4·1, the temperature being kept between 0° and 18° and the acid being allowed to act for as short a time as possible. In this way yields of 50—60% are obtained. The properties of the purified materials differ considerably from those of the original ones, the immunising effect of the anatoxins, for example, being reduced.

W. MCCARTNEY.

Insoluble precipitates in diphtheria and tetanus immunisation. A. T. GLENNY (Brit. Med. J., 1930, ii, 244—245).—The addition of aluminium sulphate or potash alum to diphtheria or tetanus toxoid produces a precipitate with high antigenic power. CHEMICAL ABSTRACTS.

Purification of bacteriophage (Shiga and typhoid phages). S. HOSOYA, K. NAGASE, and T. YOSHIZUMI (Japan. J. Exp. Med., 1930, 8, 1—2).—Bacteriophage was precipitated with zinc chloride; the zinc was removed and the filtrate dialysed. The non-dialysable fraction, concentrated at a low temperature and under reduced pressure, contained nitrogen and was precipitated by tannic and phosphotungstic acids, but did not give the protein colour reactions and was not precipitated by Nessler's reagent, ethyl or methyl alcohol, ammonium sulphate, or picrolonic acid. Treatment of the tannic acid precipitate with barium hydroxide destroyed phage activity. The non-dialysable fraction obtained from vaccine virus was inactive. CHEMICAL ABSTRACTS.

Bactericidal effect of ether and chloroform vapours. S. YASUDA (Sei-i-kwai Med. J., 1930, 49, No. 4, 51—70).—Ether vapour is less toxic towards bacteria than chloroform vapour.

CHEMICAL ABSTRACTS.

Disinfection and sterilisation. II. Constitution of terpenes and their disinfecting properties. P. K. DE. **III. Composition of essential oils and their disinfecting properties.** V. SUBRAHMANYAN (Indian J. Med. Res., 1930, 18, 83—90, 91—96).—The germicidal power of terpene hydrocarbons, determined by Rideal and Walker's method with *Bacillus typhosus*, is practically zero; derivatives containing hydroxyl, formyl, carbonyl, and oxygen groups are generally active, alcohols being more effective than ketones. Multiplication of active groups and esterification reduce the phenol coeffi-

cients; unsaturation, and increasing length of side-chains, as calculated from the position of active groups, enhance the disinfecting power. The phenol coefficients of essential oils, although largely determined by the nature and proportion of the active constituents, cannot be predicted from the composition alone. CHEMICAL ABSTRACTS.

"Virtual adrenaline": inactivation of adrenaline by formaldehyde. M. PAGET and C. P. LEBLOND (J. Pharm. Chim., 1930, [viii], **12**, 531—536).—The authors have previously demonstrated that suprarenal glands, after keeping for 24 hrs. in a vacuum over sulphuric acid, frequently show a higher adrenaline content than immediately after death, Denigès' reagent being used as a test. The action of formaldehyde on the secondary amino-group of adrenaline causes it to give a negative reaction with Denigès' reagent, but not with those of Vulpian, Folin, or Paget, which react with the pyrocatechol nucleus. The mydriatic action is considerably reduced, but still persists. T. MCLACHLAN.

Influence of adrenaline and insulin on tissue oxidation. U. VON EULER (Skand. Arch. Physiol., 1930, **59**, 123—400; Chem. Zentr., 1930, ii, 937).—For oxygen concentrations of 2—10% adrenaline (10^{-8} to 10^{-14}) increases the oxygen demand of intact or minced musculature; that of washed muscle is increased by adrenaline only after addition of glycerophosphates and hexosephosphates. The effect of nerve section is recorded. Adrenaline does not increase the oxygen demand or methylene-blue reduction of erythrocytes even in presence of glycero- or hexose-phosphate. The oxidation-promoting effect of insulin is also observed only in suboptimal oxygen concentrations; the reaction is not observed with aerated muscle. A. A. ELDRIDGE.

Phloridzin and insulin. G. ROSENFELD (Arch. exp. Path. Pharm., 1930, **157**, 149—153).—The prevention of accumulation of fat in the liver by administration of insulin to phloridzinised dogs (cf. Wertheimer, Pflüger's Archiv, 1926, **213**, 280) was confirmed. A much lower dextrose and nitrogen excretion occurred than in dogs with phloridzin alone. The significance of these changes with respect to the rôle of the pituitary gland is discussed.

F. O. HOWITT.

Initial hyperglycæmia of dogs after administration of insulin. F. RATHERY, R. KOURILSKY, and J. LAURENT (Compt. rend. Soc. Biol., 1930, **103**, 563—564; Chem. Zentr., 1930, ii, 1241).—The initial hyperglycæmia is independent of the mode of administration, the preparation, and the dose.

A. A. ELDRIDGE.

Insulin and glycogen. I. Normal dogs. II. Depancreatised, fasting, and phloridzinised dogs. F. RATHERY and B. KOURILSKY [with S. GIBERT and J. LAURENT] (Ann. Physiol. Physicochim. biol., 1930, **6**, 32—72, 73—128; Chem. Zentr., 1930, ii, 1240—1241).—I. Blood issuing from the liver after injection of insulin was richest in sugar, that of the portal vein being poorest. Insulin hypoglycæmia is not attributed to inhibition of glycogenolysis. Shortly after injection the liver-glycogen diminishes by 45—85% simultaneously with the hyperglycæmia. Muscle-glycogen also diminishes, the average fall being 22%.

II. Changes in the liver-glycogen and blood-sugar after injection of insulin are recorded.

A. A. ELDRIDGE.

Oral influence of insulin–bile acid. A. W. ELMER and M. SCHEPS (Munch. med. Woch., 1930, **77**, 931—932; Chem. Zentr., 1930, ii, 936—937).—"Cholosulin," when administered orally, has no hypoglycæmic action. A. A. ELDRIDGE.

Influence of substances of the thyroid gland on the total creatine content of liver and muscle. I. ABELIN and W. SPICHTIN (Biochem. Z., 1930, **228**, 250—256).—Administration of thyroid substances causes in rats a considerable decrease of the total creatinine of liver of muscles as well as loss of glycogen and fat. P. W. CLUTTERBUCK.

Thyroxine and the thyroid. I. ABELIN (Biochem. Z., 1930, **228**, 233—249).—A difference in the action of thyroxine and of the whole substance of the thyroid gland is investigated. When rats are given dried thyroid for 8—10 days and again after a rest of 2—3 months, it is found that the second dose is tolerated more readily than the first, the liver being then able to store considerable amounts of glycogen. When thyroxine is injected, both the first and the second treatments render the liver unable to retain carbohydrate as glycogen and the effect on the gaseous metabolism is established more quickly and strongly with the second than with the first injection.

P. W. CLUTTERBUCK.

Effect of long-continued administration of parathyroid on the body-calcium and -phosphorus of albino rats. P. L. DAY (J. Nutrition, 1930, **3**, 157—160).—No measurable effect was observed. CHEMICAL ABSTRACTS.

Parathyroid hormone and regulation of calcium level. C. BOMSKOV (Arch. exp. Path. Pharm., 1930, **157**, 220—233).—The curve of blood-calcium level before and after oral or subcutaneous administration of calcium gluconate in normal and parathyroid-treated animals and the effect of the hormone on the normal blood-calcium were studied in rabbits. The significance of the results together with those of corresponding serum-phosphorus values are discussed.

F. O. HOWITT.

Growth-promoting hormone of the pituitary body. H. B. VAN DYKE and Z. WALLEN-LAWRENCE (J. Pharm. Exp. Ther., 1930, **40**, 413—422).—The finely-ground anterior lobes of the pituitary gland are extracted with dilute sodium hydroxide solution at 0° and the extract is brought by the addition of dilute hydrochloric acid to 7·2 and the precipitate removed. The active principle is then precipitated by the addition of sodium sulphate (20 g. per 100 c.c.). The precipitate after washing in 20% sodium sulphate is suspended in distilled water, the mixture brought to p_H 7·5, the insoluble residue discarded, and the solution is filtered. For clinical use it is further purified by precipitation with sodium sulphate, dialysis, and treatment with N-acetic acid, which at p_H 4·75 produces a precipitate which is removed. The supernatant fluid is readjusted to p_H 7·5—8·0 by N-sodium hydroxide solution. The biological assay of this

extract by the use of hypophysectomised or normal adult rats is discussed. It is proposed to name the growth-promoting principle of the anterior lobe "Phyone." These extracts have no effect on the œstrous cycle of normal female rats. When treated with norite the extracts lose their activity.

W. O. KERMACK.

Conditions of action of extract of the posterior pituitary lobe on uterine muscle. H. KNAUS (Zentr. Gynakol., 1929, 1162—1174; Chem. Zentr., 1930, ii, 258).—An examination of the effect of the physiological condition of uterine muscle and of the function of the corpus luteum. A. A. ELDRIDGE.

Hormone of the anterior pituitary lobe. A. BIEDL (Endocrinol., 1928, **2**, 241—248; Chem. Zentr., 1930, ii, 1238).—The preparation of the hormone from urine of pregnancy or from the fresh gland, and its biological evaluation, are described.

A. A. ELDRIDGE.

Distribution of the ovarian hormone in the mammalian organism. M. GUTMAN (Monatsschr. Geburtshilfe, 1928, **79**, 433—439; Chem. Zentr., 1930, ii, 935).—Only the wall and liquor of ripe follicles of the ox, pig, and horse contain the hormone, which is absent from other parts of the ovary, the corpus luteum, and the placenta; it is absent from the placenta of the dog, cat, rabbit, and guinea-pig, but present in that of the mouse. A. A. ELDRIDGE.

Gastric absorption of the follicular hormone. M. M. MAINO (Arch. Ist. Biochim. Ital., 1930, **2**, 495—504).—Experiments with rats confirm the observation that the mucosa of the digestive apparatus serves well for the absorption of the ovarian hormone. The dose of hormone necessary by this route is treble that required parenterally; the gastric absorption is not influenced by the degree of purity of the solutions used. The nature of the vehicle in which the hormone is ingested affects the amount absorbed, alcoholic solutions being the most active. T. H. POPE.

Female sex hormone: assay; preparation. F. E. D'AMOUR and R. G. GUSTAVSON (J. Pharm. Exp. Ther., 1930, **40**, 473—488).—The factors influencing the assay of the hormone producing œstrus in ovariectomised rats have been investigated and the results of Coward and Burn (J. Physiol., 1927, **63**, 270) emphasising the variability of individual rats have been confirmed. Crystalline œstrin has been prepared having m. p. 241° after sublimation in a vacuum and recrystallisation from 70% alcohol. On assay 1 rat unit (Coward and Burn) was present in 0·38 γ. The compound was apparently identical with that described by Doisy, Veler, and Thayer (A., 1930, 821). W. O. KERMACK.

Rapid (mitogenesis) test for male sexual hormone (androkinin). H. E. VOSS and S. LOEWE (Deut. med. Woch., 1930, **56**, 1256—1258; Chem. Zentr., 1930, ii, 1237).

The male hormone. IV. C. FUNK and B. HARROW (Biochem. J., 1930, **24**, 1678—1680).—Considerable loss of activity takes place when urine is not acidified prior to the extraction of the hormone with chloroform. Ether extracts much of the principle from strongly alkaline solutions obtained by extracting strongly acidified urine with chloroform.

S. S. ZILVA.

Nutritive value of fresh grape juice and wine in relation to their vitamin content. L. RANDOIN (Rev. Viticult., 1930, **72**, 381—389; Chem. Zentr., 1930, ii, 261—262).—Vitamin-*C* was present, but the juice was equivalent in antiscorbutic value to half its volume of lemon juice. The amount of vitamin-*B* was insufficient to support life. A. A. ELDRIDGE.

Vitamins of water-cress (*Nasturtium officinale*). L. B. MENDEL and H. B. VICKERY (J. Home Econ., 1930, **22**, 581—587).—Vitamins-*A* and -*E* are present in the leaves in larger proportions than in lettuce; vitamin-*B* is present in amount comparable with that in other green leaves. The leaves are also known to be rich in vitamin-*C*.

CHEMICAL ABSTRACTS.

Determination of vitamin-*A*. K. H. COWARD, K. M. KEY, F. J. DYER, and B. G. E. MORGAN (Biochem. J., 1930, **24**, 1952—1966).—Two substances to be tested are given to two groups of rats when growth ceases on a vitamin-*A*-free diet. The mean increases in weight of each of the two groups are referred to a curve relating mean increase to dose of a particular sample of cod-liver oil, whence the relative potencies of the two substances are deduced. With 10 rats in a group the potency of a substance can usually be estimated with an error of less than 30%. The curve relating dose to mean increase of weight in a group cannot be assumed to be applicable to all vitamin-*A*-free diets.

Vitamin-*A* content of the livers of normal hogs and of hogs developing experimental rickets. R. GIBBONS and C. B. BARNEY (J. Home Econ., 1930, **22**, 491—496).—Liver of rachitic hogs, when fed to rats, produced 52% more growth than that of normal hogs, probably owing to the rachitic hogs requiring 62% more food per lb. of gain than the controls, whereby a larger proportion of vitamin-*A* was stored. CHEMICAL ABSTRACTS.

Reaction of antimony trichloride with cod-liver oil and its unsaponifiable fraction. E. L. SMITH and V. HAZLEY (Biochem. J., 1930, **24**, 1942—1951).—The unsaponifiable fraction of cod-liver oil, which can be extracted almost without loss with ether, ethyl acetate, chloroform, or light petroleum, gives with antimony trichloride in chloroform a blue colour proportional to its concentration (cf. Norris and Church, A., 1930, 379, 962). The line representing the dilution effect for the total unsaponifiable fraction is tangential at the origin to the dilution curve for the corresponding cod-liver oil; the intensity of the blue colour is not a linear function of the concentration of the oil. S. S. ZILVA.

Antimony trichloride reaction for vitamin-*A*. III. Effect of concentration of reagent and stability of chromogen towards light. E. R. NORRIS and A. E. CHURCH (J. Biol. Chem., 1930, **89**, 421—435).—With concentrations of oil giving colour values higher than 5 Lovibond units the concentration of antimony trichloride has a marked influence on the intensity of colour developed; further, with high

colour values the rate of fading may be such that the intensity of the light employed in making the observations becomes of significance. Exposure of cod-liver oil (whole or unsaponifiable fraction) in chloroform solution to light of wave-length 500 mμ or less causes rapid destruction of the chromogen, particularly in presence of oxygen; light of longer wave-length has no such effect. C. R. HARINGTON.

"Diet 4" for breeding rats for work on vitamin-*A*. S. V. GUDJÓNSSON (Biochem. J., 1930, **24**, 1591—1594).—The diet consists of 30% of skimmed-milk powder, 40% of rice flour, 15% of autolysed yeast, and 15% of hardened coconut oil and shark-liver oil. The young rats are ready for use at the age of 30 days, and, owing to their low reserve of vitamin-*A*, show deficiency-symptoms early. S. S. ZILVA.

Relation of hydrogen-ion concentration to the precipitation of purified torulin (yeast vitamin-B_1) by phosphotungstic acid. H. W. KINNERSLEY and R. A. PETERS (Biochem. J., 1930, **24**, 1856—1863).—The precipitation of the vitamin by this reagent appears to take place between p_H 8·0 and 3·5. It is possible to attain a high degree of concentration by precipitating the active fraction several times. Torulin is unstable to alkali in alcoholic solution. Identical results are not obtained in certain stages of a scheme of fractionation when different sources of the vitamin such as rice or yeast are used. S. S. ZILVA.

Maintenance nutrition in the adult pigeon and its relation to torulin (vitamin-B_1). I, II. C. W. CARTER, H. W. KINNERSLEY, and R. A. PETERS (Biochem. J., 1930, **24**, 1832—1843, 1844—1851).—I. A daily dose of marmite of 1·0 g. (equivalent to 4·3 day doses of vitamin-B_1) is sufficient to convert a falling nutrition on polished rice into maintenance at almost any point between the maximum and minimum weight. Large amounts of vitamin-B_1 do not produce this effect, which confirms the authors' previous observation that purified torulin (vitamin-B_1) does not give maintenance.

II. The factor which supplements B_1 (B-) in the production of maintenance nutrition is present in 50% alcohol extracts of the charcoal process for concentrating vitamin-B_1 (Kinnersley and Peters) and also in alkalised marmite. It is not identical with vitamin-B_3, -B_2, or -B_4. Whole wheat steamed for 5 hrs. gives rising nutrition when supplemented with small doses of vitamin-B_1. Vitamin-B_3 is therefore heat-stable under some conditions. Pigeons receiving up to 36 doses of vitamin-B_1 behave normally. Storage of vitamin-B_3 may influence markedly the behaviour of birds up to some 20 days after being placed on polished rice. S. S. ZILVA.

Quantitative comparison of the curative activity of torulin (vitamin-B_1) on the adult pigeon and the adult white rat. H. W. KINNERSLEY, R. A. PETERS, and V. READER (Biochem. J., 1930, **24**, 1820—1823).—Parallel tests on pigeons and rats by a curative and protective method with torulin (vitamin-B_1) preparations of different purity indicate that the B_1 factor for the two animals is identical and show that the dose of vitamin-B_1 required by these animals is approximately the same. S. S. ZILVA.

Curative activity of the antineuritic vitamin of rice. B. C. P. JANSEN, H. W. KINNERSLEY, R. A. PETERS, and V. READER (Biochem. J., 1930, **24**, 1824—1826).—Curative tests with the Jansen and Donath rice-vitamin crystals (A., 1927, 382) gave the following activity per day dose of vitamin: pigeon 0·007 mg. by injection, 0·009 mg. by mouth; rat, 0·005 mg. Tested on *S. corallinus* it promoted growth of the organism in a dose of 0·006 mg. *per diem*. S. S. ZILVA.

Antineuritic vitamin. A. G. VAN VEEN (Rec. trav. chim., 1930, **49**, 1178).—A note on an improved method for isolating vitamin-B_1. J. D. A. JOHNSON.

Stability of vitamin-B_2. N. B. GUERRANT and W. D. SALMON (J. Biol. Chem., 1930, **89**, 199—211).—The growth-stimulating effect on young rats of yeast and yeast extracts is diminished by heating at 120° for 4 hrs. or by autoclaving at 20 lb. Concentrated extracts suffer loss of activity when exposed to ultraviolet irradiation or to the action of nitrous acid, although in the latter case disappearance of activity is not proportional to destruction of amino-groups. Exposure to oxygen or to hydrogen sulphide at 85—90° has no effect on the vitamin-B_2 content of the extracts. C. R. HARINGTON.

Distribution of the vitamin-*B* complex. I. Leafy vegetables. M. H. ROSCOE (Biochem. J., 1930, **24**, 1754—1763).—Watercress, lettuce, spinach, and cabbage (both the outer dark green leaves and inner etiolated ones), when dry weights are considered, have a content of vitamin-B_1 and vitamin-B_2 about one fourth that of dry brewer's yeast. Their content of vitamin-B_1 is lower than that of wheat germ or ox-liver and higher than that of egg-yolk or ox-muscle. The content of vitamin-B_2 is lower than that of ox-liver, equal to that of milk, ox-muscle, or egg-yolk, and higher than that of the pulses or cereals. In their natural states, however, owing to their high water content, they are relatively poor sources of these vitamins. The onion bulb is poorer in both these vitamins than the green leaves, having about one twelfth to one sixteenth the value of dry yeast. The distribution of vitamin-B_2 appears to bear some relation to the greenness of the leaf, being greater in the dark green than in the paler leaves. No such difference is found in the case of vitamin-B_1. The vegetables tested were on the whole richer sources of vitamin-B_1 than of vitamin-B_2. In the cooking of spinach by the domestic process about half of both vitamin-B_1 and -B_2 is lost in the water and juice. When egg-white is given as a source of vitamin-B_2 there is a lack of a third factor (factor *Y*) necessary for the normal growth of the rat. This factor is present in autoclaved yeast extracts and in all the vegetables tested, but the amounts present in lettuce and etiolated cabbage leaves are less than in the dark green leaves, and the amount present in the onion bulb is still smaller. S. S. ZILVA.

Composite nature of the water-soluble vitamin-*B*. III. Dietary factors in addition to the

antineuritic vitamin-B_1 and the antidermatitis vitamin-B_2. H. CHICK and A. M. COPPING (Biochem. J., 1930, 24, 1764—1779).—Rats show a failure to sustain growth on a diet containing egg-white as a source of protein and vitamin-B_2 and Peters' antineuritic concentrate as a source of vitamin-B_1 (diet II). When the protein portion of the diet is replaced by purified caseinogen and vitamin-B_2 is supplied in the form of egg-white or concentrates prepared from it, the same result is obtained. This is due to the absence from the ration of a hitherto unknown dietary factor—factor Y (see preceding abstract). Satisfactory but not normal and indefinite development over long periods, including fertility and successful pregnancy, but unsatisfactory lactation, was attained on a similar diet containing purified caseinogen as protein, Peters' antineuritic concentrate as vitamin-B_1, and autoclaved yeast or autoclaved watery yeast extracts (5 hrs.; 120°; p_H about 5·0) as vitamin-B_2. Diet II was rendered satisfactory for growth by addition of a small daily ration of an aqueous yeast extract which had been autoclaved in alkaline solution (4 hrs.; 120—125°; p_H about 10). In this preparation vitamin-B_2 was proved to have been destroyed. Factor Y can therefore withstand prolonged heating in alkaline solution, and differs in this respect from vitamin-B_3 and -B_4. It accompanies B_1 and B_2 in nature.

S. S. ZILVA.

Alcohol-solubility of the anti-dermatitis, more heat-stable vitamin-B_2 constituent of the vitamin-B complex. H. CHICK and A. M. COPPING (Biochem. J., 1930, 24, 1744—1747; cf. Narayanan and Drummond, A., 1930, 380).—When alcohol to 56% was added to a solution at p_H 1·5 of vitamin-B_2 prepared from brewer's yeast the precipitate was inactive and the filtrate possessed only one half the potency of the original material. After further addition of alcohol to 70% the solution was completely inactive. When the original solution was less acid (p_H 3·2) total inactivation occurred with 56% alcohol.

S. S. ZILVA.

Egg-white as a source of the anti-dermatitis vitamin-B_2. H. CHICK, A. M. COPPING, and M. H. ROSCOE (Biochem. J., 1930, 24, 1748—1753).—Hen's egg-white, although a rich source of vitamin-B_2, contains no vitamin-B_1. Growth can be restored in young rats suffering from vitamin-B_2 deficiency and the characteristic skin lesions healed by daily doses of a concentrate, prepared by the removal of the heat-coagulable proteins, equivalent to 5—10 g. of the original egg-white. Attempts to purify these concentrates further by alcohol fractionation or precipitation with lead acetate have been unsuccessful. Vitamin-B_1 diffuses out when undiluted egg-yolk is kept in a cellophane membrane surrounded by distilled water for 4 days at about 0°. S. S. ZILVA.

Assay of vitamin-B_4. V. READER (Biochem. J., 1930, 24, 1827—1831).—The typical polyneuritis in rats is a mixture of symptoms due to lack of vitamin-B_1 and -B_4. By eliminating vitamin-B_1 deficiency at the critical stage the true clinical picture of vitamin-B_4 deficiency is revealed and can be used as a curative test. Using this method, vitamin-B_4 from 50% alcoholic extract of distillery yeast was concentrated from 500 mg. to 0·4 mg. per daily rat dose. This method also discloses how far a given vitamin-B_1 preparation is free from vitamin-B_4. S. S. ZILVA.

Third factor in vitamin-B complex of yeast. G. Z. WILLIAMS and R. C. LEWIS (J. Biol. Chem., 1930, 89, 275—288).—The residue left after exhaustive extraction of yeast with aqueous alcohol contains a heat-stable substance which is necessary, in addition to vitamins-B_1 and -B_2, to promote the normal growth of rats on a diet deficient in the vitamin-B complex (cf. Hunt, A., 1928, 1405).

C. R. HARINGTON.

Toxic effect of fish-liver oils and action of vitamin-B. E. R. NORRIS and A. E. CHURCH (J. Biol. Chem., 1930, 89, 437—449).—The toxic effects of certain cod-liver oils simulate those produced by deficiency of vitamin-B and can be relieved by administration of yeast. The same remarks apply to the toxic symptoms which result from continued administration of small amounts of *iso*amylamine or of choline. An adequate supply of yeast in the diet is therefore of importance in the biological assay of cod-liver oil for its vitamin-A content.

C. R. HARINGTON.

Vitamin-B deficiency in the rat. Bradycardia as a distinctive feature. A. N. DRURY, L. J. HARRIS, and C. MAUDSLEY (Biochem. J., 1930, 24, 1632—1649).—Bradycardia, which occurs only in advanced starvation and inanition, appears when young rats are deprived of the vitamin-B complex. The condition can be rapidly cured in the entire absence of food by injection or ingestion of vitamin-B concentrates. Prolonged restoration to normal heart rate is effected by the administration of vitamin-B even when the food consumption is of the same order as that ingested during the last stages of the deficiency. The curative substance was present in various vitamin-B_1 concentrates. It is comparatively thermolabile. The heart-rate response is roughly graded to the dose administered. Deficiency of vitamin-A, of vitamin-D, or of both combined has no significant influence. Excess of vitamin-D produces constantly a very slight bradycardia. S. S. ZILVA.

Heart block in pigeons, curative factor. C. W. CARTER (Biochem. J., 1930, 24, 1811—1819).—Whole wheat and yeast contain a factor, or factors, essential for the normal metabolism and nutrition of the pigeon, the absence of which from the polished rice leads to the development of heart block, among other disorders. This factor is destroyed in wheat if the cereal is previously heated at 100° for 5 hrs. and is not extracted with ether from it. The administration of a diet adequate in protein, fat, and inorganic salts instead of polished rice, or of vitamins-B_1, -B_2, -A, -D, or -E is incapable of preventing heart block or of clearing up the established condition. There is a similarity in the distribution and in the thermolability between this factor and Williams and Waterman's factor (cf. A., 1928, 1059). S. S. ZILVA.

Antiscorbutic fraction of lemon juice. IX. S. S. ZILVA (Biochem. J., 1930, 20, 1687—1698; cf. A., 1927, 487, 702; 1928, 801; 1930, 256).—In the manipulation of lemon juice variable activity is obtained under presumably the same conditions of

fractionation when a volume of a saturated lead acetate solution equal to the volume of the juice is employed for the precipitation of the vitamin. It is, however, possible by adjusting the quantity of the precipitating reagent to prepare from the same juice fractions of higher activity. When the phenolindophenol-decolorising capacity of fractions falls below a certain limit they are antiscorbutically inactive. This reducing property is not an index of antiscorbutic activity itself, but serves rather as an indication that the vitamin has been protected from spontaneous inactivation. The reprecipitation of the antiscorbutic fraction from lemon juice or from cabbage juice with lead acetate in neutral or slightly alkaline zone (p_H 8—9) yields an inactive preparation. The addition of an ethereal extract from autoclaved lemon juice (which decolorises iodine but not phenolindophenol), of quinhydrone, or of benzoquinone to unheated lemon juice accelerates markedly the destruction of the reducing principle and of the antiscorbutic factor in a neutral medium in the presence of air. It is possible that a substance of phenolic character oxidisable in the air is formed in the process of autoclaving and that this compound in its oxidised form destroys in conjunction with the peroxidase present in the juice the reducing principle that acts as an agent for the protection of the antiscorbutic factor. Decitrated lemon juice kept aerobically at p_H 1 or at 0·6—0·8 for 7 days does not lose its reducing capacity for phenolindophenol to a greater extent than when kept at p_H 7 and shows little loss of its antiscorbutic activity. S. S. ZILVA.

Antirachitic properties of shrimp oil. F. P. BROOKS, R. F. ABERNETHY, and F. C. VILBRANDT (J. Amer. Chem. Soc., 1930, **52**, 4940—4943).—Rats (suffering from rickets), fed on a rickets-producing diet supplemented by shrimp oil (the ether-soluble oil from shrimp waste), show increased calcium, phosphorus, and ash contents of the bones. H. BURTON.

Formation of antirachitic vitamin under exclusion of light. A. SCHITTENHELM and B. EISLER (Klin. Woch., 1928, **7**, 1118—1119; Chem. Zentr., 1930, i, 3075).—No provitamin of the antirachitic active substance is present in barley germ (cf. A., 1928, 1405). No increase in the antirachitic principle results from irradiation with ultra-violet light under various conditions. Ergosterol was not found in the germ nor could an antirachitic substance be prepared from barley germinated in the dark. Thus vitamin-*D* is formed during germination, but light is not essential for its origin. L. S. THEOBALD.

Action of light and increasing temperature on the assimilation of carbon dioxide by plants. K. NEYDEL (Biochem. Z., 1930, **228**, 451—486).—The effects of varying the type and intensity of the light and the temperature to which plants which grow in ordinary light are exposed have been measured and compared with those produced in plants which grow in the shade, the assimilation of carbon dioxide being taken as criterion. As regards the influence of temperature, the results of Lundegårdh (Biochem. Z., 1924, **154**, 195) and Johannson (Svensk bot. Tidskr., 1923, **17**, 215; 1926, **20**) have been confirmed, at least in part. W. MCCARTNEY.

Limnological importance of free carbonic acid. E. LINDEMANN (Naturwiss., 1930, **18**, 1113).—The carbon dioxide contents of lakes in Sumatra and Java are discussed. The effects of different vegetable organisms on the carbon dioxide content and p_H are also considered. W. R. ANGUS.

Influence of radium on the chrondriome of lower plants. P. F. MILOVIDOV (Protoplasma, 1930, **10**, 297—299).—The elements of the chrondriome of *Saprolegnia* were not affected by exposure to β- and γ-radiation for several hours (cf. Compt. rend. Soc. Biol., 1929, **101**, 676). A. G. POLLARD.

Hydrogen-ion phenomena in plants. IV. Buffers of potato (tuber and leaf). V. The buffer systems of plant juices. VI. Apparatus for measuring the effect of carbon dioxide on the reaction of plant sap. C. T. INGOLD (Protoplasma, 1930, **9**, 441—446, 447—455, 456—458; cf. *ibid.*, 1929, **6**, 51).—IV. The buffer action of potato tuber sap is attributed largely to its citrate, malate, and phosphate contents. Proteins, asparagine, and oxalate have but little effect. The substances recorded account for 60—70% of the buffer action between p_H 5 and 7, but considerably less in more acid ranges. Citrate, malate, and phosphate are also important buffers in the leaf sap.

V. In any range of p_H the buffer index (β) of a complex buffer system is the sum of the buffer indices of all single-buffer systems present. The general U-form of β curves is discussed. Proteins are not sufficiently powerful buffers to determine the shape of the β curve of plant sap. The forms of β curves in ranges $p_H < 7$ are considered and their uses in plant physiology discussed.

VI. Suitable electrometric apparatus is described. By colorimetric methods it is shown that the p_H value of distilled water 20% saturated with carbon dioxide is 4·2—4·0 and fully saturated 3·8—3·6. The importance of a consideration of carbon dioxide effects in connexion with the reaction of plant sap is indicated. A. G. POLLARD.

p_H and r_H of the sap of *Valonia* and the r_H of its protoplasm. M. M. BROOKS (Protoplasma, 1930, **10**, 505—509).—The sap of *V. ventricosa* has p_H 6·02—6·07. A new lower limit is set for the minimum value of the E_h of the sap, and the r_H recalculated from the above lies between 17·9 and 18·4. The r_H of the sap may be taken as approximately that of the protoplasm. A. G. POLLARD.

Surface tension of fresh latex of *Euphorbia lathyris*. L. BLARINGHEM and M. CHOPIN (Compt. rend., 1930, **191**, 1408—1410).—The surface tension of the latex from various parts of specimens of *E. lathyris*, of varying age but of identical descent, is uniform within limits of experimental error, averaging 30 dynes/cm. Corresponding figures for other plants are: *Taraxacum officinalis*, 40; *Papaver somniferum*, var. *Mursellii*, 20; hybrid *Papaver setigerum* × *somniferum*, 31; *Chelidonium majus*, 21. In the case of the poppies measurements must be made before coagulation sets in. C. A. SILBERRAD.

Development and ripening of peaches as correlated with physical characteristics, chemical

composition, and histological structure of the fruit flesh. II. Histology and microchemistry. III. Macrochemistry. G. T. Nightingale, R. M. Addoms, and M. A. Blake (N.J. Agric. Exp. Sta. Bulls., 1930, Nos. 507 and 494).—II. Microchemical examination of ripening peaches failed to demonstrate the presence of pectates in the flesh-cells except in the thick-walled cells adjacent to the epidermis. Protopectin occurs in all cell-walls in intimate association with cellulose, but is not uniformly distributed and tends to accumulate in areas exposed to intercellular spaces. The yellow pigment of ripe peaches is carotenoid in character and the red epidermal colouring is of the anthocyanin group. Dextrose is the principal reducing sugar in the fruit. Softening of fruit during ripening is accompanied by a gradual decrease in protopectin content.

III. A peach tree receiving nitrogenous fertiliser produced greater growth of leaf and twigs than an unfertilised tree, also the fruit ripened later and was less firm. The starch and nitrogen contents of the twigs of the fertilised tree were lower than those of the unfertilised. Fruit from the unfertilised tree had a higher sugar content (especially sucrose), and much lower nitrogen and ash contents than that receiving fertiliser. The tannin content of the green fruit of the unfertilised tree was much higher than the fertilised, but the difference gradually disappeared as the " soft-ripe " condition was approached.

A. G. Pollard.

Nutrition of fruit trees: some effects of deficiencies of nitrogen, potassium, calcium, and magnesium, with special reference to the behaviour of apple trees. M. B. Davis (J. Pomology, 1930, **8**, 316—344).—Several varieties of apple trees have been grown under controlled conditions in quartz sand and sand–soil mixtures, and different nutritional treatments studied. All treatments produced significant effects on growth features and chemical composition of the trees. Nitrogen omission was characterised by restricted shoot-growth, yellowed leaves, and delayed bud-break. Potassium omission was associated with restricted shoot-growth in some cases and increased shoot-growth in others, a certain amount of early defoliation, later retention of remaining foliage, leaf scorch, and much earlier bud-break. Phosphorus omission produced earlier defoliation, very restricted shoot-growth in some cases, typical bronzing of the foliage, and delayed bud-break. Calcium omission produced increased shoot-growth and larger leaves in the early stages, breakdown of leaf tissue either near the centre or along the margins. Magnesium omission was characterised by reduced shoot-growth in most cases, earlier defoliation, and marked breakdown of foliage. All omission treatments were reflected in the composition of ash and dry matter of one-year shoots and leaves for the first season. Nitrogen omission resulted in high dry matter in fresh weight; potassium omission showed high dry matter; magnesium omission low dry matter in fresh weight. Nitrogen omission gave high ash in dry matter; potassium omission tended to high ash in dry matter in most cases; calcium omission always gave low ash in dry matter; magnesium omission gave high ash in dry matter. Reductions of potash, phosphoric acid, lime, and magnesia in ash and in dry matter were usually effected where these elements were omitted. Low potash was associated with high lime and high magnesia; low phosphoric acid was accompanied by low potash and high lime. Low lime was associated with high potash, high magnesia, and low phosphoric acid. Low magnesia was accompanied by high lime.

E. Holmes.

Some effects of potassium deficiency on the histological structure and nitrogenous and carbohydrate constituents of plants. C. T. Nightingale, L. G. Schermerhorn, and W. R. Robins (N.J. Agric. Exp. Sta. Bull., 1930, No. 499, 36 pp.).—An accumulation of carbohydrate in potash-deficient tomato plants is ascribed to a retarded nitrogen assimilation. In such plants the translocation of sugars and the digestion of starch can take place freely. The development of mechanical tissue in plants is associated with their carbohydrate content and only indirectly with potash. Potash appears, directly or indirectly, to be essential for the initial stages of nitrate reduction in plants, for cell division, and probably for the protein synthesis in meristematic tissue. Most of the potash in plants is water-soluble and, when limited in amount, is translocated freely from older tissues to regions of active cell division. Stems and storage roots of potash-deficient plants may increase in length, but their diameters remain practically unchanged. Lack of potash frequently causes the premature death of fruiting plants.

A. G. Pollard.

The organic matter given off by algæ. A. Krogh, E. Lange, and W. Smith (Biochem. J., 1930, **24**, 1666—1671).—Culture experiments with *Scenedesmus* in artificial media and with natural lake-water in which the algæ were brought to luxuriant growth show that the organic material synthesised by the assimilation of these organisms is almost quantitatively stored in the cells of the algæ, whilst a fraction amounting at most to 10% may possibly be lost to the surrounding water. These losses are probably mainly due to dead and decomposed organism.

S. S. Zilva.

Iodine-absorbing (reducing) material in plants. D. Marine, E. J. Baumann, and B. Webster (J. Biol. Chem., 1930, **89**, 213—219).—Plant material was steamed, pulped, and extracted with water. The extract was acidified with hydrochloric acid and titrated with $0·01N$-iodine solution. The figures obtained varied greatly with different plants and at different stages of growth. In general the highest figures were observed with the growing parts of wild plants and grasses and at the period of most rapid growth. The iodine-absorbing material is reduced in amount when the plant is dried.

C. R. Harington.

Carbohydrate content of the nectar of indigenous flowering plants. R. Beutler (Sitzungsber. Ges. Morph. Physiol., 1928, **38**, 24—31; Chem. Zentr., 1930, i, 3063).—The carbohydrate concentration of the nectar varies from 8 to 70% according to the kind of plant. Only sucrose, dextrose, and lævulose could be detected, whilst non-volatile substances other than carbohydrate are present only in small amount. With the exception of that of the

plum, the nectars react more or less acid; the p_H of *Asclepias* nectar lies between 2·7 and 4·3.

L. S. THEOBALD.

Determination of maltose in plant extracts by maltase. N. NARASIMHAMURTY and M. SREENIVASAYA (Biochem. J., 1930, **24**, 1734—1736).—Maltase and invertase are used as the hydrolysing agents. The method is selective in its action and completely eliminates the errors inherent in the method of acid hydrolysis. S. S. ZILVA.

Occurrence of 2 : 6-dimethoxy-*p*-benzoquinone in *Adonis vernalis*, L. W. KARRER (Helv. Chim. Acta, 1930, **13**, 1424—1428).—Details are given for the extraction of 2 : 6-dimethoxy-*p*-benzoquinone (1·3 g.), m. p. 251° after decomp. from 240°, from 200 kg. of *A. vernalis.* The quinone is synthesised by oxidising pyrogallol trimethyl ether by Graebe and Hess' method (A., 1905, i, 698). 2 : 6-*Dimethoxyquinol* has m. p. 160°. H. BURTON.

Frangularoside, a rhamnoside of black alder bark. M. BRIDEL and C. CHARAUX (Compt. rend., 1930, **191**, 1374—1376).—The bark is dried, powdered, and macerated with 4 parts of water for 5 hrs. The dried residue is then extracted continuously with ether for 12 hrs. and a crude product obtained, the yield varying from 4·88 to 2·65%, according to the period of the year. The crude product is first crystallised from 66% acetic acid and then from a mixture of 2 vols. of octyl alcohol and 1 vol. of acetic acid. Purification can also be effected, in better yield, by crystallisation from methyl alcohol. The *frangularoside* separates from octyl alcohol in anhydrous and from methyl alcohol in hydrated form, $[\alpha]_{5461}$ −219°. With sulphuric acid containing 0·5% of selenious acid it gives a blue colour, and dissolves in dilute sodium hydroxide solution with formation of a yellow fluorescent solution which rapidly changes to an intense red colour. Hydrolysis gives rhamnose and a product, *frangularol*, of unknown composition.

P. G. MARSHALL.

Colour changes of plants during desiccation. Chromogen of *Orobus niger*, L., is arbutin. A. MEUNIER (Compt. rend., 1930, **191**, 1471—1473).—From the hot 80% alcoholic extract of the fresh plant of *O. niger*, L., is isolated a glucoside identical in all respects with arbutin. Hydrolysis of this glucoside with emulsin affords a product which darkens slowly by atmospheric oxidation. Thus the darkening of the foliage of *O. niger* during desiccation is due to a glucosidic component, unlike that of *O. tuberosus*, which has been shown to be due to the phenolic substance oroberol. J. W. BAKER.

Composition of consecutive cuttings of *Andropogon virginicus* and *Danthonia spicata*. R. B. DUSTMAN and A. H. VAN LANDINGHAM (J. Amer. Soc. Agron., 1930, **22**, 719—724).—Consecutive monthly cuttings lessen the normal decline in protein content and increase in fibre content.

CHEMICAL ABSTRACTS.

***Linum neomexicanum* (yellow pine flax) and one of its poisonous constituents.** W. W. EGGLESTON, O. F. BLACK, and J. W. KELLY (J. Agric. Res., 1930, **41**, 715—718).—Alcoholic extracts of *L. neomexicanum* yielded 6·6% of a substance ("linotoxin") poisonous to animals. It is probably a glucoside. A. G. POLLARD.

Examination of *Sida cordifolia*, Linn. S. GHOSH and A. DUTT (J. Indian Chem. Soc., 1930, **7**, 825—829).—The entire plant contains 0·085% of alkaloids (on air-dried material) in addition to fatty oil, phytosterols, resins, resin acids, mucins, and potassium nitrate. Tannin and glucosides are absent. The seeds contain most alkaloid, the chief constituent of which is ephedrine. H. BURTON.

Hydrocarbons of *Echinacea angustifolia*. E. L. WOODS (Amer. J. Pharm., 1930, **102**, 611—630).—The crude oil has b. p. 125—240°/5 mm., d^{15} 0·801, n^{25} 1·4480. The main fraction, b. p. 127—133°/5 mm., gives when redistilled large fractions, (*A*) b. p. 121—122°/3 mm., d_{25}^{25} 0·7873, and (*B*), b. p. 126—127°/3 mm., d_{25}^{25} 0·7881. The pure hydrocarbons show little tendency to undergo autoxidation in the dark. Oxidation of *A* with perbenzoic acid yields mainly a viscous *oil*, (?) $C_{15}H_{27}(OH)_3$ (oily *acetate*), with small quantities of an *erythrol*, $C_{15}H_{23}(OH)_4$, m. p. 91°, and a *substance*, m. p. 135—136°. Oxidation of *B* with aqueous potassium permanganate gives mainly a mixture of hexoic and heptoic acids, with adipic, pimelic, and myristic acids and traces of acetic acid, a *dihydroxytridecoic acid*, m. p. 126—127°, and a brown, viscous *acid*, b. p. 170—205° (decomp.). Oxidation with permanganate in acetone affords the same acids in larger yield, also an unsaturated *acid*, $C_{13}H_{24}O_2$, b. p. above 160°/15 mm. (*silver* salt), and a trace of oxalic acid. The main constituent of the oil is therefore probably the hydrocarbon,
$CHMe_2\cdot[CH_2]_3\cdot CH\!:\!CH\cdot[CH_2]_5\cdot CH\!:\!CH_2$, or a mixture of $CHMe_2\cdot[CH_2]_2\cdot CH\!:\!CH\cdot[CH_2]_5\cdot CH\!:\!CHMe$ and $CHMe_2\cdot[CH_2]_3\cdot CH\!:\!CH\cdot[CH_2]_4\cdot CH\!:\!CHMe$, none of which is derived from isoprene. The isolation of myristic acid indicates that the oil contains 5—10% of a hydrocarbon, $CH_2\!:\!CH\cdot[CH_2]_{12}\cdot Me$. The relation of the oil to the other constituents of the plant is discussed (cf. Bischoff, A., 1925, i, 760). H. E. F. NOTTON.

Constituents of essential oil of the bark of *Magnolia obovata*, Thunb. Y. SUGII and H. SHINDO (J. Pharm. Soc. Japan, 1930, **50**, 709—714).—The oil contains machilol, $C_{15}H_{26}O$, m. p. 83°, which on oxidation affords *dihydroxymachilol*, m. p. 110° (*monobenzoate*, m. p. 144—145°), and a *hydroxyketone*, $C_{13}H_{22}O_2$, m. p. 121—122° (*semicarbazone*, decomp. 216—218°; *oxime*, m. p. 107—108°). *Dihydromachilol* has m. p. 84—85°. CHEMICAL ABSTRACTS.

Lipase of the olive and of olive oil. E. PANTANELLI and S. VERDESCA (Rend. Accad. Sci. Fis. Mat. Napoli, 1930, [iii], **36**, 76—83).—Acidification of the fat of olives is due to the action of a lipolytic enzyme, the activity of which increases rapidly as the cell structure is destroyed by crushing. During the treatment of the olives, the lipase passes from the aqueous magma into the oil, as this dissolves the glycerol; hence the more acid the oil is at the time of crushing, the richer it is in lipase and the more liable to undergo further acidification. This acidification is governed by the glycerol, which determines the introduction of water and lipase into the oil. T. H. POPE.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

MARCH, 1931.

General, Physical, and Inorganic Chemistry.

Hyperfine structure formulæ for one-electron spectra. G. Breit (Physical Rev., 1931, [ii], **37**, 51—52; cf. Hargreaves, A., 1930, 832; Fermi, *ibid.*, 393).—Mathematical. The energy level separations caused by a nuclear magnetic moment in a one-electron spectrum are derived by a short and rigorous method. N. M. Bligh.

Variation of spark potential with temperature in gases. H. C. Bowker (Proc. Physical Soc., 1931, **43**, 96—112).—The effect of temperature on the spark potential in hydrogen and nitrogen at ordinary pressures has been investigated up to 860°. The spark potential depends on the density of the gas, but is independent of temperature and pressure for a given density. A. J. Mee.

Continuous spectra of atomic and molecular hydrogen. D. Chalonge and N. T. Ze (J. Phys. Radium, 1930, [vii], **1**, 416—425).—When an uncondensed discharge is passed through hydrogen at a pressure of a few mm. the secondary spectrum and a continuous spectrum of molecular origin are emitted. The energy curve of the latter has a maximum at 2350 Å. With sufficiently condensed discharges the secondary spectrum disappears, the Balmer lines become more intense, and the continuous spectrum becomes purely atomic, consisting of two spectra connected with the Balmer and Paschen series. The former is more intense than the latter, the energy in each case being evenly distributed through the spectrum. C. W. Gibby.

Intensities of Balmer lines. II. L. S. Ornstein and H. Lindeman (Z. Physik, 1931, **67**, 1—6).—A reply to the criticisms raised by Kopfermann and Ladenburg (cf. A., 1930, 1487) on the authors' earlier work (*ibid.*, 1073). R. W. Lunt.

Influence of traces of hydrogen on the sparking potential of helium. A. Gunther-Schultze and F. Keller (Z. Physik, 1930, **66**, 219—223).—Experiments with commercial types of low-voltage rectifiers consisting of iron electrodes in a helium atmosphere at 20 mm. are described. Spectroscopic examination of the arc under normal and overload conditions has shown that the former is associated with the disappearance of traces of hydrogen which are evolved rapidly under overload conditions. R. W. Lunt.

Fine structure of hydrogen-like atoms in an inhomogeneous electric field. S. Gupta (Z. Physik, 1930, **66**, 246—256).—Theoretical. The Darwin modification of Dirac's equation is used to calculate the Stark effect in an inhomogeneous electric field; the field gives rise to a quadratic as well as a linear term in the potential energy, and the effect of the quadratic term is calculated. A. B. D. Cassie.

Extension of simple spectra. F. Paschen (Sitszungsber. Preuss. Akad. Wiss. Berlin, 1930, **32**, 7 pp.).—The simple spectra due to the excitation of a single-valency electron are extended if more than one valency electron is present, and these are simultaneously excited. The two-electron spectra of helium, beryllium, magnesium, and Al II are discussed. A. J. Mee.

Hyperfine structure of *S* and *P* terms of two-electron atoms, with special reference to Li^+. G. Breit and F. W. Doermann (Physical Rev., 1930, [ii], **36**, 1732—1751; cf. Goudsmit and Bacher, A., 1930, 265).—Mainly mathematical. An expression is deduced for the interaction energy between the nuclear magnetic moment and the electronic system of a many-electron atom. Results are applied to the Li^+ 5485 Å. line and to the calculation of the magnetic moment of Li. N. M. Bligh.

Large displacements in the spectra of ionised nitrogen. K. Asagoe (Sci. Rep. Tokyo Bunrika Daigaku, 1930, **1**, 47—62).—The spectra of N II and N III were studied by a method similar to that employed in the study of the broadening and displacement of the halogen spectra (A., 1927, 2, 602). A. J. Mee.

Excitation of the negative nitrogen band by electron collisions. A. E. Lindh (Z. Physik, 1931, **67**, 67—74).—The intensities of the lines of the *R* branch of the negative nitrogen band have been measured for exciting electrons of 150 and 175 volts energy and at two different current densities. Measurements have also been made of the effective target area of the nitrogen molecule for the excitation of the above band in the range 50—350 volts. The values obtained are much lower than those of Ramsauer and Brode. R. W. Lunt.

Emission bands of sulphur. R. K. Asundi (Nature, 1931, **127**, 93—94).—Spectrograms of the bands of sulphur emitted in a discharge tube containing sulphur vapour and argon under pressure indicate that argon tends to arrest the predissociation of the sulphur molecule. New bands degraded towards the shorter wave-lengths have been photographed in the region 2100 Å. L. S. Theobald.

Spectrum of singly-ionised chlorine (Cl II). K. MURAKAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, **15**, 41—67).—The first spark spectrum of chlorine was obtained by a condensed discharge through a narrow Geissler tube with tungsten electrodes, one containing a small quantity of sodium chloride. The ground term is given as $3p^3P_2$, and the ionisation potential as 23·115 volts.

A. B. D. CASSIE.

Spectra of doubly-ionised argon, krypton, and xenon. S. C. DEB and A. K. DUTT (Z. Physik, 1931, **67**, 138—146).—The spectra of A^{++}, Kr^{++}, and Xe^{++} have been classified, and tables of the multiplets of these spectra are given. The values of the ionisation potentials are 36·75, 31·23, and 28·51 volts, respectively (cf. Déjardin, A., 1924, ii, 284, 709).

W. R. ANGUS.

Zeeman effect for quadrupole lines. E. SEGRÈ (Z. Physik, 1930, **66**, 827—829).—The potassium lines $^2S_{1/2}-^2D_{5/2}$ and $^2S_{1/2}-^2D_{3/2}$, at 4642·17 and 4641·58 Å., respectively, may be quadrupole transitions, or may be due to the influence of an inhomogeneous electric field. Photographs of the inverse Zeeman σ and π components of these lines, due to a field of 12,700 gauss, show that the transitions agree with the assumption of a quadrupole electric moment.

A. B. D. CASSIE.

Interferometric measurements in the arc spectrum of iron. C. V. JACKSON (Proc. Roy. Soc., 1931, **A**, **130**, 395—410).—Ten lines in the spectrum of the iron arc in air in the region 4000—4400 Å. have been measured by means of the usual interferometric method and found to be in almost perfect agreement with the values adopted by the I.A.U. in 1928, the mean systematic difference being only +0·0003 Å. and the mean accidental difference ±0·0006 Å. Sixty-eight lines in the region 2300—3100 Å. have also been measured interferometrically.

L. L. BIRCUMSHAW.

Spectrum of doubly-ionised arsenic. K. R. RAO (Proc. Physical Soc., 1931, **43**, 68—71).—The doublet system of doubly-ionised arsenic (As III) is considered in detail, and the work of Lang (A., 1929, 112) is amended. It is now possible to evaluate a trustworthy scheme of terms of As III by assuming a probable value for the $5g^2G$ term. The value used is 39,500 cm.$^{-1}$ A term table is given. A. J. MEE.

Spectrum of singly-ionised ziconrium. C. C. KIESS and H. K. KIESS (Bur. Stand. J. Res., 1930, **5**, 1205—1241).—Most of the lines observed in the spark spectrum of zirconium have been classified as combinations between terms of the quadruplet and doublet system of Zr II. The terms which have been found are in all cases those required theoretically for an atom with three outer electrons.

W. E. DOWNEY.

Intensity anomalies in the multiplets of silver and gold. S. SAMBURSKY (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 1025—1027; cf. A., 1930, 831). —The ratio 2 : 1 has been obtained for the relative intensities of the silver lines at 3382·8 and 3280·6 Å. and 2·4 : 1 for those of the second doublet of the principal series (λ=2069·8 and 2061·2 Å.). When Fermi's theory (A., 1930, 388) is applied to these results the ratio of the transition probabilities of the $2P$ and $3P$ levels to the ground state (I_2/I_3) is found to be 20, whereas the equivalent ratios for the alkali metals lie between 100 and 200. The intensity ratio of the gold lines $3^2S-2^2P_{3/2}$ and $3^2S-^2P_{1/2}$ (λ=4241·8 and 3650·7 Å.) is also the normal value of 2 : 1. The diffuse series 2^2P-3^2D in both silver and gold and the 2^2P-4^2D series in silver show marked departures from the theoretical ratio. This is explained by assuming the existence of a low ^2D term. J. W. SMITH.

Spectrum of doubly-ionised iodine. J. B. SETH (Nature, 1931, **127**, 165).—Many of the strong lines in the visible and ultra-violet regions originate in terms of $2O_2P_1$, $2O_2P_2$, and $2O_2P_3$ electronic configurations; all the quadruplet terms for these have been recognised. The $2O_2$ ($P_1\longleftarrow P_2$) and $2O_2$ ($P_2\longleftarrow P_3$) lines are grouped about 3900 Å. and 3100 Å., respectively. L. S. THEOBALD.

Spectrum of trebly-ionised cerium (Ce IV). J. S. BADAMI (Proc. Physical Soc., 1931, **43**, 53—58).—The spectrum of the condensed spark of cerium has been studied in the ultra-violet. The spectrum is simple, being similar in electronic structure to the spectra of Ca I, Ba II, and La III. A table of term values and ionisation potentials of La III and Ce IV is given. A. J. MEE.

Influence of pressure and temperature on the absorption of excited mercury atoms in a neon atmosphere. O. MASAKI (Z. Physik, 1930, **66**, 229—240).—The absorption of light corresponding with the transitions $2^3P_{0,1,2}-2^3S_1$ of excited mercury vapour in the presence of an excess of neon has been examined by means of a König–Martens spectrophotometer. The mechanisms suggested in explanation of the phenomena observed are discussed at length. R. W. LUNT.

Optical measurements on the mercury atom. M. SCHEIN (Helv. phys. Acta, 1930, **2**, Supp. 1, 3—111; Chem. Zentr., 1930, i, 3009).—As a sensitive method for measuring small spectroscopic wave-length differences the absorption of a monochromatic ray is employed in a monochromatic absorbing medium with the light and absorption frequencies continually out of phase. The method succeeds with mercury resonance fluorescence absorbed in mercury vapour, and has been applied to determine the Stark and Doppler effects. L. S. THEOBALD.

Mercury band system in the neighbourhood of the resonance line. (LORD) RAYLEIGH (Nature, 1931, **127**, 125).—Additional bands between that at 2540 Å. and the resonance line 2536·52 have been measured; the bands are shaded from the red and the wave-lengths are 2540·37, 2538·44, and 2537·32 Å. Two bands shaded from the red have also been measured at 2535·82 and 2535·35 Å.

L. S. THEOBALD.

High-frequency discharges in mercury, helium, and neon. C. J. BRASEFIELD (Physical Rev., 1931, [ii], **37**, 82—86; cf. A., 1930, 837).—Measurements of the potential drop at the electrodes and the electric force in the positive column of high-frequency discharges in mercury, helium, and neon for a range of gas pressures and oscillation frequencies

of 1·25—22·5 megacycles showed that, in general, the magnitude of the electric force was insufficient to produce electrons of velocity necessary to ionise or excite the gas. N. M. BLIGH.

Intensity determinations with the multiplets of mercury and neon by excitation of the lines by electron collision. W. ENDE (Z. Physik, 1931, **67**, 292—293; cf. A., 1929, 1119).—The intensity relationships given in the former paper are corrected. A. J. MEE.

Intensity distribution in the mercury triplet $2S^3{}_1-2^3P_{0,1,2}$ and the mean glow period of the triplet components. R. FRISCH and P. PRINGSHEIM (Z. Physik, 1931, **67**, 169—178).—By irradiation of the lines 5461 and 4047 Å. the fluorescence emission of the visible mercury triplet $2^3S_1-2^3P_{0,1,2}$ was obtained. The relative intensity of the three lines is independent of whether the green or the violet component is used for the excitation. It is concluded that the inequality observed by Randall (A., 1930, 970) in the life period of the three lines cannot be cleared up by consideration of hyperfine structure (cf. Richter, this vol., 8). A. J. MEE.

Polarisation of the continuous *X*-rays from single electron impacts. B. DASANNACHARYA (Physical Rev., 1930, [ii], **36**, 1675—1679).—Polarisation increased exponentially with decreasing thickness of aluminium targets, indicating nearly complete polarisation at 6×10^{-6} cm. thickness, and diminished with increasing velocity of the exciting electrons. Results are in agreement with Sugiura's theory of the polarisation of continuous *X*-rays (cf. A., 1930, 4). N. M. BLIGH.

Scattering of short *X*-rays by molecular hydrogen. H. S. W. MASSEY (Proc. Camb. Phil. Soc., 1931, **27**, 77—85; cf. Debye, A., 1930, 843).—Mathematical. From the formula deduced by Waller (cf. A., 1929, 746) the intensities of short *X*-rays scattered from molecular hydrogen are calculated. N. M. BLIGH.

Spectrum of the radiation from a high potential *X*-ray tube. C. C. LAURITSEN (Physical Rev., 1930, [ii], **36**, 1680—1684; cf. *ibid.*, 988).—Using a Seeman type spectrograph, a spectrogram with the tube at 600 kilovolts shows a continuous spectrum with a maximum intensity at about 200 kilovolts, and a short wave-length limit at about 600 kilovolts, the range covered being 100—20 Å. N. M. BLIGH.

Origin of *L*-absorption edges of heavier elements. A. SANDSTROM (Z. Physik, 1930, **66**, 784—789).—The known *L*-absorption and emission spectra for the elements tungsten to uranium indicate that *L* edges are due to a transition from the *L* level to the first incomplete group or sub-group of extranuclear electrons. A. B. D. CASSIE.

Accuracy of interference determinations with molecules with *X*- and cathode rays. L. BEWILOGUA (Physikal. Z., 1931, **32**, 114—117).—The accuracy attainable by the use of *X*-rays and of cathode rays in determinations based on interference is discussed. *X*-Rays provide a more accurate result than cathode rays, although the latter possess the advantage of requiring shorter exposure time. A. J. MEE.

Discontinuous absorption of *X*-radiation. B. B. RAY (Z. Physik, 1930, **66**, 261—268).—*X*-Radiation scattered in a direction inclined to a primary beam suffers a change in wave-length depending on the vector change in momentum, *i.e.*, the change in wave-length is due to the Compton effect, and broadens the spectral line in the direction of longer wave-lengths. Any Raman line is therefore obscured. Radiation scattered in the direction of the primary beam shows no Compton modification in wave-length, but might show an anti-Stokes Raman line due to atoms excited by Compton collisions. Cu$K\alpha$, Ni$K\alpha$, Ni$K\beta$, $WL\alpha$, and Fe$K\beta$ radiations scattered by carbon, nitrogen, and oxygen were examined, and anti-Stokes lines corresponding with $CK\alpha$, $NK\alpha$, and $OK\alpha$ were found. A. B. D. CASSIE.

Angular intensity distribution of the continuous *X*-ray spectrum. Y. SUGIURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, **15**, 37—39).—Mathematical. A. B. D. CASSIE.

Change of wave-length of *X*-rays on traversing an absorbing medium. J. M. CORK (Compt. rend., 1931, **192**, 153—155).—The new lines stated by Ray (cf. A., 1930, 972) to be produced on passing copper $K\alpha$ radiation through carbon etc. were not obtained when his experiment was repeated, nor could any such effect be obtained with boron. C. A. SILBERRAD.

Vacuum spectrograph for precise measurements of *X*-rays of long wave-length. C. E. HOWE (Rev. Sci. Instr., 1930, [ii], **1**, 749—757).—A plane grating spectrograph and special features of design for securing high precision are described. N. M. BLIGH.

Multiple scattering in the Compton effect. J. W. M. DUMOND (Physical Rev., 1930, [ii], **36**, 1685—1701).—Theoretical. Possible errors due to the neglect of multiple scattering in a study of the spectral distribution of *X*-radiation scattered by light elements are reviewed. N. M. BLIGH.

Double-crystal spectrometer. J. W. M. DUMOND and A. HOYT (Physical Rev., 1930, [ii], **36**, 1702—1720).—The uses, theory, design, and technique of operation of the double-crystal spectrometer are described. N. M. BLIGH.

Infra-red absorption bands in the spectra of the greater planets. R. WILDT (Naturwiss., 1931, **19**, 109—110).—The spectra of Neptune and Jupiter were photographed up to 8600 Å. and compared with the spectra of the sun and Capella obtained in the same way. W. R. ANGUS.

Photo-electric and thermionic properties of rhodium. E. H. DIXON (Physical Rev., 1931, [ii], **37**, 60—69).—A thin ribbon of pure rhodium was submitted to rigorous heat treatment in a pyrex tube at 950—1450° for 1050 hrs. in a vacuum. During heating, the long-wave limit shifted from 2530 to 3150 and back to 2509 Å.; the photo-electric current, measured by a Compton electrometer, increased about 130% for the temperature range 25—950°, with a

sudden increase at 240°. The thermionic current curve showed an irregularity at 1100°.

N. M. BLIGH.

Photo-electricity. J. WERNER (Z. Physik, 1931, **67**, 207—226).—Metals and salts show, in a high vacuum, an increase in the photo-electric emission with time, which is independent of the radiation. The cause of this increased sensitivity, shown only by the unsaturated emission, is the removal or diminution of the layer of gas adsorbed on the metal or salt.

A. J. MEE.

Connexion between the effect of nitrogen-oxygen compounds and that of their components on the photo-electric sensitivity of potassium. R. FLEISCHER and H. TEICHMANN (Z. Physik, 1931, **67**, 184—191; cf. A., 1930, 391).—An examination of the effect of nitrogen dioxide, nitric oxide, nitrogen, and oxygen on the sensitivity of the potassium cell shows that the change in position of the selective maximum from 334 to 365 mμ is due to the formation of nitrogen dioxide.

A. J. MEE.

Temperature relationship of the unidirectional layer photo-effect. H. TEICHMANN (Z. Physik, 1931, **67**, 192—193; cf. this vol., 9).—In the temperature range down to −180°, emission of the copper-copper oxide cell reaches a maximum between −80° and −110°.

A. J. MEE.

Avoidance of an infinite singularity at the electron. W. ANDERSON (Z. Physik, 1930, **66**, 712—720).—Ambarzumian and Ivanenko concluded (cf. A., 1930, 1335) that electrons in crystal formation could not approach closer than $6{\cdot}34e^2/m_0c_2$, and this is precisely the minimum diameter possible for electrons when considered as gas of compressible electric particles (cf. A., 1929, 1137). No explanation of this coincidence could be found.

A. B. D. CASSIE.

New method for recording electrons. P. H. CARR (Rev. Sci. Instr., 1930, [ii], **1**, 711—743).—The use of photographic plates for recording electrons is reviewed. Using a slightly modified apparatus, the experiments of Cole (cf. A., 1926, 1189) were repeated, and it was found that photographic plates are rendered more sensitive to electrons by the application of small amounts of certain oils, provided the electrons strike the plate at speeds not less than 25 equivalent volts. The sensitivity is mainly due to cathodo-luminescence of the oil, and the failure at low speeds is due to the high electrical resistance of the photographic emulsion. The regions of metal surfaces bombarded by electrons react differently from the unbombarded regions towards certain vapours, the effect being observed for electron speeds down to 12 equivalent volts. Experimental details are given for gold and silver, for which mercury and iodine vapours, respectively, were found the most satisfactory developers. The effect was also investigated for other metals, and possible explanations are discussed. The advantages and scope of the two methods are compared.

N. M. BLIGH.

Longitudinal distribution of photo-electrons. L. SIMONS (Nature, 1931, **127**, 91—92).—Assuming the wave-mechanical principle of interference $P(\theta)\propto\sin^2\theta$ and that independent groups of photo-electrons originate from a small, plane circular area of radius b normal to the ray, and a small spherical volume, radius a, the probability $P(\theta)d\theta\propto(A^1\pi a^2+B^1\text{–}b^2\cos\theta)\sin^3\theta d\theta$, where A^1 and B^1 are independent of θ, is obtained. This expression must be regarded as unilateral and integrable only between the limits 0 to $-/2$. Experiment has confirmed the existence of longitudinal symmetry.

L. S. THEOBALD.

Electron diffraction at oxygen adsorbed on tungsten. W. BOAS and E. RUPP (Ann. Physik, 1930, [v], **1**, 983—1000).—An apparatus for studying the diffraction of electrons of 100—2000 volts energy at surfaces the temperature of which could be raised to 3000°, is described, and the possible errors are discussed. Results are given for pure tungsten and for tungsten with an adsorbed layer of oxygen.

A. B. D. CASSIE.

Capture of electrons by protons. K. WOLF (Ann. Physik, 1930, [v], **7**, 937—946).—An apparatus which brings protons and electrons of variable relative velocity into the same stream is described. The stream is subsequently analysed into electrons, protons, and hydrogen atoms. According to Davis and Barnes' results for α-particles (A., 1929, 971), neutral hydrogen atoms should appear at definite relative velocities. No such phenomenon was observed.

A. B. D. CASSIE.

Angular scattering of electrons in gases. F. L. ARNOT (Proc. Camb. Phil. Soc., 1931, **27**, 73—76; cf. A., 1930, 1493).—The error introduced into experiments on the angular scattering of electrons in gases by the potential gradient between the electron beam and a point outside it resulting from the slight difference in concentration between the positive ions and electrons due to the greater mobility of the former is discussed.

N. M. BLIGH.

Diamagnetism of the free electron. C. G. DARWIN (Proc. Camb. Phil. Soc., 1931, **27**, 86—90).—Mathematical. Landau, in his calculation of the diamagnetic effect due to the motion of electrons in a magnetic field (cf. A., 1930, 1355), made an allowance for boundary considerations. A special case is considered, admitting of exact solution, in which the boundary is replaced by a weak field of force. The result reduces to Landau's formula, and shows Bohr's argument of the creeping of the electron round the boundary wall.

N. M. BLIGH.

Diffraction of an electron wave at a single layer of atoms. M. VON LAUE (Physical Rev., 1931, [ii], **37**, 53—59).—A mathematical examination of the treatment by Morse of the incidence and reflexion of electrons at the surface of a space lattice (cf. A., 1930, 976).

N. M. BLIGH.

Effect of resolving power on measurements of the absorption coefficient of electrons in gases. R. R. PALMER (Physical Rev., 1931, [ii], **37**, 70—81).—Using a Mayer type apparatus with an opening of variable aperture at the end of the scattering chamber, the absorption coefficient of electrons in helium and mercury vapour for the range 20—135 volt electrons was studied as a function of the aperature for 2—11°.

N. M. BLIGH.

Photographic detection of asymmetrical angular distribution of doubly-reflected elec-

trons. E. RUPP (Naturwiss., 1931, **19**, 109).—Using a non-rotating analyser an asymmetry has been observed in the angular distribution of doubly-reflected electrons. A pencil of electrons was reflected by gold foil of a fibrous structure inclined at 45° to the incident pencil. Using 220-kilovolt electrons diffraction patterns have been obtained showing definite asymmetrical intensity distribution of the doubly-reflected electrons, the intensity being greatest in the plane of the incident and reflected pencils and towards the side of the electron source. The intensities at right angles to this plane were equal. This asymmetry was not due to the fibrous structure of the foil, since the same effect was observed with the foil turned through 90°. The effect is not observable when aluminium foil is substituted for gold. J. W. SMITH.

Discrete range groups of *H*-particles expelled from aluminium. II. Dependence of sharing and energy of *H*-particles on the angle between the primary and secondary rays. H. POSE (Z. Physik, 1931, **67**, 194—206; cf. A., 1930, 1086, 1232).—It is shown that the backward sharing is about 30% smaller than that in the forward direction. The velocities of the *H*-particles calculated from the ranges decrease as the angle between the primary and secondary ray increases. A. J. MEE.

Recoil atoms in gases. L. GOLDSTEIN (Compt. rend., 1930, **191**, 1450—1452; cf. A., 1929, 1358).—The curve showing the relation of yield of activation to pressure shows a rapid rise to a maximum of 50% for a pressure of about 2 cm. mercury, followed by an asymptotic decline to about 26% for pressures in excess of 45 cm. It is suggested that the maximum occurs when the field is just strong enough to bring all recoil atoms on to the electrode, the subsequent decline being caused by increased ionic density due to increased pressure resulting in more complete utilisation (in ionisation) of the α-particles.

C. A. SILBERRAD.

Method of ion counting in the free atmosphere. Y. ITIWARA (Physikal. Z., 1931, **32**, 97—106).—The use of the ion counting tube for determining the number of ions in the free atmosphere is discussed. It is shown that if it is used by the charge method, *i.e.*, the outer electrode of the cylindrical condenser is raised to a constant potential, then the charge on the inner electrode which was originally earthed measures only a fraction of the total number of ions. The counting tube of Gockel, as used by Hess, counts only the large ions, and if a suitable correction is applied to his figures, they agree more closely with those of other observers. A. J. MEE.

[Method of ion counting in the atmosphere.] V. F. HESS (Physikal. Z., 1931, **32**, 106).—Doubt is cast on the quantitative value of the work of Itiwara (cf. preceding abstract). The experiments of Itiwara in no way touch the work of Hess on the ionisation balance of air over land and open sea.

A. J. MEE.

Formation of negative ions in gases. W. HEY and A. LEIPUNSKY (Z. Physik, 1930, **66**, 669—685).—Experiments to determine the probability of the formation of negative ions in argon, mercury, and iodine vapours as a function of the electron velocity are described in which care has been taken to eliminate the sources of error to which are attributed the discrepancies in the data of other workers. The probability in all cases is of the order of 10^{-5} in the range 0—20 electron volts. Iodine vapour exhibits a well-defined maximum in the neighbourhood of 2·5 volts and thereafter the probability attains an approximately constant value. Below 10 volts the probability in argon and mercury vapour is very small and rises rapidly in the range of 10—20 volts. R. W. LUNT.

Production of high-speed canal rays without the use of high voltages. E. O. LAWRENCE and D. H. SLOAN (Proc. Nat. Acad. Sci., 1931, **17**, 64—70).

Value of M/m. W. N. BOND (Nature, 1931, **127**, 164).—Evidence against Eddington's suggested value of 1849·6 for M/m is quoted. L. S. THEOBALD.

Masses of the electron, the proton, and the universe. (SIR) A. S. EDDINGTON (Proc. Camb. Phil. Soc., 1931, **27**, 15—19; cf. A., 1930, 518).—An extension of the theory of the value 137 for the constant $hc/2\pi e^2$ is outlined; it gives satisfactory values for the masses of the electron, proton, and universe.

N. M. BLIGH.

Eleventh report of the German commission on atomic weights. M. BODENSTEIN, O. HAHN, O. HONIGSCHMID, and R. J. MEYER (Ber., 1931, **64**, [*B*], 1—21).—The report follows the general lines of its predecessors. The following changes are adopted: As=74·93 instead of 74·96; Ta=181·36 instead of 181·5; Re=186·31 instead of 188·7. H. WREN.

Fundamental at. wts. IX. At. wt. of sulphur. Synthesis of silver sulphide. O. HONIGSCHMID and R. SACHTLEBEN (Z. anorg. Chem., 1931, **195**, 207—227; cf. A., 1929, 370).—By direct combination of silver and sulphur vapour at 250° the value of 1·148621 has been obtained for the ratio $Ag_2S:2Ag$, which gives 32·0664 for the at. wt. of sulphur. Silver sulphide does not dissociate at 150—300°.

R. CUTHILL.

Revision of at. wt. of calcium. At. wt. of calcium from sylvine. O. HONIGSCHMID and K. KEMPTER (Z. anorg. Chem., 1931, **195**, 1—14).—Determination of the ratios $CaCl_2:2Ag$ and $CaCl_2:2AgCl$ has given the value 40·085+0·00060 for the at. wt. of calcium. The at. wt. of calcium obtained from sylvine is normal, indicating the absence of any appreciable amount of the calcium isotope Ca^{41}.

R. CUTHILL.

At. wt. of uraninite lead from Wilberforce, Ontario, Canada. G. P. BAXTER and A. D. BLISS (J. Amer. Chem. Soc., 1930, **52**, 4851—4853).—The at. wt. of lead extracted from uraninite is found to be 206·195 and on certain assumptions the thorium/uranium constant is computed to be 0·27.

J. G. A. GRIFFITHS.

At. wt. of uranium lead from Swedish kolm. G. P. BAXTER and A. D. BLISS (J. Amer. Chem. Soc., 1930, **52**, 4848—4851).—The at. wt. of uranium lead extracted from Swedish kolm, in which thorium could not be detected, is 206·01. J. G. A. GRIFFITHS.

Determination of the isotope ratio from intensity measurements of the boron monoxide spectrum. A. ELLIOTT (Z. Physik, 1931, **67**, 75—

88).—The intensity of a spectral line depends on the number of molecules in the original state, and on the transition probabilities. If the curve showing the number of molecules with a given energy is selective to a range of energies, as is the case with boron monoxide in an active nitrogen discharge tube, then because of the difference between the energies of vibration of two isotopic molecules, the isotope ratio may not be proportional to the relative intensities of the corresponding lines. The error in assuming this proportionality for boron monoxide isotopes is 4—7%. The corrected isotope ratio is $3{\cdot}63 \pm 0{\cdot}02$, and the corresponding at. wt. is $10{\cdot}794 \pm 0{\cdot}001$. The effective temperature of active nitrogen in such a discharge tube is 470°. A. B. D. CASSIE.

Isotopic constitution and at. wts. of zinc, tin, chromium, and molybdenum. F. W. ASTON (Proc. Roy. Soc., 1931, **A**, **130**, 302—310).—With the object of determining the relative abundance of isotopes in a number of elements, attempts have been made to measure the photometric intensity of mass spectra lines. The use of cadmium methyl and germanium ethyl led to unsatisfactory results for these metals. In the experiments on zinc, zinc methyl was used. The packing fraction of Zn^{64} was found to be $-9{\cdot}9$, the percentage of this isotope being 48·0. The at. wt. of the metal was calculated to be $65{\cdot}38_0 \pm 0{\cdot}02$, in exact agreement with the best chemical determinations. The methyl compound was also used for tin, which gave a packing fraction of $-7{\cdot}3$ for Sn^{120} and at. wt. $118{\cdot}72 \pm 0{\cdot}03$. Chromium hexacarbonyl was used for chromium, and four isotopes, 50, 52, 53, and 54, were discovered, 52 being much the strongest. A provisional value for the packing fraction of Cr^{52} is -10, giving at. wt. $52{\cdot}011 \pm 0{\cdot}006$. The hexacarbonyl was also used for molybdenum and seven isotopes, 92, 94, 95, 96, 97, 98, and 100, were observed. This group shows a similarity of abundance more striking than that of any other element of such complexity. The packing fractions of Mo^{98} and Mo^{100} were found to be the same, $-5{\cdot}5$ (approx.), giving at. wt. $95{\cdot}97 \pm 0{\cdot}06$.
L. L. BIRCUMSHAW.

Constitution of osmium and ruthenium. F. W. ASTON (Nature, 1931, **127**, 233).—The mass spectrum of osmium tetroxide indicates that the metal has four strong and two weak isotopes, one of the latter being isotopic with tungsten, W^{186}. The mass numbers and % relative abundances (provisional) are 186 and 1·0, 187 and 0·6, 188 and 13·5, 189 and 17·3, 190 and 25·1, and 192 and 42·6, respectively. The packing fraction is $-1{\cdot}0 \pm 2{\cdot}0$ and the deduced at. wt. is $190{\cdot}31 \pm 0{\cdot}06$, suggesting that the accepted value of 190·9 is too high. The behaviour of ruthenium tetroxide in the discharge makes the following data uncertain, but six isotopes, with possibly a faint seventh, appear to be present. The mass numbers and percentage abundances are 96 and 5, (98) and —, 99 and 12, 100 and 14, 101 and 22, 102 and 30, and 104 and 17, respectively. Assuming a packing fraction of approximately -6, these give an at. wt. of 101·1, but the divergence from the accepted value of 101·7 can be partly explained in this case.
L. S. THEOBALD.

Isotopes and living organisms. W. VERNADSKY (Compt. rend., 1931, **192**, 131—133).—To determine whether living organisms have the power of separating isotopes, compounds of potassium, iron, magnesium, zinc, calcium, silicon, and sulphur have been prepared from them and the at. wts. are to be determined (cf. Lowry, this vol., 141).
C. A. SILBERRAD.

Removal of radon from an emanation chamber after use. C. L. UTTERBACK and D. DEVAPUTRA (Rev. Sci. Instr., 1931, [ii], **2**, 53—54).—An apparatus and method are described for the rapid removal of radon after work on solutions containing radium up to 10^{-7} g. per litre, by alternate evacuation of the emanation chamber and sweeping out with specially dried air.
N. M. BLIGH.

Magnetic spectra of α-rays. S. ROSENBLUM (J. Phys. Radium, 1930, [vii], **1**, 438—444).—Two pieces of apparatus are described. It is shown that all the α-rays from thorium-*C* do not travel with identical speeds, but in groups. C. W. GIBBY.

Anomalous scattering of α-particles by light nuclei. E. GUTH and T. SEXL (Z. Physik, 1930, **66**, 577—580).—A method is indicated for the exact calculation of anomalous scattering of α-particles by a Gamow–Gurney–Condon potential field, instead of by the usual successive approximation method.
A. B. D. CASSIE.

Capture of electrons by α-particles. H. C. WEBSTER (Proc. Camb. Phil. Soc., 1931, **27**, 116—130).—The capture of one and two electrons by swift α-particles, reported by Davis and Barnes (cf. A., 1929, 971; 1930, 393), was investigated, using an electrical counter instead of a scintillation screen, with completely negative results. Detailed considerations of various aspects of the experimental conditions and interpretation of data show no possibility of reconciliation with the reported effect. N. M. BLIGH.

Scattering of slow α-particles by helium. P. M. S. BLACKETT and F. C. CHAMPION (Proc. Roy. Soc., 1931, **A**, **130**, 380—388).—Mott has shown (A., 1930, 269), from consideration of the symmetry of the wave functions, that the scattering of particles by an inverse square field is quite different from that of the classical theory when the scattering and scattered particles are identical. By using an automatic Wilson chamber containing a mixture of helium and oxygen, the scattering of α-particles by helium has been followed down to a velocity of 10^8 cm. per sec., corresponding with a range of 0·5 mm. in air at *N.T.P.* L. L. BIRCUMSHAW.

Attempt to demonstrate the existence of short-range α-particles from radium-*C*. G. H. HENDERSON and J. L. NICKERSON (Proc. Nova Scotia Inst. Sci., 1930, **17**, 256—258).—An attempt to detect short-range particles from radium-*C* by the Wilson chamber method showed that no group of particles of definite range could be detected above the general background. H. BURTON.

Absorbable radiation accompanying α-rays from polonium. (MME.) I. CURIE and F. JOLIOT (J. Phys. Radium, 1931, [vii], **2**, 20—28).—A more detailed account of work already noted (A., 1930, 130).

Loss of energy by β-particles, and its distribution between different kinds of collisions. E. J. Williams (Proc. Roy. Soc., 1931, **A**, **130**, 328—346).—Theoretical. The requirements of the classical and quantum theories are compared, and it is shown that the quantum theory is in general agreement with experiment and provides an explanation of several previously obscure effects, particularly in connexion with primary ionisation.

L. L. Bircumshaw.

Rate of loss of energy by β-particles in passing through matter. E. J. Williams (Proc. Roy. Soc., 1931, **A**, **130**, 310—327).—Most of the previous experimental work which has been carried out on β-particles is vitiated by the effects due to scattering and straggling. Experimental values which are practically free from these effects are now given for the rate of loss of energy by β-particles with velocities ranging from about 0·1 to 0·97*c*.

L. L. Bircumshaw.

Photographic effects of γ-rays. J. S. Rogers (Proc. Phys. Soc., 1931, **43**, 59—67).—Although slow, a photographic method can be used for measuring intensities of γ-rays, even when very small. The photographic action of γ-rays from radium and radon in equilibrium with their short-lived products has been investigated. The variation of photographic density with time of exposure (using constant intensity) and the variation of density with intensity (constant time) were examined for γ-rays filtered through lead screens of different thicknesses. The index in the Schwarzschild relation is unity for all lead filters. A photographic method has been developed for the determination of absorption coefficients. The absorption coefficient of lead for γ-rays is 0·533 cm.$^{-1}$ for thicknesses of lead from 1 to 7 cm. This is the same value as was found by Kohlrausch for the harder rays from radium-*C*, but is somewhat less than that obtained by Ahmad with a filter of lead 1 cm. thick.

A. J. Mee.

Absorption coefficients of γ-radiation from radium-*D* and -*E*, and the number of emitted quanta. (Miss) S. Bramson (Z. Physik, 1930, **66**, 721—740).—Absolute measurements have been made of ionisation currents due to γ-radiation from radium-*D* and -*E*, after passage through aluminium and copper. Radium-*D* showed absorption coefficients corresponding with the wave-length $2·6\times10^{-9}$ cm., and radium-*E* the wave-lengths 1·55 and $0·5\times10^{-9}$ cm. The longer radium-*E* wave-length is a $K\alpha$ radiation from polonium, but the shorter probably arises in the radium-*D* nucleus. The magnitude of ionisation currents showed that every 100 disintegrating radium-*D* atoms emitted $3·1\pm1·2$, and every 100 disintegrating radium-*E* atoms emitted $0·5\pm0·25$ γ-quantum. The internal absorption coefficient is known for radium-*D*, and indicates that every disintegrating radium-*D* nucleus emits one γ-quantum.

A. B. D. Cassie.

Number of γ-quanta emitted from radium-*D*. E. Stahel and G. J. Sizoo (Z. Physik, 1930, **66**, 741—747).—The number of γ-quanta emitted from radium-*D* due to disintegration was determined by means of an ionisation chamber containing methyl iodide. *L*-Radiation from excited atoms was absorbed by 1 mm. of aluminium and β-radiation was deflected by a magnetic field. Energy absorbed by the methyl iodide that does not contribute to ionisation was allowed for. Every 100 disintegrating radium-*D* atoms emit $2·4\pm0·7$ γ-quanta.

A. B. D. Cassie.

Methods of investigating the intensities of γ-rays. C. D. Ellis and D. Skobeltzyn (Nature, 1931, **127**, 125).—The methods of Skobelzyn (A., 1930, 8) and of Ellis and Aston (*ibid.*, 1339) for measurements of the intensities of the γ-rays of radium-*B* and -*C* are discussed in relation to each other and are shown to be complementary. Confidence in the values of the individual intensities of the γ-rays measured by the photo-electric method is also given by this agreement. L. S. Theobald.

Photo-electric absorption of γ-rays. L. H. Gray (Proc. Camb. Phil. Soc., 1931, **27**, 103—112).—Available data for the derivation of a formula for the photo-electric absorption coefficient of *X*-rays and γ-rays are reviewed. N. M. Bligh.

Absorption law for short wave-length γ-rays. L. Meitner and H. H. Hupfeld (Z. Physik, 1931, **67**, 147—168).—The absolute scattering coefficient of γ-rays of wave-length 4·7 X from thorium-*C″*, filtered through 4 cm. of lead, was determined for different substances and was found to correspond with that calculated from the formula of Klein and Nishina (A., 1929, 373) for carbon only; in general, σ_e increases with increasing nuclear charge. For γ-rays for radium-*C* the scattering coefficients for aluminium and carbon are identical and accord with the theory.

A. J. Mee.

Theory of atomic disintegration. II. G. Beck (Z. Physik, 1931, **67**, 227—239; cf. A., 1930, 1233; this vol., 16).—The case of a heavy nucleus is considered where the incident α-rays cannot penetrate far, and the excitation of a nucleus by direct collision with α-rays is discussed. A. J. Mee.

Present status of theory and experiment as to atomic disintegration and atomic synthesis. R. A. Millikan (Science, 1931, **73**, 1—5).—An address. L. S. Theobald.

Microcalorimetric measurements of a thermic effect varying with time. A. Dorabialska (Rocz. Chem., 1931, **11**, 35—39).—The increase in heat production of 2·2 mg. of radium separated from emanation and from slowly disintegrating products can be measured by means of an adiabatic microcalorimeter, and is a measure of the accumulation of emanation.

R. Truszkowski.

Radiation and molecular properties. R. D. Kleeman (Z. anorg. Chem., 1931, **195**, 164—172).—Theoretical. It is shown that the author's theory of a static atom is capable of affording a comprehensive explanation of the phenomena of photochemistry (cf. A., 1930, 1340). It also yields a satisfactory physical interpretation of radiation and ionisation potentials.

R. Cuthill.

Quantum-mechanical motion of free electrons in electromagnetic fields. E. H. Kennard (Proc. Nat. Acad. Sci., 1931, **17**, 58—63).

Transfer of energy between atoms on collision. O. N. RICE (Proc. Nat. Acad. Sci., 1931, **17**, 34—39).—Mathematical. An outline is given of a modification of Born's treatment of the question of energy exchange between atoms or molecules which takes into account the relative translational energy and also meets the objections raised by Kallmann and London (A., 1930, 395) to Frenkel's view that Born's method may be applied directly (*ibid.*, 132). The method yields in any given case an upper limit for the radius of action which is considerably smaller than that found by Kallmann and London (A., 1929, 487).

H. F. GILLBE.

Absorption coefficient of earth radiation in air. G. A. SUCKSTORFF (Naturwiss., 1931, **19**, 87—88).—The absorption coefficient of earth radiation for free air (10 metres above ground level) was found to be $3{\cdot}4\times10^{-5}$ cm.$^{-1}$; for air in an iron tower 10 metres high the value was $4{\cdot}5\times10^{-5}$ cm.$^{-1}$ The absorption curve in free air can be represented by the addition of three absorption curves with coefficients, 4·6, 3·2, and $2{\cdot}6\times10^{-5}$ cm.$^{-1}$, which correspond with the ionising influences of radium, thorium-*C''*, and potassium, respectively. W. R. ANGUS.

Transformation of light into heat in solids. I. J. FRENKEL (Physical Rev., 1931, [ii], **37**, 17—44; cf. A., 1930, 126, 132).—Mainly mathematical. From the analogy between a crystal and a molecule the electronic excitation forming the first step in the process of light absorption is distributed among the atoms in the form of "excitation waves," similar to sound waves, which are used to describe the heat motion in the same crystal. N. M. BLIGH.

Building up of elements in stars. W. ANDERSON (Z. Physik, 1931, **67**, 294—295).—The statement of Atkinson and Houtermans (A., 1929, 738) that the temperature of stars is of the order of $4\times10^{7\circ}$ and that the density is about 10 g. per c.c. does not agree with Milne's value of $10^{11\circ}$. A. J. MEE.

Van der Waals forces for hydrogen and helium at large inter-atomic distances. H. R. HASSE (Proc. Camb. Phil. Soc., 1931, **27**, 66—72; cf. Eisenschitz, A., 1930, 525; Lennard-Jones, this vol., 17).—Mathematical. The interatomic force at large distances is calculated from the principle of minimum energy by a method based on that used for the polarisability of helium (cf. this vol., 14).

N. M. BLIGH.

Separation of the two types of iodine molecule and the photochemical reaction of gaseous iodine with hexene. R. M. BADGER and J. W. URMSTON (Proc. Nat. Acad. Sci., 1930, **16**, 808—811).—Wood and Loomis (J. Franklin Inst., 1928, **205**, 481) found that the fluorescence spectrum of iodine excited by the green mercury line (5461 Å.) contained only half the number of lines of the fluorescence spectrum excited by white light. The lines appearing under excitation by 5461 Å. are ascribed to an "ortho" type of iodine molecule. Therefore by irradiating iodine with 5461 Å. it is possible to activate selectively "ortho" molecules. Experiments were performed in which the activated "ortho" molecules reacted with hexene are discussed. It is claimed that after irradiating a mixture of iodine and hexene with 5461 Å. for 24 hrs., the residual iodine consists largely of molecules which cannot absorb the mercury green line. W. R. ANGUS.

Photometric properties of ground and frosted glass. J. DOURGNON and P. WAGUET (Compt. rend., 1931, **192**, 155—156). C. A. SILBERRAD.

Highly-attenuated flames of alkali metal vapours with halogen hydrides. G. SCHAY (Z. physikal. Chem., 1930, **B**, **11**, 291—315; cf. A., 1930, 832).—Reactions between opposing streams of halogen hydrides and vapours of sodium or potassium have been studied by the methods described in earlier papers. The primary reaction is $M+HX=MX+H$, and the luminescence observed is due to subsequent reaction of the hydrogen atoms. A part of the emitted light is due to a reaction $H+HX=H_2+X$ and the remainder probably to combination of hydrogen atoms with sodium adsorbed on the walls of the tube, and subsequent reaction of the hydride with atomic hydrogen. The light emitted by the sodium flames is that of the sodium *D* line, whereas the potassium flames give a continuous spectrum.

F. L. USHER.

Ammonia discharge tube. G. I. LAVIN and J. R. BATES (Proc. Nat. Acad. Sci., 1930, **16**, 804—808).—The active products in the exit tube of an ammonia discharge tube have been examined and seem to consist of atomic hydrogen and NH or NH_2. The catalytic effects of certain substances and the characteristic luminescences at various surfaces have been examined (A., 1930, 659) and are discussed.

W. R. ANGUS.

Band spectrum intensities for symmetrical diatomic molecules. II. E. HUTCHISSON (Physical Rev., 1931, [ii], **37**, 45—50).—Mathematical. The approximate expression previously deduced (cf. A., 1930, 1331) is extended, using the Schrödinger perturbation theory and removing the restriction of linear oscillations. N. M. BLIGH.

Theoretical values of the quantum of energy of vibration of unexcited gaseous alkali iodides. H. J. VAN LEEUWEN (Z. Physik, 1930, **66**, 241—245).—Theoretical. Brück's method (A., 1929, 381) is used to calculate the energy of interaction of a comparatively small positive ion and the electrons of a completed *O* shell, where the *O* shell moves in a field of force due to a nucleus of effective charge *Z*. Examples discussed are lithium, sodium, and rubidium iodide. A. B. D. CASSIE.

Analysis and interpretation of hydrogen chloride bands in the ultra-violet. M. KULP (Z. Physik, 1931, **67**, 7—23).—The band spectrum obtained by a Geissler discharge in streaming gaseous hydrogen chloride was measured (cf. A., 1930, 1089; this vol., 19). W. R. ANGUS.

Influence of the crystal lattice on the absorption spectrum of a compound. H. FESEFELDT (Z. Physik, 1931, **67**, 37—41).—Absorption spectra between 180 and 600 mμ are given for silver and thallium iodides at one temperature below the inversion point, and at another above the inversion point. Variation of the absorption constant with temperature of silver iodide at 480 mμ is also given.

The curves indicate that silver and thallium iodides have not simple ionic lattices like those of the alkali halides. A. B. D. CASSIE.

Intensity relationships in the spectra of alkali mixtures and the possibility of quantitative spectral analysis of these elements. H. LUCAS (Z. anorg. Chem., 1931, **195**, 321—337).—With the object of establishing a technique for the spectroscopic determination of sodium and potassium in a mixture of salts the intensity ratios of suitable spectral lines of the two metals have been measured. When the carbon arc is used not only the intensities but also the ratios of the intensities vary from point to point in the arc; in the coolest region, where the field strength is small, the more readily excited potassium spectrum becomes relatively more intense. By measuring the emission always from the same zone of the arc and maintaining constant voltage, current, and length of arc the intensity ratios of sodium or potassium lines of different series but of which the upper terms have approximately the same excitation potential are constant to within 10%. For lines of the same series the error may be 40—50%, and deviations of this order are obtained also when comparing the lines of sodium with those of potassium. The intensity ratio, however, bears a definite relationship to the composition of the salt mixture, and by employing the doublet ratios of either metal as a control, the error of a determination may be reduced to about 20—25%. The error is of the same order if the spark at the surface of a solution of the salts be employed as the source of light. H. F. GILLBE.

Emission spectra of benzene derivatives. J. B. AUSTIN and I. A. BLACK (J. Amer. Chem. Soc., 1930, **52**, 4755—4762; cf. A., 1930, 660; McVicker, Marsh, and Stewart, J.C.S., 1923, **123**, 642, 2147).—The ultra-violet emission band spectra of the vapours of toluene, *o*-, *m*-, and *p*-xylene, and ethylbenzene, excited in a Tesla discharge, have been photographed and the wave-lengths of bands between 2600 and 3000 Å. determined to within ±0·5 Å. The toluene and ethylbenzene bands are displaced towards the red, as compared with those of benzene, and those of *o*-, *m*-, and *p*-xylene exhibit progressively larger displacements. The application of these spectra to qualitative and quantitative analysis is limited.

J. G. A. GRIFFITHS.

Simple relations between molecular spectra and structure. H. DESLANDRES (Compt. rend., 1930, **191**, 1404—1407). The formula $\nu = qd_1/rs \pm q'd'_1/r's'$ (cf. A., 1925, ii, 1023) and the theory of a fundamental frequency ($d_1=1062\cdot5$) are examined in regard to their applicability to certain vibration bands, residual rays, and Raman spectra. The frequencies are shown to be integral multiples of various fractions (from $\frac{1}{3}$ to 1/160) of the fundamental frequency.

C. A. SILBERRAD.

Absorption spectra of dibenzyl and its derivatives. (MME.) RAMART-LUCAS and J. HOCH (Compt. rend., 1931, **192**, 53—55).—Dibenzyl prepared in hexagonal plates by the action of sodium and magnesium on three specimens of benzyl chloride of different origins showed the *a* and *b* absorption bands observed by Baly and by Castille (A., 1927, 186, 608), the former varying in intensity. Condensation of two specimens of bromoethylbenzene and benzene in the presence of aluminium chloride gave prismatic needles of dibenzyl showing only the *b* band (2700—2300 Å.). The differences in absorption and crystal structure are accounted for by the presence in the former specimen of about 0·05% of stilbene.

J. GRANT.

Ultra-violet absorption spectra of the quinoline group. C. S. HICKS (Austral. J. Exp. Biol., 1930, **7**, 171—181).—The following ultra-violet absorption bands have been determined: quinine λλ 3268—3058, 2805—2570, 2390—? Å. (in alcohol); quinine hydrochloride, λλ 3295—3035, 2800—2580, 2325—? (in water); methylquinine sulphate, λλ 3285—3020, 2776—2581, 2385—? (in water); cinchonine, λλ 3150—3125, 2818—2450, 2240—? (in alcohol); cinchonine hydrochloride λλ 3150—3125, 2850—2470, 2280—? (in water); cinchotoxin, λλ 3100—2630, 2376—2322, 2174—? (in alcohol); cupreine, λλ 3340—3040, 2815—2578, 2190—? (in alcohol); hydrocupreine λλ 3335—3049, 2840—2685, 2413—? (in alcohol); optochin hydrochloride, λλ 3355—3400, 2872—2570, 2840—? (in water); eucupine dihydrochloride, λλ 3305—2700, 2350—? (in water); euquinine, λλ 3305—3005, 2800—2575, 2300—? (in alcohol); hydrochinotoxin, λλ 3390—2865, 2265—? (in water); hydrochininone, λλ 3465—2840, 2265—? (in alcohol); yohimbine λλ 2745—2445, 2190—? (in water). The absorption bands of the quinine alkaloids are determined almost entirely by the quinoline nucleus and not by the quinuclidine group. W. O. KERMACK.

Infra-red spectra of water, hydrogen sulphide and selenide. W. MISCHKE (Z. Physik, 1931, **67**, 106—126).—The spectra of hydrogen sulphide and selenide were plotted between 0·8 and 18 μ. Hydrogen sulphide showed bands at 14·6, 8·1, 4·27 μ (fundamental frequencies), and at 2·70, 1·92, and 1·57 μ (combination frequencies); hydrogen selenide showed bands at 8·5, 4·25, 3·33, and 2·3 μ. Partial resolution was obtained for most of the bands. *P–R* branch separations give a moment of inertia $2\cdot0\times10^{-40}$ g.-cm.^{2} Hund's model (A., 1925, ii, 479) of hydrogen sulphide gives $J_1=3\cdot5$, $J_2=1\cdot3$, $J_z=4\cdot8\times10^{-40}$ g.-cm.^{2}, and the mean value $\sqrt[3]{J_1J_2J_3}$ agrees with $2\cdot0\times10^{-40}$ g.-cm.^{2} An alternation in the intensities of resolved lines in the 8·1 μ band is ascribed to two forms of hydrogen sulphide corresponding with parallel and with anti-parallel hydrogen nuclear spins.

A. B. D. CASSIE.

Absorption of ultra-violet rays by transparent liquids. J. CLUZET and T. KOFMAN (Compt. rend. Soc. Biol., 1930, **103**, 783—785; Chem. Zentr., 1930, ii, 12).—Using a cadmium cell, the ultra-violet absorption in the region 3000—2300 Å. has been investigated for the commoner organic solvents and acids, and for aqueous solutions of common inorganic salts. L. S. THEOBALD.

Ultra-violet absorption spectrum of lignin derivatives. E. HAGGLUND and F. W. KLINGSTEDT (Z. physikal. Chem., 1931, **152**, 295—312).—The positions of the maxima and minima in the absorption spectra, and the molecular extinction coefficients, are given for methyl-, ethyl-, and *iso*amyl-lignin, for

lignosulphonic acid, and for alkali lignins derived from different species of wood. There is comparatively strong selective absorption. F. L. USHER.

Optical effects (absorption and fluorescence) caused by salt formation of substituted cinnamic acids. H. LEY and R. DREINHÖFER (Z. wiss. Phot., 1930, **29**, 134—154).—Quantitative measurements of the absorption of *o*-hydroxy- and *o*-amino-cinnamic acids and their alkali salts show that the spectra in the region down to 220 mμ consist of two bands, one of long and the other of short wave-length. The fluorescence centres in the molecules are the groups C_6H_4·OH (or C_6H_4·O′ in the more strongly fluorescing alkali *o*-hydroxycinnamate) and C_6H_4·NH_2. The absorption of rays in the long-wave-length bands produces the fluorescence. J. W. GLASSETT.

Thermoluminescence in glasses which contain two activators. B. E. COHN and W. D. HARKINS (J. Amer. Chem. Soc., 1930, **52**, 5146—5154; cf. Nyswander and Cohn, A., 1930, 520).—The progressive addition of manganese to zinc borate glass containing cerium at first increases and then decreases the thermoluminescence. Similar affects are produced by the addition of cerium to the glass containing manganese. As to whether the addition of a definite proportion of cerium will activate or damp the luminescence depends on the concentration of the manganese. The emission spectrum from zinc borate glass containing manganese is a band occupying the green, yellow, and red. The ultra-violet absorption bands of zinc borate glass containing cerium, manganese, or thorium have single ends on the longer wave-length side and the energy of luminescence may be derived from near these boundaries. It is concluded that different light sources will excite thermoluminescence of different relative intensity with different solutes in the same solvent. Absorption curves of these glasses are given and that of zinc borate containing manganese is anomalous.
J. G. A. GRIFFITHS.

Decay of phosphorescence in sylvine containing thallium chloride and its dependence on temperature. W. BÜNGER and W. FLECHSIG (Z. Physik, 1931, **67**, 42—53).—A method for determining the decay of phosphorescence at different wave-lengths is described. The total radiation emitted as phosphorescence decays exponentially with time. It has a definite physical significance, and with this is associated a threshold energy necessary for emission of phosphorescence. This is calculated to be 1·5 μ, where preliminary experiments have shown the excited KCl–TlCl system to have high absorption.
A. B. D. CASSIE.

Raman spectrum of nitric oxide. F. RASETTI (Z. Physik, 1930, **66**, 646—649).—An exposure of 72 hrs. gave a plate with displacements corresponding with $^2\Pi_{1/2} \longrightarrow {}^2\Pi_{3/2}$ and indicates that the doublet separation is 122 cm.$^{-1}$ The instrument did not resolve individual rotation lines, but the photographs suggest that the transitions $\Delta J = \pm 1$ and ± 2 occur, as theoretically predicted for a Π level.
A. B. D. CASSIE.

Raman effect and constitution of molecules. III. The fundamental frequencies of molecules of type XY_4. Effect of mixed halides. B. TRUMPY (Z. Physik, 1930, **66**, 790—806; cf. A., 1930, 1499).—Raman displacements due to the molecules CCl_4, $SiCl_4$, $TiCl_4$, $SnCl_4$, and $SnBr_4$ were obtained, and the corresponding infra-red frequencies calculated. The chlorides each show four intense infra-red fundamental frequencies, which diminish regularly as the mass increases from carbon to tin. Dennison's expressions (A., 1926, 659) for the normal vibration frequencies of such tetrahedral molecules are used to deduce ratios of the fundamental frequencies, and these ratios show that theory and experiment agree to within 10%. The infra-red fundamental frequencies of $SnBr_4$ are less than those of $SnCl_4$, agreeing with the greater mass of bromine. Mixtures of $SnCl_4$ and $SnBr_4$ in the ratios 1 : 1, 1 : 3, and 3 : 1 were investigated and showed new Raman displacements. The lines due to $SnCl_4$ and $SnBr_4$ were considerably weakened, and new lines were even more intense than the original lines. Results support the hypothesis that $SnCl_2Br_2$, $SnBr_3Cl$, and $SnBrCl_3$, respectively, are the chief intermediate products in these mixtures.
A. B. D. CASSIE.

Chemical constitution and the Raman effect: ethylenic compounds. R. LESPIEAU and BOURGUEL (Bull. Soc. chim., 1930, [iv], **47—48**, 1365—1376; cf. A., 1930, 1091).—When the double linkings are of different types, *i.e.*, closed or open chain, numerous lines appear in the neighbourhood of the frequency 1600 cm.$^{-1}$ The substitution by methyl of a hydrogen atom attached to an ethylenic carbon atom causes an increase of the characteristic Raman frequency, but the effect is less marked than in acetylenic compounds. The existence of conjugated double linkings is indicated by increased intensity of the lines due to each linking. Comparison of the Raman spectra of phenyltrimethylene with those of allyl- and propenyl-benzene shows that the first-named contains a three-membered ring, in confirmation of the view previously expressed (A., 1930, 1041).
H. F. GILLBE.

Chemical constitution and the Raman effect: acetylenic compounds. BOURGUEL and P. DAURE (Bull. Soc. chim., 1930, [iv], **47—48**, 1349—1365).—A detailed account of work mostly published elsewhere (A., 1930, 978). In addition to the lines previously reported, there appears to be a fairly strong line of frequency about 350 cm.$^{-1}$ due to the triple linking, but its position depends on the nature of the compound under investigation. The linking ⁝C·Me is characterised by a rather strong line of frequency 1375. The effect of substitution in an acetylenic side-chain in aromatic compounds is described. H. F. GILLBE.

Raman effect in monohalogen derivatives of methane. G. N. BALL (Z. Physik, 1930, **66**, 257—260).—The Raman spectra due to methyl chloride, bromide, and iodide were investigated with a spectrometer of dispersion 50—90 Å. per mm. in the range 3650—4916 Å. Methyl chloride gave displacements corresponding with 13·85, 7·36, and 3·37 μ, methyl bromide 16·8 and 3·38 μ, methyl iodide 19·6, 8·00, and 3·38 μ. Thus only the fundamental frequencies of vibration appear. The 16·8 μ displacement for the

bromide and 19·6 μ for the iodide were predicted, from infra-red measurements, by Bennett and Meyer (A., 1929, 239). A. B. D. CASSIE.

Ionisation of air by the oxidation of phosphorus. J. TAUSZ and H. GORLACHER (Physikal. Z., 1931, **32**, 91—97).—The dependence of the ionisation on the velocity of streaming of the gas over the phosphorus, the temperature, and the area of the phosphorus surface is examined. For air it was found that there was a marked increase of ionisation with time. When the oxidation has once begun there is a rise of temperature which increases the ionisation. With increasing velocity of streaming, the ionisation increases. It appears that when the gas is still the oxidation zone is round the phosphorus, but when the gas is in motion the oxidation zone is inside the ionisation chamber. In moist streaming oxygen, there is no increase in ionisation at atmospheric pressure. For dry oxygen, however, there is an increase, the increase depending on the degree of dryness. With dry oxygen and dry phosphorus there was strong ionisation and cloud formation, but no glow. The effect on the ionisation of the admixture of foreign substances (isoprene, *cyclo*hexene, *cyclo*hexane, and benzene) with the air was determined. There was smaller ionisation with isoprene and *cyclo*hexene than with *cyclo*hexane and benzene. The ionisation decreases with increasing concentration of the foreign substance. A. J. MEE.

Influence of adsorbed gas layers on the photo-effects of salts. J. KLAPHECKE (Naturwiss., 1931, **19**, 87).—The properties arising from an adsorbed layer of gas in Geiger counting chambers is discussed (cf. Bosch and Klomb, this vol., 142). Water vapour promotes the escape of electrons from salts. Salts which have been heated strongly in a vacuum show little or no photo-electric effect on cooling. If a salt is produced by sublimation and then introduced into a photo-cell, a certain photo-stream is obtained which is increased ten-fold by treating the salt for a short time with water vapour; the same salt prepared from an aqueous solution gives a much higher photo-stream. Therefore adsorbed and occluded water both act as promoters for the escape of electrons. The influence of gases on the phenomena which concern the escape of surface electrons has been examined, but the results are not conclusive. The gases may have been imperfectly dried or small quantities of hydrogen and oxygen present in the gas may have united. If adsorbed layers of gases, other than water vapour, exert a similar effect, its magnitude will be considerably less than that of water vapour.

W. R. ANGUS.

Conductivity of liquid hydrocarbons in thin layers. L. BRUNINGHAUS (Compt. rend., 1931, **192**, 151—153; cf. A., 1930, 282).—The conducting stage has been further examined with means for more accurately measuring the distance between the electrodes. C. A. SILBERRAD.

Polarisation in photo-electric conductivity arising from *X*-ray excited rock-salt. P. TARTAKOVSKI (Z. Physik, 1930, **66**, 830—833).—A thin plate of rock-salt was placed between the poles of an electromagnet, and the Hall effect was used to give a preponderance of free electrons towards one side of the plate. When the magnetic field was removed, the corresponding half of the plate showed a lower conductivity. Hence free electrons increase the polarisation. A. B. D. CASSIE.

Dielectric constant and conductivity of ionised gases. J. V. JONESCU and C. MIHUL (Compt. rend., 1930, **191**, 1436—1438).—An apparatus is described by means of which variations in dielectric constant and conductance ($1/\rho$) of a gas due to change in degree of ionisation are determined. It is shown that the conductance is proportional to the intensity of ionisation when the square of the wave-length of the oscillator is taken into account. C. A. SILBERRAD.

Dielectric constant of supercooled sulphur and some sulphur solutions. S. ROSENTAL (Z. Physik, 1930, **66**, 652—656).—A condenser consisting of a double-walled glass vessel is described. The outside and inside of the vessel are metal-coated, and the substance to be investigated is contained between the walls. Sulphur, supercooled to 25° below f. p., showed a linear relation between dielectric constant and temperature. At 130°, the dielectric constant is $3{\cdot}720\pm0{\cdot}003$; on solidification it rose by 5—10%. Solutions in benzene followed the Clausius–Mossotti relation, but in carbon tetrachloride small increases in polarisation occurred with rise in temperature.

A. B. D. CASSIE.

Dielectric constant of liquid bromine. D. DOBORZYNSKI (Z. Physik, 1930, **66**, 657—668).—The condenser described by Rosental (see preceding abstract) and the resonance method were used to determine the dielectric constant of bromine in the range 0—53·8°. The experimental method and possible errors are discussed. The dielectric constant is given by $\varepsilon=1{\cdot}0730+671{\cdot}42/T$. Bromine, which can be considered as a non-associated liquid, has therefore a dipole moment of $0{\cdot}49\times10^{-18}$ e.s.u.

A. B. D. CASSIE.

Dielectric measurements on vapours of amines. O. STEIGER (Helv. phys. Acta, 1930, **3**, 161—162; Chem. Zentr., 1930, ii, 1343).—The following dipole moments ($\times10^{-18}$ e.s.u.) have been determined: methylamine $1{\cdot}23+0{\cdot}02$, dimethylamine $0{\cdot}96\pm0{\cdot}01$, trimethylamine $0{\cdot}60\pm0{\cdot}02$. A. A. ELDRIDGE.

Electrical moments of certain organic compounds. A. SANGER (Helv. phys. Acta, 1930, **3**, 162; Chem. Zentr., 1930, ii, 1343).—The following values ($\times10^{-18}$ e.s.u.) are recorded: dimethyl ether $1{\cdot}316\pm0{\cdot}012$, methyl chloride $1{\cdot}861\pm0{\cdot}008$, ethyl chloride $2{\cdot}019\pm0{\cdot}025$, propyl chloride $2{\cdot}040\pm0{\cdot}08$. Hence the polarising effect of the chlorine atom reaches only to the second carbon aton in the chain.

A. A. ELDRIDGE.

Change of the electric polarisation of ethyl ether with temperature. M. WOLFKE and J. MAZUR (Nature, 1931, **127**, 236; cf. A., 1930, 1501).—The value of the dielectric polarisation of ethyl ether, calculated by means of the Clausius–Mossotti formula, increases slowly with a fall in temperature from the value 0·5858 at 35° to a maximum of 0·9209 at −105·4°, and then decreases rapidly. This marked change suggests that the structure of the molecule of

ethyl ether suffers a modification at $-105\cdot4°$ (cf. A., 1930, 1554). L. S. THEOBALD.

Dense space charges (polarisation) in calcite. A. JOFFÉ, D. ROJANSKI, and K. SINELNIKOV (Z. Physik, 1930, 66, 143—171).—Measurements relating to the dielectric polarisation in calcite due to continuous potentials are described. Polarisation is confined to a very thin region, a few μ, in the neighbourhood of the cathode. The polarisation is conveniently expressed in terms of that capacity which may be regarded as proportional to the total charge per cm.^{2} in those layers adjacent to the cathode in which the space charge falls from its maximum value to $1/e$th. When an equilibrium state of polarisation is attained the conductivity of the medium attains a constant value which is much smaller than the normal conductivity. Related data are given for a large number of materials. R. W. LUNT.

Electrical conductivity and [high-tension] polarisation in sodium nitrate crystals. B. HOCHBERG and V. JOFFÉ (Z. Physik, 1930, 66, 172—191).—The experiments on dielectric polarisation described in the preceding abstract have been extended to sodium nitrate. The polarisation is again found to be confined to regions in the neighbourhood of the electrodes. The temperature variation of the conductivity in the polarised state is found to have the same form as that of the normal state. R. W. LUNT.

Dielectric properties of potassium sodium tartrate. P. KOBEKO and J. KURTSCHATOV (Z. Physik, 1930, 66, 192—205).—The abnormally high values of the dielectric constant of potassium sodium tartrate reported by earlier workers has been confirmed, and provided that a good contact is made between the electrodes and the specimen values up to 20,000 may be obtained. The dielectric constant of a given specimen diminishes as the potential across the specimen is increased. It is shown that these abnormal values cannot be attributed to the polarisation effect in the neighbourhood of the electrodes such as is observed in calcite (cf. preceding abstracts). R. W. LUNT.

Refractive indices of some heavy metal halides in the visible, and determination of interpolation formulæ for the dispersion curves. H. SCHRÖTER (Z. Physik, 1931, 67, 24—36).—The refractive indices of silver chloride and bromide, and of thallium chloride and bromide, were measured in the range 4500—7000 Å. accurately to the third decimal place. The prisms of silver bromide and chloride were single crystals; those of thallium consisted of three or four crystals. The method of obtaining these crystals is described. A. B. D. CASSIE.

Dispersion of potassium bromide crystals in the infra-red. E. GUNDELACH (Z. Physik, 1930, 66, 775—783).—The refractive index of crystalline potassium bromide was determined between 0·8 and 18 μ with two Wadsworth prism spectrometers, using either rock-salt or sylvine prisms, and between 18 and 28·5 μ by means of an étalon interferometer and a prism of potassium bromide. A radiomicrometer was used to measure intensity of radiation. The refractive indices are accurate to one unit in the third decimal place. A. B. D. CASSIE.

Mechanical double refraction of liquids in relationship to the molecular form. II. D. VORLÄNDER and U. KIRCHNER (Z. physikal. Chem., 1931, 152, 47—66).—Data are given relating to the specific double refraction of unitary anisotropic "oils," including glycerol, aliphatic and aromatic esters, and aromatic aldehydes and ketones, and of homogeneous mixtures of isotropic "oils," solutions of colloids in oils, and a variety of aqueous solutions. The measurements show the influence of double linkings, *p*-substituents, chain length, and branched molecules such as tolyl phosphate. The simple aliphatic alcohols do not exhibit mechanical double refraction; glycol, despite its high viscosity, is also inert, and cannot be of the simple structure expressed by its formula. Among the normal monobasic fatty acids the effect first becomes evident with nonoic esters, and among the dibasic acids with succinic esters. Aqueous solutions, even of high viscosity, of simple inorganic compounds such as calcium and zinc chlorides do not exhibit the effect to any marked extent, whereas with potassium acetate solutions there is a definite positive effect which reverses sign as the chain length of the anion increases. H. F. GILLBE.

Measurement of circular dichroism. J. P. MATHIEU (Compt. rend., 1931, 192, 156—158).—A method is described for measuring circular dichroism by which both rotation and ellipticity are determined with the same apparatus, the essential point being the use as compensator of one birefringent plate for the whole visible spectrum. C. A. SILBERRAD.

Photo-elastic dispersion of vitreous silica. L. N. G. FILON and F. C. HARRIS (Proc. Roy. Soc., 1931, A, 130, 410—431).—By means of a modification of the spectrometer method previously described (Filon, Proc. Camb. Phil. Soc., 1902, 12, 55), measurements have been made of C, the stress-optical coefficient of vitreous silica for light of wave-length λ, and the formula $C=C_0/(1-\lambda_0/\lambda)$ is found to hold with fair accuracy. L. L. BIRCUMSHAW.

Magnetic rotation of gaseous halogen derivatives of saturated hydrocarbons. R. DE MALLEMANN and P. GABIANO (Compt. rend., 1931, 192, 278—280).—Magnetic rotations of eleven halogen derivatives of the lower paraffins have been determined in the liquid and gaseous states. From these results and those previously obtained (cf. this vol., 148) the following values have been deduced for the atomic rotations ($\times 10^2$) of H, C, Cl, Br, and I respectively: 5·5, 10, 33, 66, and 143. The figure for hydrogen is but slightly lower than that for the free gas; the figures for the halogens are very much lower than those for the corresponding ions (Cl′ 108, Br′ 208, and I′ 450). C. A. SILBERRAD.

Magnetic rotatory power of a uniaxial crystal in directions oblique to the axis; determination of the rotation of tysonite in a direction approximately that of a binary axis, at the temperature of liquid nitrogen. J. BECQUEREL (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 913—925).—An

extension of the work on tysonite at the ordinary temperature. A compensation method is used. The optical and magnetic axes are in a horizontal plane and different orientations are given to the crystal and to the field. With a magnetic field of given orientation and constant intensity, the rotation of the principal axis of the emerging elliptically polarised light is measured for different orientations of the crystal. An equation is deduced for the magnetic rotation of tysonite under the conditions of the experiment, which is verified by the results. The ratio of the rotatory powers normal and perpendicular to the optical axis is much less at liquid nitrogen temperatures than at the ordinary temperature.

J. Farquharson.

Determination of the paramagnetic rotatory power of a crystal of tysonite in a direction normal to the optical axis at the temperature of liquid hydrogen. J. Becquerel and W. J. de Haas (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 926—936).—Two methods of measurement may be used: (*a*) a compensation method (see preceding abstract), (*b*) the field is oriented perpendicularly to the optical axis and the component of the effect is measured directly in a direction normal to the optical axis. Experiments were made by both methods at 20° and by method (*a*) at 14°. J. Farquharson.

Magneto-optical anisotropy in a plane normal to the optical axis of a hexagonal crystal. Paramagnetic rotatory powers in directions approximating to the binary axes at very low temperatures. J. Becquerel and W. J. de Haas (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 937—948).—At the temperature of liquid helium, method (*b*) (see preceding abstract) is applicable. Measurements are made with two tysonite plates of different thicknesses. After correction for the thickness of the plates curves are obtained for the magnetic rotation as a function of H/T. The magnetic rotations in the directions of the two species of binary axes are different; the deviation of the two curves is greater than can be ascribed to experimental error. This is the first example of an optical anisotropy in a plane normal to the optical axis of a uniaxial crystal. The anisotropy has a paramagnetic origin, for the saturation rotations in the directions of the binary axes are the same, showing that the uniaxial crystal is optically isotropic for all directions normal to the optical axis. J. Farquharson.

General theory of paramagnetic rotation in crystals. H. A. Kramers (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 959—972).—Theoretical. If the divergence from isotropy is small, the introduction of a rotation vector permits a simple explanation of the properties of a beam of light in any direction. An atomic system of odd number of electrons, in a purely electrical external field, has doubly degenerate energy levels. The magnetisation produced in such an atom by a magnetic field in any direction is discussed, as is the paramagnetic rotation in a crystal containing these atoms. J. Farquharson.

Theory of Kossel and Magnus. Allard (Bull. Soc. chim., 1930, [iv], **47**, 1333—1342).—A lecture describing the Kossel–Magnus theory, and particularly its bearing on the structure of hydrates and ammines. H. F. Gillbe.

Structural principles of compounds of boron and hydrogen. E. Wiberg (Z. anorg. Chem., 1931, **195**, 288).—A correction (cf. A., 1930, 524).

R. Cuthill.

Molecular structure of triatomic gases. II. H_2O, H_2S, and N_2O. P. C. Mahanti (Physikal. Z., 1931, **32**, 108—110; cf. A., 1929, 1365).—The available data for dipole moments, Raman spectra, and infra-red absorption bands for these three molecules are discussed with a view of settling their structure. The H_2O molecule has a triangular structure which explains the existence of three moments of inertia. The H_2S molecule has a finite dipole moment and hence there can be no central symmetry, so that again the molecule has a triangular structure. For the N_2O molecule, the dipole moment is $0{\cdot}249\times10^{-18}$, which is very small. All observations point to a linear symmetrical structure for this molecule.

A. J. Mee.

Natural classification of chemical compounds. F. M. Schemjakin (Z. physikal. Chem., 1931, **152**, 235—244).—Theoretical. An attempt is made on the basis of Grimm's method to develop a system of classification of inorganic and organic compounds.

F. L. Usher.

Chemistry and geochemistry of the titanium group. G. von Hevesy (J.C.S., 1931, 1—16).—A lecture. N. M. Bligh.

Surface tension in a magnetic field. H. Auer (Z. Physik, 1930, **66**, 224—228).—A discussion of the effect of surface tension in the capillary method of measuring magnetic susceptibility and a method for controlling it. J. Farquharson.

Parachors of two isomeric chlorodinitrobenzenes. S. A. Mumford and J. M. C. Phillips (J. Amer. Chem. Soc., 1930, **52**, 5295—5297; cf. A., 1929, 1219).—A correction of statements by and polemical against Sickman and Menzies (A., 1930, 1279). J. G. A. Griffiths.

Parachors of isomeric chlorodinitrobenzenes. D. V. Sickman and A. W. C. Menzies (J. Amer. Chem. Soc., 1930, **52**, 5297).—A reply (see preceding abstract). J. G. A. Griffiths.

Parachor and chemical constitution. XVI. Silicon compounds. S. Sugden and H. Wilkins (J.C.S., 1931, 126—128).—Owing to divergent values of the atomic parachor of silicon from existing data for silicon tetrachloride, measurements of surface tension and density were made for methyl and ethyl orthosilicate and for tetra-ethyl-, -propyl-, and -phenylsilicane. Results give 28 for the parachor.

N. M. Bligh.

Determination of atomic distances in gas molecules by means of Röntgen and cathode rays. J. M. Bijvoet and H. J. Verweel (Chem. Weekblad, 1930, **27**, 648—650).—A discussion of recent results obtained with chloroform and ethylene chloride vapours; the existence of *cis-* and *trans-*forms in the latter is not regarded as established.

S. I. Levy.

Part-absorption phenomena of X-rays. R. C. MAJUMDAR (Nature, 1931, **127**, 92; cf. A., 1930, 1334).—Details of part-adsorption of iron and nickel radiations by carbon, nitrogen, and aluminium are recorded and discussed. L. S. THEOBALD.

Dependence of the width and intensity of Debye lines and rings on the dimensions of the X-ray source, of the preparation, and of the camera. W. BUSSE (Z. Physik, 1930, **66**, 285—288; cf. A., 1930, 1240).—Results deduced in the earlier paper are applied to an apparatus of average dimensions, and the conditions for its most efficient use are given. A. B. D. CASSIE.

Dependence of width and intensity of Debye lines and rings on tube-focus etc. W. BUSSE (Z. Physik, 1931, **67**, 296; cf. A., 1930, 1240).—The criticism made by Bredig (*ibid.*, 1502) of the form of apparatus used previously has been applied. A. J. MEE.

Relation of the liquid to the crystalline state. K. BANERJEE (Nature, 1931, **127**, 92—93).—The partial "crystallinity" of liquids manifested by the maximum, shown by X-ray diffraction, in the molecular arrangements in liquids corresponding with the crystalline structure of the substance in the solid state is responsible for the modified scattering reported by Gross (A., 1930, 1237). Gross' explanation of the broadening of Raman lines is criticised and another explanation is advanced. L. S. THEOBALD.

Theory of recrystallisation. J. A. M. VAN LIEMPT (Z. anorg. Chem., 1931, **195**, 366—386).—A mathematical attack on the problem of recrystallisation in metals. By consideration of the velocity of interchange of position of the atoms in uni-crystalline materials as a function of the temperature, the equation $D=(-p^2\nu/6)e^{-kb^2T_s/T}$ is derived, where D is the diffusion coefficient of a metal A, of relatively low m. p., into another metal, B, at temperature T, p is the minimum distance between the atoms of B, ν is the characteristic atomic frequency and T_s the m. p. of A, $b=+2$, and k is theoretically 3, but is subject to deviations from Dulong and Petit's law. The recrystallisation process in mixed crystals is discussed and the influence of impurities on the recrystallisation temperature of metals is to some extent elucidated. H. F. GILLBE.

Growth and dissolution of non-polar crystals. I. N. STRANSKI (Z. physikal. Chem., 1930, **B**, **11**, 342—349; cf. A., 1928, 1178).—A theoretical discussion of the differences between homopolar and heteropolar crystals with reference to their growth, dissolution, and function in heterogeneous catalysis. F. L. USHER.

Crystal etchings. G. T. FAUST (Bull. Wagner Inst. Sci., 1930, **5**, 35—41).—The results of etch figure studies of the quartz trigonal pyramid *s* (1121) are given and establish a symmetry identical with that previously indicated by the etchings of the commoner forms. The symmetry of orthoclase was also investigated by the etching method. W. GOOD.

Fractional precipitation. V. Inclusion of foreign matter in the crystal lattice. O. RUFF (Z. anorg. Chem., 1931, **195**, 60; cf. A., 1930, 286).—A correction. R. CUTHILL.

Recrystallisation of rock salt. K. PRZIBRAM (Z. Physik, 1931, **67**, 89—105).—Recrystallisation of rock-salt can be followed by use of a radium preparation. Discoloration due to radiation from the radium follows crystal planes, and only extends throughout recrystallised portions. Dependence of rate of recrystallisation on temperature and pressure (400—3000 kg./cm.^{2}) was thus studied. A. B. D. CASSIE.

Crystalline structure of the inert gases. Krypton. A. NASINI and G. NATTA (Atti R. Accad. Lincei, 1930, [vi], **8**, 141—147).—Application of the powder method of X-ray analysis to krypton indicates a face-centred cubic lattice; the cells containing four atoms have edges of 5·78 Å., corresponding with a volume of 193×10^{-24} c.c.; $d_{calc.}$ 2·83. F. G. TRYHORN.

Physical properties of rhenium. C. AGTE, H. ALTERTHUM, K. BECKER, G. HEYNE, and K. MOERS (Naturwiss., 1931, **19**, 108—109).—Rhenium crystallises hexagonally in the densest packing. The lattice constants are a 2·765, c 4·470 Å., c/a 1·616. The smallest atomic distance being 2·765 Å., the atomic radius is 1·382 Å. The m. p. determined by the drill-hole method is 3440±50° Abs. The coefficient of linear expansion measured by the X-ray method is $12\cdot45\times10^{-6}$ in the direction of the hexagonal axis and $4\cdot67\times10^{-6}$ in the direction perpendicular to this axis. The density of a highly-sintered rod was measured as 20·9, the density from X-ray measurements being 21·4. This indicates at. wt. 186·31±0·02. The tensile strength of a rhenium wire of 0·25 mm. cross-section with a tungsten core of 0·03 mm. cross-section was 50·6 kg./mm.^{2} The extension was 24%. The specific electrical resistance at the ordinary temperature is $0\cdot21\times10^{-4}$ ohm 15%, and the temperature coefficient of the resistance $3\cdot11\times10^{-3}$ between 0° and 100° and $1\cdot98\times10^{-3}$ between 0° and 2710°. The ratio of the specific resistances at 2710° and 0° is 6·34. Measurements of the electron emission between 1900 and 2700° Abs. give the following values for the constants in Richardson's emission equation $i=AT^2\varepsilon^{b/T}$: $A=200$ amp./cm.^{2} degree^2; $b=59{,}500$, and the work of evaporation of electrons calculated therefrom is 5·1 volts. J. W. SMITH.

Crystal structure of thallium. S. SEKITO (Z. Krist., 1930, **74**, 189—201; Chem. Zentr., 1930, ii, 1945).—α-Thallium, stable below 225°, hexagonal, has a 3·450 Å., c/a 1·600, 11·83; β-thallium, stable above 225°, cubic face-centred, has a 4·841 Å., d 11·86. Measurements were also made with various thallium alloys. A. A. ELDRIDGE.

Crystal structure of ice. E. BRANDENBERGER (Z. Krist., 1930, **73**, 429—430; Chem. Zentr., 1930, i, 3528).—Polemical (cf. Barnes, A., 1930, 20). A. A. ELDRIDGE.

X-Ray diffraction in water: the nature of molecular association. G. W. STEWART (Physical Rev., 1931, [ii], **37**, 9—16).—Using a method previously described (cf. A., 1927, 1015) the X-ray diffraction intensity–angle distribution for water and its variation for the temperature range 2—98° was

investigated. Periodicities were found at 3·24, 2·11, and 1·13 Å. in agreement with Meyer (cf. A., 1930, 1097). N. M. BLIGH.

Crystal structure of molybdenum trioxide. N. WOOSTER (Nature, 1931, **127**, 93).—Small, thin, lustrous plates parallel to *b* (010) of sublimed molybdenum trioxide show orthorhombic symmetry with a 3·93±0·02 Å., b 13·91±0·05 Å., and c 3·57±0·02 Å. There are four mols. per cell and the space-group is Q_h^{16} (*bnm*). With the centre of symmetry as origin, the co-ordinates of the molybdenum atoms are $uv\frac{1}{4}$: $u+\frac{1}{2}, v+\frac{1}{2}, \frac{1}{4}$; $u+\frac{1}{2}, v+\frac{1}{2}, \frac{1}{4}$; $uv\bar{\frac{1}{4}}$, where $u=36°$, and $v=30°$, approximately.

L. S. THEOBALD.

X-Ray investigation of potassium fluoborate. B. PESCE (Gazzetta, 1930, **60**, 936—939).—Examination of the two supposed dimorphous forms of potassium tetrafluoborate by means of X-rays shows that they are identical. For the precipitated product dried at 100° d^{15} is 2·555. O. J. WALKER.

X-Ray analysis of the structure of potassium dihydrogen phosphate. J. WEST (Z. Krist., 1930, **74**, 306—332; Chem. Zentr., 1930, ii, 1658).—Hendricks' view (A., 1927, 1013) is supported after some modification. A. A. ELDRIDGE.

Pearlite: its structure and mechanical properties. N. T. BELAIEV (Rev. Met., 1930, **27**, 680—685).—A review of recent work of the author and of Green in which expressions are deduced for determining the width of the lamellæ of cementite and ferrite in the pearlite eutectic. A. R. POWELL.

Structure of silicates. W. L. BRAGG (Z. Krist., 1930, **74**, 237—305; Chem. Zentr., 1930, ii, 1657).—A discussion. A. A. ELDRIDGE.

Crystallographic relationships between epidote–zoisite and orthite–allanite. F. MACHATSCHKI (Zentr. Min. Geol., 1930, **A**, 89—96, 154—158; Chem. Zentr., 1930, ii, 536).

Crystal structure of loparite and pyrochlore. H. R. VON GAERTNER (Neues Jahrb. Min., 1930, **A**, **61**, 1—30; Chem. Zentr., 1930, ii, 536).—The pseudocubic unit cell of loparite has a 3·854±0·018 Å. Pyrochlore has a 10·34 Å., with 8 mols. in the unit cell; space-group O_h^7. A. A. ELDRIDGE.

Structural and molecular unit of eudialyte. B. GOSSNER and F. MUSSGNUG (Zentr. Min. Geol., 1930, **A**, 81—88; Chem. Zentr., 1930, ii, 537).—The rhombohedral unit cell has a 14·31, c 30·15 Å.

A. A. ELDRIDGE.

Structural and molecular unit of petalite. B. GOSSNER and F. MUSSGNUG (Z. Krist., 1930, **74**, 62—66; Chem. Zentr., 1930, ii, 1355).—The unit cell, a 11·77, b 5·13, c 15·17 Å., β 112° 44′, contains 4 mols. of $LiAlSiO_4,3SiO_2$; space-group C_{2h}^6. The crystals are monoclinic pseudocubic. The constituents, particularly lithium, are subject to replacement.

A. A. ELDRIDGE.

Structure of melilite. B. E. WARREN (Z. Krist., 1930, **74**, 131—138; Chem. Zentr., 1930, ii, 1964).—Melilite, $(Ca,Na)_2(Mg,Al)(Si,Al)_2O_7$, tetragonal, has a 7·73, c 5·01 Å., the unit cell containing 2 mols.; space-group D_{2d}^3 (V_d^3). A. A. ELDRIDGE.

Structure of sodalite and helvine. L. PAULING (Z. Krist., 1930, **74**, 213—225; Chem. Zentr., 1930, ii, 1965).—Sodalite, cubic, has a 8·870 Å.; the unit cell contains 2 mols.; d 2·290; space-group T_d^4. Helvine has a 8·25 Å., space-group T_d^4.

A. A. ELDRIDGE.

Crystal structure of benoitite, $BaTiSi_3O_9$. W. H. ZACHARIASEN (Z. Krist., 1930, **74**, 139—146; Chem. Zentr., 1930, ii, 1964—1965).—Benoitite has a 6·60±0·01, c 9·71±0·01 Å.; the trigonal unit cell contains 2 mols.; space-group D_{3h}^3. The ionic condition of the ions is discussed. A. A. ELDRIDGE.

Spinels. III. Cobalt and zinc titanates. L. PASSERINI (Gazzetta, 1930, **60**, 957—962; cf. A., 1930, 1007).—*Cobalt orthotitanate*, Co_2TiO_4, and zinc orthotitanate, Zn_2TiO_4, which were prepared by heating a mixture of 2 mols. of the corresponding nitrate and 1 mol. of titanic acid at 900°, are shown to crystallise in the cubic system with a lattice of the spinel type. Co_2TiO_4, a 8·420±0·005, v 596·94×10^{-24} c.c., $d_{calc.}$ 5·12, and Zn_2TiO_4, a 8·410±0·005, v 594·82×10^{-24} c.c., $d_{calc.}$ 5·43; the unit cell contains 8 mols. in each case. O. J. WALKER.

Influence of shape and polarity of molecules on the X-ray spectra of liquids. III. Appearance of two intense "amorphous rings" in substances the molecules of which are probably disc-shaped. J. R. KATZ and J. SELMAN (Z. Physik, 1930, **66**, 834—857; cf. A., 1928, 222).—Experiments on colloidal solutions of disc-shaped colloidal particles have shown that these particles tend to orient in parallel layers, separated by a definite distance. Experiments described suggest that disc-shaped molecules, such as naphthalene, quinoline, *iso*quinoline, coumarin, and like molecules with short side-chains also form groups of parallel molecules, when at a temperature considerably below the critical temperature. This parallel grouping of molecules gives rise to a second amorphous ring, the comparatively large width of which shows that the group is small in size, and the intensity of which indicates that few, if any, of the molecules are not in groups. As the critical temperature is approached, the outer ring becomes more diffuse, and finally disappears; that for quinoline disappears at 150°. Hydration of the molecules also tends to destroy the outer ring. Molecular dimensions deduced from the diameter of these rings are given. A. B. D. CASSIE.

Centres of addition as centres of co-ordination. E. HERTEL (Z. physikal. Chem., 1930, **B**, **11**, 279—290; cf. A., 1930, 668).—*C*-Diethylbarbituric acid crystallises in rhombic bipyramids; translation-group Γ_0', space-group V_h^{14}, molecular symmetry C_{2v}, a 7·11, b 14·4, c 9·7 Å. The unit cell contains four molecules. Structural models are given.

F. L. USHER.

Molecular layers of fatty acids. A. JOFFÉ and P. LUKIRSKY (J. Phys. Radium, 1930, [vii], **1**, 405—410).—Measurements have been made by an ionisation method of the changes of potential at layers of stearic acid 1, 2, and 3 mols. thick, on a gold-plated surface. The values obtained are +0·13, 0, and +0·09 volt, respectively, showing that the molecules in adjacent layers lie with similar ends adjacent. If the

gold surface is first washed with acid, −0·14 volt is obtained for a unimolecular layer, in agreement with Frumkin and Guyot (cf. A., 1926, 1093), showing that the first layer is then attached by the other end of the molecule. C. W. GIBBY.

Alternation in properties of long-chain carbon compounds. T. MALKIN (Nature, 1931, **127**, 126—127).—Theoretical. It is suggested that the essential feature of an alternating series is that the zig-zag chain is tilted with respect to the terminal planes; non-alternating series possess vertical as opposed to tilted chains. L. S. THEOBALD.

***X*-Ray study of mannitol.** G. W. McCREA (Nature, 1931, **127**, 162—163).—*X*-Ray analysis gives for *d*-mannitol *a* 8·66, *b* 16·58, *c* 5·50 Å.; space-group Q^4; $d_{calc.}$ 1·522 g./c.c.; 4 mols. per unit cell (cf. Marwick, this vol., 152). L. S. THEOBALD.

***X*-Ray examination of liquid-crystalline substances. I. *p*-Azoxyanisole.** P. W. GLAMANN, K. HERRMANN, and A. H. KRUMMACHER (Z. Krist., 1930, **74**, 73—94; Chem. Zentr., 1930, ii, 1493).—*X*-Ray photographs of *p*-azoxyanisole in the liquid-crystalline and amorphous phases show two liquid-rings; the liquid-crystalline phase oriented in a magnetic field also gives the two rings, but modified in a manner which is not observed in the amorphous phase. When Mo$K\alpha$ radiation is used a third ring is observed. A. A. ELDRIDGE.

***X*-Ray investigations of optically active compounds. II. Diphenyl and its active and inactive derivatives.** G. L. CLARK and L. W. PICKETT (J. Amer. Chem. Soc., 1931, **53**, 167—177).—Rotation and oscillation photographs of diphenyl, dimesityl, *d*- and *l*-3 : 3′-diaminodimesityl, hexachlorodiphenyl, diphenic acid, and *o*-tolidine are used for the determination of the crystal structures. The systems, unit cell dimensions, space-group, and number of mols. per unit cell are given. Of the compounds examined, only diphenyl has a centre of symmetry. H. BURTON.

Influence of impurities on some physical and crystallographical properties of hemimellitic acid. V. AGAFONOV (Compt. rend., 1931, **192**, 99—101).—The ultra-violet polychroism of hemimellitic acid is probably due to the distribution in the crystal lattice of small quantities of α- and β-acids. These were isolated by fractional crystallisation as flat plates or elongated yellow prisms (α), and as needles (β), *d* 1·54 and 1·66, n_g 1·63 and 1·68, respectively, m. p. (α) 182—185°, β infusible. The former contained about 0·5% of ash (calcium, aluminium, and manganese), whilst the β-crystals were calcium hemimellitate. Crystallographic data are also given, and show the birefringence of the acid to be greater than that of the α- or β-crystals. J. GRANT.

Transformation of lattice of cellulose nitrate. General phenomenon in cellulose compounds. J. J. TRILLAT (Compt. rend., 1930, **191**, 1441—1443).—*X*-Ray examination of cellulose nitrate (12·95% N) as prepared and in the form of film obtained by evaporation of an acetone solution shows, respectively, the usual crystalline cellulose nitrate diagram, and a modified form also crystalline, due to an admixture of what may be merely a new form of the nitrate, or of a combination thereof with acetone —of which about 1% is obstinately retained (cf. A., 1930, 1519). Films of cellulose nitrate containing 10—12% N are amorphous; undissolved nitrate shows a crystalline structure diminishing in definiteness with decrease in content of nitrogen. It is inferred that only the trinitrate is a well-defined compound (cf. Hess etc., *ibid.*, 750). C. A. SILBERRAD.

Structure of cellulose nitrates. DESMAROUX and MATHIEU (Compt. rend., 1931, **192**, 234—236).—Cellulose nitrates of nitrogen contents between 13·9 and 11·5% give, on *X*-ray examination, Debye–Scherrer diagrams in each of which there appears a clearly-defined ring corresponding with a lattice spacing which increases from 6·6 to 7·5 Å. with increasing nitrogen content. Cellulose nitrate containing 13·9% N gives two definite intense rings corresponding with lattice spacings of 4·5 and 4 Å., respectively. The intensity and definition of these rings diminish with decreasing nitrogen content. The homogeneity of nitration can thus be investigated. In the *X*-ray diagrams of films prepared from cellulose nitrate of 12·10% N the definite internal ring has become a feeble halo and the external bands have coalesced. A. RENFREW.

Volta effect. E. DUBOIS (Ann. Physique, 1930, [x], **14**, 627—725).—Detailed investigations of the Volta effect for a number of metals are described with reference to the degree of heating, influence of time, and presence of impurities. The effect shows a positive variation for moderate heating, becoming negative for higher temperatures, and a variation with the time elapsing after heating. The temperature variations are due to the elimination of impurities, in particular oxygen and water vapour. On heating, oxygen is expelled first and a positive variation results; water vapour is removed on raising the temperature, and a negative variation is observed. Traces of salts of the alkali metals distilled on to the metallic electrodes rendered them more electropositive. The variation with time is found even after heating the metal in argon, and corresponds with a decrease in density of electron emission of the pure metal. N. M. BLIGH.

Measurements of contact potentials between pure metals. H. KOSTERS (Z. Physik, 1930, **66**, 807—826).—Contact potentials between tungsten, molybdenum, nickel, copper, and chromium were measured in a high vacuum by Monch's method (*ibid.*, 1926, **47**, 522). The metals were freed from adsorbed and occluded gases by induction heating. This heating and the measurements of potential were carried out with the apparatus surrounded by liquid air. Tungsten, tantalum, and molybdenum gave results in good accord with the work required to transfer an electron across the surface, but nickel and copper gave uncertain results. A. B. D. CASSIE.

Theory of the polarity effects in solids during passage of currents. P. BONING (Z. Physik, 1930, **66**, 581—597).—A theory of the mechanism of the partial unidirectional conductivity characteristic of some crystalline materials which are relatively poor

conductors of electricity is developed with particular reference to the role played by polarisation in such phenomenon. It is claimed that the theory has important bearings on the mechanism of the electrical breakdown of insulating materials. R. W. LUNT.

Contact potentials. I. The contact potentials between metals and insulators. F. POLEDNIK (Z. Physik, 1930, **66**, 619—631).—A method involving the use of Henkel's thread electrometer has been developed for the determination of the contact potential between a metal and glass or fused quartz in a vacuum. The following values in volts are given for quartz or glass, respectively: platinum +2·22, +1·15, iron +1·99, +1·15, copper +1·60, +0·58, gold +1·42, +0·58, silver +1·42, +0·14, aluminium +0·93, +0·14, magnesium, +0·93, +0·14, zinc +0·45, −0·29, lead +0·16, −0·60, and tin −0·30, −1·14. When these values are plotted against the m. p. of the metal the points are found to lie on two smooth curves approximately parabolic.

R. W. LUNT.

Contact potentials. II. Contact potential between salts and their saturated (aqueous) solutions. (FRL.) M. LEDERER (Z. Physik, 1930, **66**, 632—645).—The possibility of measuring the contact potential between a salt and its saturated solution has been examined, to which end a special form of Dolezalek electrometer was designed. The errors inherent in the method do not permit absolute values to be obtained; it has, however, been possible to determine the absolute value of the difference between the potential for salt-solution pairs. The following data are given: sodium chloride–potassium chloride, −0·18+0·08; sodium chloride–sodium nitrate, −0·04±0·07; sodium nitrate–barium nitrate, −0·21±0·06. R. W. LUNT.

Conductivity of thin metal foils. L. TISZA (Naturwiss., 1931, **19**, 86—87).—The specific resistance of thin metal foils slowly increases as the thickness of the foil is diminished until at a limiting thickness of 10—20 μμ, when there is a sudden increase in its value. Theories propounded to account for this behaviour take no account of the relation between conductivity and temperature. The conductivity of silver at −253° is 150 times that at the ordinary temperature. Limiting thicknesses are expressed as a function of the mean free path in the compact metal, on the assumption that surface electrons are reflected diffusely and thereby lose a forward impulse.

W. R. ANGUS.

Curie points. L. F. BATES (Proc. Physical Soc., 1931, **43**, 87—95).—Three temperatures may require to be specified in a description of the magnetic behaviour of a ferromagnetic substance. The term "Curie point" is loose and it is better to call it the ferromagnetic critical point, since it is not enough to state that a change in specific heat occurs at the Curie point. The second important temperature is the ferromagnetic Curie point at which the intrinsic magnetisation may be considered to become zero. It is obtained by extrapolation of the curve of intrinsic magnetic moment against temperature, that portion of the curve being used where the rate of change is a maximum. The third temperature is the paramagnetic Curie point, and comes into account when the variation of susceptibility with temperature after the substance has passed into the paramagnetic state is considered. This temperature may vary considerably from the ferromagnetic Curie point. In the case of iron, the separation is 80°. There are cases where the paramagnetic Curie point is lower than the ferromagnetic Curie point; *e.g.*, the ferrocobalts. The significance of these two points in connexion with a theory of ferromagnetism is discussed. An extension of the view that ferromagnetism is due to the association of atoms in groups may account for the paramagnetic behaviour of iron, cobalt, and nickel, and of more complex substances such as the ferrocobalts, magnetite, and manganese arsenide. The experimental evidence in the case of the elements iron, nickel, and cobalt leaves some doubt as to the existence of a true paramagnetic Curie point, but it may be assumed for the purpose of an approximate calculation of the Weiss constant of the internal molecular field. A. J. MEE.

Critical anisotropic point of ferromagnetic crystals. N. S. AKULOV (Physikal. Z., 1931, **32**, 107—108).—Theoretical. A. J. MEE.

Paramagnetism independent of temperature. Existence of electronic isomerides in polyatomic ions. S. FREED and C. KASPER (J. Amer. Chem. Soc., 1930, **52**, 4671—4679; cf. A., 1930, 1102).—The susceptibilities of uranyl sulphate, sodium tungstate, and potassium dichromate have been determined at temperatures between 70° and 293° Abs. The susceptibility of the uranyl ion decreases slightly and uniformly with depression of the temperature. The permanganate ion (Ishiwara, A., 1915, ii, 141) probably behaves similarly. The susceptibilities of the tungstate and dichromate ions are $5·93\times10^{-6}$ and $62·1\times10^{-6}$ per g.-mol., respectively, and within experimental error ($<0·1\times10^{-6}$) these susceptibilities exhibit no variation with temperature. The properties of these ions indicate that the least stable electrons are localised near the metallic kernel and are shielded from the external fields of neighbouring ions. Hence, modern theories of magnetism may be applied (van Vleck, A., 1928, 572) and as a consequence the existence of electronic isomerides in these polyatomic ions is recognised.

J. G. A. GRIFFITHS.

Thermal analogy of the Barkhausen effect. B. DEL NUNZIO (Atti R. Accad. Lincei, 1930, [vi], **11**, 125—129).—Measurements of the magnetisation of nickel at temperatures between 0° and 400° in a constant magnetic field show that the magnetisation falls slowly up to 300°, and then abruptly to almost zero near the Curie point 357°. F. G. TRYHORN.

Thermomagnetic property of manganese. Y. SHIMIZU (Sci. Rep. Tohoku, 1930, **19**, 411—417).—The magnetic susceptibility of 99·9% manganese is $7·55\times10^{-6}$ at 20° and falls in a smooth curve to $5·22\times10^{-6}$ at 805°. At 810° the change to β-manganese is accompanied by a rise in the susceptibility to $6·0\times10^{-6}$; this is followed by a slow fall to $5·4\times10^{-6}$ at 1090°, when there is a sudden increase to $8·41\times10^{-6}$ at 1100° corresponding with the change to γ-manganese.

A. R. POWELL.

Range of brittleness of iron at low temperatures. F. Sauerwald, B. Schmidt, and G. Kramer (Z. Physik, 1931, 67, 179—183).—For technical soft iron there was a sharp limit to the brittleness at $-155°$. For a two-crystalline system of a special soft iron, the limit for brittleness can be raised to $-90°$ to $-98°$. A. J. Mee.

Determination of mol. wt. in liquid ammonia. H. H. Strain and J. H. C. Smith (J. Amer. Chem. Soc., 1930, 52, 5291—5293).—The method is similar to those of Schwarz (A., 1929, 1416) and Signer (A., 1930, 531), involving the diffusion of a vapour, in this case ammonia, until two solutions (one is the unknown, the other a standard) have the same molecular concentration. Ammonium chloride appears to exist in the bimolecular form in liquid ammonia. The results for lævulose are low, probably owing to interaction with the solvent. Results are given for 21 substances. H. Burton.

Vapour-pressure determination of the mol. wt. of sucrose. S. Oguri (Mem. Fac. Sci. Eng. Waseda, 1930, 7, 93—96).—A current of dry air is saturated first in an aqueous sugar solution of known concentration and secondly in pure water. If p' is the vapour pressure of the solvent and p that of the sugar solution at the temperature of experiment, the losses in weight of the solution and of the solvent are proportional to p and to $p'-p$, respectively. Application of the usual molecular vapour-pressure depression equation to the above weight losses enables the mol. wt. of the sugar to be calculated directly. The apparatus used is described. E. A. Ryder.

Thermoanalysis of metal single crystals and a new thermoelectric effect of bismuth crystals grown in magnetic fields. A. Goetz and M. F. Hasler (Physical Rev., 1930, [ii], 36, 1752—1781).—Crystals of bismuth having any desired orientation predetermined by a seed crystal were grown by the method previously described (cf. A., 1930, 401), one half normally, and the other under a transverse magnetic field, by the continuous and discontinuous process. A thermoanalyser is described for measuring and localising changes of the thermoelectric properties along the crystal length by progressive local heating without application of mechanical stress. It was found that the normal half of a crystal has a thermo-*E.M.F.* against the magnetic half; this effect was investigated in relation to the orientation of the crystal to the magnetic field and thermoelectric current, the method of growth, the presence of impurities, the strength of the applied field, and the temperature. The results obtained are brought into relation with the diamagnetic anisotropy of bismuth. N. M. Bligh.

Measurements with the aid of liquid helium. XI. Resistance of pure metals at low temperatures. W. Meissner and B. Voigt (Ann. Physik, 1930, [v], 7, 761—797).—Measurements of the electrical resistance of the metals in the first and second groups of the periodic table and of boron, aluminium, indium, and thallium in the third group down to temperatures of about 1·1° Abs. have been made and superconducting metals determined. W. Good.

Measurements with the aid of liquid helium. XI. Resistance of pure metals at low temperatures. W. Meissner and B. Voigt (Ann. Physik, 1930, [v], 7, 892—936).—Tables showing the resistance between 1·2° and 273° Abs. are given for all elements in the fourth group excepting hafnium, for vanadium, tantalum, arsenic, antimony, and bismuth, for chromium, molybdenum, tungsten, uranium, selenium, and tellurium, manganese and rhenium, iron, ruthenium, cobalt, rhodium, iridium, nickel, palladium, and platinum. A. B. D. Cassie.

Properties of pure nickel. L. Jordan and W. H. Swanger (and others) (Bur. Stand. J. Res., 1930, 5, 1291—1307).—Fairly pure electrolytic nickel was further purified by annealing in hydrogen. The ingots finally prepared were of a purity of 99·94% and contained not more than 0·001% O. The density as cast is 8·907 g. per c.c. at 23°. The length of the side of unit cube is 3·525 Å. The m. p. is 1455°. Electrical resistivity is 7·236 microhms-cm. at 20° with a temperature coefficient of 0·0067 ohm per 1° per ohm at 0°. Saturation value of intrinsic induction is 6150 gauss. Magnetic transformation takes place at 370—380° and thermal transformation at 350°. The thermal *E.M.F.* against platinum (towards which nickel is negative) are 1·485 millivolts at 100°, 6·165 millivolts at 500°, 12·130 millivolts at 1000°. The average coefficient of thermal expansion is $13·3\times10^{-6}$ (25—100°), $14·4\times10^{-6}$ (25—300°), $16·5\times10^{-6}$ (300—600°), and $17·8\times10^{-6}$ (600—900°). W. E. Downey.

Damping of sound waves in a homogeneous gaseous medium. Y. Rocard (J. Phys. Radium, 1930, [vii], 1, 426—438).—Theoretical. C. W. Gibby.

Equation of state of easily liquefiable hydrocarbons. IV. Density and compressibility of *n*-butane. M. Beckers (Bull. Soc. chim. Belg., 1930, 39, 470—495; cf. A., 1930, 25).—Methods available for the preparation and purification of butane have been critically examined. The progress of purification by fractional distillation may be followed accurately by measurement of the vapour pressure of the liquid before fractionation and of the initial and final fractions obtained; the usual criterion of purity, viz., constancy of pressure during distillation, is untrustworthy. Measurements with *n*-butane by the balloon method previously described yield for the density at 0° mean values of 2·5185 (710 mm.), 1·79876 (510 mm.), and 1·07568 (310 mm.). The extent to which the vapour deviates from the gas law has been calculated. The mol. wt. of *n*-butane, calculated from the density, is 58·188, giving at. wt. of carbon 12·0275. H. F. Gillbe.

Magnetic susceptibility and absorption spectra of complex cyanides. L. Szego and P. Ostinelli (Gazzetta, 1930, 60, 946—957).—Measurements have been made of the magnetic susceptibility and of absorption spectra of the following complex cyanides: $K_3Cr(CN)_6$; $K_4Cr(CN)_6$; $K_3Mn(CN)_6$; $K_4Mn(CN)_6$; $K_5Mn(CN)_6$; $K_3Co(CN)_6$; $K_4Co(CN)_6$; $K_2Ni(CN)_4$, and $K_2Ni(CN)_3$. As in the case of ferro- and ferri-cyanides, greater optical activity is associated with the paramagnetic than with the diamagnetic state, except with the complex cyanides of bivalent

cobalt and of uni- and bi-valent nickel. Potassium cobaltocyanide, for example, is diamagnetic, but shows a greater absorption than the cobalticyanide. The results are discussed in terms of the electronic theory. O. J. WALKER.

Determination of the susceptibility of cerium fluoride at low temperatures. W. J. DE HAAS and C. J. GORTER (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 949—952).—The susceptibility of cerium fluoride has been measured from very low temperatures up to the ordinary temperature. At higher temperatures the Curie–Weiss law is followed. At the temperature of liquid nitrogen and at lower temperatures deviations occur. The result is in disagreement with the theory of Becquerel and Kramers as applied to tysonite, which has the same crystal structure and the same central atom as cerium fluoride. J FARQUHARSON.

Dependence of certain electrical and electro-optical constants of nitrobenzene and nitrotoluene on the purity. W. ILBERG (Z. tech. Physik, 1930, **11**, 283; Chem. Zentr., 1930, ii, 1342) — Polemical (cf. Hehlgans, A., 1930, 142). F. HEHLGANS (*Ibid.*, ..83 285).—A reply. A. A. ELDRIDGE.

Quantum theory of null-point temperature. G. BECK, H. BETHE, and W. RIEZLER (Naturwiss., 1931, **19**, 39).—The absolute null point is characterised by a cessation of all motion within the lattice. Each electron, according to Eddington, possesses $1/\alpha$ degrees of freedom, where α is the Sommerfeld fine-structure constant. Besides electrons the crystal also contains protons, for which, obviously, the number of degrees of freedom is the same, since, according to Dirac, a proton can be considered as a hole in electron gas. To arrive at the absolute null point it is necessary to subtract $2/\alpha-1$ degrees of freedom for each neutron (=1 electron+1 proton). By doing this the expression for the null point temperature is obtained, $T_0=-(2/\alpha-1)$ degrees. Substitution of 273° for T_0 gives the value 137 for $1/\alpha$, which agrees, within the limits of error, with values previously deduced in other ways. A hexagonal crystal was studied, but the same result is obtained irrespective of the type of crystal structure. W. R. ANGUS.

F. p. of nickel as a fixed point on the international temperature scale. H. T. WENSEL and W. [illegible] ESER [illegible] Stand. J. Res., 1930, **5**, 1309—1318). The f. p. of nickel was determined by measuring with an optical pyrometer the ratio of brightness of red light of wave-length $0{\cdot}6533\,\mu$ [illegible] y black bodies at the f. p. of nickel and gold, respectively. The nickel was frozen in magnesia crucibles in a vacuum. The f. p. was found to be 1455±1° on the International temper- scale based on the value 1063° for the f. p of gold 1432 cm.-degree for C_2. W. E. DOWNEY.

Christiansen three-plate method for the determination of the heat conductivity of gases. H [illegible] IERKES (Physikal. Z, 1931, **32**, 84—91).—This method has been investigated in an endeavour to increase its accuracy so as to render it a precision method. The apparatus is accordingly modified in several ways, the temperatures being determined by thermo-elements. Results are given for the heat conductivity of hydrogen and carbon dioxide relative to air. The results obtained were for hydrogen, 5·3, and for carbon dioxide, 0·71. Compared with the generally accepted values the former is too small, and the latter too great. If the Schleiermacher method is correct, and there appears to be no doubt of this, there must be other errors in the Christiansen method. It may be that the temperature inside the plates is not identical with that at the surfaces, and adsorption of gas on the plates may occur. A. J. MEE.

Spec[illegible] heats of gases at high pressures. II. Method and apparatus at high temperatures. [illegible]. KRASE and [illegible] MACKEY (J. Amer. Chem. Soc., 1930, **52**, 5111—5114; cf. A., 1930, 403).—The constant-temperature, adiabatic, flow calorimeter described may be used for the determination of the specific heats of gases at temperatures as high as 350° and at pressures up to 1000 atm. Data for nitrogen are recorded. J. G. A. GRIFFITHS.

I. Specific heats of thallium, calcium, and magnesium at 10° Abs. II. Entropy and chemical constants of magnesium from spectroscopic data. K. CLUSIUS and J. V. VAUGHEN (J. [illegible] Chem. Soc., 1930, **52**, 4686—4699; cf. A., 19..9, 635).—I. The specific heats have been determined at temperatures between 10° and 250° Abs. in the apparatus described. Previous values recorded for thallium are too low, whilst those for calcium and magnesium are too high. At temperatures above 1[illegible] Abs., the results for thallium are reproduced by inserting the characteristic temperature $\theta=94°$ in the Debye function; at lower temperatures, θ decreases to 84°. With calcium, θ approaches a constant value, 219, at low temperatures. With magnesium, the values of θ increase with fall of temperature, but above 30° Abs. θ is about 322.

II. The vapour-pressure constant of magnesium is $0{\cdot}443\pm0{\cdot}1$ as compared with the value 0·493 calculated statistically. The entropy of the monatomic vapour at 1 atm. and 25° is 35·29 g.-cal./1° (cf. theoretical value 35·5). J. G. A. GRIFFITHS.

Specific heat of liquid diphenyl. R. F. NEWTON, B D. KAURA, and T. DE VRIES (Ind. Eng. Chem., 1931, **23**, 35—37).—The specific heat of liquid diphenyl determined over the range 100—300° was $0{\cdot}388+0{\cdot}00057t$ (t in °C.). An accuracy of 1% is claimed for the results. H. INGLESON.

Specific heat of diphenyl. H. O. FORREST, E. W. BRUGMANN, and L. W. T. CUMMINGS (Ind. Eng. Chem., 1931, **23**, 37—39).—The specific heat of diphenyl has been measured from 77° to 347° by two methods. A curve of the variation of specific heat with temperature reproduces the experimental results with an accuracy of about 2%. H. INGLESON.

Measurement of the true specific heats of solid and liquid metals at high temperatures. H. SEEKAMP (Z. anorg. Chem., 1931, **195**, 345—365).—A method has been developed for measuring the specific heats of metals at temperatures up to 600—700°. A hollow cylinder of the metal encloses an insulated tungsten spiral which can be heated electrically;

after passage of the current for a known time with a measured fall of potential the temperature of the metal is measured with a thermocouple inserted in a hole in the wall of the cylinder. Results for the specific heat of copper (18—700°), aluminium (18—600°), and magnesium (18—500°) agree in general with those of other observers. Measurements with thallium at temperatures up to 500° yield for the transition temperature 226·7° and for the heat of transition 98 g.-cal./g.-atom, and show the existence of minima in the temperature-specific heat curve at about 254° and 380°. H. F. GILLBE.

Influence of period of heating on b. p. of liquids used in ebullioscopy. Testing purity of volatile liquids by isothermal distillation. S. L. WRIGHT, jun and A. W. C. MENZIES (J. Amer. Chem. Soc., 1930, **52**, 4699—4708).—A pair of differential isoteniscopes (Smith and Menzies, A., 1910, ii, 1036) is employed to determine directly any differences of the vapour pressure of two samples of a liquid, one having been maintained at the b. p. for several hours and the other having been elevated to the b. p. immediately before the determination. The results obtained with acetic acid, bromine, benzene, and carbon tetrachloride are taken to indicate that the vapour pressure is independent of the above treatment, and delay in the attainment of internal equilibrium is therefore without influence on the b. p. The purity of the liquids was verified by isothermal distillation in the apparatus. The presence of impurities in quantities too small to be detected by ordinary means causes errors in vapour-pressure measurements when circumstances favour fractionation (cf. Washburn, A., 1928, 10). J. G. A. GRIFFITHS.

Vapour pressure of ice at low temperatures. C. DEI (Atti R. Accad. Lincei, 1930, [vi], **11**, 119—124).—Measurements have been made of the potential required to produce an explosive discharge in water vapour at a series of known low pressures. The curve giving the relationship between discharge potential and pressure of water vapour was then applied to calculate the vapour pressure of ice at low temperatures from measurements of the discharge potential over ice. At the temperatures −22·3°, −55°, and −66° the respective vapour pressures of ice are 0·58±0·023, 0·0166±0·0008, and 0·0037±0·0002 mm. F. G. TRYHORN.

Vapour pressures of selenium tetrachloride. Existence of selenium dichloride. D. M. YOST and C. E. KIRCHER (J. Amer. Chem. Soc., 1930, **52**, 4680—4685; cf. Simons, A., 1930, 1356).—The vapour pressure of selenium tetrachloride at temperatures between 109° and 181° is given by $\log_{10} P$(mm.) $=11{\cdot}2040-0{\cdot}05223\times 73{,}990/T$. By means of vapour-pressure measurements with excess of chlorine and vapour density determinations it is found that between 109° and 226° the vapour consists of chlorine and selenium dichloride. The heat of the reaction $SeCl_4(s)=SeCl_2(g)+Cl_2(g)$ is (ΔH) 35,380 g.-cal and the heat of formation of $SeCl_2(g)$ is (ΔH) −10,780 g.-cal. J. G. A. GRIFFITHS.

B. p. and vapour-pressure formulæ for organic liquids. E. W. MADGE (Z. anorg. Chem., 1931, **195**, 338).—It is shown that the formula derived by Herz (A., 1930, 1104) must be applicable to substances which obey Trouton's rule. H. F. GILLBE.

M p of pure chromium. F. HOFFMANN and C. TINGWALDT (Z. Metallk., 1931, **23**, 31—32).—The m. p. of electrolytic and of alumino-thermic chromium has been determined by melting the metal in a magnesia crucible and by observing the temperature of a hole in a bar of chromium during melting in a vacuum by the passage of a high current. The first method gave 1800±10° and the second 1765 ±10°. A. R. POWELL.

Heat of dissociation of fluorine. H. VON WARTENBERG and J. TAYLOR (Nachr. Ges. Wiss. Gottingen, 1930, 119—123; Chem. Zentr., 1930, ii, 1660).—The heat of dissociation of fluorine, calculated from the band spectrum, is 63·5±0·7 kg.-cal. Irradiation with ultra-violet light does not accelerate the union of hydrogen and fluorine. A. A. ELDRIDGE.

Entropy of hydrogen and the third law of thermodynamics. Free energy and dissociation of hydrogen. W. F. GIAUQUE (J. Amer. Chem. Soc., 1930, **52**, 4816—4831; cf. Giauque and Johnston, A., 1929, 138).—Band spectrum data for the hydrogen molecule are employed in conjunction with the equations previously developed (this vol., 295) to evaluate the proportions of ortho- and para-hydrogen present in equilibrium at temperatures between 0° and 298° Abs. The energy contents and heat capacities of para- and ortho-hydrogen, their equilibrium mixtures, and mixtures of para and ortho in the ratio 1 : 3 have been calculated for the range 0—298° Abs. The free energy of dissociation, equilibrium constants, and percentage dissociation of the hydrogen molecule at temperatures between 298° and 5000° Abs. have been calculated and are in satisfactory agreement with Langmuir's data. The absolute entropy of hydrogen is 33·98 g.-cal./1° per mol. In agreement with the experimental value, the ordinary application of the third law of thermodynamics gives 29·59, based on the assumption that the lowest levels of ortho- and para-hydrogen, with their total of 10 quantum species, are present in the solid state as a perfect solution, the relative proportions being those determined by the equilibrium at the ordinary temperature. It is concluded that for most substances (*e.g.*, Giauque and Wiebe, A., 1929, 755) the absolute entropy resulting from nuclear spin will persist to temperatures below those at which measurements are ordinarily made, and hydrogen is probably the only exception. A value, 31·23, is derived for the entropy of hydrogen and may be used in conjunction with data obtained for other substances by the ordinary methods. J. G. A. GRIFFITHS.

Superheating and intensive drying of liquids. E. COHEN and W. A. T. COHEN-DE MEESTER (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 1003—1014).—From many experiments it is found that the true b. p. of water, benzene, or carbon tetrachloride can never be obtained when a heating bath is used. even when all the precautions detailed by Smits are introduced (cf. A., 1930, 1102). Heating with a free flame always led to a slight degree of superheating, but this was less than that which appeared when a

heating bath was used. No superheating whatever occurs when an electrically heated platinum wire in the liquid is used. The b.-p. measurements of Baker and of Smits are believed to be inconclusive (cf. Lenher, A., 1929, 1372). J. W. SMITH.

Second virial coefficient for gases: critical comparison between theoretical and experimental results. H. MARGENAU (Physical Rev., 1930, [ii], **36**, 1782—1790).—Mainly mathematical. From London's recent theory of the attractive forces between molecules (cf. A., 1930, 1239) the second virial coefficient is computed for the gases: hydrogen, neon, argon, helium, nitrogen, oxygen, carbon dioxide, ammonia, and water vapour. For the two last named, which have a dipole moment, the contribution of the dipole interaction is also calculated (cf. Margenau, *ibid.*, 1349). Results are compared graphically with experimental values computed from Beattie and Bridgeman's constants; agreement is satisfactory except in the case of helium and hydrogen, where the discrepancy can be accounted for by the presence of zero point energy. N. M. BLIGH.

Lattice energy from the thermodynamic view point. J. H. HILDEBRAND (Z. Physik, 1931, **67**, 127—134).—Theoretical. Restrictions on the electrostatic equation giving lattice energies are pointed out. The thermodynamic equation determines these energies from the elastic properties of the crystal at the ordinary temperature. The lattice energy calculated for potassium iodide agrees with Mayer's value (A., 1930, 836). A. B. D. CASSIE.

Equation of state explicit in the volume. G. SCATCHARD (Proc. Nat. Acad. Sci., 1930, **16**, 811—813).—Beattie (A., 1930, 534) has derived an equation of state in the virial form $V/n-RT/p+\beta/RT+\gamma p/(RT)^2+\delta p^2/(RT)^3$ as an approximation of the Beattie–Bridgeman equation, $p=RT(n/V)+\beta(n/V)^2+\gamma(n/V)^3+\delta(n/V)^4$ (A., 1927, 819), where β, γ, and δ are functions of the temperature. A new approximation of the Beattie–Bridgeman equation has been derived, $V/n=RT/p+\beta/RT+[\gamma/(RT)^2-\beta^2/(RT)^3]p+[\delta/(RT)^3-3\beta\gamma/(RT)^4+2\beta^3/(RT)^5]p^2$. The accuracy of the two approximate equations in reproducing the values obtained by using the Beattie–Bridgeman equation is compared for hydrogen, oxygen, nitrogen, methane, ethylene, and carbon dioxide; the new approximation fits more closely. The limitation of the approximation at higher pressures is indicated. W. R. ANGUS.

Chemical constant of hydrogen vapour and the entropy of crystalline hydrogen. T. E. STERN (Proc. Roy. Soc., 1931, **A**, **130**, 367—379; cf. Fowler, A., 1928, 469).—Mathematical. By the use of the Einstein–Bose statistics, a result is obtained for the vapour pressure of hydrogen crystals at low temperatures which yields a value for the chemical constant of hydrogen in even closer agreement with experiment than that obtained by Fowler (*loc. cit.*). As the result of the Einstein–Bose statistics, slight variations are found to occur in the composition of the mixed crystal of ortho- and para-hydrogen as it is allowed to build up from the gas at low temperatures. Thus at temperatures very near the absolute zero the ratio of the two kinds of molecules, when the crystal is small, may be as great as 3·2 : 1, whilst at higher temperatures the ratio is always nearly 3 : 1. The vapour-pressure equation which is correct at low temperatures is followed through to the ordinary temperature. L. L. BIRCUMSHAW.

Calculation of free energy from spectroscopic data. W. F. GIAUQUE (J. Amer. Chem. Soc., 1930, **52**, 4808—4815; cf. Lewis and Mayer, A., 1929, 648).—Theoretical. A general expression for the absolute entropy of ideal gases is derived and includes terms for molecular rotation, vibration, electronic excitation, nuclear spin, and other states which the molecule may assume. The equations given afford a basis for the evaluation of the free energy of gases and equilibrium constants from spectroscopic data. J. G. A. GRIFFITHS.

Specific gravities of liquid and solid sulphuric acid. D. MCINTOSH (Proc. Nova Scotian Inst. Sci., 1930, **17**, 259—261).—Sulphuric acid of d 1·7—1·84 is denser in the solid (frozen) state than in the liquid. The f.-p. diagram of the system water–sulphuric acid is given. H. BURTON.

Determination of critical temperatures. Critical temperature of hydrogen fluoride. P. A. BOND and D. A. WILLIAMS (J. Amer. Chem. Soc., 1931, **53**, 34—37).—The substance to be investigated is enclosed in a monel metal tube 15 cm. long, 1 cm. diameter, inclined at about 20° to the horizontal and supported at its centre by knife edges; the lower end is attached to the arm of a sensitive balance by a vertical wire which passes through the top of the oven enclosing the tube. When the oven has cooled to the critical temperature, the formation of the liquid phase in the lower end of the tube sets the balance in motion. The critical temperature of hydrogen fluoride is 230·2° (cf. Van Laar, A., 1921, ii, 83). J. G. A. GRIFFITHS.

Measurement of very small vapour pressures. Vapour pressure of mercury and potassium. III. H. MAYER (Z. Physik, 1931, **67**, 240—263).—A method for the determination of vapour pressures of the order 10^{-7} to 10^{-2} mm. is described. The vapour pressure of potassium ($2·0\times10^{-6}$ mm. at 69·8° and $4·78\times10^{-4}$ at 143·2°) is given by $\log p\,.\,T=-21087/4·571T+10·418$. The results in general agree with those of Weiler and of Killian (A., 1926, 653), but the values of Edmondson and Egerton (A., 1927, 103) are 20—30% lower. A. J. MEE.

Vapour pressure of Ramsay greases. H. MAYER (Z. Physik, 1931, **67**, 264—269; cf. preceding abstract).—The vapour pressure of the gum grease of Ramsay at ordinary and higher temperatures has been determined by means of the apparatus previously described. It is shown that these greases can be regarded as having a definite and constant vapour pressure only if left in a vacuum desiccator at a temperature above m. p. for some time in order to outgas them. The vapour pressure of a grease so treated was $1·1\times10^{-5}$ mm. at 12·6°. A. J. MEE.

Density of mixtures of chloroform (U.S.P.) and benzyl alcohol. S. M. GORDON (J. Amer. Pharm. Assoc., 1931, **20**, 15—17).—A graph of the densities of mixtures of chloroform and benzyl

alcohol is a straight line joining the densities of the two components, 1·4843 and 1·0468, respectively, at $20 \pm 0·5°$. E. H. SHARPLES.

Viscosities of binary mixtures. L. PIATTI (Z. physikal. Chem., 1931, **152**, 36—46).—The viscosity isotherms of binary mixtures of *m*-cresol and of anisole with ethyl alcohol and with benzene have been determined at temperatures from 0° to 60°. In the cresol systems the curves are continuous, with neither maxima nor minima, but the viscosities are much lower than the values calculated additively, and indicate that the strongly associated cresol molecules are largely dissociated in presence of the second component. The anisole–alcohol isotherms exhibit minima at all temperatures, but in the anisole–benzene system the curves follow closely the additive law, especially at temperatures above 50°. The b.-p. curves of the four systems have been determined, and the results are compared with the viscosity measurements. H. F. GILLBE.

Theory of concentrated solutions. M. HOEPPENER and A. VON ANTROPOFF (Z. physikal. Chem., 1931, **152**, 95—109).—The vapour pressure, density, and composition of the vapour phase in equilibrium with liquid mixtures of benzene and carbon tetrachloride have been determined at 15°. The deviations of the saturated vapour from the ideal gas law amount to about 3·5%. The deviations from the Raoult law for the vapour pressure of solutions, from Henry's law, and from the Nernst law when expressed in terms of the fractional molar concentration, are of the same order. H. F. GILLBE.

Empirical correction of Raoult's law applied to concentrated solutions. G. A. ROSNER (Rocz. Chem., 1931, **11**, 13—18).—The empirical formula $a/N_1 = 1 + KN_2$ is derived, in which $a = p'/p$, where p and p' are the partial pressures of the solvent and the solution, respectively, $N_1 = N/(n+N)$ and $N_2 = n/(n+N)$, where n and N are respectively the number of molecules of solvent and solute present, and K is a constant. R. TRUSZKOWSKI.

Influence of b. p. on composition of azeotropic mixtures. B. KAMIEŃSKI (Rocz. Chem., 1931, **11**, 1—12).—The expressions $\Delta p' = p'\Delta p'_0/p'_0$ and $\Delta p'' = p''\Delta p''_0/p''_0$ are derived, in which $\Delta p'$ and $\Delta p''$ represent the increase in the partial pressures p'_0 and p''_0 of the components of a binary azeotropic mixture, occasioned by a rise in temperature of 1° above the b. p., and p' and p'' are the partial pressures at the higher temperature. The application of these formulæ to the calculation of the composition of azeotropic mixtures of various b. p. gives results in better agreement with experiment than those given by Merriman's formula (J.C.S., 1913, **103**, 1801). R. TRUSZKOWSKI.

Mol. wt. of nitrosobenzene in solid solution. C. DRUCKER and T. FLADE (Z. wiss. Phot., Schaum Festschr., 1930, **29**, 29—41).—The mol. wt. of nitrosobenzene has been determined cryoscopically with dried nitrobenzene as the solvent. The results indicate that the compound is almost dimeric in dilute solid solutions. Pure nitrosobenzene is therefore at least dimeric and probably exists in a higher state of association. The sublimation pressure, heat of sublimation, and heat of combustion have also been determined. J. W. GLASSETT.

Miscibility and variation in the properties of supersaturated silver–copper alloys. N. AGEEV, M. HANSEN, and G. SACHS (Z. Physik, 1930, **66**, 350—376).—The influence of concentration and annealing temperature on the hardness and electrical resistance of the alloys has been studied by *X*-ray measurements. The mixing and annealing processes are the same for alloys at the copper and silver ends of the series, although copper dissolved in silver separates at a temperature about 100° above that at which silver separates from copper. The velocity of reaction is determined primarily by the concentration, and has a negative temperature coefficient. When separation takes place, an abnormal increase in resistance occurs. Experimental results are insufficient for a theoretical discussion of this, and of the abnormal hardness effects. A. B. D. CASSIE.

Heat of mixture in molten metals. M. KAWAKAMI (Sci. Rep. Tohoku, 1930, **19**, 521—549; cf. A., 1928, 21).—The heat of mixing has been measured for twenty-five systems of binary alloys containing magnesium, antimony, aluminium, silver, copper, or gold. The results show that the intermetallic compounds which exist in the solid state up to their m. p. do not decompose into their components on melting, but exist as such in the liquid phase. W. E. DOWNEY.

Thermal [and *X*-ray] analysis of the system lithium–copper. S. PASTORELLO (Gazzetta, 1930, **60**, 988—992; cf. A., 1930, 1359).—Thermal and *X*-ray analyses of the above system show that no compounds or solid solutions are formed between lithium and copper. The eutectic point is at the m. p. of pure lithium, which is given as 180°. O. J. WALKER.

System bismuth–selenium. N. PARRAVANO and V. CAGLIOTI (Gazzetta, 1930, **60**, 923—933).—The existence of two bismuth selenides (cf. A., 1913, ii, 415), Bi_2Se_3 and BiSe, is confirmed by *X*-ray examination of pure bismuth and selenium and of a series of alloys of the two elements. Taking the most probable values of the axial ratio shown, the following lattice constants are obtained: Bi, c/a 2·706, a_0 4·531; Se, c/a 1·14 or 2·66, a_0 4·360; Bi_2Se_3 c/a 1·68, a_0 6·702; BiSe, c/a 1·60, a_0 5·021. For the two selenides in the above order the values of d are 7·398 and 7·98. O. J. WALKER.

Equilibrium diagrams of the aluminium–manganese, copper–manganese, and iron–manganese systems. T. ISHIWARA (Sci. Rep. Tohoku, 1930, **19**, 499—519).—As a preliminary to the investigation of ternary systems containing manganese, the above binary systems have been examined thermally, microscopically, and dilatometrically and also by electrical resistance measurements and *X*-ray observations. Equilibrium diagrams which differ from those of earlier workers are given. W. E. DOWNEY.

System iron–carbon. E. L. DUPUY (Rev. Mét., 1930, **27**, 686—692).—Modern knowledge of the equilibria at the iron end of this system is summarised,

and the development of the equilibrium diagram from that first proposed by Roberts-Austen to that now generally accepted is traced. A. R. POWELL.

Equilibrium diagram of the iron–vanadium–carbon system. M. ÔYA (Sci. Rep. Tohoku, 1930, **19**, 449—472).—The system has been investigated by X-ray, micrographic, and thermal analysis up to a content of 9·9% C. The system contains no ternary compounds. There are five liquidus surfaces, six binary eutectic reactions, one binary peritectic reaction, two ternary eutectic reactions, and a ternary peritecto-eutectic reaction. The composition and temperature of the non-variant points are: (*a*) liquid $\gamma+[Fe_3C]+\varepsilon$; 3·4% V, 4·2% C, 92·4% Fe, 1122°; (*b*) liquid $\rightleftharpoons\alpha+\beta+\varepsilon$; 35% V, 1% C; (*c*) δ+liquid$\rightleftharpoons\gamma+\varepsilon$; 7% V, 2·3% C, 1330°. In the field of existence of the γ-phase there are three solubility surfaces in which α, ε, and $[Fe_3C]$, respectively, begin to separate and three binary eutectoid curves along which the following reactions occur: $\gamma\rightleftharpoons\alpha+\varepsilon$, $\gamma\rightleftharpoons\alpha+Fe_3C$, and $\gamma\rightleftharpoons Fe_3C+\varepsilon$. The complete and various sectional diagrams as well as several characteristic micrographs of the alloys are included.

A. R. POWELL.

Solubility of hydrogen fluoride in benzene and in octane. J. H. SIMONS (J. Amer. Chem. Soc., 1931, **53**, 83—87).—Data are recorded between 20° and 65°. The vapour pressure of hydrogen fluoride over benzene solutions exhibits negative deviations from Raoult's law at very low concentrations and large positive deviations at higher concentrations. This phenomenon is attributed to the strong polarity of the hydrogen fluoride molecule. J. G. A. GRIFFITHS.

Solubilities [of salts] in hydrogen fluoride. P. A. BOND and V. M. STOWE (J. Amer. Chem. Soc., 1931, **53**, 30—34; cf. Fredenhagen and Cadenbach, A., 1930, 421).—Solubility data for lithium hydrogen fluoride at 0—40° are recorded. The solubility of calcium, zinc, and magnesium fluorides is less than 0·01 at 0°. J. G. A. GRIFFITHS.

Solubilities of silver salts. K. MASAKI (Bull. Chem. Soc. Japan, 1930, **5**, 345—348).—Solubilities of some sparingly soluble silver salts have been determined potentiometrically. The values obtained are: cyanide $2·1\times10^{-7}$, thiocyanate $1·10\times0^{-6}$, bromide $7·0\times10^{-7}$, and carbonate $1·1\times10^{-4}$ mol. per litre.

F. L. USHER.

Reaction between polyhydric alcohols or phenols and arsenic compounds, in particular arsinoacetic acid. III. B. ENGLUND (J. pr. Chem., 1931, [ii], **129**, 1—23).—The constant *L* (cf. A., 1930, 330) has been evaluated for the increase in solubility of arsenious oxide in 95% *n*-butyl alcohol in presence of propane-αβ- and -αγ-, *meso*- and *r*-butane-βγ-, hexane-αζ-, heptane-αη-, octane-αθ-diols, and pinacone, the results being parallel to those already described.

The comparatively small increases in the solubility of arsinoacetic acid in glacial acetic acid caused by the aliphatic glycols $(CH_2)_n(OH)_2$, where $n=4$—10, show an irregular oscillating effect when plotted against *n*. *cis*-α-Glycols of cyclic hydrocarbons exert a greater effect than corresponding aliphatic glycols, but the *trans*-compounds are much less effective, the ratio *L trans* : *L cis* being 1 : 11, 5, 10, and 22, respectively, for *cyclo*pentane, *cyclo*hexane, hydrindene, and tetrahydronaphthalene. The results are in general agreement with those required on stereochemical grounds, assuming the formation of a five-membered heterocyclic ring, except that ease of addition to the two forms of *cyclo*hexane-1 : 2-diol should be about the same in the two cases.

Arsenic and arsinoacetic acid derivatives of ethylene glycol are found to be unimolecular in boiling acetone. Similar derivatives of pinacone, in contrast to those of ethylene glycol, are stable to alcoholic alkali: with phenolphthalein as indicator they behave as monobasic acids. The arsenic acid complex of pinacone in addition shows marked stability towards aqueous alkali, with which it can be titrated at 0°; it is rapidly and completely hydrolysed in aqueous solution, however, with regeneration of arsenic acid. A kinetic study by titrimetric and conductometric methods indicates also that hydrolysis is markedly accelerated by small quantities of mineral acids.

The preparation of butane-αδ-, pentane-αε-, octane-αθ-, and nonane-αι-diols, by reduction of the corresponding dicarboxylic acids with sodium and alcohol (cf. A., 1903, i, 597; 1928, 43), is described.

H. A. PIGGOTT.

Laws of distribution of small amounts of substances in crystalline precipitates. O. HAHN, H. KADING, and R. MUMBRAUER (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1930, **30**, 11 pp.).—The separation of small quantities of a foreign substance which is admixed with a crystalline precipitate may take place in two ways. It may separate in the mass of the precipitate so as to be independent of the area of surface of the precipitate, its polar nature, and its charge; by this method, mixed crystals are formed. In the second case, the separation is greatly dependent on the surface properties, and is in fact an adsorption phenomenon. The method used to study the separation of foreign substances was to crystallise salts (especially barium salts) from a radioactive solution. In this way it was possible to determine how the radium had been taken up. Mixed crystals may be formed under these conditions, even if, in the macroscopic state, no isomorphism is known.

A. J. MEE.

Frenkel and Huckel's theories of adsorption. A. GANGULI (Z. Physik, 1930, **66**, 704—707).—Frenkel and Hückel's adsorption formulæ are both contained in the formula deduced by Kar and Ganguli (A., 1930, 151). A. B. D. CASSIE.

Correction for adsorption in physico-chemical determinations of mol. and at. wts. E. MOLES (Anal. Asoc. Quím. Argentina, 1930, **18**, 114—123).—An historical account is given of the part played by adsorption in earlier work with gases, and of the corrections which have been applied to the data. Adsorption corrections cannot be eliminated by the employment of vessels of differing capacities, and the most satisfactory conditions are obtained with 1-litre vessels. Results obtained by the author and by other workers are reviewed. H. F. GILLBE.

Activation energy of adsorption processes. H. S. Taylor (J. Amer. Chem. Soc., 1930, **52**, 5298—5299).—A preliminary discussion.

J. G. A. Griffiths.

Specific adsorptive properties of active charcoals. I. M. M. Dubinin (J. Russ. Phys. Chem. Soc., 1930, **62**, 1627—1633).—A theoretical consideration of the laws governing adsorption.

R. Truszkowski.

Theory of gas adsorption. II. V. B. Mecklenburg (J. Russ. Phys. Chem. Soc., 1930, **62**, 1723—1747).—An exposition and experimental confirmation of Kubelka's theory (Z. Elektrochem., 1925, **31**, 488) of the adsorption of gases by activated charcoal.

R. Truszkowski.

Influence of subdivision of carbon on the adsorption of fatty acids. B. Bruns (Kolloid-Z., 1931, **54**, 33—35).—Extremely finely-divided non-activated carbon adsorbs relatively greater quantities of the higher members of the fatty acid series than of the lower members. Consequently, an adsorbent which normally shows an inversion of Traube's rule may be made to behave in accordance with the rule by fine subdivision. It is suggested that the inversion of Traube's rule is due to the opening up of small pores on subdivision, which are not accessible to the larger molecules.

E. S. Hedges.

Poisoning effects of water vapour on the adsorption of carbon dioxide by manganese dioxide [at 25°]. H. W. Foote and J. K. Dixon (J. Amer. Chem. Soc., 1931, **53**, 55—58; cf. A., 1930, 990).—The adsorption of carbon dioxide at pressures as high as 500 mm. by manganese dioxide, with and without adsorbed water, has been investigated. The adsorption is reversible and is diminished by 50% when about 35% of the surface of the manganese dioxide is covered with water. This indicates the presence of active adsorption patches. Similar experiments with carbon monoxide in place of carbon dioxide show that the adsorption of the former is highly irreversible, although results were obtained qualitatively similar to those for carbon dioxide.

J. G. A. Griffiths.

Adsorption of electrolytes by crystalline surfaces. III. (Mlle.) L. de Brouckère (J. Chim. phys., 1930, **27**, 543—565; cf. A., 1928, 831; 1929, 757).—The previous work has been extended to the study of the adsorption of sodium and potassium iodide and bromide and of cadmium iodide on the microcrystalline surface of barium sulphate; the results indicate complete reversibility, the attainment of a definite equilibrium, and the formation of a unimolecular layer. The isotherms resemble in general those obtained with the chlorides, and when plotted logarithmically consist of two linear portions of which the first indicates that in sufficiently dilute solution the quantity adsorbed increases almost linearly with the concentration, whilst the second portion corresponds with saturation of the surface of the adsorbent. In the case of cadmium iodide the isotherms indicate that simple and complex molecules are adsorbed more readily than are simple ions. By comparison of the curves obtained with a series of salts having a common on it appears that the main factor in the adsorption process is direct adsorption of the anions and that the equivalent number of cations are retained solely by electrostatic forces. The ease of adsorption of the alkali metal halides increases with increase of the at. wt. of the anion.

H. F. Gillbe.

Exchange of ions at the surface of colloidal platinum. S. W. Pennycuick (Kolloid-Z., 1931, **54**, 21—32).—The hydrogen ions liberated from the surface of colloidal platinum when the colloid is coagulated by the addition of electrolytes have been determined by a conductometric method. Salts of univalent cations undergo little exchange adsorption and neither hydrochloric nor nitric acid is adsorbed at all by colloidal platinum. Barium, calcium, and aluminium chlorides undergo exchange adsorption, but hydrolytic adsorption occurs simultaneously. The effect of hydrolysis is most marked in the addition of potassium cyanide. A comparison of the amount of exchange of ions with the lowering of the electrokinetic potential shows a very close connexion and points to exchange adsorption as the cause of coagulation. Actually, no discontinuity occurs at the point of coagulation and ion-exchange is not then complete. The explanation is probably that the first coagulum consists of particles in loose contact, which still contain replaceable hydrogen ions, but that when these are replaced the particles adhere more firmly, or coalesce. With colloidal platinum ion-exchange does not appear to take place in stoicheiometric ratio, but this observation is probably due to partial hydrolysis of the salts concerned.

E. S. Hedges.

Adsorption of aluminium and thorium chlorides on clays and kaolins. N. A. Held (J. Russ. Phys. Chem. Soc., 1930, **62**, 1553—1570).—Aluminium and thorium can be determined electrotitrimetrically in the same solution, using a quinhydrone electrode. Adsorption of aluminium and thorium but not of chloride ions takes place on clay, which at the same time gives up calcium and magnesium ions; this process is accompanied by acidification of the solution, as a result of the reactions: $AlCl_3+2H_2O \rightleftharpoons Al(OH)_2Cl+2HCl$ and $ThCl_4+3H_2O \rightleftharpoons Th(OH)_3Cl+3HCl$.

R. Truszkowski.

Influence of hydrogen ions on the adsorption of barium and aluminium ions by clays. N. A. Held and M. N. Sokolova (J. Russ. Phys. Chem. Soc., 1930, **62**, 1571—1575).—The adsorption of barium and aluminium ions varies with the of the solution; at a given p_H the adsorption series Ba<Al<Th is obtained.

R. Truszkowski.

Density, surface tension, and adsorption in the water–ammonia system at 20°. H. H. King, J. L. Hall, and G. C. Ware (J. Amer. Chem. Soc., 1930, **52**, 5128—5135; cf. Berthoud, A., 1918, ii, 310; Rice, A., 1928, 582).—A closed apparatus for the simultaneous determination of the density and surface tension of a liquid is described. The surface tension of liquid ammonia at 0°, 10°, and 20° is 26·43, 24·28, and 22·03, respectively. The Ramsay–Shields constant is 1·662, corresponding with an apparent mol. wt. of 24·5. The surface tension and density of 0—100% ammonia–water mixtures at 20° are recorded (cf. Mittasch and others, A., 1927, 104). The surface tension generally agrees with the mixture

law except in the middle region, where the values rise to a maximum deviation of 6 dynes per cm. If this deviation is due to adsorption of ammonia in the surface, the adsorption is 1—5% of the normal surface concentration. J. G. A. GRIFFITHS.

Unimolecular films on water and mercury. II. Surface films on mercury. E. FAHIR (J. Chim. phys., 1930, **27**, 587—603).—Mercury, in an atmosphere of nitrogen, has been used for the study of surface films owing to the absence of disturbances due to the slight solubility of the second phase and on account of its high surface tension. Films of long-chain organic compounds on mercury exhibit the same phenomena as similar films on water. Observations with oleic and myristic acids and with cetyl alcohol films confirm Marcelin's views (A., 1929, 1001) and yield results for the chain length which accord well with those derived from X-ray measurements. The isotherm of the system oleic acid–mercury has been plotted from 15 to 59·5 dynes per cm.^{2}; the latter is the saturation pressure and is approximately twice the value for oleic acid films on water. An attempt is made to interpret the behaviour of such films by regarding them as composed of dipoles oriented by the action of the electric field of the liquid. Calculation shows that the energy of a film of this type on mercury is roughly twice that of a similar film of water, in accordance with the relative saturation pressures of oleic acid films. H. F. GILLBE.

Adhesive forces in surface films. T. M. LOWRY (Nature, 1931, **127**, 165).—The conception of the co-ordination of hydrogen can be used to account for the adhesion between contiguous molecules in a unimolecular film of a fatty acid on the surface of water. L. S. THEOBALD.

Ultramicroscopic structure of unimolecular soapy water films. C. SPIERER (Kolloid-Z., 1931, **54**, 17—21).—The thinnest films obtainable with 5% sodium oleate solution have been examined in the ultramicroscope. They initially contain particles which are in Brownian movement, but later this ceases and formations resembling clouds appear. These are frequently striated like cirrus clouds, the period being a few $\mu\mu$. Finally, the whole surface becomes a gel. The appearance of the dark spot is described. The thinnest part of the film is about 4·5 $\mu\mu$. E. S. HEDGES.

Elliptical polarisation at the surface of liquids. Application to study of unimolecular surface films. C. BOUCHET (Ann. Physique, 1931, [x], **15**, 5—130).—The elliptical polarisation produced by reflexion at liquid surfaces, using the green mercury line 546, has been studied. Water gives the value $K = +0{\cdot}00040$. The negative values previously reported are due to impurities in the surface. The values obtained for organic liquids are all positive and there is no distinction between aliphatic and aromatic compounds. The value $K(n—1)$, where n is the refractive index, varies inversely with the surface tension for a number of liquids. The thickness of the surface film calculated by the application of Drude's equation is of the order of molecular dimensions deduced from X-ray investigations; in the case of pure fatty acids, the ellipticity varies little with the number of carbon atoms and thus depends on the diameter rather than on the length of the molecule. The value of elliptical polarisation for salt solutions is independent of the nature and concentration of the salt and is identical with that of pure water; this is apparently due to a film of adsorbed water at the surface. A study was made of the elliptical polarisation of unimolecular films of fatty acids. The values for the acids which are completely miscible with water are not proportional to the concentration; for butyric acid, K passes through a minimum. In the case of the higher fatty acids, K decreases as the concentration increases and tends towards a limiting minimum as saturation is reached. The value of the minimum is related to the length of the carbon chain as determined by X-ray methods. These results afford independent evidence of the existence of a single layer of molecules oriented vertically. The films adsorbed at the surface of solutions of soluble fatty acids are identical in structure with unimolecular films of insoluble fatty acids. E. S. HEDGES.

Surface potentials of unimolecular films of long-chain fatty acids. I. Experimental method. II. Evaluation of the resolved electric moments. III. Potentials of solid, liquid condensed, and double layer films. J. H. SCHULMAN and E. K. RIDEAL (Proc. Roy. Soc., 1931, A, **130**, 259—270, 270—284, 284—294).—I. The work of Frumkin and Guyot is briefly reviewed. Using a modification of the apparatus employed by these workers, giving an accuracy in the potential measurements of ± 2 millivolts, measurements have been made of the potential rise at a 0·01N-hydrochloric acid–air interface by the surface solution of a crystal of myristic acid. It is found that the value of ΔV, the change of potential, which equals $4\pi n\mu$ (where n is the number of molecules per sq. cm. of the film-forming substance and μ is the effective vertical component of the average electric moment) shows an arrest for a period of 10—20 min. at 150—160 millivolts. This corresponds with the transition from vapour to liquid expanded film. Measurements were also made by spreading the film in the usual way from a solution in light petroleum. With certain precautions the values obtained for the potential could be repeated both on expansion and contraction of the film, but two critical regions where marked hysteresis occurred were observed—one over the region of area 88—100 Å.^{2}, and one from 40 to 30 Å.^{2} The ΔV–area curves showed three well-defined arrest points at 39·5, 53·5, and 88 Å.^{2}, with one less defined between 26 and 30 Å.^{2}

II. The value of (see above) was calculated from the Helmholtz equation to be $2{\cdot}29\times10^{-19}$ e.s.u. for a molecule of myristic acid in the expanded state. The value obtained from the $\Delta V—n$ curve gives for the true value of $\bar{\mu}$ $2{\cdot}5\times10^{-19}$ e.s.u., the difference being due to a change in the zero potential after the deposition of an expanded film on the surface. On the surface of 0·01N-hydrochloric acid the value of $\bar{\mu}$ for a molecule in the liquid condensed state at a pressure corresponding with equilibrium in the expanded state is $1{\cdot}56\times10^{-19}$ e.s.u., and has small values in the vaporous state. It rises for both the

solid condensed and the expanded state, and for the latter it has a constant value of $2 \cdot 5 \times 10^{-19}$ e.s.u. Identical results were obtained for palmitic and pentadecoic acids in similar states of aggregation. The transition from the expanded or liquid state to the vaporous state occurs at constant potential, from which it can be deduced that an intermediary state exists between these two which has been designated the "pre-homalic" state and appears on expansion of a liquid phase beyond a critical area. Just previous to the disappearance of this phase the electric moment of the molecules in the highly expanded film reaches the large value $\mu = 3 \cdot 7 \times 10^{-19}$ e.s.u., and experimental evidence is obtained which suggests that in the vaporous state the molecules are horizontally oriented. A comparison is made between the values of $\bar{\mu}$ obtained and those derived from measurements of refractive index and dielectric constant.

III. Measurements have been made of the surface potential of films of palmitic acid in various states of compression on a series of buffer solutions varying from p_H 2 to 7·3, and from the variation of ΔV with the nature of the substrate the contribution of the double layer to the interfacial potential can be calculated from the equation $\Delta V = 4\pi n \bar{\mu} + \Delta V_u$, where $4\pi n \mu$ is the real contribution of the film-forming material, whilst ΔV_u is the contribution of the underlying double layer to the air–liquid *P.D.* observed. It is concluded that μ calculated from the apparent surface potential change $\Delta V = 4\pi n \mu$ depends on the hydrogen-ion concentration of the underlying surface layer which differs from that of the bulk phase, on the character of the anion and its capillary activity, and also on the phase of the film. The value of $\bar{\mu}$, calculated from the increase in surface potential due to an increase in the number of mols. per cm.^{2} from $\Delta V = 4\pi n \bar{\mu} + \Delta V_u$, is independent of the p_H of the substrate, and depends only on the phase of the film. The vertical component of the electric moment of palmitic acid in the liquid condensed state is found to be $1 \cdot 59 \times 10^{-19}$ e.s.u., whatever the acidity of the substrate, but the apparent electric moment may vary from 2·06 to $1 \cdot 7 \times 10^{-19}$ e.s.u., owing to the effect of the underlying ionic layer. The borate and citrate ions, which are distinguished by different capillary activities, have a marked effect on the ionic double layer. Similar effects are observed for the molecule on compression of a film in the solid condensed state. L. L. BIRCUMSHAW.

Relationships between phase boundary potential, adsorption, surface tension, and particle size. F. K. V. KOCH (Phil. Mag., 1931, **11**, 585—592).—The Nernst formula for the variation of electrode potential with the concentration of ions is derived on the assumption that the ideal gas laws apply to the solution and that the charge at the interface is directly proportional to the number of ions or molecules adsorbed. Expressions for the adsorption isotherm and the surface tension isotherm are derived mathematically on the assumption of the Helmholtz double layer, but the adsorption isotherm has a different mathematical form from that of Freundlich. The following expression is derived for the variation of interfacial potential with particle size: $\Delta e = (RT/nF) \log_e P_w/P - 2\sigma M/r\rho nF$, where Δe is the difference in potential between a spherical particle of radius r and the plane surface, P_w and P are the Nernst solution pressures, M is the mol. wt. of the liquid, σ the surface tension, and ρ the density. E. S. HEDGES.

Relation between ballo-electric phenomena and *P.D.* at the interface gas/solution. A. FRUMKIN and A. OBRUTSCHEVA (Kolloid-Z., 1931, **54**, 2—7).—The charge acquired by droplets of finely-dispersed water containing a surface-inactive electrolyte and a surface-active non-electrolyte depends on the concentration of the electrolyte and is qualitatively connected with the potential at the gas–solution boundary. When the positive end of the molecular dipole is oriented towards the gas phase the droplets assume a positive charge and when the negative end is towards the gas a negative charge is assumed. With increasing concentration of the capillary-active non-electrolyte the ratio of the ballo-electric effect to the interfacial potential is constant for ethyl acetate and trichloroacetic acid, but rises to a steady maximum for propionic acid. Although the concentration of the electrolyte has a large influence on the ballo-electric effect, it has little influence on the interfacial potential. The sign of the ballo-electric effect changes when a non-electrolyte is converted into an electrolyte, *e.g.*, by the addition of an acid to aniline or the addition of alkali to a phenol. E. S. HEDGES.

Surface tension of aqueous sucrose solutions. K. SMOLEŃSKI and W. KOZŁOWSKI (Rocz. Chem., 1931, **11**, 29—34).—The surface tension of sucrose solutions is expressed by the equation $\sigma = 73 \cdot 0 + 0 \cdot 089c$, where c is the percentage sucrose content. The temperature coefficient of surface tension is 0·0018 for M solutions. R. TRUSZKOWSKI.

Measurement of wetting tension and some results. W. HALLER (Kolloid-Z., 1931, **54**, 7—13).—The method described for the measurement of wetting tension consists in determining the displacement of the liquid meniscus in a horizontal capillary tube under the application of varying pressures. The values for the wetting tension of *iso*amyl alcohol, *n*-heptyl acetate, petroleum, *n*-hexyl and benzyl alcohols, lactic acid, aniline, acetophenone, glycol water, and glycerol on a glass wall are tabulated. In many cases a marked hysteresis was observed. By slowly withdrawing the liquid the meniscus becomes semicircular and leaves a thin film on the glass wall, which is very stable for water, glycol, glycerol, and lactic acid. The wetting tension of water against ceresin, cellulose nitrate, cellulose acetate, and gelatin has been measured by coating the glass capillary with films of these substances. An ageing effect is shown by cellulose acetate, films obtained from freshly prepared solutions giving a higher value than those obtained from solutions which had been kept for a few days. Capillary-active substances form a layer at the solid–liquid interface; they may form (1) unstable films, which do not alter the wetting tension, but reduce the velocity of wetting, (2) metastable films, which reduce the wetting tension, (3) stable films, which increase the wetting tension.

Sugar solutions on glass give exceedingly thin films, which show interference colours. E. S. HEDGES.

Mechanical properties of surface energy. V. DUCCESCHI (Kolloid-Z., 1931, **54**, 13—17).—Mechanical energy can be obtained from surface energy by the following method. A small and light turbine is lowered into a glass trough containing water, so that the vanes of the turbine cut the water surface. An aluminium plate, the surface of which is covered with a layer of camphor, menthol, or thymol, is then placed in the water a few cm. away from the turbine. As the film of camphor or other substance spreads over the water surface the turbine rotates and may continue for 10—15 min. The addition of capillary-active substances, such as ethyl ether and amyl alcohol, in the neighbourhood of the turbine stops the movement. E. S. HEDGES.

Kinetics in [metal] solid solutions. H. HANEMANN (Z. Metallk., 1930, **22**, 404).—When a supersaturated solid-solution alloy is allowed to cool under certain conditions the new phase separates in layers the orientation of which depends on the orientation of the original mixed crystals; *e.g.*, the ferrite in steels having a Widmanstatten structure is in layers parallel to the cube and octahedron surfaces of the γ-crystals. This behaviour is explained by assuming that the atoms move in a definite direction in the lattice during the decomposition of the unstable γ-phase. Since the carbon atoms in this phase are situated in the centre of the elementary cube they can move only in the (011) direction without coming into collision with an iron atom; hence if movement of the carbon atoms away from the nuclear point of the α-phase takes place along this direction the resulting iron layers must be parallel to the cube and octahedron surfaces of the original γ-crystals. The term "perfusion" is suggested for this type of movement of one kind of atom in a mixed crystal where no interchange of position with another atom takes place. A. R. POWELL.

Optical investigations on the passivity of iron and steel. L. TRONSTAD (Nature, 1931, **127**, 127—128).—Mirrors of iron and steel show a change in reflected light as soon as they are rendered passive. The change corresponds with the formation of a surface film of refractive index approximately 3·0 and with an average thickness of approximately 30 Å. The mean refractive index agrees with that of ferric oxide. The optical properties of the mirrors are constant during continuous anodic treatment independently of the current densities used. Reactivation does not completely remove the oxide film, but its destruction on the ferrite grains is more pronounced than on the grains of cementite. L. S. THEOBALD.

Recovery of transmissivity of newly repassivated iron wires in nitric acid. R. S. LILLIE (J. Gen. Physiol., 1931, **14**, 349—361).—Steel wire (No. 20 piano wire) activated in 70 vol.-% nitric acid was immersed in nitric acid of varying concentrations until recovery was complete, and finally in nitric acid of 70—100 vol.-%, in which it is re-activated by touching one end with zinc. The distance travelled by the activation wave was then measured. Automatic repassivation requires a certain minimal concentration of nitric acid. The conditions governing the primary phase of recovery in irritable living tissue are analogous to those obtaining in newly repassivated iron wires, in which the agent responsible for such an effect is a layer of iron oxide. P. G. MARSHALL.

Microscopic and cinematographic study of Liesegang rings. (MME.) S. VEIL and L. BULL (Compt. rend., 1931, **192**, 282—284).—A detailed illustrated account of the formation of these rings when a drop of silver nitrate solution is placed on a moist dichromated gelatin jelly. C. A. SILBERRAD.

Properties of protein-cellulose membranes. L. VELLUZ and J. LOISELEUR (Compt. rend., 1931, **192**, 306—308).—In both artificial and natural protein-cellulose membranes each constituent exhibits its own characteristic properties, the membrane behaving as a solid solution. Cellulose renders the membrane insoluble in water and confers on it its typical mechanical properties, whilst the protein is responsible for the various colour reactions obtained. Thus such membranes give the xanthoprotein reaction when boiled with dilute nitric acid. A membrane containing 30% of casein is coloured mauve by the action of 1% potassium hydroxide solution after immersion in boiling 5% copper sulphate solution and subsequent washing; it also gives Axenfeld's reaction, due to the presence of the colloidal metal, when treated with gold chloride solution and subsequently reduced (reddish-brown colour by reflected, blue by transmitted light), the intensity of colour running parallel to the protein content. In a series of artificial gelatin membranes with 5% of this protein the properties of the membrane are exclusively those of cellulose, with 10% the Tyndall effect becomes apparent, with 75% the mechanical properties of cellulose are still apparent, but with 80%, gelatin properties predominate. J. W. BAKER.

Diffusion of electrolytes, non-electrolytes, and colloidal electrolytes. J. W. McBAIN and T. H. LIU (J. Amer. Chem. Soc., 1931, **53**, 59—74).—The method of Northrop and Anson (A., 1929, 587) yields accurate results which are independent of the porosity of the diaphragm. The Nernst and Einstein equations are combined to include all cases of diffusion. The diffusion coefficient, D, is then given by the relation $D=iRT/\Sigma(1/U_m)$, where $1/U_m$ is the resistance to movement of a particular species and i is the van 't Hoff coefficient. When data for the diffusion of 0·025—0·5N-potassium laurate into more dilute solutions and into 0·0015N-potassium hydroxide at 25° are analysed on the basis of the above considerations, the results are found to accord with previous conclusions as to the nature of the solutions (McBain and Jenkins, J.C.S., 1922, **121**, 2328). Data for sucrose and other solutions show that the viscosity attributable to the solute is not that which determines the rate of diffusion, and also that non-reacting solutes have a mutual influence on their individual rates of diffusion. J. G. A. GRIFFITHS.

Dependence of viscosity of cellulose ester solutions on temperature. II. E. KARRER, E. BERL, and H. UMSTATTER (Z. physikal. Chem., 1931, **152**,

150—152).—An equation derived theoretically by one of the authors becomes when simplified $\log(1/\eta)=A-B/T$, where $1/\eta$ is the fluidity, A is proportional to the mean energy which must be acquired by a molecule before it can move past neighbouring molecules, and B is a function of the size, number, and weight of the mobile molecules. Since the experimental results obtained for cellulose ester solutions (A., 1930, 1115) conform to this equation at all temperatures between 20° and 48°, it follows that the ester molecules undergo no chemical change over this temperature interval. H. F. GILLBE.

Viscosity–temperature relations of solutions of cellulose esters. III. E. BERL, H. UMSTÄTTER, and E. KARRER (Z. physikal. Chem., 1931, **152**, 284—294; cf. A., 1930, 1115).—Viscosities of solutions of nitrates and acetates of celluloses of varying origin in tetrachloroethane, butyl acetate, and acetone have been determined. The formulæ $\log\eta=kc$, and $\log\eta=B/T-A$ (where c denotes volume concentration and T the absolute temperature, k, A, and B being constants) express the results satisfactorily. Values of the viscosity are accurately reproducible provided no free acid is present in the solvent.
F. L. USHER.

Density of acid copper sulphate solutions. G. CHAPAS, C. CHARMETANT, and A. RAME (Chim. et Ind., 1930, **24**, 794—796).—Diagrams are given showing lines of equal density in the ternary system $CuO-SO_3-H_2O$ (up to the limit of homogeneous solutions) and in the system $H_2SO_4-CuSO_4$. The saturated solution of copper sulphate in water at 15° has d 1·186. From solutions containing more than 47% SO_3 the sulphate crystallises as the monohydrate.
A. R. POWELL.

Viscosity of electrolytes. W. R. BOUSFIELD (Nature, 1931, **127**, 129).—Certain general statements of Joy and Wolfenden (this vol., 164) are criticised.
L. S. THEOBALD.

Variations of colour of solutions of cobalt chloride. E. TOPORESCU (Compt. rend., 1931, **192**, 280—282).—Solutions containing 0·717% of cobalt chloride in methyl, ethyl, n-propyl, n-butyl, and amyl alcohols change colour from blue to rose when cooled to +3°, −18°, −32°, −45°, and −65°, respectively. The dielectric constants of these solvents at these temperatures (with one doubtful exception) decrease in the same order. Addition to a red solution (*e.g.*, in methyl alcohol or water) of a substance which diminishes the dielectric constant, *e.g.*, ether, acetone, or hydrochloric acid, tends to turn the colour from red to blue; addition of one that raises the constant, *e.g.*, carbamide or glycine, has the opposite effect. It would therefore seem that the change in colour depends on the dielectric constant of the solvent, and consequently on its state of polymerisation, rather than on any change in the cobalt chloride itself.
C. A. SILBERRAD.

Potassium chromate and potassium dichromate as light filters and the constitution of chromic acid from absorption measurement. W. V. BHAGWAT and N. R. DHAR (J. Indian Chem. Soc., 1930, **7**, 913—921).—Absorption measurements have been made for potassium chromate and dichromate solutions of various concentrations in different regions of the visible spectrum. The results are expressed as extinction coefficients and the percentage transmission has been determined. A saturated solution of potassium chromate transmits wave-lengths longer than 5150 Å., and a saturated solution of potassium dichromate can conveniently be used to cut off all the wave-lengths shorter than 5600 Å. Very dilute solutions of chromates and dichromates behave similarly and it appears that chromic acid in dilute solution exists mainly as $H^{\cdot}$, $HCrO_4'$, and CrO_4'' ions, and dichromates as $HCrO_4'$ and CrO_4'' ions.
E. S. HEDGES.

Absorption of aqueous solutions of tartaric acid. R. LUCAS and M. SCHWOB (Compt. rend., 1931, **192**, 225—227).—In view of the discrepant results of other investigators (cf. Bruhat and others, A., 1930, 10, 18, 1090, 1094, 1341) the absorption of ultra-violet light (λ 2654 and 2536) by solutions of tartaric acid has been determined, using silica vessels, and water distilled in a platinum vessel, and measuring the absorption photoelectrically (cf. Halban and Siedentopf, A., 1922, ii, 332). Differences of more than 100% are shown by the results for the two samples of tartaric acid used, and for both the absorption is smaller than the recorded values. The data also show clearly that Beer's law is not followed, the specific absorption for dilute solutions being more than three times that for concentrated solutions.
C. A. SILBERRAD.

Nomenclature of atmospheric disperse systems. H. GRIMM (Kolloid-Z., 1931, **54**, 1—2).—A review of the literature relating to disperse systems in gases directs attention to the numerous terms in use for the same kind of system. A plea is made for a unified system of nomenclature. E. S. HEDGES.

Method for measuring average particle size of emulsions. W. P. DAVEY (J. Physical Chem., 1931, **35**, 115—117).—The particle size is obtained from measurements of the spreading of the emulsion on a clean surface of water. The volume of the droplets of the disperse phase is obtained independently by curdling a known volume of emulsion with one of a suitable electrolyte. The limitations of the method are discussed. L. S. THEOBALD.

Photometric measurement of concentration and dispersity in colloidal solutions. II. T. TEORELL (Kolloid-Z., 1931, **54**, 58—66; cf. this vol., 164).—The dispersity of a sol can be defined by the ratio of the absorption constants for light of short and of long wave-length (the "dispersity quotient") This quotient has a higher value for highly-disperse than for coarsely-disperse systems, and for sols with particles of medium size the dispersity quotient is proportional to the size of particle. The light absorption method has also been applied to observations on the coagulation and ageing of mastic sols.
E. S. HEDGES.

Diffusivity of colloids. Determination of diffusion velocity of very slowly diffusing substances. H. R. BRUINS (Rec. trav. chim., 1931, **50**, 121—128).—Measurements of the rate of diffusion of colloids are rendered invalid by the long duration of the experiments and an attempt has therefore

been made to develop a method by which the concentration differences occurring during the first rapid stages of diffusion can be measured. An optical interference method is described. Two parallel, interfering light beams from the same source pass vertically through the diffusion apparatus, one passing through the cell containing the sol and the other through pure water. They are then united by means of a lens and are examined by an optical device similar to the Zeiss water interferometer. The calculation of the diffusion coefficient from the optical data is described. Experiments with a sol of soluble starch indicate a diffusion coefficient of $0{\cdot}026\times10^{-5}$, from which the mean particle radius is calculated to be 8×10^{-7} cm. The method yields results which are in accordance with the diffusion law, and the degree of reproducibility is 1—2%. E. S. HEDGES.

Ultrafiltration as a test for colloidal constituents in aqueous and non-aqueous systems. J. W. McBAIN and S. S. KISTLER (J. Physical Chem., 1931, **35**, 130—136).—Cellophane provides a membrane which retains all but the smallest colloidal particles and allows simple molecules to pass through; the membranes can be thickened so as to retain the larger molecules and ions such as those of sucrose, and sodium or potassium chloride. The presence of colloidal constituents in non-aqueous solutions of electrolytes which show anomalous behaviour in electrical conductivity and osmotic measurements has been demonstrated. Such systems are silver bromate in diethylamine, silver nitrate in piperidine, ammonium iodide in aniline, barium perchlorate or cadmium iodide in amyl alcohol, potassium acetate or pyridine in acetic acid. Colloidal constituents also occur in aqueous solutions of potassium iodate. L. S. THEOBALD.

Preparation of colloids from molecular streams by the condensation method. N. TOMASCHEVSKI (Kolloid-Z., 1931, **54**, 79—81).—Colloid systems have been prepared by simultaneously distilling the disperse phase and the dispersion medium on to a surface cooled by liquid air, and then allowing the solid condensate to melt. Such systems are mercury in water, cadmium in ethyl ether, selenium in water, sodium in ethyl ether, benzene, xylene, and hexane, potassium in ethyl ether and xylene, rubidium and cæsium in ethyl ether. The properties of these systems are described and their absorption spectra have been examined. The stability of the sols of alkali metals in ethyl ether is particularly high. E. S. HEDGES.

Preparation of colloidal gold by Zsigmondy's method. I. Influence of the nature of the distilled water. Action of traces of hydrogen sulphide. R. WERNICKE and R. B. LOSSON (Anal. Asoc. Quim. Argentina, 1930, **18**, 74—97).—The conditions under which red gold sols may be obtained consistently by Zsigmondy's method, *viz.*, reduction of an alkaline auric chloride solution with formaldehyde, have been investigated. By employing water distilled twice from glass vessels satisfactory sols cannot be obtained, but if the water is allowed to remain in contact with vulcanised rubber for 24 hrs. or is boiled with a trace of rubber for 3—5 min. it acquires the property of yielding excellent sols, although it becomes inert again on boiling. After repeated treatment the rubber becomes inactive, but reacquires its activity after about 24 hrs. Crude rubber produces the same effect, and although the water becomes opalescent it retains its activity on boiling. Contact with air also activates distilled water, but dissolved hydrogen sulphide is not the sole cause. Excellent sols, containing up to 0·33 part of gold per million parts, may be prepared by employing water containing sodium sulphide at a concentration of $1{\cdot}23\times10^{-7}M$; at concentrations above $4{\cdot}9\times10^{-6}M$ sol formation is inhibited. Zsigmondy's results are attributed to the action of atmospheric hydrogen sulphide and of the rubber tubing used. H. F. GILLBE.

Colloidal platinum and its behaviour as a typical acidoid sol. S. W. PENNYCUICK (J. Amer. Chem. Soc., 1930, **52**, 4621—4635; cf. A., 1929, 643, etc.).—In continuation of previous work, it is shown that the surface oxide layer is reduced on passing hydrogen through the sol and that the acidoid properties disappear, but are regenerated on passing oxygen. The charge on the colloidal particles is increased by hydrocyanic acid, and conductometric measurements indicate that this substance probably displaces from the surface the hexahydroxyplatinic acid which is combined, in the form of Werner compounds, with part of the surface oxide. J. G. A. GRIFFITHS.

Chromic hydroxide. J. LISIECKI (Rocz. Chem., 1930, **10**, 736—742).—Stable chromic hydroxide sols are obtained by adding washed chromic hydroxide, prepared by the action of ammonia on chromic nitrate solution, to a solution of chromic chloride; such sols do not need to be dialysed. R. TRUSZKOWSKI.

Preparation of electrolytic-free sol of manganese dioxide. S. SARVOTTAM and T. S. NARAYAN (J. Indian Chem. Soc., 1930, **7**, 882—885).—The stability of sols of manganese dioxide prepared by different methods has been investigated. The most stable sols are obtained when potassium permanganate is reduced by concentrated ammonia solution, added drop by drop. The negatively-charged sol coagulated slowly on electrodialysis, the duration of its stability increasing with the negative potential applied. With an applied potential of 220 volts stable sols were obtained, in which no sensible amount of potassium hydroxide could be detected. The electrolyte-free sol was more sensitive to electrolytes. The sol can also be rendered electrolyte-free by dialysis of the hot solution. E. S. HEDGES.

Silicic acid hydrosol. I. Preparation from ethyl silicate by hydrolysis. II. Electrical properties. K. INABA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, **15**, 1—15, 16—31).—I. Silicic acid hydrosol may be prepared by the hydrolysis of ethyl silicate in the presence of a small quantity of peptising agent in the form of a mineral acid or alkali. In acid solution the maximum concentration of silica giving a clear sol was 7—8%, coagulation taking place at higher concentrations; a higher concentration was obtained in alkaline solutions. The acid sol was particularly stable in the presence of 0·01—0·02*N*-acid and on electrodialysis it began to coagulate when the

concentration of acid was reduced to about 0·0002*N*. On the other hand, the alkaline sol could be electrodialysed until completely free from alkali without coagulation, thus giving a neutral sol. The acid sol had a lower electrical conductivity and a higher viscosity than the neutral sol. On the addition of hydrochloric acid to the neutral sol, coagulation quickly occurred at concentrations between 0·0001 and 0·0002*N*, but at higher concentrations of acid the sols were stable.

II. The cataphoretic migration velocity of the particles of silicic acid sols prepared by different methods and in the presence of various electrolytes has been measured. The acid sols were found to have a relatively low degree of dispersion and a small charge ($\zeta=-0{\cdot}003$ to $-0{\cdot}01$ volt). Neutral or alkaline sols had a high degree of dispersion and a high charge ($\zeta=-0{\cdot}02$ to $-0{\cdot}04$ volt). On the addition of hydrochloric acid or the chlorides of potassium, barium, cerium, or thorium coagulation did not occur, but the migration velocity decreased to the isoelectric point, after which the direction of migration was reversed. Exceptions occurred in the addition of barium chloride or cerium chloride to alkaline sols, in which cases coagulation ensued. A viscosity minimum was observed in the neighbourhood of the isoelectric point. It is deduced that the charge of the acid sols is due to the chlorine ion or corresponding anion adsorbed from the dispersion medium, and that the charge of the neutral sol is due to silicate ions.

E. S. HEDGES.

Effect of multivalent hydroxy-compounds in the synthesis of hydrosols. IV. Sugars. A. DUMANSKI and L. G. KRAPIVINA (Kolloid-Z., 1931, **54**, 73—79, and J. Russ. Phys. Chem. Soc., 1930, **62**, 1713—1721).—The peptising effect of sugars in the formation of colloidal ferric hydroxide by the reaction of ferric chloride with sodium and ammonium hydroxides has been investigated and the results have been expressed in the form of triangular equilibrium diagrams. The sugars examined can be arranged in the following order of decreasing effectiveness: lactose > lævulose > maltose > galactose > dextrose > sucrose > raffinose. Sugars of the maltose type, containing a carbonyl group, are the best peptising agents. The stability of the sols produced by this method depends on both the charge and hydration of the particles. E. S. HEDGES.

Influence of hydrolysis temperature on some properties of colloidal ferric oxide. IV. Variation of density and relative viscosity with sol concentration. G. H. AYRES and C. H. SORUM (J. Physical Chem., 1931, **35**, 412—416; cf. this vol., 164).—The density of the sols varies linearly with concentration and is not affected by the temperature of preparation. The densities of 17 different sols prepared between 100° and 140° and containing 2·0 g. Fe_2O_3 per litre gave a mean value at 25° of 0·9988 with a maximum variation of $\pm 0{\cdot}0002$. No generalisation relating to the shape of the viscosity–concentration curve can be drawn even for concentrations up to 0·5%. L. S. THEOBALD.

Unusual properties of colloidal dispersions. R. V. WILLIAMSON (J. Physical Chem., 1931, **35**, 354—359).—Experiments which show the marked changes in the plastic and elastic properties of dispersions produced by changes in temperature or in the magnitude and rate of application of stress are described. The flowing properties of paints, the behaviour of thixotropic dispersions of gas black in petroleum and of zinc oxide in gasoline, certain unusual properties of sodium silicate dispersions, and the liquefaction of viscose gels by a fall in temperature are described. L. S. THEOBALD.

Complexity of the magnetic properties of elements in the colloidal state. S. S. BHATNAGAR (J. Indian Chem. Soc., 1930, **7**, 957—958).—The reported changes in magnetic susceptibility of metals when reduced to colloidal dimensions should be viewed with reserve. In the case of bismuth, the colloidal particles contain oxide, which can account for the differences observed. E. S. HEDGES.

Action of electrolytes added to a colloidal solution in quantities insufficient to bring about coagulation. G. ROSSI and A. MARESCOTTI (Gazzetta, 1930, **60**, 993—996).—Hydrochloric acid when added to a colloidal solution of arsenious sulphide in amounts which are insufficient to bring about coagulation may, according to the quantity added, exert either a stabilising or a destabilising influence on the sol in regard to the coagulating action of hydrochloric acid itself. These two effects are accompanied by an increase and a decrease, respectively, of the degree of dispersion of the sol.

O. J. WALKER.

Equilibrium phenomena in the coagulation of colloids. E. F. BURTON and M. ANNETTS (J. Physical Chem., 1931, **35**, 48—59).—Measurements of the light scattered and transmitted by sols of gum mastic and arsenious sulphide indicate that distinct changes occur in the sol on the addition of small traces of electrolytes even before coagulation sets in. On the addition of small amounts of aluminium nitrate, aluminium sulphate, or magnesium sulphate to sols of gum mastic the intensity of the scattered light decreases to a constant value until the particles settle visibly. The time required to reach this value depends on the amount of electrolyte added, and the curves obtained by plotting this time against the quantity of electrolyte show two maxima and minima in the case of aluminium, but only one maximum and minimum in the case of magnesium. With arsenious sulphide, no such zonal effects are obtained. The successive addition of small amounts of electrolyte to sols of gold, mastic, or arsenious sulphide shows the existence of stages of partial coagulation, some of the colloidal material being precipitated. The constitution of arsenious sulphide sol is discussed, and it is suggested that after being adsorbed by the colloidal particle hydrogen sulphide dissociates, leaving HS^- to provide the charge on the surface, whilst the hydrogen ion is associated with the diffuse outer region of the Helmholtz double layer. L. S. THEOBALD.

Effect of hydrogen-ion concentration on flocculation values of ferric oxide sols. I. F. HAZEL and C. H. SORUM (J. Amer. Chem. Soc., 1931, **53**, 49—54).—The p_H of ferric oxide sols acidified (p_H 5·9—2·9) with hydrochloric acid and of the

coagulated media obtained by adding the critical concentration of electrolytes has been determined by means of the glass electrode. The stability of the sol towards potassium chloride, bromide, chromate, dihydrogen phosphate, ferricyanide, and ferrocyanide, ammonium and barium chlorides increases with increasing acidity, but the reverse is true of the sulphates of potassium, ammonium, and calcium. The stability towards ferric and aluminium chlorides is independent of the initial acidity, but depends on the constant value to which the is altered by the hydrolysis of the salt. J. G. A. GRIFFITHS.

Coagulation of methylene-blue by means of mercuric chloride. N. N. ANDRONIKOVA (Kolloid-Z., 1931, **54**, 82—84).—A certain minimal concentration of mercuric chloride is required to produce rapid coagulation of a methylene-blue solution. The coagulation is reversible in the sense that the precipitate is redissolved on heating or on the addition of a large volume of water. The character of the precipitate varies with the concentration of the mercuric chloride; low concentrations of the precipitant produce a coarse, blue precipitate, but higher concentrations give a violet precipitate. Mercuric chloride is adsorbed by the precipitate, the amount increasing with the concentration until the ratio is 2 mols. of mercuric chloride to 1 mol. of methylene-blue; at higher concentrations the composition of the precipitate falls to the ratio 3 mols. of mercuric chloride to 2 mols. of methylene-blue, after which the amount of mercuric chloride rises again. Similar effects were observed on the addition of potassium thiocyanate to methylene-blue solutions. E. S. HEDGES.

Acceleration produced by light in the flocculation of colloidal solutions in a fluorescent medium. A BOUTARIC and J. BOUCHARD (Compt. rend., 1931, **192**, 95—97).—Flocculation of colloids (mastic and other gums, arsenic sulphide, ferric hydroxide) by electrolytes (sulphuric acid and salts of alkali metals) in the presence of fluorescent substances (rhodamine, eosin, fluorescein, erythrosin) is accelerated by exposure to daylight and, to a much greater extent, to ultra-violet light. No acceleration occurs if the fluorescent material and/or electrolyte is absent. The quantity of electrolyte required for flocculation is also lowered in a fluorescent medium. Non-fluorescent dyes have no such influence, and (anti-oxygenic) substances, which inhibit fluorescence, repress the acceleration of flocculation. J. GRANT.

Dissolution of colloid particles on dilution of sols. A. J. RABINOVITSCH and V. A. KARGIN (Z. physikal. Chem., 1931, **152**, 24—35).—The phenomena observed with silica sols (A., 1928, 835) have been found to occur in other cases. On dilution of a tungstic acid sol the p_H rises at first, then remains constant for a considerable range of dilution, and finally increases. The buffer effect is due to hydration of the colloidal particles and the consequent liberation of hydrogen ions from the nuclei, whilst at extreme dilutions (1 : 5000) the whole of the colloidal material enters into true solution; the velocity of the transition from the colloidal state is much greater than with silica sols. Potentiometric and spectrophotometric measurements with vanadium pentoxide sols demonstrate the occurrence of a similar sequence of changes; a series of colourless complex polyvanadic acids is probably formed as an intermediate stage. The p_H changes which occur on dilution of arsenious sulphide sols indicate only slight hydrolysis at high dilutions, whilst with ferric hydroxide sols there is a small linear increase of the chloride-ion concentration; in neither case is there any evidence of true solution formation, and this phenomenon appears to be confined to acidic sols.
H. F. GILLBE.

Investigation of stream-double-refraction in very low concentrations. H. FREUNDLICH, J. V. TAMCHYNA, and H. ZOCHER (Z. wiss. Phot., Schaum-Festschr., 1930, **29**, 102—109).—The limiting concentrations at which colloidal solutions of certain metallic oxides and dyes exhibit stream-double-refraction have been determined by macroscopic and microscopic methods. The effect is enhanced by ageing the sols, and with sols of vanadium pentoxide, ferric oxide, tungsten trioxide, cotton-yellow GX, benzopurpurin 4B and 6B, and aniline-blue can be detected at concentrations of 10^{-6} g. of substance per c.c. With aluminium oxide and titanium dioxide the limiting concentration is considerably higher.
J. W. GLASSETT.

Density of water adsorbed on silica gel. D. T. EWING and C. H. SPURWAY (J. Amer. Chem. Soc., 1930, **52**, 4635—4641).—A gas dilatometer, with helium as the inactive gas, has been used to determine the density of water adsorbed on silica gel at 25·02°. With quantities of water up to 4·36 wt.-% of the gel, the vapour pressure of the liquid is very small. The density of the adsorbed water is about 1·027 and the pressure on the liquid is calculated to be about 750 atm. Quantities of adsorbed water greater than about 5% have a mean density less than that of free liquid water, suggesting the presence of the three phases—compressed, liquid, and gaseous water,
J. G. A. GRIFFITHS.

State of water in colloidal and living systems. R. A. GORTNER (Trans. Faraday Soc., 1930, **26**, 678—686).—Emphasis is laid on the distinction between free and bound water in lyophilic colloidal systems and on the importance of this conception in relation to biological problems. W. O. KERMACK.

Optical properties of protein sols and the influence of neutral salts and p_H. N. JERMOLENKO (Kolloid-Z, 1931, **54**, 66—78).—The refractive index of gelatin solutions does not vary with time and is independent of the treatment of the solution. Since the viscosity of the solution is affected considerably by the temperature at which the solution has been heated, by mechanical agitation, etc., whilst the refractive index is unchanged, it would seem that refractive index is not a function of the state of aggregation of the colloid. This point was also established in the case of glutin solutions. The refractive index is a linear function of the concentration for gelatin, glutin, and egg-albumin. The refractive index of gelatin scarcely changes with the hydrogen-ion concentration. The refractive index of glutin is constant for a given temperature and concentration, independently of whether the dispersion

medium is water or various salt solutions. No lyotropic effect is observed. E. S. HEDGES.

Changes in viscosity of gelatin sols in the process of gelation. S. N. BANERJI and S. GHOSH (J. Indian Chem. Soc., 1930, 7, 923—931).—An investigation of the hysteresis of the sol–gel transformation of gelatin has shown that the setting and melting temperatures are identical, provided that sufficient time is allowed for observation. The greater is the concentration of the gel, the shorter is the time at which the melting and setting temperatures become the same. Similar results were observed with soap gels in various alcohols and water. No firm gels of gelatin at any concentration can be obtained above 33°. Viscosity measurements show that there is a considerable difference according to whether the gelatin sol has been prepared at a temperature higher or lower than that at which the measurement is made. The sol prepared at a higher temperature has a higher viscosity than that prepared at a lower temperature. The viscosity increases with time when a gelatin sol prepared at a higher temperature is kept in a bath at a lower temperature, but the sol obtained by melting a gel shows a decrease in viscosity with time at a temperature higher than the m. p. of the gel. The ageing effect becomes appreciable within a short interval of time and is at a maximum in the region near the gelation temperature. It is supposed that a gelatin solution represents an equilibrium between simple molecules and aggregated molecules of gelatin and also that the aggregated molecules are in equilibrium with colloidal particles of gelatin. Gelation occurs when a sufficient quantity of aggregated molecules and colloidal particles is present, a view which explains the influence of concentration on the setting temperature.

E. S. HEDGES.

Hydrogels. Manganese dioxide hydrates. X. A. SIMON and F. FEHER (Kolloid-Z., 1931, 54, 49—58).—Manganese dioxide prepared in six different ways, after washing with water, alcohol, and acetone, gave on analysis a water content of 0·45—0·50 mol. of water to 1 mol. of manganese dioxide. In each case loss of water began at 70° and the vapour-pressure curves showed that the water is not bound by ordinary valency forces, but is colloid-chemically bound. The relatively small amount of water retained by the compound after treatment with alcohol and acetone is an indication of its lyophobic nature. It is deduced that no stable, stoicheiometric, chemical compounds of manganese dioxide and water exist. Native manganese dioxide stores a certain amount of its water in the capillaries of its structure, but this part is removed by the treatment with acetone. The action of sulphuric, oxalic, acetic, and hydrochloric acids on freshly-precipitated manganese dioxide and on old preparations was examined. The freshly-prepared substance was peptised only by $2N$-hydrochloric acid, and a precipitate which had been kept for 1½ years was not affected by any of these reagents. When kept, the preparations slowly lose water.

E. S. HEDGES.

Properties of starch with relation to time of formation of starch gels. O. W. CHAPMAN and J. H. BUCHANAN (Iowa State Coll. J. Sci., 1930, 4, 441—450).—The viscosity at first increases with rise of temperature, thereafter decreasing; the maximum is reached in the order potato, wheat, maize, rice starch, *i.e.*, in the order of decreasing grain size. Rapid heating increases, and addition of acid ($0·0025N$) decreases, the viscosity; addition of alkali causes an increase followed by a decrease in the viscosity. Sodium chloride ($0·5M$) has little effect. Sodium sulphate retards the attainment of maximum viscosity; sodium phosphate increases the maximum at a lower temperature. Acetates, sulphates, oxalates, and citrates hasten syneresis; other salts retard or prevent it. CHEMICAL ABSTRACTS.

Distribution of ions in gels. E. J. BIGWOOD (Trans. Faraday Soc., 1930, 26, 704—719).—The rate of diffusion of sodium hydroxide from an aqueous solution of constant concentration into an agar gel as indicated by the alteration in the colour of an indicator present in the gel is approximately independent over a wide range of the concentration of agar, and the distance penetrated is approximately proportional to the square root of the time. In the case of gelatin gels these statements are true only for relatively high concentrations of sodium hydroxide and relatively low concentrations of gelatin. When the gelatin concentration is high and the sodium hydroxide concentration is low the rate of penetration decreases as the concentration of gelatin increases. The distance of penetration is not proportional to the square root of the time, but after a certain time a steady state may be reached in which equilibrium is apparently established. These results are probably related to the power of gelatin to neutralise small concentrations of sodium hydroxide.

W. O. KERMACK.

Behaviour of proteins towards colloids and towards electrolytes. W. PAULI (Trans. Faraday Soc., 1930, 26, 723—737).—The interaction of a highly-purified Congo-red sol with highly-purified protein is described (cf. Pauli and Weiss, A., 1929, 395). A theory of the phenomena is advanced in which emphasis is laid on the zwitterion constitution of proteins and this is applied generally to the mutual interaction and precipitation of lyophobic and lyophilic colloids, more particularly in the neighbourhood of their isoelectric points. W. O. KERMACK.

Influence of volume on swelling. D. J. LLOYD (Kolloid-Z., 1931, 54, 46—49).—The observation that the degree of swelling of gelatin in sodium hydroxide solutions varies with the volume of solution is due to hydrolytic decomposition of the gelatin. When pure gelatin swells in sodium hydroxide solutions at a sufficiently low temperature (0°) to prevent hydrolysis, the amount of swelling is independent of the volume of liquid. The swelling of gelatin in solutions of inorganic salts is independent of the volume of the solution over a wide range of temperature and of concentration, whether the swelling reaches a maximum or leads to dissolution. E. S. HEDGES.

Swelling power of thiocyanates and [formation of] compounds of cellulose and neutral salts. J. R. KATZ and J. C. DERKSEN (Rec. trav. chim., 1931, 50, 149—152).—When cellulose is immersed in

dilute solutions of thiocyanates no change occurs in the X-ray diagram, the salt being adsorbed at the surface or penetrating only a small way into the structure of the fibre. When cellulose swells in concentrated solutions of thiocyanates a definite X-ray spectrum is obtained, indicating the formation of a chemical compound between the cellulose and the salt. At extremely high concentrations of lithium thiocyanate a different X-ray spectrum is obtained, suggesting that in this case two different compounds can be formed. Mercerised and native cellulose give different X-ray spectra after swelling in concentrated lithium thiocyanate solution. E. S. HEDGES.

Adsorption and protection phenomena in complex colloidal media. C. MARIE and N. MARINESCO (Compt. rend., 1931, **192**, 92—94).—The value of ε for aqueous solutions of gelatin, glycine, and *l*-leucine is greater than that for water, indicating permanent polarity of the solutes, whilst with aqueous suspensions of animal charcoal the similar difference is attributed to induced moments. Binary mixtures of these two types depress ε below that for water, indicating that the free dipoles are masked by the global polarisation of the system. Protection of colloids may thus be explained, the polarised protecting body surrounding the protected colloid and completely masking its properties. Permanently polarised gelatin added to a solution of amino-acid lowers ε owing to condensation of the dipoles of the latter by the former, although here simple association or molecular coupling results instead of pure protection. Dielectric analysis may therefore be used to determine the nature and amount of protective colloid required. J. GRANT.

Mitogenic radiation, and the effect of volatile substances from crushed onion root on colloidal phenomena. H. KOWARCZYK (Acta Biol. Exp., Warsaw, 1930, **6**, 29—36).—The disturbing effect on the formation of Liesegang rings of placing crushed onion root in the vicinity of a gelatin surface on which rhythmic deposition of silver dichromate is proceeding is due to volatile products and not to mitogenic radiation. The formation of Liesegang rings is not affected by ultra-violet light. The above volatile substances enhance the rate of coagulation of gold sols.

R. TRUSZKOWSKI.

State of division of lichosan in the dissolved and solid state. H. PRINGSHEIM and C. LAMM (Kolloid-Z., 1931, **54**, 36—42).—Lichosan precipitated by alcohol in the cold appears in daylight to be identical with that precipitated from a solution at 80° by the addition of boiling alcohol, but the fluorescence of the specimen prepared in the cold is considerably less. Mol. wt. determinations by the cryoscopic method gave a value of about 850 for the lichosan precipitated from hot solutions and a value of about 200 for the lichosan precipitated in the cold. The latter varies with time, however, increasing ultimately to about 850; simultaneously an increase in the viscosity of the solution is observed. The mol. wt. varies with the method of preparation. E. S. HEDGES.

Application of ternary co-ordinate systems to the graphical representation of the composition of colloidal systems. A. DUMANSKI (J. Russ. Phys. Chem. Soc., 1930, **62**, 1649—1663).—An exposition of the application of triangular co-ordinates to the study of colloidal systems. R. TRUSZKOWSKI.

Thermodynamics of mixtures. V. FISCHER (Z. Physik, 1930, **66**, 269—279).—For dilute solutions of gases in liquids it is shown that, neglecting the vapour pressure of the liquid and assuming a perfect gas, the osmotic pressure of the gas in solution is given by the ratio of the volume of the gas absorbed (at 760 mm. and the temperature at which dissolution is considered to take place) to the volume of the pure solvent in which the gas is dissolved. The ratio is identified with the absorption coefficient. Data for the following systems are used in illustration: acetylene–acetone, acetylene–acetone–water, acetylene–acetone–ethyl alcohol, acetylene–acetone–methyl alcohol. R. W. LUNT.

Calculation of entropy constants. I. Calculation of gas equilibria from spectroscopic data. J. M. BIJVOET (Chem. Weekblad, 1931, **28**, 26—37). —Theoretical. It is shown that all the quantities necessary for the calculation of equilibria in gaseous systems can be derived from spectroscopic data.

H. F. GILLBE.

Oxidation of carbon monoxide by steam. R. NITZSCHMANN (Metallbörse, 1930, **20**, 5—6, 118—120; Chem. Zentr., 1930, ii, 171).—The constants for the equilibrium $CO+H_2O \rightleftharpoons CO_2+H_2+10{,}400$ g.-cal. between 327° and 2090° have been derived, and the composition of the products after 95—99% conversion at 327°, 427°, and 452° have been calculated.

A. A. ELDRIDGE.

Water-gas process with addition of oxygen. R. NITZSCHMANN (Metallbörse, 1930, **20**, 285—286, 397—399, 510—511, 566—567, 678—679, 847—848, 903—904, 958—959; Chem. Zentr., 1930, ii, 171).—The equilibrium relations in the system $CO+H_2O \rightleftharpoons CO_2+H_2$ with the addition of oxygen in admixture with nitrogen have been examined, the results for varying conditions being tabulated.

A. A. ELDRIDGE.

Electrolytic dissociation of weak acids and bases. H. VON EULER and H. HELLSTRÖM (Svensk Kem. Tidskr., 1930, **42**, 300—302).—The ionisation of weak electrolytes is discussed on the hypothesis that the separation of the constituent ions takes place in a series of stages which result in the formation of active, although not fully dissociated, molecules, in which the distance between the ions is relatively great. On the assumption that the ionisation energy of a molecule is employed in increasing the mean distance between the ions it becomes less difficult to assign a physical significance to extremely small ionisation constants. Methods of investigating the hypothesis experimentally are indicated.

H. F. GILLBE.

Relative strengths of bases in non-aqueous solutions. III. E. I. JOHNSON and J. R. PARTINGTON (J.C.S., 1931, 86—92; cf. A., 1929, 1011).—The esterification of phenylacetic acid in dry alcoholic solution in presence of hydrogen chloride is slightly accelerated by small amounts of benzil and furan, retarded by diphenylpyrone, phenylmethylpyrone, and unsubstituted γ-pyrone, and not affected by small quantities of di-*n*- and -*iso*-propyl ethers and glycerol.

The velocity data have been used to calculate the relative basic strengths of the pyrones as compared with water (cf. Lapworth, J.C.S., 1908, **93**, 2187).
R. CUTHILL.

Recalculations of first dissociation constant of phosphoric acid in aqueous solution at 18°. Incidental determination of activity coefficients of undissociated acid molecules. J. W. H. LUGG (J. Amer. Chem. Soc., 1931, **53**, 1—8).—From existing data (Abbott and Bray, A., 1909, ii, 660), and correcting for secondary dissociation, the equivalent conductivity at infinite dilution of $(Na^{\cdot}+H_2PO_4{}')$ and $(H^{\cdot}+H_2PO_4{}')$ is computed to be 70·1 and 340·5, respectively, at 18°. Values of the first stoicheiometric dissociation constant of phosphoric acid are given by $pK_1=2{\cdot}09-\mu^{\frac{1}{2}}/(1+1{\cdot}0\,\mu^{\frac{1}{2}})-1{\cdot}8\,\mu$. The activity coefficient of the undissociated acid in dilute phosphoric acid solution is given by $p\gamma_{H_3PO_4}=-1{\cdot}8\mu$.
J. G. A. GRIFFITHS.

Thermodynamic properties of weak acids and bases in salt solutions, and an exact determination of their dissociation constants. H. S. HARNED and B. B. OWEN (J. Amer. Chem. Soc., 1930, **52**, 5079—5091; cf. Harned and Robinson, A., 1929, 140).—The *E.M.F.* data for cells without liquid junction are applied to acetic acid (*loc. cit.*) and formic acid in sodium chloride and potassium chloride solutions. The logarithm of the activity coefficient of the electrolyte, referred to unity at infinite dilution in water, varies linearly with the concentration of weak acid. This relation is valid at zero ionic strength and is believed to be very nearly true at all concentrations of salt. From the above data the dissociation constants of acetic and formic acids at 25° are computed to be $1{\cdot}75\times10^{-5}$ and $1{\cdot}77\times10^{-4}$, respectively. The dissociation constants of ammonia, mono-, di-, and tri-methylamine are calculated to be 1·79, 43·8, 52·0, and $5{\cdot}45\times10^{-5}$, respectively (*loc. cit.*).
J. G. A. GRIFFITHS.

Acid and base constants of glycine from cells without liquid junction. H. S. HARNED and B. B. OWEN (J. Amer. Chem. Soc., 1930, **52**, 5091—5102; cf. preceding abstract).—An exact thermodynamic method, which eliminates the use of liquid junctions and takes into account certain previously neglected medium effects, is developed for the evaluation of the acid and base constants of an ampholyte. From determinations at 25° of the *E.M.F.* of the cells Pt,H_2|NaOH(0·1*M*)|Na(0·1%),Hg|sodium glycine(0·1*M*),NaCl(*m*)|H_2,Pt; Pt,H_2|sodium glycine(0·1*M*),NaCl(*m*)|AgCl,Ag; and Pt,H_2|glycine hydrochloride(0·1*M*),NaCl(*m*)|AgCl|Ag, and existing *E.M.F.* data, the apparent dissociation constants of glycine at 25° are computed to be K_A, $4{\cdot}92\times10^{-3}$ and K_B, $5{\cdot}56\times10^{-5}$ (cf. Branch and Miyamoto, A., 1930, 542).
J. G. A. GRIFFITHS.

Strength of organic bases in glacial acetic acid solution. N. F. HALL (J. Amer. Chem. Soc., 1930, **52**, 5115—5128; Conant and Werner, this vol., 40).—A large number of bases at 0·05*M* concentration in glacial acetic acid at 25° have been titrated electrometrically with perchloric acid (cf. Hall and Werner, A., 1928, 1188). The titration curves obtained with the weakest bases show an initial rapid rise of *E.M.F.*, but no break; bases of intermediate strength give an initial rise and a break, whilst the strongest bases show a break only. There appears to be a close parallelism between the relative strengths of bases in glacial acetic acid and in water, and this affords a method for predicting the strength in water of bases which cannot be studied in the latter solvent. Data for the strengths of bases in water are collected and reviewed.
J. G. A. GRIFFITHS.

Temperature coefficient of dissociation of acetic acid in potassium and sodium chloride solutions. H. S. HARNED and G. M. MURPHY (J. Amer. Chem. Soc., 1931, **53**, 8—17; cf. Harned and Owen, above).—The *E.M.F.* of the cells H_2|HCl(0·01*M*),XCl(0—3*M*)|AgCl|Ag and H_2|acetic acid (0·2*M*), XCl(0·05—3*M*)|AgCl|Ag has been determined at 20°, 25°, and 30°. The activity coefficients of hydrochloric acid decrease slightly with rise of temperature and the decrease becomes more pronounced with increasing concentration of salt. The relative partial heat contents of 0·01*M*-hydrochloric acid in the salt solutions have been computed (Harned, A., 1920, ii, 664), and the excess or electrical contribution to partial molal heat content of hydrochloric acid in these solutions is approximately proportional to the square root of the total molarity. The hydrogen-ion concentrations in the acetic acid solutions have been computed. The dissociation constant of the acid is $1{\cdot}75\times10^{-5}$ between 20° and 30°. The ionic activity coefficient of acetic acid in the salt solutions varies similarly to that of hydrochloric acid.
J. G. A. GRIFFITHS.

Hydrolysis equilibria of triphenylchloromethane and triphenylbromomethane. Free energy of reactions of triphenylchloromethane, triphenylbromomethane, and triphenylcarbinol. J. O. HALFORD (J. Amer. Chem. Soc., 1931, **53**, 105—112).—Solubilities at 25° of triphenylchloromethane, triphenylbromomethane, and triphenylcarbinol in benzene have been determined and vapour-pressure data are recorded. By means of partition experiments between water and benzene, the free energies, ΔF_{298}, of the reactions are found to be CPh_3Cl (in benzene)$+H_2O(g)=CPh_3{\cdot}OH$ (in benzene) $+HCl(g)$, 1755 g.-cal.: $CPh_3Cl(s)+H_2O(g)=CPh_3{\cdot}OH(s)+HCl(g)$, 900; CPh_3Br (in benzene)$+H_2O(g)=CPh_3{\cdot}OH$ (in benzene)$+HBr(g)$, 4310. The results, together with existing data, afford information concerning the reactions of triphenylchloromethane with bromine, hydrogen bromide, and bromides. In benzene, the dissociation of triphenylbromomethane into neutral molecules is 10^6 times that of the chloro-compound, and of the two the bromo-compound has a slightly greater tendency to ionise.
J. G. A. GRIFFITHS.

Effect of light on the ferrocyanide–ferricyanide iodine–iodide equilibrium. R. G. DICKINSON and S. F. RAVITZ (J. Amer. Chem. Soc., 1930, **52**, 4770—4778; cf. La Mer and Friedman, A., 1930, 542).—At 0°, where the thermal reaction is very slow, it is found that irradiation of the system $2Fe(CN)_6{}'''+2I'$—$2Fe(CN)_6{}''''+I_2$ effects a shift of the equilibrium in the direction of increased free iodine. It is shown that the light absorbed by the $I_3{}'$ ion is

effective and that the quantum efficiency of the reaction is very nearly the same as that in the reaction $2Fe^{\cdots}+2I'—2Fe^{\cdot\cdot}+I_2$ (cf. Kistiakowsky, A., 1927, 528). Possible mechanisms for the reaction are discussed. J. G. A. GRIFFITHS.

Vapour pressures and activities of volatile components in binary alloys at high temperatures. K. JELLINEK and G. A. ROSNER (Z. physikal. Chem., 1931, **152**, 67—94).—The vapour pressure of cadmium at 567° is 48·2 mm. Vapour-pressure measurements have been made with binary alloys of cadmium with lead, tin, and copper at temperatures from 500° to 700° and over a fractional molar concentration range of 0·1—0·6, and with zinc–copper alloys between 600° and 800°. The activity coefficients a of cadmium and zinc in the alloys have been calculated; the a-concentration curves are very similar for the cadmium–lead and cadmium–tin alloys, but for the cadmium–copper alloys are of a different form owing to the limited solubility of copper in cadmium. The zinc–copper alloys are noteworthy in that a is almost independent of temperature, and the a-concentration curve intersects the theoretical curve at 52 mol.-% zinc. Since the log p–$1/T$ curves for all the alloys are roughly parallel, the latent heats of evaporation of cadmium and zinc in the alloys can differ but little from their values in the pure state. The latent heats and the heats of mixing have been calculated, and the results, together with the calculated activity coefficients for the cadmium–lead and cadmium–zinc alloys, are compared with the results of Taylor's *E.M.F.* measurements (A., 1924, ii, 89). H. F. GILLBE.

Activity coefficients of electrolytes. V. Principle of specific interaction in cadmium and magnesium sulphate and chloride solvents. H. B. FRIEDMAN and V. K. LA MER (J. Amer. Chem. Soc., 1931, **53**, 103—105; cf. La Mer and Goldman, A., 1929, 1387).—The solubility data for thallium and lanthanum iodates in 0·1N-solutions of the chlorides and sulphates of magnesium and cadmium at 25° show that the principle of specific interaction does not apply when cadmium chloride is concerned. J. G. A. GRIFFITHS.

Activity coefficient of copper iodate in aqueous salt solutions. B. H. PETERSON and E. L. MEYERS (J. Amer. Chem. Soc., 1930, **52**, 4853—4857; cf. La Mer and Goldman, A., 1929, 1387).—The solubility of copper iodate in aqueous solutions of the chlorides and sulphates of potassium and magnesium has been determined at 25°. The activity coefficients of copper iodate approach values given by the Debye–Hückel limiting law with increasing dilution of the salts. Positive deviations from this law are observed when solutions of potassium sulphate are used as solvent. J. G. A. GRIFFITHS.

Reduction of nitric acid by nitric oxide. I. Equilibrium. II. Electrochemical potential. H. BODE (Z. anorg. Chem., 1931, **195**, 195—200, 201—206).—I. From observations of the decrease in pressure of nitric oxide when confined over nitric acid the equilibrium constant of the reaction $H^{\cdot}+NO_3'+2NO+H_2O=3HNO_2$ is found to be 29·4 and 51 at 25° and 35°, respectively (cf. Klemenc and Hayek, A., 1930, 543).

II. From measurements of the *E.M.F.* of the cell $Pt|NO, HNO_2, HNO_3$ (in equilibrium)$|HCl|H_2(Pt)$ the normal potentials of the reactions $NO+NO_3'=2NO_2'+\oplus$ and $NO+2H_2O=NO_3'+4H^{\cdot}+3\ominus$ have been found to be 0·517+0·003 and 0·960 volt, respectively. R. CUTHILL.

Thermodynamic properties of molten solutions of lead chloride in lead bromide. E. J. SALSTROM and J. H. HILDEBRAND (J. Amer. Chem. Soc., 1930, **52**, 4641—4650).—The density at 500° of lead bromide, lead chloride, and mixtures of the two have been determined. The molal volumes are additive. The *E.M.F.* of the cell $Pb(l)|PbBr_2(l)+PbCl_2(c_1)|Br_2(g)$,graphite, where c_1, the molar fraction of lead chloride, is 0·0—0·55, has been determined between 438° and 584°. If c_1 is 0·6, or larger, the reaction $PbCl_2(l)+Br_2=PbBr_2(l)+Cl_2$ (ΔF_{773}, 11,090 g.-cal.) interferes. The free energy of dilution of lead bromide with lead chloride and the activity coefficients are calculated. If both salts are assumed to be un-ionised, the results correspond with negative deviations from Raoult's law. The assumption of complete ionisation leads to results corresponding with positive deviations. It is desirable to attempt to take into account changes in interionic forces. J. G. A. GRIFFITHS.

Thermodynamic properties of molten solutions of lithium bromide in silver bromide. E. J. SALSTROM and J. H. HILDEBRAND (J. Amer. Chem. Soc., 1930, **52**, 4650—4655).—Density data for the fused salts and mixtures are recorded. From the *E.M.F.* of the cell $Ag(s)|AgBr(l)+LiBr$(0·0—0·89 mol. fraction)$|Br_2(g)$,graphite, between 440° and 615° the energy changes of molten silver bromide on dilution with lithium bromide have been calculated and the free energy of formation of molten silver bromide is given by $\Delta F=-21{,}510+6{\cdot}7t$, where $t=440$—575°. The activity exhibits a large positive deviation from Raoult's law. J. G. A. GRIFFITHS.

Thermodynamic properties of solutions of molten lead chloride and zinc chloride. A. WACHTER and J. H. HILDEBRAND (J. Amer. Chem. Soc., 1930, **52**, 4655—4661; cf. A., 1927, 418).—Density data for the fused chlorides are recorded. From the *E.M.F.* of the cell $Pb(l)|PbCl_2(l)+ZnCl_2$(0·0—0·8 mol. fraction)$|Cl_2$ between 493° and 602° the free energy of dilution and activity coefficients have been calculated. The values correspond with negative deviations from Raoult's law and the assumption of either no ionisation or complete ionisation of both salts does not account for the results, which moreover are only partly explained by assuming that the lead chloride is ionised and the zinc chloride is not. The *E.M.F.* of the cells $Pb(l)|PbCl_2(l)|Cl_2$ and $Zn(l)|ZnCl_2(l)|Cl_2$ is $1{\cdot}2730-6{\cdot}25\times10^{-4}(t-500)$ and $1{\cdot}5725-6{\cdot}95\times10^{-4}(t-500)$ volts, respectively (cf. Lorenz and Velde, A., 1929, 1241). The heats and free energies of formation of the molten chlorides are calculated. J. G. A. GRIFFITHS.

Heats of dilution at 25° for certain uni-bivalent salts at high dilutions. I. Magnesium, calcium, strontium, and barium chlorides and

bromides. E. LANGE and H. STREECK (Z. physikal. Chem., 1931, **152**, 1—23; cf. A., 1930, 997).—The molecular heats of dilution V_m of a number of alkaline-earth halides have been determined at concentrations from 0·1 to 0·0001*M*, and the results, together with the differential heats of dilution, are presented graphically. The $V_m-\sqrt{m}$ curves are linear at concentrations up to 0·01*M*, and the deviations from the linear law at higher concentrations become still greater if V_m is plotted against $m^{\frac{1}{2}}$. The extrapolated initial slope ($m=0$), which is in accordance with the Debye–Hückel limiting law, is 6·7 times that obtained for uni-univalent salts. For all the compounds investigated the values of V_m at high dilutions almost coincide. The results are discussed in relation to the Debye–Hückel theory and to activity and osmotic coefficients. The values of *a* between 0·1 and 0·0001*M*, derived from the V_m curves, vary in the same order as the radii of the non-hydrated ions, but this is not true of the values derived from the osmotic and activity coefficients. The individual behaviour of these salts in comparable concentration ranges cannot therefore be elucidated in terms of specific values of *a*. Certain discrepancies observed at concentrations above 0·01*M* cannot be explained on the assumption either of incomplete ionisation or of a change of dielectric constant. H. F. GILLBE.

Binary systems. III. J. H. KOERS and F. E. C. SCHEFFER (Rec. trav. chim., 1931, **50**, 139—148).—A mathematical treatment of the crystallisation of a solid phase. E. S. HEDGES.

Phase equilibria in binary systems with continuous series of mixed crystals. E. KORDES (Z. physikal. Chem., 1931, **152**, 161—196; cf. A., 1927, 1132).—Equations formally similar to the author's empirical equation connecting the vapour pressures of a binary mixture with the composition of the liquid phase (A., 1929, 994) are found to express the composition of the liquid or solid phase in binary systems where a continuous series of mixed crystals is formed, the m. p. of the pure components and the temperature at which fusion or solidification begins being known. Curves and tables are given to show the agreement between experimental values and those given by the formula. The same formula can also be applied to isotropic-anisotropic transformations in the liquid state, as shown in mixtures of *p*-azoxyanisole and *p*-azoxyphenetole. Application of the formula to the system albite-anorthite leads to the conclusion, which is supported by thermal considerations, that albite is polymerised in the liquid state. The usefulness of the method in dealing with geochemical problems, and in fractional crystallisation, is discussed. F. L. USHER.

Tensiometric stabilisation of crystalline hydrates. M. AUMERAS (Compt. rend., 1931, **192**, 229—231).—Sodium sulphate decahydrate remains unchanged in a desiccator over sulphuric acid so dilute that the pressure of water vapour lies between the values for the vapour pressure of the saturated solution and the dissociation pressure of the decahydrate. C. A. SILBERRAD.

Hydrated calcium silicates. I. System CaO–SiO_2–H_2O. II. Hillebrandite and foshagite. V. A. VIGFUSSON (Amer. J. Sci., 1931, [v], **21**, 67—78).—I. Earlier work on the system CaO–SiO_2–H_2O is discussed.

II. *X*-Ray investigations of hillebrandite and foshagite show that the two are practically identical. Probably both have the same formula $2CaO,SiO_2,H_2O$, differences in the analyses being explicable by partial hydrolysis and carbonation of foshagite. C. W. GIBBY.

System MgO–FeO–Fe_2O_3 in air at one atm. [pressure]. H. S. ROBERTS and H. E. MERWIN (Amer. J. Sci., 1931, [v], **21**, 145—157).—The ternary system has been investigated at temperatures above 1000° and at 0·2 atm. oxygen pressure. In the system Fe_3O_4–Fe_2O_3 the stable phase at temperatures above 1386±5° is a hæmatite solid solution containing less oxygen than Fe_2O_3, whilst at the higher temperatures the stable phase consists of magnetite solid solutions containing more oxygen than Fe_3O_4. The only compound in the MgO–Fe_2O_3 system is MgO,Fe_2O_3, which dissociates somewhat on heating; the resultant solid solution begins to melt in air at 1750±25°. In the ternary system there are two solid solution fields, of which the first begins at MgO below 1000° and with rising temperature extends towards MgO,Fe_2O_3 and FeO; a liquid phase appears at 1770±25°, when the solid phase contains iron oxide equivalent to 73% Fe_2O_3. The second solid solution extends from MgO,Fe_2O_3 to the iron oxide boundary (1386±5°). There is probably little dissociation in either of the solid solutions up to 1770°. Solid solutions of about 1% MgO in MgO,Fe_2O_3 may exist at temperatures from 1750° to 1000° or lower. Differential heating curves appear to support the conclusion derived from *X*-ray diagrams, viz., that magnesium ferrite and magnetite are isomorphous. H. F. GILLBE.

System wollastonite–anorthite–pyroxene. L. KOCH (Neues Jahrb. Min., 1930, **A**, **61**, 277—320; Chem. Zentr., 1930, ii, 1684).—The system $CaSiO_3$–anorthite–diopside forms a ternary eutectic. A fourth substance corresponding with that present in slags from coal ash was not detected. A. A. ELDRIDGE.

System water–potassium nitrate–calcium nitrate. M. A. HAMID and R. DAS (J. Indian Chem. Soc., 1930, 7, 881—882).—The equilibrium diagram for the system has been constructed. E. S. HEDGES.

Polytherms of the ternary systems containing water, alkali sulphate, and a sulphate of the vitriol type. III. A. BENRATH (Z. anorg. Chem., 1931, **195**, 247—254; cf. A., 1930, 702).—The isotherms for the systems manganous sulphate–thallous sulphate–water and manganous sulphate–rubidium sulphate–water between 0° and 100° are described. Data for the 100° isotherm and various points on the 12·5° and 40° isotherms of the system manganous sulphate–ammonium sulphate–water are also recorded. R. CUTHILL.

Phase-rule studies on metallic thiocyanates. I. Systems $Ba(CNS)_2$–$NaCNS$–H_2O and $Ba(CNS)_2$–$KCNS$–H_2O at 25°. V. J. OCCLESHAW (J.C.S., 1931, 55—60).—The isotherms show the existence of the double *salt* $3KCNS,2Ba(CNS)_2,5H_2O$.

The solubilities of barium, sodium, and potassium thiocyanates are 62·61, 58·78, and 70·89 g. per 100 g. of solution, respectively. At 25° the stable form of sodium thiocyanate appears to be the dihydrate, and not the monohydrate as reported by Hughes and Mead (A., 1929, 1375). At about 30·3° the dihydrate passes into the anhydrous salt. R. CUTHILL.

Reaction between water vapour and sodium chloride at high temperature. S. BRETSZNAJDER (Rocz. Chem., 1930, **10**, 729—735).—Sodium chloride undergoes hydrolysis with the production of sodium hydroxide and hydrogen chloride on heating with water at 750° in a crucible lined with sodium chloride. The equilibrium constant of the reaction is approximately $1{\cdot}6\times10^{-7}$ at 750°. The hydrolysis is accelerated by the addition of dried silica gel, which combines with the sodium hydroxide produced. The analogous reaction with calcium chloride begins at a lower temperature. R. TRUSZKOWSKI.

Reversibility of reactions between sulphur dioxide and calcium oxide and between calcium sulphide and sulphate. J. ZAWADZKI and Z. SYRYCZYNSKI (Rocz. Chem., 1930, **10**, 715—728).—Direct determination of the free sulphur liberated in the reaction between calcium sulphide and sulphate and between sulphur dioxide and calcium oxide is not possible, owing to the formation of a suspension of sulphur in the reaction gases. Measurements of the partial sulphur dioxide pressure in the reaction $CaS+3CaSO_4$ $4CaO+4SO_2$ give values in accordance with theory, in spite of the fact that the reaction is not strictly reversible, as a result of the side-reaction $CaS+2SO_2\rightleftharpoons CaSO_4+S_2$. The thermal effect of the first reaction is $-238{\cdot}6$ g.-cal., and that of the second $+58{\cdot}9$ g.-cal. These values are in good agreement with those calculated from Nernst's theorem. R. TRUSZKOWSKI.

Equilibrium of the reciprocal system sodium chloride–magnesium sulphate in its application to natural salt waters. Conditions of formation of Glauber's salt at Karabugaz. N. S. KURNAKOV and S. F. SHEMTSCHUSHNI (Akad. Nauk, U.S.S.R., Material, 1930, **73**, 339—409).—The equilibrium diagram is characterised at 0° by four and at 25° by seven surfaces or fields of crystallisation. The diagram is in accord with conditions observed at Karabugaz and other salt lakes in Aralo-Caspian territory. CHEMICAL ABSTRACTS.

Solid-phase rule in the system cellulose–cuprammonium hydroxide–sodium hydroxide. I. SAKURADA (Kolloid-Z., 1931, **54**, 43—46).—The amount of cellulose dissolved by a mixture of cuprammonium hydroxide and sodium hydroxide increases at first with the concentration of the reagent, reaches a maximum, and falls at higher concentrations. This behaviour is in accordance with many other observations on the influence of the amount of solid phase on swelling and peptisation. E. S. HEDGES.

Heat of formation of cobaltous oxide. W. A. ROTH and H. HAVEKOSS (Z. anorg. Chem., 1931, **195**, 239—240).—By combustion of metallic cobalt the value of $57{\cdot}5\pm0{\cdot}2$ kg.-cal. has been obtained for the heat of formation of cobaltous oxide under constant pressure at 20°. R. CUTHILL.

Conductivity of electrolytes in nitromethane. C. P. WRIGHT, D. M. MURRAY-RUST, and (SIR) H. HARTLEY (J.C.S., 1931, 199—214).—The conductivities of various electrolytes in nitromethane solution have been measured at 25° and at concentrations of 0·0001—0·002N. With tetraethylammonium nitrate, perchlorate, picrate, iodide, and thiocyanate the graph obtained by plotting Λ_c, the equivalent conductivity at concentration c, against $\sqrt{c}$ is a straight line, the slope of which is in good agreement with the Debye–Hückel–Onsager equation. For lithium thiocyanate, perchlorate, and iodide, sodium thiocyanate and perchlorate, potassium thiocyanate and iodide, ammonium thiocyanate and perchlorate, thallium perchlorate, silver perchlorate, and perchloric acid, however, there are large deviations from the ideal behaviour, and it is found empirically that a straight line is obtained only by plotting Λ_c against $c^{2/3}$. Since these salts behave as strong electrolytes in methyl and ethyl alcohols, which have lower dielectric constants than nitromethane, it must be concluded that the association of ions is not determined solely by the electrical forces between them. It seems possible that hydroxylic solvents prevent association by forming sheaths round both anions and cations and that nitromethane, which has donor properties only, can attach itself by co-ordinate linkings only to the cation. This theory is supported by the observation that the increase in conductivity on addition of water to the solutions of the non-ideal electrolytes is far too great to be explained by change in dielectric constant. The mobility of the hydrogen ion in nitromethane is not abnormally high, as in hydroxylic solvents.

At 25° nitromethane has d 1·1312 and its viscosity is 0·00627; addition of water lowers the viscosity. The approximate mutual solubilities of nitromethane and water are: water in nitromethane, 2%; nitromethane in water, 10%. R. CUTHILL.

Conductivity of electrolytes in nitrobenzene. D. M. MURRAY-RUST, H. J. HADOW, and (SIR) H. HARTLEY (J.C.S., 1931, 215—219).—As an ionising solvent nitrobenzene is comparable with nitromethane, but there is a somewhat greater tendency to ionic association. At 25° and at concentrations of 0·0001—0·002N, tetraethylammonium picrate and perchlorate behave as strong electrolytes and obey the Debye–Hückel–Onsager equation, whereas silver perchlorate is only partly ionised, and perchloric acid occupies an intermediate position. Approximate measurements show that hydrogen chloride, benzenesulphonic acid, and trinitrobenzoic acid are only very slightly ionised at a concentration of about 0·01N. The mobility of the hydrogen ion in nitrobenzene is not abnormally high as it is in hydroxylic solvents. R. CUTHILL.

Conductivity and viscosity of solutions of lithium nitrate in binary alcoholic systems [at 25°]. J. L. WHITMAN and D. M. HURT (J. Amer. Chem. Soc., 1930, **52**, 4762—4770; cf. Whitman and Spencer, A., 1928, 957).—Viscosity and density data for the solvents water, ethyl, n-propyl, and *iso*propyl alcohols and their binary mixtures are recorded. The

conductivities of 0·0625—0·1*M* solutions of lithium nitrate in these solvents have been determined. The water–alcohol mixtures exhibit a maximum viscosity at some intermediate composition, but the conductivity–composition curves do not show minima. No maxima or minima occur in either the viscosity or conductivity curves for mixtures of two alcohols.

J. G. A. GRIFFITHS.

Relation between thermo-electric power, thermolysis, and ionic mobility in solid salts and mixed crystals. H. REINHOLD (Z. physikal. Chem., 1930, B, **11**, 321—341; cf. A., 1928, 846).—A discussion of experimental results published elsewhere. The treatment follows the lines laid down by Wagner (A., 1930, 1341) and Eastman (A., 1928, 365, 370). Thermodynamic analysis of the total thermo-electric effect in the system M|MX|M (where M denotes a metal and MX a conducting solid salt) enables the "homogeneous effect" due to the gradient of activity of the mobile ions along the temperature gradient to be calculated by difference. In the systems studied (halides of lead and silver, and silver sulphide, selenide, and telluride) the thermo-electric effect at the phase boundaries is small compared with the "homogeneous effect," except for salts with abnormally high conductivity. At present only a qualitative relation between "heat of transfer" and the temperature coefficient of mobility of the ions has been established. The former quantity is generally not identical with the heat of activation.

F. L. USHER.

Calculation of the electrical conductivity of the disperse phase of a suspension. A. SLAWINSKI (J. Chim. phys., 1930, **27**. 604—610; cf. A., 1929, 1142).—Two glass tubes of the same size, fitted with metal end-plates, are filled with the suspension and placed one horizontally and the other vertically; a third tube is filled with the disperse medium. The ratios of the conductivities of the contents of the tubes and the height of the deposit are measured after settling, and from the results the conductivity of the disperse phase may be calculated by use of the formulæ and tables which are given. The method is applicable to all suspensions which give uniform deposits.

H. F. GILLBE.

Cadmium-lead chloride voltaic cell. R. T. PRIEPKE and W. C. VOSBURGH (J. Amer. Chem. Soc., 1930, **52**, 4831—4837).—*E.M.F.* measurements between 17° and 40° are recorded. The *E.M.F.* of the cell $Cd(Hg)|CdCl_2,2·5H_2O(sat.)|CdCl_2,2·5H_2O(sat.), PbCl_2|Pb(Hg)$ in presence of solid cadmium chloride hemipentahydrate agrees with values given by Obata (Proc. Phys. Math. Soc. Japan, 1921, [3] **3**, 64, 136), but when cadmium chloride monohydrate is in true (above 34°) or metastable (below 34°) equilibrium with the electrolyte, the values of the *E.M.F.* agree with those recorded by Vosburgh (A., 1927, 1033). The *E.M.F.* of the cell $Cd(Hg)|CdCl_2,2·5H_2O(sat.)|CdCl_2,2·5H_2O(sat.),Hg_2Cl_2|Hg$ is 0·2 millivolt lower than that recorded by Lipscomb and Hulett (A., 1916, ii, 213). The transition point is 34° and not 26° (cf. Vosburgh, *loc. cit.*). The *E.M.F.* of the cell $Pb(Hg)|PbCl_2(sat.)|PbCl_2(sat.),Hg_2Cl_2|Hg$ agrees with values recorded by Gerke (A., 1922, ii, 682).

J. G. A. GRIFFITHS.

Temperature coefficients of certain reference electrodes. P. PUTZEYS (Bull. Soc. chim. Belg., 1930, **39**, 454—457).—The temperature coefficients of the potentials of the deci- and centi-normal hydrogen electrodes have been determined from measurements with cells of the type $Pt|H_2|0·1N\text{-}HCl(25·2°)|0·1N\text{-}HCl(T°)|H_2|Pt$ at a series of temperatures between 14° and 41°. The *E.M.F.* of the 0·1*N*-electrode is given by $E_T-E_{25}=0·334(T-25)+0·00279(T-25)^2$, and of the 0·01*N*-electrode by $E_T-E_{25}=0·391(T-25)+0·00335(T-25)^2$.

H. F. GILLBE.

Electrode potential and solvent: solvation activity coefficient. F. K. V. KOCH (Phil. Mag., 1931, [vii], **11**, 579—584).—Absolute normal potential may be regarded as the difference of two potentials, one dependent only on the solvent and the ion and the other dependent only on the element electrode and the ion. The Nernst electrolytic solution tension may be regarded as the distribution coefficient of the metal ion between the pure solvent and the element electrode and is thus equal to the ratio of two solvation activities. Values of the solvation potential have been calculated for a number of ions in water from the free energies of hydration. The solvation activity coefficient is defined as the factor by which the activity of solvated ions must be multiplied in order to give the electromotively equivalent activity of hydrated ions and is identical with the ionic distribution coefficient of the ion between two solvents when one solvent is water. The solvation activity coefficient is not only a function of the dielectric constant of the solvent, but depends also on specific intermolecular forces. The solvation of the electron is discussed.

E. S. HEDGES.

Potential of passive iron. A. TRAVERS and J. AUBERT (Compt. rend., 1931, **192**, 161—163).—A measure of the degree of passivity of iron is said to be given by the potential set up by immersion of a polished electrode of electrolytic iron in different media. In 1% aqueous sodium sulphate the *P.D.* (—0·73 volt) decreases as the alkalinity of the solution is increased, the iron becoming quite passive at p_H 14. Immersion in a series of oxidising solutions of various types gives potentials equal to those obtained with platinum and these are therefore characteristic of the medium. On removing and washing the iron its activity is completely regained. It is difficult to harmonise this behaviour with the "oxide film" theory of Evans (A., 1929, 270), and attempts to render the metal passive by oxidation with air or oxygen failed when tested by this method.

H. A. PIGGOTT.

Reduction potential of ceric-cerous electrode. A. H. KUNZ (J. Amer. Chem. Soc., 1931, **53**, 98—102).—From the *E.M.F.* data at 25°, for the cell $Pt,H_2|H_2SO_4(c_3)|H_2SO_4(c_3),Ce_2(SO_4)_3(c_1),Ce(SO_4)_2(c_2)|Pt$, where c_1+c_2 is 0·001—0·02*M*, c_2/c_1 is 0·1—18, and c_3 is 0·5 or 1·0 formal, the molal reduction potential of ceric and cerous sulphate in 1·0 formal sulphuric acid is found to be $-1·44\pm0·01$ volt.

J. G. A. GRIFFITHS.

Potentiometric study of acid-base titration systems in the very strongly acid solvent formic acid. L. P. HAMMETT and N. DIETZ, jun. (J. Amer.

Chem. Soc., 1930, **52**, 4795—4807).—Potentiometric titrations at 25° in formic acid solution have been made with cells of the type Au|quinhydrone, sodium benzenesulphonate (sat.), 0·098M|sodium formate| sodium benzenesulphonate (sat.)|base (c), quinhydrone|Au, where the solvent in each cell compartment is anhydrous formic acid. Quinhydrone reacts slowly with formic acid in the presence of benzenesulphonic acid and hence titrations are commenced in basic solution. In formic acid, benzene sulphonic acid is a strong acid, water and ether are very feeble bases, whilst sodium formate, triphenylcarbinol, and carbamide are strong bases. The complete ionisation of the last two demonstrates the extremely high degree of acidity which is attainable in formic acid as compared with acetic acid (cf. Conant and Werner, this vol., 40) and water. Titration data are given and it is shown that the ion product constant of formic acid is about 10^8 times that of water (cf. Schlesinger and others, A., 1919, ii, 91, etc.) and thus formic acid does not differ from water as much in basicity as in acidity. Large salt effects are absent and in this respect formic acid resembles water rather than acetic acid as a solvent (*loc. cit.*). J. G. A. GRIFFITHS.

Potential differences at air–liquid interfaces. J. W. WILLIAMS and V. A. VIGFUSSON (J. Physical Chem., 1931, **35**, 345—353).—The uncertainties involved in the measurement of interfacial potential differences are discussed. Many experimental difficulties must be overcome before such data can be used to calculate the electric moments of molecules. The results of an unsuccessful attempt to reproduce the data of other workers by the air ionisation method of Guyot and of Frumkin are recorded and discussed. With this method, the potential varies with the distance of the radioactive electrode from the liquid surface. A temperature effect appears to exist.

L. S. THEOBALD.

Explanation of the electro-capillary Becquerel effect. H. FREUNDLICH and K. SOLLNER (Z. physikal. Chem., 1931, **152**, 313—314).—A correction of an error in an earlier paper (A., 1929, 145). The only condition for the separation of metal is a positive value of the decomposition potential, and an impressed *E.M.F.* is not required. F. L. USHER.

Dependence of yield on temperature. E. N. GAPON (Ukraine Chem. J., 1930, **5**, [Sci.], 165—168).—The following expressions are derived from the kinetic equations of velocity of reaction : $\log\log A/(A-x)=a_1-b_1/T$ for unimolecular, and $\log x/(A-x)=a_2-$ for bimolecular reactions, in which x represents the yield of products per minute, A is the initial concentration of substrates, T the absolute temperature, and a and b are constants.

R. TRUSZKOWSKI.

Relation between energy of activation and the constant S of Arrhenius' equation. E. N. GAPON (Ukraine Chem. J., 1930, 5, [Sci.], 169—180).—The expressions $\log S=\log K_i-E/RT_i$, $\log K_i=\log\psi+\phi/RT_i$, and $K_i=\psi e^{-\psi/RT_i+E/RT_i-E/RT}$ are derived, in which S is Arrhenius' constant, T_i is the temperature at which the velocity coefficients K_i of a given group of reactions possess the same value, E is the energy of activation, and and ϕ are characteristic constants for all reactions. The above expressions apply to unimolecular reactions.

R. TRUSZKOWSKI.

Uniform propagation of flame. N. R. SEN and H. K. SEN (Nature, 1931, **127**, 125—126).—Mathematical analysis shows initial uniform flame propagation to be possible provided that pressure plays no part during the short interval concerned. The condition for uniform propagation is $\theta=aQ/\rho C$, where θ is the ignition temperature, ρ is the density of the inflammable mixture, C is the specific heat, and aQ is the fraction of the total heat of combustion which is utilised for conduction. The average flame temperature is twice that of ignition of the mixture, a relation which receives support from the experimental data of Dixon and McDavid. L. S. THEOBALD.

Propagation of flame in electric fields. I. Distortion of the flame surface. E. M. GUENAULT and R. V. WHEELER (J.C.S., 1931, 195—199).—The influence of an electric field on the movement of the flame in mixtures of carbon monoxide and oxygen ignited at the centre of a glass vessel has been studied photographically. When the flame surface is between the plates of a charged condenser not only is there no evidence of movement of the flame caused by travel of the flame electrons towards the positive plate, but, on the contrary, there is a movement bodily towards the negative plate. The effect is probably mechanical and due to the positive ions carrying the flame with them rather than to an effect on the chemical reactions in the flame. H. F. GILLBE.

Radiation from the cyanogen–oxygen flame. K. TAWADA (J. Soc. Chem. Ind. Japan, 1930, **33**, 504—506B).—The total radiation from the explosion of cyanogen–oxygen mixtures was measured (cf. Garner and Tawada, A., 1930, 263). The reduction in radiation caused by the addition of water or hydrogen is distinctly shown; the effect is about the same in amount for either, and increases with increase of initial pressure. Addition of hydrogen or water appears also to alter the reaction velocity, since explosion of wet mixtures is audible at pressures above 30 cm., whilst the explosion of dry mixture is inaudible. When more than 46% of cyanogen is present water seems to prevent liberation of carbon and consequently to reduce "black body" radiation; in the presence of excess of oxygen the reduced radiation is considered to be due partly to lowering of the flame temperature and partly to the analogous procedure occurring in the carbon monoxide flame. Only qualitative information was obtained by measuring the persistence of ionisation phenomena.

E. LEWKOWITSCH.

Kinetics of the acetylene–oxygen reaction. R. SPENCE and G. B. KISTIAKOWSKY (J. Amer. Chem. Soc., 1930, **52**, 4837—4847; cf. A., 1930, 1528).—The intermediate compounds glyoxal, formaldehyde, and formic acid have been isolated by means of a circulating method. At 320°, the rate of reaction is accelerated or slightly retarded by oxygen according as acetylene or oxygen is in excess. When the concentration of oxygen is less than optimal, the rate of reaction is proportional to a power of the acetylene concentration less than two. Nitrogen has a very

slight retarding effect. From determinations of the temperature coefficient the energy of activation is computed to be 34,700 g.-cal. at 320°. The mechanism of the reaction is discussed.

J. G. A. GRIFFITHS.

Effect of intensive drying on the velocity of gaseous reactions. C. C. COFFIN and O. MAASS (Canad. J. Res., 1930, 3, 540—542).—Intensively dried gaseous ammonia and carbon dioxide do not react, but on liquefaction immediate combination takes place. This observation supports the view previously put forward, viz., that the liquid state is in itself a catalytic factor, and it is suggested that the effect of intensive drying is due to removal of all traces of the liquid phase rather than to the removal of water. H. F. GILLBE.

Velocity of reaction of sodium with halogen hydrides. H. VON HARTEL (Z. physikal. Chem., 1930, B, 11, 316—320; cf. Schay, this vol., 282).—The velocities of the reaction of highly-diluted sodium vapour with hydrogen chloride, bromide, and iodide have been measured by determining, by means of a sodium resonance lamp, the distribution of sodium vapour in the reaction zone. With hydrogen iodide every collision is effective, with the bromide 1 in 6, and with the chloride 1 in 86. The respective heats of activation calculated from the Arrhenius–Trautz relationship are 200, 1900, and 4500 g.-cal. For the reaction with hydrogen chloride the heat of activation was also calculated, from the measured increase in velocity caused by raising the temperature of the reaction tube, to be 6200 g.-cal. Thus the heats of activation are nearly completely determined by the respective negative heats of reaction.

F. L. USHER.

Attempt to measure velocity of dissociation of nitrogen tetroxide by the method of sound waves. G. B. KISTIAKOWSKY and W. T. RICHARDS (J. Amer. Chem. Soc., 1930, 52, 4661—4671).—The velocity of sound at 25° in nitrogen tetroxide at pressures between 760 and 140 mm. is, within the experimental error of 0·5%, independent of frequencies between 10 and 80 kilocycles per sec. It is shown that these results indicate a minimum value ($2 \cdot 5 \times 10^4$) of the velocity coefficient of the dissociation of nitrogen tetroxide not greatly less than the maximum velocity coefficient deduced from the kinetic theory, assuming that the activation of a nitrogen tetroxide molecule involves a large number of degrees of freedom.

J. G. A. GRIFFITHS.

Kinetics of the polymerisation of vinyl acetate. H. W. STARKWEATHER and G. B. TAYLOR (J. Amer. Chem. Soc., 1930, 52, 4708—4714; cf. Whitby and others, A., 1928, 1186).—The velocity of polymerisation of vinyl acetate has been determined dilatometrically at 82°, 101°, and 111°. The polymerisation of vacuum-distilled vinyl acetate follows a unimolecular law and is probably a chain reaction. The temperature coefficient is 2·7 per 10° and the heat of activation is 25,000 g.-cal. The velocity coefficient falls rapidly during the reaction in toluene, but benzoyl peroxide catalyses the reaction and is destroyed in the process. Sulphur is a negative catalyst. J. G. A. GRIFFITHS.

Permanganate decomposition in alkaline media. [Manganese dioxide gel.] R. H. FERGUSON, W. LERCH, and J. E. DAY (J. Amer. Chem. Soc., 1931, 53, 126—137).—The interaction at 50°, 75°, and 95° of sodium and potassium permanganates with the corresponding hydroxides at various concentrations, up to 6N, has been investigated, solutions of the pure substances being employed. No decrease of available oxygen (determined by titration in acid solution) seems to occur when the concentration of alkali is below certain limiting values, but greater concentrations lead to a diminution of the minimum towards which the available oxygen slowly approaches. Rise of temperature accelerates the reaction, and, in general, the final minimum of available oxygen in a solution of given alkalinity diminishes with rise of temperature. The products of the reaction are oxygen and the manganates of the metals. No precipitated or colloidal manganese dioxide could be detected, and the initial presence of this substance brings about a comparatively rapid decomposition of the permanganate to manganese dioxide. The reaction is probably bimolecular, and whilst at 50° and 75° it is accounted for by the equation $4MnO_4' + 4OH' \longrightarrow 4MnO_4'' + 2H_2O + O_2$, more available oxygen than is thus indicated is lost at 95°; the results are explained if the existence of a continuous series of soluble double salts or oxides of manganese and the alkali metal is assumed. Manganese dioxide gel is obtained by diluting 400 c.c. of the dark green alkali–permanganate reaction mixture with 100 c.c. of water and evaporating the product.

J. G. A. GRIFFITHS.

Kinetics of reaction between persulphate and thiosulphate ions in dilute aqueous solution. C. V. KING and O. F. STEINBACH (J. Amer. Chem. Soc., 1930, 52, 4779—4795; cf. Schwicker, A., 1928, 1107).—The velocity of the reaction $S_2O_8'' + 2S_2O_3'' = 2SO_4'' + S_4O_6''$ in aqueous solution is very sensitive to impurities. The reaction is unimolecular with respect to persulphate and almost independent of concentration of thiosulphate. The salt effect is large and positive, and indicates that the velocity is determined by reaction between two negative ions. From determinations of the catalytic effect of iodide ions the bimolecular constant of the persulphate–iodide reaction is calculated (cf. Jette and King, A., 1929, 771; Kiss, *ibid.*, 772). Copper has a very large catalytic effect and the results are taken to indicate that oxidation of the negative cuprous ion–thiosulphate complex (produced from cupric ion by reduction with thiosulphate) to cupric ion by persulphate is bimolecular. As compared with copper, iron has a smaller and silver a very small catalytic effect. Sucrose catalyses the persulphate–thiosulphate and the persulphate–iodide reactions (cf. Kiss and Hatz, A., 1929, 271). J. G. A. GRIFFITHS.

Velocity of decomposition of carbonatotetramminocobaltic ion and its dependence on hydrogen-ion concentration. K. J. PEDERSEN (J. Amer. Chem. Soc., 1931, 53, 18—30).—The kinetics of the reaction $[Co(NH_3)_4CO_3]^{\cdot} + 2H^{\cdot} + H_2O \longrightarrow [Co(NH_3)_4(H_2O)_2]^{\cdot\cdot\cdot} + CO_2$ have been investigated at 25° in 0·01M-solutions at various hydrogen-

ion concentrations by means of the pressure of carbon dioxide developed. In glycollate buffers the decomposition proceeds almost to completion, whilst in some of the acetate buffers employed the reaction is balanced and appears to involve several consecutive reactions. There is a positive neutral salt effect, but no general acid catalysis. Provided that the pressure of carbon dioxide is low and the hydrogen-ion concentration is not too small, the velocity may be expressed as the sum of two terms, one being proportional to and the other independent of the hydrogen-ion concentration. J. G. A. GRIFFITHS.

Molecular attractive forces and the velocity of chemical reactions. C. C. COFFIN and O. MAASS (Canad. J. Res., 1930, **3**, 526—539).—In the liquid state Δ^{γ}-butylene reacts readily with hydrogen chloride, the α-isomeride much more slowly, and the β-isomeride very slowly. The initial velocity is with the α- and β-compounds greater than with propylene, but as the hydrogen chloride concentration diminishes the velocity falls more rapidly; the reaction does not proceed to completion, on account of polymerisation of the hydrocarbon. In presence of an excess (2 mols.) of hydrogen chloride the reaction time is reduced to 0·07—0·1 of its normal value, and the acceleration is a linear function of the acid concentration. With Δ^{γ}-butylene the reaction is practically instantaneous at 0° and requires only 1 min. for completion at −78°. In the case of Δ^{β}-butylene an excess of the hydrocarbon also accelerates the reaction to a small extent. The products of the reaction, which is homogeneous, are from Δ^{α}-butylene *sec.*-butyl chloride with about 25% of a mixture of octyl chloride and octylene, from Δ^{β}-butylene about 65% of *sec.*-butyl chloride, and from the γ-isomeride almost pure *tert.*-butyl chloride, m.p. −26·5°. The f.-p. curve of hydrogen chloride–Δ^{β}-butylene mixtures indicates the formation of an equimolecular compound. In the gaseous state only the γ-isomeride reacts with hydrogen chloride, the reaction being bimolecular and heterogeneous. The results, which are discussed from the point of view of the influence of molecular attraction on reaction velocity, support the view previously put forward, and suggest that in the liquid state there exists a catalytic factor due possibly to the state of molecular strain caused by the proximity of other molecules or to the existence of orientation resulting from the mutual attractions of polar molecules. H. F. GILLBE.

Effect of sulphur trioxide on decomposition of oxalic acid by sulphuric acid. E. O. WIIG (J. Amer. Chem. Soc., 1930, **52**, 4737—4741; cf. Lichty, A., 1907, ii, 445).—The rate of decomposition of oxalic acid in sulphuric acid containing 0—30% of free sulphur trioxide has been investigated at 15° and 25°. The rate of decomposition increases at first rapidly and then more slowly with increasing concentration of sulphur trioxide until a maximum is attained in acid containing approximately 14% of sulphur trioxide. The results, including the existence of a maximum velocity, when considered in conjunction with the equilibrium $H_2SO_4 \rightleftharpoons H_2O + SO_3$, indicate that water is a powerful anticatalyst, whilst sulphur trioxide is relatively very weak. J. G. A. GRIFFITHS.

Decomposition of citric acid by sulphuric acid. E. O. WIIG (J. Amer. Chem. Soc., 1930, **52**, 4729—4737).—The velocity of decomposition of citric acid at 15°, 25°, and 35° by sulphuric acid containing 0—5% of water and 0—1·5% of sulphur trioxide has been measured by the rate of evolution of carbon monoxide. The reaction is quantitative, homogeneous, follows the unimolecular law, and is retarded very strongly by sulphur trioxide and by the products (acetonedicarboxylic acid and water). As the concentration of water is decreased, the rate of reaction rises to a maximum, varying with the temperature, and on further removal of water the rate decreases. The existence of a maximum is explained on the view that sulphur trioxide is a stronger inhibitor than water, taken in conjunction with the existence of the equilibrium H_2SO_4—$H_2O + SO_3$. The temperature coefficient per 10° ranges between 3·5 and 4·4 and increases as the water content of the sulphuric acid is increased. The reaction is considered to proceed by way of an unstable citric acid–sulphuric acid complex which is stabilised by water.
J. G. A. GRIFFITHS.

Mechanism of the decomposition of chlorohydrin by alkali. L. SMITH [with N. T. HOLM and B. SVENONIUS] (Z. physikal. Chem., 1931, **152**, 153—156).—The reaction between chlorohydrins and alkali is bimolecular; previous reports to the contrary are ascribed to the use of mixtures of isomerides having different decomposition velocities, and to the influence of atmospheric carbon dioxide, the volatility of the chlorohydrin, and the presence of non-hydrolysable impurities. The velocity coefficients of the hydrolysis of ethylene chlorohydrin (25°) and propylene chlorohydrin (18°) are 0·62—0·68 and 6·49—6·52, respectively. H. F. GILLBE.

Kinetics of the formation of malonamide from ethyl malonate and ammonia in homogeneous solution. Reaction of the third order. K. C. BAILEY (Proc. Roy. Irish Acad., 1930, 39*B*, 567—573).—In homogeneous solution in ethyl alcohol–water mixtures at temperatures between 0° and 33·8° the reaction between ethyl malonate and ammonia is homogeneous and termolecular, and when the solvent medium contains 44·5% of alcohol has a velocity coefficient of 0·0311 at 0°; the temperature coefficient of the velocity is 1·68—1·70. By increasing the alcohol content of the solvent to 73% the velocity coefficient falls to less than one sixth of its previous value, but the reaction is still termolecular; this effect is probably due to the formation of a molecular compound. Although ethyl alcohol is one of the products of the reaction the velocity rises during the later stages of the reaction; the reason is obscure.
H. F. GILLBE.

Chemical kinetics in mixed solvents. VIII. Velocity of formation of tetra-substituted ammonium salts in mixtures of acetone and chloroform. G. E. MUCHIN and R. B. GINSBURG (Ukraine Chem. J., 1930, **5**, [Sci.], 147—158).—The values of the velocity coefficient of reactions between allyl bromide and pyridine or dimethylaniline are higher in mixtures of acetone and chloroform than those calculated for each solvent separately. The deviation of K may

amount to 50%, and is greater at higher than at lower temperatures. R. TRUSZKOWSKI.

Chemical kinetics in mixed solvents. IX. G. E. MUCHIN and R. I. BARANOVA (Ukraine Chem. J., 1930, **5**, [Sci.], 159—163).—The velocity of reaction at 35° and 45° of pyridine and allyl bromide dissolved in various esters varies inversely with the mol. wt. of the solvent for esters of the same homologous series. K is greatest in methyl salicylate, in which both the benzene nucleus and the hydroxyl group appear to activate the reaction. R. TRUSZKOWSKI.

Velocity measurements on the opening of the furan ring in hydroxymethylfurfuraldehyde. II. H. P. TEUNISSEN (Rec. trav. chim., 1931, **50**, 1—20).—The velocity of hydrolysis of hydroxymethylfurfuraldehyde into formic and lævulic acids has been determined by methods similar to those previously employed (A., 1930, 1256) in various mixtures of water and ethyl or methyl alcohol in the presence of $0{\cdot}5N$-hydrochloric acid at 100° (sealed tubes) and at the b. p. of the mixtures. The value of the pseudo-unimolecular coefficient $k\times10^3$ in 10, 15, 25, 35, 50, and 75% alcohol at 100° is 1·39, 1·31, 0·90, 0·55, 0·22, and ±0, respectively, and in 10, 20, 30, and 40% methyl alcohol it is 1·11, 0·63, 0·20, and ±0, respectively. The amount of humin produced decreases as the concentration of alcohol is increased. In aqueous ethyl alcohol the temperature coefficient of the reaction between 90° and 100° is 2·0. Although hydrolysis no longer occurs in 40% methyl alcohol, evidence of alcoholysis is found in the increasing amounts of iodoform obtained by the action of iodine and potassium hydroxide as the heating is continued. An unidentified p-nitrophenylhydrazone, m. p. 125—130°, was obtained from the reaction product. Hydrolysis of a 1% solution of furfuryl alcohol into lævulic acid in the presence of 0·1, 0·05, and $0{\cdot}02N$-hydrochloric acid and 0·4 and $0{\cdot}02N$-oxalic acid was similarly investigated, but in all cases large amounts of resinous products are obtained and hence the unimolecular coefficient decreases rapidly as the reaction proceeds, whilst the yield of lævulic acid never exceeds 40—50%. Furfuryl alcohol is hydrolysed by water alone at 100°. J. W. BAKER.

Denaturation of proteins. VII. Denaturation in the presence of alcohol. N. BOOTH (Biochem. J., 1930, **24**, 1699—1705).—The unimolecular velocity coefficients of the denaturation of hæmoglobin increase with increasing alcohol content under otherwise similar conditions. The minimum point of the p_H-velocity curve is shifted considerably from the neutrality point of water to the acid side by addition of alcohol, and becomes more abrupt on the side of lower than on that of greater p_H values. The critical increment of activation increases appreciably with the amount of alcohol present. The magnitude of the critical increment is inversely proportional both to the dielectric constant of the medium and to the percentage of water present. S. S. ZILVA.

Electromotive activation of oxygen. [Oxidation of ferrous sulphate.] A. B. LAMB and L. W. ELDER, jun. (J. Amer. Chem. Soc., 1931, **53**, 137—163).—The kinetics of the oxidation of ferrous sulphate (chiefly $0{\cdot}15M$) solutions at 30° by air have been investigated in relation to the catalytic effects of various substances. The progress of oxidation in the solution is determined from the potential of a bright platinum electrode which is calibrated empirically. The velocity of oxidation is independent of the rate of stirring (1250 r.p.m.) if the oxygen is absorbed at a rate less than 0·01 equivalent per litre per hr. The reaction is approximately unimolecular with respect to oxygen and bimolecular with respect to ferrous sulphate; the velocity is almost independent of concentration of sulphuric acid between $3M$ and $0{\cdot}1M$, but increases rapidly with further progressive decrease of acidity. Of the metallic ions investigated, chromic has a slight retarding action and cupric a catalytic effect which increases greatly with progressive increase of acidity. $0{\cdot}023M$-Sodium pyrophosphate increases the rate of oxidation by about 1000 times, but the actual velocity is markedly dependent on the rate of stirring (cf. Smith and Spoehr, A., 1926, 249). The oxidation potential of this solution is low. Equally large catalytic effects are produced by sufficient ground steam-activated coconut charcoal and by platinum-black; silica gel is inactive in comparison. The effect of charcoal is approximately proportional to the weight added and is maximal in solutions 0·5—$1M$ with respect to sulphuric acid; in these liquids copper sulphate has little effect. Potassium ferrocyanide in neutral solution is oxidised by air about half as rapidly as corresponding solutions of ferrous sulphate in 0·01—$3{\cdot}0M$-sulphuric acid; copper salts have negligible catalytic action.

In confirmation of the view that the catalysis is due to the formation of specific peroxides, minute quantities of such a substance have been extracted from aerated charcoal by means of sulphuric acid—the greatest activity being manifest in M-acid; further, the catalysis by copper sulphate or charcoal is depressed by traces of amyl alcohol etc.

From direct measurements of the depolarising action of the acid solutions of ferrous sulphate containing charcoal, it is found that electrodes utilising these solutions possess great advantages as compared with the oxygen electrodes previously investigated at the ordinary temperature (cf. Hofmann, A., 1919, ii, 8; von Náray-Szabó, A., 1927, 208). J. G. A. GRIFFITHS.

Kinetics of heterogeneous formation of formate. G. BIRSTEIN and N. LOBANOV (Z. anorg. Chem., 1931, **195**, 173—194; cf. A., 1927, 319).—In the reaction between formaldehyde and sodium hydroxide in aqueous solution in presence of cupric oxide the primary reaction is $H{\cdot}CHO+NaOH=H{\cdot}CO_2Na+2H$, half the hydrogen being used up in reducing the copper oxide to copper and the remainder being liberated as gas. The reaction exhibits a period of induction due to the autocatalytic effect of the copper formed. When the reactants are present in equivalent amounts the rate of the reaction may be represented by the equation $dx'/dt=ka^{4/3}x'(1-x')^{4/3}$, where x' is the quotient of the amount which has reacted in time t by a, the initial concentration, and the temperature coefficient is comparable with that of a normal chemical reaction. If, however, either reactant is present in excess, the velocity equation is

$dx'/dt-kax'(1-x')$, the velocity coefficient, k, diminishing with increase in the concentration of the reactant present in excess. The former equation can be deduced by combining the usual equation for the velocity of a homogeneous bimolecular equation with the adsorption isotherm, and it is believed that the seat of reaction is the surface of the solid phase. When formaldehyde and sodium hydroxide react in presence of copper prepared by reducing cupric oxide with formaldehyde and alkali, the reaction is $2H\cdot CHO+NaOH=H\cdot CO_2Na+MeOH$, but is kinetically bimolecular, probably because adsorption processes still play an important part. R. CUTHILL.

Photography of waves and vortices produced by the discharge of an explosive. D. B. GAWTHROP, W. C. F. SHEPHERD, and G. ST. J. PERROTT (J. Franklin Inst., 1931, **211**, 67—86).—Photographic records have been made, by the Schlieren method, of the shock waves and other disturbances sent out by the detonation of small charges of explosive fired in the open and at one end of cellophane tubes. The "wave-speed" camera of Payman and Shepherd (Safety in Mines Res. Bd., Paper 29, 1926) was used. The spherical shock wave has a high initial speed, which, however, falls rapidly, so that the wave is soon overtaken by solid particles scattered by the explosion. The plane shock wave sent along a tube, when the explosive is confined at one end, maintains its high initial speed for some time. On emerging from the tube the plane wave changes to a spherical wave and gives rise to a vortex ring, which travels more slowly. J. LEWKOWITSCH.

Theory of combustion of colloidal powders in a closed vessel. H. MURAOUR (Compt. rend., 1931, **192**, 227—229).—The theory supposes that the powder burns because its temperature is raised to that of its decomposition by the shock of the gaseous molecules already given off, and that the temperature of the layer immediately in contact with the powder, and in which combustion is incomplete, is lower than that of explosion. The temperature rises with the more complete combustion at increased distance from the surface of the powder. At high pressures layers of gas parallel to such surface do not intermix, owing to their high density, but do so at lower pressures, thus increasing in this case the temperature of the layer at the surface of the powder. Hence the increased velocity of combustion at low densities of loading. Other deductions are drawn, and shown to be in accord with the author's experimental results (cf. A., 1930, 1530; B., 1930, 442).

C. A. SILBERRAD.

Evaluating results of corrosion tests of ferrous metals. K. PITSCHNER.—See B., 1931, 160.

Initial corrosion rate of steels. H. O. FORREST, B. E. ROETHELI and R. H. BROWN.—See B., 1931, 116.

Adsorption and promoter action in catalysis. A. C. ROBERTSON (J. Amer. Chem. Soc., 1931, **53**, 382—383; cf. Elissafoff, A., 1915, ii, 681).—Investigations of the decomposition in quartz vessels of hydrogen peroxide in the presence of copper sulphate and glass wool indicate that a tenfold increase of glass wool increases the rate very little, and a filtered extract of the glass wool is as catalytically active as the solid material. It is considered that the reaction is probably homogeneous in the absence of glass wool and that the mechanism is different under "promotion" conditions. The reaction cannot be regarded as an example of the effect of adsorption on catalytic reaction rates (cf. Rudel and Haring, B., 1931, 110).

J. G. A. GRIFFITHS.

Catalytic decomposition of hydrogen peroxide by acetates. M. O. CHARMANDARIAN and E. A. ALEXEEVA (J. Russ. Phys. Chem. Soc., 1930, **62**, 1677—1683).—Nickel sulphate and acetate do not catalyse the decomposition of hydrogen peroxide, chromic sulphate and acetate and manganese and copper sulphates have a feeble effect, cobaltous sulphate and manganous and lead acetates a slightly greater effect, and cupric and cobaltous acetates exert a powerful catalytic influence which appears in the case of copper salts to depend on the presence of ionic copper. R. TRUSZKOWSKI.

Inhibition in decomposition of organic acids by sulphuric acid. E. O. WIIG (J. Amer. Chem. Soc., 1930, **52**, 4742—4751).—Available data of the reactions of sulphuric acid with oxalic (Bredig and Lichty, A., 1906, ii, 602; Wiig, this vol., 315), formic (Schierz, A., 1923, ii, 230), malic (Whitford, A., 1925, ii, 559; Dittmar, A., 1930, 1131), *o*-benzoylbenzoic (Gleason and Dougherty, A., 1929, 318), triphenylacetic (Dittmar, A., 1929, 656), and citric acid (Wiig, *loc. cit.*) are considered. In all cases the inhibiting effect of water is an exponential function of the concentration of the inhibitor. In the three cases fully examined, maximal velocities are obtained when the sulphuric acid contains specific concentrations of water or sulphur trioxide, the latter also being an inhibitor. In general, the addition of an inhibitor increases the temperature coefficient, which is increased by increasing concentrations of the inhibitor. The mechanisms of the decompositions are discussed in relation to Taylor's theory (A., 1923, ii, 399).

J. G. A. GRIFFITHS.

Effect of copper and lead ions on the rate of decomposition of hydrogen peroxide at various acidities. H. W. RUDEL and M. M. HARING.—See B., 1931, 110.

Catalytic oxidation of carbon monoxide. J. C. W. FRAZER (J. Physical Chem., 1931, **35**, 405—411).—A *résumé* of previous results on the catalytic oxidation of carbon monoxide by means of oxides specially prepared to be free from impurities which poison the surface. The high catalytic activity of these purified oxides is attributed to their indefinite composition and to the ease with which oxygen can be taken up or released according to conditions.

L. S. THEOBALD.

Photo-electric properties of ammonia catalysts. A. K. BREWER (J. Amer. Chem. Soc., 1931, **53**, 74—83; cf. Kunsman, A., 1927, 603).—The photo-electric properties of reduced magnetite, alone and promoted by aluminium and potassium oxides, have been investigated in a vacuum, and in the presence of nitrogen, hydrogen, and traces of oxygen, at temperatures up to 700°. The unpromoted iron catalyst has the same photo-electric threshold as electrolytic iron;

neither has a temperature coefficient. The presence of gases had only small effects. The catalyst promoted with 1·3% of aluminium oxide has similar properties, thus indicating that the surface contains a very low concentration of aluminium oxide and no metallic aluminium. The photo-electric emissivity of the catalyst containing 0·2% of potassium oxide, alone or in addition to alumina, increases to a maximum at about 300°, followed by a minimum at about 450°, and thereafter increases rapidly with rise of temperature. When the temperature is lowered, the minimum at 450° almost disappears. Nitrogen and hydrogen increase the emissivity; oxygen has a pronounced depressing action. When the temperature is raised, the photo-electric thresholds extend towards the red, and the results point to the dissociation of potassium oxide at elevated temperatures and the sparse distribution of metallic potassium over the surface, the ratio of free to total potassium being greatly diminished by the presence of alumina. It is suggested that whilst the photo-electric properties of the doubly-promoted catalyst are due to the potassium oxide which remains uncombined with the alumina, the catalytic properties are due to $K_2Al_2O_4$, which more than offsets the anti-catalytic effects of potassium oxide alone. J. G. A. GRIFFITHS.

Dissociation of gypsum in presence of catalysts. J. E. ADADUROV D. E. DERIBAS, and P. Y. KRAINI (J. Appl. Chem., Russia, 1930, 3, 509—531).—By proper choice of catalyst the yield of sulphur trioxide at 600° can be raised from 0·18 to 25·85%, whilst that of sulphur dioxide is reduced to 0·54% (with manganese dioxide as catalyst). Numerous catalysts were employed. The results are in accord with the resonance theory of catalysis. When the wave-length of an element is identical with that of the catalysed substance the element is a catalyst. The catalytic activity diminishes with increase in the wave-length. There is a minimum temperature for activity at each wave-length. CHEMICAL ABSTRACTS.

Reaction between metallic magnesium and aqueous chloride solutions. I. IITAKA (Proc. Imp. Acad. Tokyo, 1930, 6, 363—366).—Magnesium is attacked rapidly by $0·01M$-sodium chloride solutions at $p_H<4$; at higher p_H values the reaction is very slow. F. J. WILKINS.

Catalysis of reactions between solids. II. Reaction mechanism of the catalytic formation of stannate. S. TAMARU and N. ANDÔ (Z. anorg. Chem., 1931, 195, 309—320; cf. A., 1930, 171).—The equilibrium constants of the following reactions have been determined at 900°: $CaSnO_3+CaO+H_2O=Ca_2SnO_4+H_2$, p_{H_2}/p_{H_2O}, 1·98; $CaSnO_3+H_2=CaO+Sn+H_2O$, p_H/p_{H_2O}, 1·98; $Ca_2SnO_4+CO=CaSnO_3+CaO+CO_2$, p_{CO}/p_{CO_2}, 5, approximately. It is considered that the action of hydrogen in catalysing the formation of stannate from stannic oxide and lime is to be attributed to the consecutive reactions $SnO_2+H_2=SnO+H_2O$, $SnO+CaO=CaSnO_2$, and $CaSnO_2+H_2O+CaO=Ca_2SnO_4+H_2$, the further reaction $CaSnO_3+H_2=CaO+Sn+H_2O$ finally setting in when the formation of stannate is complete. A convenient method of opening up cassiterite consists in converting it into stannate by heating with excess of lime in a reducing atmosphere. R. CUTHILL.

Adsorption catalysis. M. BORN and J. FRANCK (Nachr. Ges. Wiss. Gottingen, 1930, 77—89; Chem. Zentr., 1930, ii, 1654).—A discussion of the part played in adsorption catalysis by the fact that a protracted association between the reaction partners is established, with particular reference to the reaction $2H_2+N_2=N_2H_4$. A. A. ELDRIDGE.

Catalytic researches with a high-pressure circulating apparatus. E. BERL and R. BEMMANN (Z. angew. Chem., 1931, 44, 34—39).—An apparatus for carrying out catalytic reactions with gas mixtures at high temperatures and pressures is described; the gas can be continuously circulated through the hot catalyst and the liquid products of the reaction continuously condensed and removed under a constant high pressure. Treatment of water-gas in the apparatus, using a zinc oxide catalyst free from alkali, results in the production of methyl alcohol of high quality, whereas when a catalyst containing alkali is used a complex mixture of higher alcohols, acids, aldehydes, and other compounds is obtained. These results are obtained only when the gas mixture is circulated rapidly through the catalyst; slow circulation induces the reaction to proceed more nearly towards completion, and methane and carbon dioxide are the chief products. The presence of sulphur in the gas mixture reduces the activity of the catalyst and promotes the more rapid formation of the end products of the reaction. A. R. POWELL.

Electrodeposition of chromium. J. W. CUTHBERTSON.—See B., 1931, 162.

Heat-treatment of chromium deposits to increase their resistance to corrosion. R. J. WIRSHING.—See B., 1931, 162.

Electrodeposition of chromium–iron alloy. G. FUSEYA and K. SASAKI.—See B., 1931, 118.

Electrodeposition of lead–thallium alloys. C. G. FINK and C. K. CONARD, jun.—See B., 1931, 162.

Electrodeposition of iron–nickel alloys from cyanide solutions. L. E. STOUT and J. CAROL.—See B., 1931, 161.

[Electro]deposition of nickel–cobalt alloys. C. G. FINK and K. H. LAH.—See B., 1931, 161.

[Electro]deposition of nickel at a low p_H. W. M. PHILLIPS.—See B., 1931, 161.

Preparation of metal powders by electrolysis of fused salts. II. Thorium. F. H. DRIGGS and W. C. LILLIENDAHL.—See B., 1931, 118.

Spectroscopic study of decomposition and synthesis of organic compounds by electrical discharges. I. Electrodeless discharge. W. D. HARKINS and D. M. GANS (J. Amer. Chem. Soc., 1930, 52, 5165—5175; cf. A., 1930, 1171; Austin, *ibid.*, 1268).—The spectra of the decomposition products in the electrodeless discharge of benzene, acetylene, naphthalene, *n*-heptane, aniline, nitrobenzene, phenol, and chlorobenzene are reproduced. The colours of the initial ring discharge and of the glow discharge are listed. In all cases, insoluble brown solid pro-

ducts are obtained, but only in minute yield from *n*-hexane. In addition to the gaseous products C_2, CH, C^+, and H, given by benzene, acetylene, and naphthalene, aniline yields CN, NH, N_2, and N_2^+, nitrobenzene yields CN, N_2, N_2^+, CO and OH, phenol yields CO and OH, and chlorobenzene yields Cl. J. G. A. GRIFFITHS.

Relationship of photochemical reaction velocity to the intensity of illumination. E. GAVIOLA (Anal. Asoc. Quim. Argentina, 1930, 18, 133—136).—An expression has been derived for the relationship between the number N_0 of excited molecules present in an irradiated gas and the intensity I of the illumination. By consideration of the average life of an excited molecule it is shown that $N_0=[(a^2+4ckI)\cdot-a]/2$, where c is the probability of removal of the excited molecule by collision, a the probability of its removal by other causes, such as collision with the containing walls, absorption or emission of radiation, etc., and k is a constant. The equation is of general application to photochemical systems.

H. F. GILLBE.

Photochemical kinetics of mixtures of hydrogen and chlorine. Oxygen-free gases. M. BODENSTEIN and W. UNGER (Z. physikal. Chem., 1930, B, 11, 253—278; cf. Cremer, A., 1927, 947).—In the mechanism previously suggested for the photochemical combination of hydrogen and chlorine, the reaction chain was assumed to be broken only in the gas phase by union of chlorine and of hydrogen atoms with oxygen. Chapman and Grigg (A., 1929, 154) and Trifonov (*ibid.*, 776) showed that a retarding process occurred also at the walls of the reaction vessel. The problem has now been further attacked by studying the reaction in gases from which oxygen had been very thoroughly removed, with the object of eliminating the retardation in the gas phase. In these circumstances only the chlorine atoms are destroyed, and the process has been shown to take place, not by re-combination at the walls, but by their reaction in the gas phase with a compound of silicon produced by the attack of the glass or silica walls by activated chlorine. In oxygen-free gas the reaction conforms to the simple law $d[HCl]/dt=kI_{abs.}[H_2]$, $I_{abs.}$ denoting the intensity of the absorbed light. Apparent discrepancies in earlier work are explained by taking into account the conditions under which each of the two mechanisms predominates.

F. L. USHER.

Influence of radiation on the coloration of glasses. P. GILARD and A. LECRENIER.—See B., 1931, 158.

Latent photographic image. F. C. TOY and G. B. HARRISON (Nature, 1931, 127, 129).—A reply to Trivelli (A., 1930, 1534). The authors' experiments show that illumination produces little, if any, increase in the electrolytic conductivity of silver bromide. Trivelli's theory also requires the temperature coefficient of photographic sensitivity to be comparable to some extent with that of electrolytic conductance; this is not so. L. S. THEOBALD.

Relation between photographic reversal and the sensitivity of the silver halide grain. F. E. E. GERMANN and D. K. SHEN (J. Physical Chem., 1931, 35, 93—99; cf. A., 1929, 893).—Development in the case of silver iodide grains in a one-grain layer emulsion is shown to be a slow process; certain grains in a developer containing no soluble halide were still incompletely developed after 15 min. Maximum developability is reached with an exposure of 64 sec. and only 17% of the iodide grains are developable. The developability–exposure curves for large- and small-grained fractions separated by centrifuging coincide with that of the uncentrifuged emulsion, indicating that the undevelopability of 83% of the grains is not due to depletion of a material in the solution which promotes sensitivity. No appreciable difference in sensitivity appears between large and small grains of the same emulsion. Treatment of the grains before exposure with quinol or pyrogallol results in increased developability with time of treatment up to 100%, and after thorough washing with water the plate does not return to its initial state of low developability. Silver iodide plates are also sensitised by solutions of acetonesemicarbazone, sodium nitrite, sodium sulphite, and sodium hydrogen sulphite. The sensitisers only increase the developability of the grains and have no effect on their speed. The terms sensitisers and desensitisers should be restricted to substances which increase or decrease developability of the grains; substances which increase or decrease the speeds should be termed accelerators or retarders, respectively. The rôle of sensitisers appears to be one of preventing or delaying reversal in an emulsion possessing a wide range of speeds of the various grains. The insensitivity of pure silver iodide emulsions is due probably to the existence of this wide range of speeds combined with quick reversal. Reversal is discussed and a case of rapid photo-retrogression of a silver iodide plate pointed out.

L. S. THEOBALD.

New photographic effect. F. E. POINDEXTER (J. Opt. Soc. Amer., 1931, 21, 59—69).—Various mechanisms of the formation of latent images about sensitivity centres as nuclei in the silver halide grain are discussed. An apparatus for the measurement of the relative reduction in photographic density on parts of an emulsion subjected to mechanical pressure is described. The formation of a latent image was largely prevented by the application of pressure. Consideration is given to the difficulty of accounting for the pressure effect on the basis of existing assumptions as to matter and radiation, since the compression of the film and silver bromide crystals is unlikely to hinder the passage of electrons or photo-conduction currents. N. M. BLIGH.

Effect of light and salts on gelatin. A. GALINSKY (Biochem. J., 1930, 24, 1706—1715).—When gelatin is made insoluble by treatment with potassium dichromate and exposure to light a change in the protein allied to denaturation, which does not involve a change in the Hausmann numbers or in the digestibility of the protein, takes place first. The chromium is then fixed in the form of the sesquioxide without forming a definite compound with the gelatin. The reaction does not proceed to completion and is probably reversible, equilibrium being attained when

90% of the gelatin has become insoluble. The reaction is catalysed by the insoluble gelatin.

S. S. ZILVA.

Irradiated ergosterol. A. WINDAUS (Nachr. Ges. Wiss. Gottingen, 1930, 36—57; Chem. Zentr., 1930, ii, 1391).—Irradiation of ergosterol leads to the formation of at least five or six products which are not precipitable by digitonin. The nature of these products is discussed. A. A. ELDRIDGE.

Conversion and action of ergosterol. W. HIRSCH (Med. Welt, 1930, 4, 655—658; Chem. Zentr., 1930, ii, 83).—It appears probable that by the use of monochromatic radiation the proportion of the antirachitic substance could be increased and that of the three by-products diminished.

A. A. ELDRIDGE.

Chemical effects of cathode rays. I. Decomposition of ammonia. G. R. GEDYE and T. E. ALLIBONE (Proc. Roy. Soc., 1931, A, **130**, 346—366).—An apparatus is described in which measurements were made of the decomposition of gaseous ammonia at pressures between 71·4 and 0·02 cm. by high-velocity cathode rays of maximum voltage 240 kilovolts. Over the pressure range the rate of formation of permanent gas (nitrogen and hydrogen) is approximately proportional to the pressure and independent of the nature of the surface. Hydrazine is also formed, the relative yield for the same relative amount of decomposition being greater at low pressures. If hydrazine is an intermediate product it must be decomposed much faster than ammonia, and two possible hypotheses, both of which agree with the experimental results, are advanced to explain this. Most of the chemical reaction is considered to be due to simple ionisation. Two possibilities are discussed: (*a*) the combination of a positive ion and an electron, and (*b*) the combination of a positive and a negative ion. The latter is preferred and a possible mechanism, which permits a maximum efficiency of two molecules of ammonia decomposed per ion pair, is $NH_3+NH_3=2NH+2H_2$, $2\{NH+NH_3=N_2H_4\}$, $2N_2H_4=2NH_3+N_2+H_2$. It is calculated that 1·2 molecules are decomposed for each ion pair formed. The results are compared with those obtained by the decomposition of ammonia by α-rays and other radiations. No confirmation is obtained of McLennan and Greenwood's conclusion that at 4 mm. pressure equilibrium is entirely on the side of formation and that the initial rate of decomposition is independent of pressure. The advantages of the cathode-ray method are indicated.

L. L. BIRCUMSHAW.

Thermal hydrogen–oxygen combination. Formation of hydrogen peroxide, and influence of surface nature. R. N. PEASE (J. Amer. Chem. Soc., 1930, **52**, 5106—5110).—The reaction between hydrogen and oxygen at total pressures between 5 and 760 mm. has been investigated in pyrex vessels by a flow method at temperatures between 510° and 650°. At 760 mm., quantities of hydrogen peroxide which can be determined are formed together with water which is produced autocatalytically. The results indicate that the peroxide is a primary product of the reaction which is favoured by a high hydrogen : oxygen ratio and by high temperature. The initial presence of traces of water vapour is not essential for the reaction. At low total pressures there is immediate, but not complete, reaction up to a limiting pressure and then a rapid decrease in velocity with progressively higher pressures (cf. Thompson and Hinshelwood, A., 1929, 403). Hydrogen peroxide could not be detected in the products of the rapid reaction. The previous treatment of the pyrex glass surface has a very marked effect on the velocity of the reaction. A very pronounced retarding effect is produced by covering the surface with potassium chloride, potassium hydroxide, and other substances.

J. G. A. GRIFFITHS.

Separation as carbonates of the constituents of sylvine. E. URBAIN (Compt. rend., 1931, **192**, 232—233).—Sylvine is dissolved to saturation in water, sodium hydrogen carbonate and excess of magnesium carbonate are added, and the mixture is agitated in an atmosphere of carbon dioxide. The potassium is almost completely precipitated as $KHMg(CO_3)_2$, whence it is extracted as carbonate with regeneration of magnesium carbonate. The great excess of sodium chloride has no appreciable effect on the solid phase; $MgCO_3+NaHCO_3+KCl=MgKH(CO_3)_2+NaCl$. The solution is treated by the ammonia-soda process to regenerate sodium hydrogen carbonate, the residual solution of ammonium chloride being advantageously cooled to −10°, and the residual liquid used to dissolve fresh sylvine, as in this way a considerable quantity of sodium hydrogen carbonate usually lost is recovered. C. A. SILBERRAD.

Everitt's salt. III. Reaction of formaldehyde with potassium ferrocyanide solution. T. KIRIGAKUBO (J. Soc. Chem. Ind. Japan, 1930, **33**, 513—515B).—The micro-crystalline (rhombohedral) greenish-white precipitate obtained by the reaction between potassium ferrocyanide and formaldehyde is identical in crystallographic and chemical properties and composition with the crystalline component of Everitt's salt prepared by the method of Hofmann, Heine, and Hochtlen (A., 1905, i, 38), but is obtained in a purer form. The minutely granular impurity accompanying the crystals in Everitt's salt may be isomeric, and is analogous to the pale yellow precipitate from the ferrocyanide–formaldehyde reaction (cf. A., 1930, 454, and J. Soc. Chem. Ind. Japan, 1929, **32**, 1123). E. LEWKOWITSCH.

Preparation of basic cupric acetate from the neutral salt. Z. A. IOFA, S. M. KOBRIN, and L. L. KLYACHKO.—See B., 1931, 156.

Reaction of calcium carbonate with magnesium salts in solution under pressure. E. SAUER and J. HUTER (Z. anorg. Chem., 1931, **195**, 241—246).—When a dilute solution of magnesium chloride or sulphate is heated under pressures of up to 15 atm. in an autoclave there is no detectable amount of hydroxide formed, but in presence of calcium hydrogen carbonate or the solid carbonate the magnesium salt is largely converted into hydroxide. R. CUTHILL.

Calcium, strontium, and barium stannites. S. TAMARU and H. SAKURAI (Z. anorg. Chem., 1931, **195**, 24—34).—By condensing the vapour of stannous

oxide on the carbonate of calcium, barium, or strontium heated in a vacuum at about 900°, the *stannites*, $CaSnO_2$, $BaSnO_2$, and $SrSnO_2$, respectively, are formed. When calcium stannite is subjected to the action of steam at 800° in presence of stannous oxide the product is the metastannate, $CaSnO_3$, whereas in absence of stannous oxide the orthostannate, Ca_2SnO_4, results. R. CUTHILL.

Calcium, barium, and strontium thioxystannites. S. TAMARU and Y. TANAKA (Z. anorg. Chem., 1931, **195**, 35—40).—The *thioxystannites* of calcium, barium, and strontium, SnS,2CaO, SnS,2BaO, and SnS,2SrO, may be prepared by heating the corresponding carbonates or oxides with excess of stannous sulphide; they have d^{25} 3·683, 4·464, and 3·880, respectively. They react with water according to the equation $SnS,2MO+2H_2O=SnS+2M(OH)_2$. R. CUTHILL.

Contamination of mercury by gold. W. SWIENTOSŁAWSKI and S. ZAGRODZKI (Rocz. Chem., 1931, **11**, 19—28).—An apparatus for the repeated submission to a high-tension current of a sample of mercury is described. The gold content of mercury so treated is the same at the end as at the beginning of the experiment when iron parts are used in the apparatus, but increases when platinum parts are employed. By dissolving mercury in nitric acid and examining the residue microscopically 0·001 mg. of gold can be detected. Gold-free mercury cannot be prepared by redistillation, or by electrolysis or reduction of mercuric nitrate; the purest samples prepared contained about 10^{-8} g. of gold per 100 g. R. TRUSZKOWSKI.

Preparation of luminescent substances. N. F. ZHIROV (J. Appl. Chem., Russia, 1930, **3**, 675—680).—Phosphorescence of boric acid with fluorescein (1 in 10^4) as activator can be used to detect 0·02 mg. of boric acid. Triphenylmethane gives a weak yellow luminescence. Complete luminophores possess no advantage. The boric acid was purified by crystallisation from concentrated nitric acid containing hydrogen peroxide. CHEMICAL ABSTRACTS.

Neodymium selenates. J. MEYER and (FRL.) C. KITTELMANN (Z. anorg. Chem., 1931, **195**, 121—126).—From a mixed solution of neodymium sulphate octahydrate and potassium sulphate *potassium neodymium sulphate*, $KNd(SO_4)_2,H_2O$, separates, and the corresponding *rubidium* salt, $RbNd(SO_4)_2$ or $RbNd(SO_4)_2,2H_2O$, may be obtained in a similar way, the anhydrous salt crystallising from a hot solution and the dihydrate in the cold. By the action of selenic acid on neodymium oxide or nitrate, *neodymium selenate*, $Nd_2(SeO_4)_3,8H_2O$, may be prepared; the *pentahydrate*, $Nd_2(SeO_4)_3,5H_2O$, is formed by evaporating a solution of the octahydrate on a water-bath. Neodymium selenate forms double *selenates* with the alkali selenates: $KNd(SeO_4)_2,4H_2O$, $RbNd(SeO_4)_2,4H_2O$, and $NaNd(SeO_4)_2,2H_2O$. All the above salts are red in colour. Approximate solubility determinations at 0° and 20° have been made. R. CUTHILL.

Mechanism of the combustion of carbon at low pressures. A. EUCKEN (Z. angew. Chem., 1930, **43**, 986—993).—The mechanism of the production of 2 mols. of carbon monoxide and 1 mol. of carbon dioxide in the primary reaction between graphitic carbon and oxygen at low pressures, and of the influence of the two oxides on the course of the reaction, is discussed in the light of Sihvonen's results (A., 1930, 1379). The conclusions reached do not accord fully with those of Sihvonen, but this may be due in part to the experimental difficulties of the work. H. F. GILLBE.

Oxidation of carbon monoxide by dissociated water vapour. G. I. LAVIN and W. F. JACKSON (J. Amer. Chem. Soc., 1931, **53**, 383—384; cf. Taylor and Lavin, A., 1930, 870).—The 5% oxidation of carbon monoxide by oxygen in the discharge tube (Harteck and Kopsch, A., 1930, 1388) is attributed to the presence of small quantities of water; this is a source of hydroxyl which reacts thus: $OH+CO=CO_2+H$ (cf. Bonhoeffer and Haber, A., 1929, 11). Under the conditions water vapour oxidises carbon monoxide, and the oxidation in oxygen is progressively increased by increasing concentrations of water vapour. J. G. A. GRIFFITHS.

Variation of hydrogen-ion concentration with carbon dioxide pressure above 1 atm. I. Colorimetric measurement. M. B. MOORE and J. H. BUCHANAN (Iowa State Coll. J. Sci., 1930, **4**, 431—439).—The p_H was determined (±0·1) by the use of bromophenol-blue. The value at 25° is minimal at about 6 atm., not decreasing appreciably with further increase of pressure to 33·3 atm. At 0° the p_H is 0·1—0·2 lower than at 25° up to 23·4 atm. The limiting value is not affected by the addition of citric acid until this alone would account for the low value. Hence the power of carbon dioxide to inhibit the growth of organisms in carbonated beverages is due to a cause other than high hydrogen-ion concentration. CHEMICAL ABSTRACTS.

Formation of carbon tetrachloride from its elements. A. STOCK, H. LUX, and W. WUSTROW Z. anorg. Chem., 1931, **195**, 149—157).—At 400—600° activated carbon combines very slowly with chlorine to form carbon tetrachloride. R. CUTHILL.

Thermal decomposition of carbonyl chloride. II. A. STOCK, W. WUSTROW, H. LUX, and H. RAMSER (Z. anorg. Chem., 1931, **195**, 140—148; cf. A., 1925, ii, 987).—At 400° neither the reaction $2COCl_2=CO_2+CCl_4$ nor the reverse change occurs to any measurable extent, even in presence of activated carbon, silica, or aluminium chloride. R. CUTHILL.

Behaviour of the various modifications and varieties of silica when mixed with carbon and heated in a current of chlorine. E. GRUNER and J. ELOD (Z. anorg. Chem., 1931, **195**, 269—287).—The conditions under which the various forms of silica yield silicon tetrachloride when mixed with carbon and heated in chlorine have been studied. Amorphous silica prepared by precipitating sodium silicate or hydrolysing silicon tetrafluoride and dehydrated by heating at dull redness starts to react appreciably at 740°, tridymite at 1060—1070°, cristobalite at 1060—1070°, and quartz at 1220°. With naturally-occurring forms of silica gel, such as

flint, opal, and chalcedony, the reaction temperature varies from 800° to 1100°, according to the age of the mineral; the reactivity of the more recent minerals is comparable with that of the artificial amorphous silica. Quartz glass is attacked at 1130—1140°. The relative reactivities seem to depend chiefly on the density; the higher is the density the smaller is the reactivity. By a process of differential chlorination the amounts of the various modifications in a mixture may be approximately determined. The temperature is first so adjusted that only the amorphous silica reacts, then when reaction is complete the temperature is raised until the cristobalite and tridymite react, and finally the quartz is caused to react. The tetrachloride given off at each stage is absorbed in alkali, from which the silica is precipitated by addition of acid and weighed. This method of separation is not, however, applicable to mixtures containing aged silicic acid gels. It seems most probable that in the reaction of silica with chlorine and carbon the first step is the reaction $SiO_2+2Cl_2=SiCl_4+O_2$, followed by $2C+O_2=2CO$ (cf. Spitzin, A., 1930, 874). R. CUTHILL.

Pneumatolytic synthesis of silicates. I. C. J. VAN NIEUWENBURG and H. B. BLUMENDAL (Rec. trav. chim., 1931, **50**, 129—138).—Silica volatilises in superheated steam (365—410°, 200—350 atm.). When silica and certain metallic oxides in separate crucibles are simultaneously treated with superheated steam reaction takes place through the volatilisation, and in this way the syntheses of β-wollastonite, strontium metasilicate, alamosite, willemite, tephroite, antigonite, and diopside have been effected. The mineralogical significance of these results is discussed. Similar results were obtained when ferrosilicon was used in place of silica, but whether these were due to oxidation to silica by the steam or occurred through the intermediary of silicon hydride has not been established. E. S. HEDGES.

Germanium. VIII. Action of ammonia on germanium tetrachloride: germanium imide. J. S. THOMAS and W. PUGH (J.C.S., 1931, 60—71).—It is suggested that the substance $GeCl_4,6NH_3$ is merely a mixture of ammonium chloride and germanium imide. The solution obtained on washing the substance with liquid ammonia in an apparatus designed to prevent the ingress of water yields on evaporation crystals of ammonium chloride practically free from germanium, whilst the insoluble residue consists of germanium imide of 97·2% purity. The imide forms a light, white powder which is immediately decomposed by water; it reacts rapidly with 2 mols. of hydrogen chloride and the resulting salt reacts further with formation of the tetrachloride. No evidence has been obtained of the formation of germanium amide at temperatures above −20° during the action of ammonia on the tetrachloride. On heating the mixture of imide and ammonium chloride at various temperatures between 130° and 300° a constant amount of ammonia is evolved, but no definite equilibrium pressure is attained. The reactions which occur are probably: $2Ge(NH)_2 \rightleftharpoons Ge_2N_3H + NH_3$ and $Ge_2N_3H + 2NH_4Cl \rightleftharpoons Ge_2N_3H,2HCl+2NH_3$, together with either $Ge(NH)_2+4NH_4Cl \rightleftharpoons GeCl_4+6NH_3$ or $Ge_2N_3H+8NH_4Cl \rightleftharpoons 2GeCl_4+11NH_3$. H. F. GILLBE.

Nitrogen compounds of germanium. I. Preparation and properties of germanic nitride. W. C. JOHNSON (J. Amer. Chem. Soc., 1930, **52**, 5160—5165).—Germanium nitride, Ge_3N_4, is prepared by the action of ammonia on the metal at 650—700° or on the oxide at 700—750°. The nitride is stable towards air, water at 100°, and boiling sodium hydroxide, and is only slowly attacked by strong acids, but at 600—700° hydrogen effects reduction to ammonia and the metal, whilst oxidation occurs in oxygen at 800—900°. At 600—1000° germanium nitride is decomposed into its elements and a brown volatile substance, possibly *germanous nitride*, Ge_3N_2. The brown colour of germanium nitride (cf. Schwarz and Schenk, A., 1930, 437) is not entirely due to finely-divided metal, since chlorine does not react below 575°; between 600° and 700° the reaction is probably $Ge_3N_4+6Cl_2=3GeCl_4+2N_2$. J. G. A. GRIFFITHS.

Heteropoly-acids of germanium. I. Germanomolybdic acid. C. G. GROSSCUP (J. Amer. Chem. Soc., 1930, **52**, 5154—5160).—*Germanomolybdic acid* is prepared by the gradual addition of 70 g. of molybdic oxide to a boiling solution of 5 g. of germanic oxide and 7 g. of sodium hydroxide in 200 c.c. of water. Yellow efflorescent crystals of the acid, $H_8[Ge(Mo_2O_7)_6],24—26H_2O$, m. p. 65° (approx.), are obtained by extraction by Drechsel's method (A., 1887, 703). The acid is analysed by distillation with 9*N*-hydrobromic acid. The following reaction occurs with alkali: $GeO_2,12MoO_3,aq.+24NaOH=GeO_2,aq.+12Na_2MoO_4+aq.$, and titration may be effected with chlorophenol-red as the indicator (cf. Scroggie, A., 1929, 779). The acid yields sparingly soluble compounds with salts of metals, guanidine, and the alkaloids, and 0·00183 g. of the free acid (=0·082 mg. of germanic oxide) imparts a yellow colour to 5 c.c. of water, thus indicating a possible method for the colorimetric determination of germanium. J. G. A. GRIFFITHS.

Germanochlorides of alkaloids, cæsium [and rubidium]. A. TCHAKIRIAN (Compt. rend., 1931, **192**, 233—234).—Germanochlorides of quinine, $C_{20}H_{24}O_2N_2,HCl,GeCl_2$, and of pilocarpine, $C_{11}H_{16}O_2N_2,HCl,GeCl_2$, are precipitated on mixing 10% solutions of the two chlorides. Both compounds are very hygroscopic, and are hydrolysed by water. The quinine compound is insoluble in alcohol or chloroform, but soluble in a warm mixture of the two. On mixing hydrochloric acid solutions of germanous and cæsium or rubidium chlorides, the double salt $CsGeCl_3$ or $RbGeCl_3$ is precipitated. The cæsium salt melts without decomposition and is unaffected by gaseous hydrogen chloride at 100°; it is concluded therefore that its constitution is $Cs[GeCl_3]$. C. A. SILBERRAD.

Zirconium and hafnium sulphates. G. VON HEVESY and E. CREMER (Z. anorg. Chem., 1931, **195**, 339—344).—The behaviour of zirconium and hafnium sulphates on heating shows that whether prepared from the tetrahalides or from the oxides there is always present an excess of sulphate radical; it is

for this reason that at. wt. determinations based on analysis of the sulphates are always low. The excess of sulphuric acid is removed only by heating at temperatures at which decomposition commences. The temperature-dissociation pressure curves give no indication of the formation of a definite basic sulphate. Zirconium sulphate has the higher decomposition pressure. The heat of decomposition of the hafnium salt is about 95—100 kg.-cal. and of the zirconium salt about 60—70 kg.-cal. Both compounds yield on thermal decomposition the monoclinic–tetragonal form of the oxide. Debye–Scherrer diagrams of the two sulphates after heating at 500° indicate that the lattice dimensions do not differ by more than 1%.

H. F. GILLBE.

Stannic ethoxide and the stannic acids. P. A. THIESSEN and O. KOERNER (Z. anorg. Chem., 1931, **195**, 83—104).—Electrolyte-free stannic ethoxide with the composition $Sn(OEt)_4,2EtOH$ is obtained by interaction of stannic chloride and sodium ethoxide in absolute alcohol solution. By slow hydrolysis of alcoholic solutions of this compound there are formed gels of hydrated stannic oxide in which the pores are large enough not to hold water by capillary condensation and the smallest particles are of such size that their vapour pressure does not depend on their dimensions. The isothermal dehydration curves of such preparations show "steps" corresponding with the hydrates $2SnO_2,5H_2O$, $SnO_2,2H_2O$, $4SnO_2,7H_2O$, $2SnO_2,3H_2O$, SnO_2,H_2O, and $2SnO_2,H_2O$, of which only the last two are stable in dry air. By controlled dehydration the various hydrates have been obtained in the pure state, and subjected to *X*-ray examination, the results indicating that in detecting crystalline compounds in solids with very fine grains *X*-ray methods are sometimes less useful than isothermal dehydration.

From a solution of stannic chloride in absolute alcohol a *compound* $SnCl_4,2EtOH$ crystallises.

R. CUTHILL.

Ceric selenate. J. MEYER and F. SCHULZ (Z. anorg. Chem., 1931, **195**, 127—128).—By the action of a 50% solution of selenic acid on ceric hydroxide yellow *ceric selenate*, $Ce(SeO_4)_2$, is obtained.

R. CUTHILL.

Mechanism of precipitation processes. II. Reaction between sulphuric acid and lead bromide. Z. KARAOGLANOV and B. SAGORTSCHEV. **III. Reaction between sulphuric acid and lead bromide.** Z. KARAOGLANOV [with B. SAGORTSCHEV] (Z. anorg. Chem., 1931, **195**, 105—112, 113—120; cf. this vol., 182).—II. When lead bromide reacts with sulphuric acid in aqueous solution the precipitate always contains bromine, apparently in the form of a secondary product of reaction, possibly $(PbBr)_2SO_4$. The amount of this substance in the precipitate is at its highest immediately after the reactants are mixed, and at once starts to fall owing to conversion into the pure sulphate, which has a smaller solubility product. This process takes place at the interface secondary product/solution and leads to the deposition of a layer of sulphate on the surface of the solid phase. As a result, the reaction is progressively retarded, and ultimately practically ceases before reaction is complete. The rate of reaction probably also depends on the temperature, stirring, the composition of the liquid phase, the surface area of the solid phase, and the rates of diffusion. If equal amounts of sulphuric acid are precipitated with equivalent amounts of lead chloride and bromide under the same conditions, equivalent amounts of the secondary products are formed.

III. The behaviour of the above system can be explained satisfactorily by supposing that the secondary product of reaction, the estimated solubility product of which is 10^{-4}—10^{-5}, is formed by the reaction $2PbBr^{\cdot}+SO_4'' = (PbBr)_2SO_4$, and decomposes according to the equation $(PbBr)_2SO_4 = PbSO_4 + PbBr_2$. This latter process seems to proceed in the main in accordance with Nernst's theory of heterogeneous reactions, although the deposition of one of the products of reaction at the interface complicates it somewhat.

R. CUTHILL.

Reduction of nitrates by ferrous hydroxide. C. SANDONNINI and S. BEZZI (Gazzetta, 1930, **60**, 693—700).—The oxidation of ferrous hydroxide by sodium nitrate in neutral and alkaline solutions has been followed by determination of the ammonia evolved on boiling. At 100° and in neutral solutions the hydroxide is oxidised to black ferrosoferric oxide, according to the equation $12Fe(OH)_2+NaNO_3 \longrightarrow 4Fe_3O_4+NH_3+NaOH+10H_2O$. Prolonged boiling does not cause further oxidation. The rate of oxidation is retarded in faintly alkaline solution, by reason of the rapid agglomeration of the ferrous hydroxide. Oxidation becomes much more rapid in strongly alkaline solution and proceeds to a higher stage: $8Fe(OH)_2+NaNO_3 \longrightarrow 4Fe_2O_3+NH_3+NaOH+6H_2O$.

F. G. TRYHORN.

Structure of PCl_4Br. J. H. KOLITOWSKA (Rocz. Chem., 1930, **10**, 743—750).—Phosphorus tetrachlorobromide reacts with phenol to yield chlorobromophosphorus triphenoxide, $(OPh)_3PClBr$, indicating that the bromine atom and one chlorine atom differ in their mode of combination from the remaining three chlorine atoms.

R. TRUSZKOWSKI.

Preparation of arsenic tri-iodide by the wet method. P. G. PATERNOSTO (Rev. fac. cien. quim. La Plata, 1930, 7, 43—46).—Arsenious oxide (2 g.) is treated with hydrochloric acid (*d* 1·19, 30 c.c.); a hot solution of potassium iodide (10 g.) in water (10 c.c.) is added, the precipitate being collected on asbestos after 4—5 min. and dried in a vacuum. Arsenic tri-iodide (yield, 94%; purity, 99·8%) is extracted from the mixture by means of carbon disulphide.

CHEMICAL ABSTRACTS.

Non-existence of the sub-iodides of bismuth, BiI_2 and BiI. V. CAGLIOTI (Gazzetta, 1930, **60**, 933—935).—An *X*-ray examination of the system bismuth–iodine shows that only the tri-iodide BiI_3 exists.

O. J. WALKER.

Preparation of sulphuryl chloride. J. MEYER (Z. angew. Chem., 1931, **44**, 41—42).—The gases are bubbled through sulphuric acid, then passed downwards through a six-bulb condenser, each bulb of which is half filled with glass wool which supports a thin layer of granular activated charcoal. At the beginning of the preparation the uppermost charcoal layer is

moistened with a little sulphuryl chloride and the gas stream is passed at the rate of 3—4 bubbles a second; after 20 min. liquid sulphuryl chloride collects in the receiver at the rate of 150 g. per hr.

A. R. POWELL.

Interaction between iodine pentoxide and nitric oxide. M. S. SHAH and T. M. OZA (J.C.S., 1931, 32—36).—The reaction between iodine pentoxide and nitric oxide commences at 80° and is rapid at 120°; the time required for completion varies with the quantity of nitric oxide used. Iodine is liberated and in presence of moist sodium hydroxide all the gas evolved is converted into nitrate and nitrite. The mechanism of the reaction is discussed. The initial product may be nitrogen peroxide, formed according to the equation $10NO+2I_2O_5=2I_2+5N_2O_4$, and subsequently oxidation takes place to pentoxide: $5N_2O_4+I_2O_5=I_2+5N_2O_5$; or nitrogen pentoxide may be the primary product: $10NO+3I_2O_5=3I_2+5N_2O_5$, and nitrogen peroxide may be formed by the further action of nitric oxide.

H. F. GILLBE.

Preparation of iodine trichloride. E. C. TRUESDALE and F. C. BEYER (J. Amer. Chem. Soc., 1931, 53, 164—165).—Details of a rapid and economical method for the preparation of definite (large) quantities of iodine trichloride are given. When the iodine in a bulb-tube has been converted into the monochloride by a current of chlorine, the temperature is raised to just below 100°, chlorine is then passed more rapidly, and the iodine trichloride carried over is solidified in a bulb immersed in ice.

J. G. A. GRIFFITHS.

Reactions involving hydrogen peroxide, iodine, and iodate ion. I. Introduction. W. C. BRAY and H. A. LIEBHAFSKY. **II. Preparation of iodic acid. Preliminary rate measurements.** W. C. BRAY and A. L. CAULKINS (J. Amer. Chem. Soc., 1931, 53, 38—44, 44—48; cf. A., 1921, ii, 629; Abel, A., 1928, 1194; Auger, A., 1912, ii, 40).—I. The effects of variation of concentration of reactants and of hydrogen ions on the reactions of hydrogen peroxide with iodine and iodate or iodide are discussed in relation to the mechanisms.

II. The above considerations afford a method for the preparation of iodic acid. 10 G. of finely-divided iodine, 10 c.c. of concentrated nitric acid, and 50 c.c. of 3% hydrogen peroxide are heated at 70°. Whenever the colour, which decreases when the reaction starts, becomes deeper, more hydrogen peroxide, to a total of 300 c.c., is added as required. The product is evaporated to dryness.

The unimolecular velocity coefficient (k, 0.6 ± 0.1) at 25° of the homogeneous reaction in the system potassium iodate 0·0069—0·042M, sulphuric acid 0·015—0·3N, hydrogen peroxide 0·006—0·21M, and iodine 0·5—$8\times10^{-4}M$ is independent of the first three, but decreases rapidly with decrease of concentration of iodine below 3×10^{-4}. The first-order reaction is interpreted as the rate of hydrolysis of iodine, $I_2+H_2O\longrightarrow HIO+H^{\cdot}+I'$, and the diminution of k is due to the effect of the reverse reaction as equilibrium is approached.

J. G. A. GRIFFITHS.

Formation of a ferromagnetic iron sesquioxide by decomposition of van Bemmelen's hydrated sesquioxide. G. CHAUDRON and A. GIRARD (Compt. rend., 1931, 192, 97—99).—Thermal analysis shows that the compound Fe_2O_3,H_2O prepared by hydrolysis of sodium ferrite is less stable than the natural hydrates and loses water at 100° (*e.g.*, after 48 hrs. in boiling water) to 140°, forming a strongly ferromagnetic oxide which above 675° is converted rapidly into oligist or ordinary iron sesquioxide (cf. Huggett, A., 1929, 1369). The Curie point varies according to the thermal history of the oxide or ferrite (cf. Huggett, A., 1927, 207; 1928, 841). The ferrite, hydrate, and oxide all form birefringent hexagonal tablets, whilst slow oxidation of magnetite (Malaguti) yields a cubic form.

J. GRANT.

Production and properties of pure metals. M. L. V. GAYLER (Metall-Wirt., 1930, 9, 677—679; Chem. Zentr., 1930, ii, 2179).—Crucibles of the corresponding oxides are used, but for iron, manganese, and chromium alumina crucibles are employed. The production of electrolytic iron is described. Chromium, prepared electrolytically with a rotating cathode, contains only hydrogen (removed at 600°) and oxide (removed by treatment with hydrogen at 1500—1600°); with removal of hydrogen the metal becomes soft and ductile. The properties of pure manganese and beryllium are described.

A. A. ELDRIDGE.

Ferrous ferrites. I. Ferrites from ortho- and meta-ferric hydroxides. A. KRAUSE and J. TULECKI (Z. anorg. Chem., 1931, 195, 228—238).—Ferrous ferrites of various compositions have been prepared from metaferric hydroxide by addition of ammonia to a mixed solution of ferric chloride peptised with hydrochloric acid and ferrous chloride and from orthoferric hydroxide by addition of ammonia to a mixed solution of ferrous and ferric chlorides. By heating the reacting mixture at the b. p. the proportion of ferrous iron in the product is increased, the maximum having been observed in a ferrite prepared from the meta-hydroxide, the composition of which when air-dry was $FeO,1{\cdot}13Fe_2O_3,0{\cdot}54H_2O$. The ferrites obtained from the meta-hydroxide are much more resistant to atmospheric oxidation than those prepared from the ortho-hydroxide, and in the air-dry state they also contain more ferrous iron and less water. This difference in properties is ascribed to the difference between the isoelectric points of the two hydroxides, the ortho-hydroxide having acid properties only in an alkaline solution. All the ferrites obtained were ferromagnetic.

R. CUTHILL.

Higher oxides of group VIII elements. III. Nickel peroxides. D. K. GORALEVITSCH (J. Russ. Phys. Chem. Soc., 1930, 62, 1577—1625).—A number of oxides, Ni_6O_{11}, Ni_5O_7, Ni_3O_4, Ni_8O_{13}, Ni_3O_5, Ni_9O_{17}, Ni_2O_3, Ni_7O_{12}, Ni_8O_{15}, Ni_2O_3,H_2O, Ni_5O_8, $Ni_{11}O_{17}$, and Ni_9O_{16} are obtained by the oxidation of powdered nickel or of nickelic salts. These oxides evolve oxygen (6—15%) on treatment with sulphuric acid. Certain of these oxides represent mixtures in various proportions of the oxides NiO, Ni_2O_3, Ni_3O_4, and NiO_2, whilst others are nickelous salts of pernickelic acid, H_4NiO_4, such as Ni_3O_4 ($=Ni_2NiO_4$), or of the condensation products of this acid. The struc-

tural formulæ of the fifteen peroxides prepared are given. R. TRUSZKOWSKI.

Photo-electric microanalysis. M. MATSUI and T. NODA (J. Soc. Chem. Ind., Japan, 1930, **33**, 517—518B).—The concentration of a dilute solution may be determined from its quantitative relation to log I_0/I, where I_0 and I are the photo-electric currents corresponding with the light transmitted through a cell containing water and the test solution, respectively. A cæsium cell filled with argon was used as photo-electric cell and an incandescence lamp as light source: the determination is accurate to 5% or less.

E. LEWKOWITSCH.

Determination of small amounts of hydrogen and oxygen in activated carbons. A. STOCK, H. LUX, and J. W. R. RAYNER (Z. anorg. Chem., 1931, **195**, 158—163).—The carbon is rendered gas-free and then burnt in a known amount of oxygen. From the weight of water formed the amount of hydrogen in the carbon may be calculated and the amount of oxygen can be obtained from the amount of carbon dioxide formed and the amount of oxygen remaining uncombined. R. CUTHILL.

Todt's "spot apparatus" for the colorimetric determination of p_H. I. M. KOLTHOFF (Chem. Weekblad., 1931, **28**, 78—79).—A criticism of the apparatus and of the claims made for it. Since colorimetric methods yield satisfactory results for unbuffered solutions only when the indicator solution has the same as the solution tested, and the indicators supplied are not neutralised, determinations made with the apparatus are valueless.

H. F. GILLBE.

Determination of small amounts and traces of water and carbonic acid in silicates. I. E. DITTLER and H. HUEBER (Z. anorg. Chem., 1931, **195**, 41—59).—Lindner's method for the determination of water by liberation of hydrogen chloride from α-naphthyloxychlorophosphine (A., 1925, ii, 901) has been applied to the determination of the water expelled from silicates by heating. In the analysis of micas and epidotes this method is capable of much greater precision than the usual gravimetric methods, but its applicability is restricted to such minerals of low water content. R. CUTHILL.

Drop method for detection of bromides. A. V. PAVLINOVA (Ukraine Chem. J., 1930, **5**, [Sci.], 231—232).—Filter-paper is soaked in feebly alkaline fluorescein solution and dried; a drop of a solution of sodium nitrite (10%) and hydrogen peroxide (3%) and of dilute sulphuric acid are placed side by side on the paper, and a drop of the solution under examination at the confluence of the two drops, when a red stain, due to the formation of eosin, indicates the presence of bromide (minimum concentration 1 in 12,500). The coloration obtained can be intensified by exposure to ammonia vapour. Should iodine be present, the stain should first be treated with thiosulphate solution. R. TRUSZKOWSKI.

Bromo-iodometric investigations. V. J. H. VAN DER MEULEN (Chem. Weekblad, 1931, **28**, 82—86). In a solution half saturated with sodium chloride bromide is completely oxidised to bromate by an excess (2·5 times the theoretical quantity) of hypochlorite in presence of a weak acid such as carbonic or boric; for quantitative work the temperature should be 80—90°. The excess of hypochlorous acid is destroyed by addition of hydrogen peroxide and the excess of peroxide is removed by boiling the solution; the bromate may then be determined by addition of potassium iodide to the acidified solution and titration with thiosulphate. The method may be applied to the determination of bromide in admixture with iodide, iodate, and bromate after determination of the other anions by the method previously described (this vol., 55); it is necessary to add the potassium hydrogen carbonate before addition of the bromine employed to oxidise the iodide. H. F. GILLBE.

Determination of iodide in presence of chloride and bromide. F. L. HAHN (Z. anorg. Chem., 1931, **195**, 75—82; cf. A., 1927, 124).—In confirmation of the observations of Gorbatschev and Kasatkina (A., 1930, 1143) it is found that in the potentiometric titration of iodide with permanganate in presence of chloride and bromide the first inflexion on the titration curve occurs when 1 equivalent of permanganate per mol. of iodide has been added and the second when the amount of permanganate is double this. If the mol. ratio of bromide to iodide does not exceed 10 : 1, the first inflexion gives the more exact result.

R. CUTHILL.

Analysis of dilute iodine solutions. H. A. LIEBHAFSKY (J. Amer. Chem. Soc., 1931, **53**, 165—166; cf. Bray and Caulkins, this vol., 324).—Sufficient of the aqueous iodine solution is extracted with 25 c.c. of carbon tetrachloride to supply iodine equivalent to 1—5 c.c. of 0·004N-sodium thiosulphate. The carbon tetrachloride is added to 50 c.c of 1% potassium iodide made 0·001N with respect to acid. Starch solution is added when titration with thiosulphate is almost complete. Conditions at the carbon tetrachloride–aqueous layer interface favour the formation of the blue starch–iodide compound.

J. G. A. GRIFFITHS.

Quantitative precipitation of sulphides in buffered solutions. I. Cobalt sulphide. M. M. HARING and M. LEATHERMAN. **II. Nickel sulphide.** M. M. HARING and B. B. WESTFALL (J. Amer. Chem. Soc., 1930, **52**, 5135—5141, 5141—5145).—I. Hydrogen sulphide precipitates cobalt sulphide quantitatively from a boiling solution of the chloride containing about 0·2 g. of the metal, if the solution has been treated with 25 c.c. of 0·4N-ammonium acetate, 4·5 c.c. of 6·8N-acetic acid, and 70 c.c. of water to make the p_H 3·93. The precautions to be observed during the precipitation and the subsequent conversion of the precipitate into the metal are enumerated. The precipitation of the sulphide is quantitative when the initial p_H of the solution is greater than 3·93.

II. To 10—15 c.c. of solution containing 0·2 g. of nickel are added 34 c.c. of 0·4N-ammonium acetate, 2·8 c.c. of 6·8N-acetic acid, and about 40 c.c. of water. The liquid (p_H 4·4) is heated at 90° before the hydrogen sulphide is passed. Precautions to be observed during the precipitation and subsequent conversion of the sulphide into the oxide are given. Complete

precipitation of the sulphide occurs when the initial p_H of the solution is greater than 4·4.

J. G. A. GRIFFITHS.

Determination of sulphite ions in the presence of thiosulphate ions, using fuchsin. V. E. MALINOVSKI (Ukraine Chem. J., 1930, **5**, [Sci.], 181—186).—0·3 Mg. of sulphite ion in 0·001*M* solution decolorises 1 drop of 0·001*M*-fuchsin reagent containing 0·0002*M*-sulphuric acid. The presence of thiosulphate at concentrations less than 0·1*M* does not interfere with this reaction. This reaction cannot be applied to the determination of sulphite.

R. TRUSZKOWSKI.

Volumetric determination of sulphate in water. R. SCHMIDT.—See B., 1931, 180.

Volumetric determination of Caro's acid, persulphuric acid, and hydrogen peroxide in presence of each other. K. GLEU (Z. anorg. Chem., 1931, **195**, 61—74).—The method described depends on the observation that in a solution containing sulphuric acid hydrogen bromide reduces Caro's acid completely long before it reacts appreciably with persulphuric acid and hydrogen peroxide and that arsenious acid reacts immediately with the bromine liberated, but only slowly with the hydrogen peroxide and persulphuric acid. The solution for analysis is slightly acidified with sulphuric acid and then 5 c.c. of *N*-potassium bromide and a known excess of 0·1*N*-arsenious acid are added. After 1—2 min. 0·1*N*-potassium bromate is added gradually until there is permanent slight yellow coloration due to free bromine, which is removed by titrating with arsenious acid until the solution is colourless. After the addition of 5 c.c. of 2*M*-manganous sulphate the hydrogen peroxide is titrated with 0·1*N*-permanganate, the end-point being indicated by the appearance of the yellow colour of bromine. Finally a known excess of arsenious acid and 10 c.c. of 10*M*-sulphuric acid are added and the mixture is boiled for 10 min. to reduce the persulphuric acid, after which the excess of arsenious acid is titrated back with bromate. R. CUTHILL.

Detection of tellurium in bismuth. H. TOPELMANN.—See B., 1931, 161.

Determination of nitrate by Grandval and Lajoux' method. B. A. SKOPINTZEV (J. Appl. Chem., Russia, 1930, **3**, 747—758).—Loss of nitrate during evaporation owing to the presence of sulphur compounds in the gas is avoided by addition of 0·1*N*-sodium hydroxide (0·5—1·0 c.c.). The volume of the standard sample should be 1—3 c.c., and the burette must be read to 0·01 c.c. The presence of ammonium compounds is objectionable only if the content is greater than the equivalent amount of alkalis.

CHEMICAL ABSTRACTS.

Determination of hypophosphites and arsenites by the mercurimetric method. A. IONESCO-MATIU and (MME.) A. POPESCO (J. Pharm. Chim., 1931, [viii], **13**, 12—19).—Hypophosphites and arsenites are determined volumetrically by reaction with mercuric chloride, the metallic mercury so formed being transformed into sulphate, which is determined as previously described (B., 1929, 698).

E. H. SHARPLES.

Permanence of standardised arsenious acid solutions. I. TANANAEV (Ukraine Chem. J., 1930, **5**, [Sci.], 217—226).—The diminution in titre of arsenious acid solutions is due to oxidation to arsenic acid: the velocity of this process is proportional to the alkali content, the daily oxidation of a 0·1*N* solution in *N*-sodium hydroxide amounting to 0·176%. Feebly alkaline solutions (p_H 7—9) do not change their titre during 18 months. Arsenious acid solutions are best prepared by dissolving arsenious oxide in carbonate-free sodium hydrogen carbonate solution. Micro-organisms do not develop in such solutions, nor do the latter evolve arsine. R. TRUSZKOWKSI.

Quantitative study of the boric acid–alcohol flame reaction. W. STAHL (Latvij. Univ. Raksti, 1930, **1**, 369—400).—The flame reaction of boric acid with methyl or ethyl alcohol can be observed when the temperature of the liquid is 100° below the b. p. of the alcohol, but is most marked near the b. p., and with a mixture of 1 vol. of sulphuric acid to 5 vols. of alcohol. A modification of Rosenbladt's apparatus, by means of which it is possible to detect 0·005 mg. of boric acid with methyl alcohol, or 0·02 mg. with ethyl alcohol, is described. The flame colour with methyl alcohol is less influenced by water than is the case with ethyl alcohol. F. L. USHER.

Rapid determination of small quantities of boric acid by intensity of flame coloration. W. STAHL (Latvij. Univ. Raksti, 1930, **1**, 401—407; cf. preceding abstract).—Boric acid, in quantities of 0·3 mg. and upwards, may be roughly estimated by comparing the colour intensity of a Bunsen flame fed with the vapour of the methyl ester with that given by a series of standard solutions. Preliminary separation of the ester by distillation is unnecessary.

F. L. USHER.

Analysis of products of [thermal] decomposition of carbonyl chloride. A. STOCK and W. WUSTROW [with H. LUX, H. RAMSER, and A. SCHEIDER] (Z. anorg. Chem., 1931, **195**, 129—139).—The separation and analysis of mixtures of carbonyl chloride, carbon monoxide, carbon dioxide, chlorine, carbon tetrachloride, and hydrogen chloride by fractional condensation and the use of mercury vapour, alkali, aniline, and sodium amalgam as absorbents are described (cf. A., 1925, ii, 987).

R. CUTHILL.

Drop method of detection of thiocyanate and ferrocyanide ions together. A. V. PAVLINOVA and T. N. BACH (Ukraine Chem. J., 1930, **5**, [Sci.], 233—234).—A drop of ferric chloride solution is placed on a filter-paper, then a drop of dilute sulphuric acid, and finally a drop of the solution under examination, when a blue stain enclosed in a red ring indicates the presence of ferrocyanide and thiocyanate ions.

R. TRUSZKOWSKI.

Quality of filter-paper and sensitivity of the drop method. A. V. PAVLINOVA and T. N. BACH (Ukraine Chem. J., 1930, **5**, [Sci.], 235—236).—Potassium ferrocyanide can be detected by the drop method at a dilution of *N*/8445 using ash-free filter-paper, and of *N*/5000 using ordinary filter-paper.

R. TRUSZKOWSKI.

Helium. VIII. Determination of minute quantities of helium. IX. Helium content of iron, of the accessory components of ferrous meteorites, and of terrestrial metals. F. PANETH and W. D. URRY (Z. physikal. Chem., 1931, **152**, 110—126, 127—149).—VIII. By employing a heated wire manometer in a manner similar to that previously described (A., 1930, 1543) quantities of helium of from 7×10^{-9} to 1×10^{-4} c.c. may be determined with an error which falls from 50% to 1% as the quantity increases within the limits stated. The variation of the galvanometer deflexion with the gas pressure is described, and details are given of the precautions which are necessary to obtain accurate results.

IX. An apparatus whereby metals and other materials may be dissolved in acid without admission of air or of radioactive impurities is described; the helium and radium contents may thus be determined in one specimen. By employing this apparatus in conjunction with the heated wire manometer the helium content of iron derived from 38 meteorites has been found to lie between 0·23 and 36×10^{-6} c.c. per g.; the non-ferrous constituents appear to contain only slightly smaller quantities of helium. In certain stony meteorites the helium content of the ferrous constituent is only about one sixth of that of the stony part, and the distribution in the latter is irregular. Two specimens of commercial copper contained no helium of radioactive origin, whereas one specimen of iron contained 10^{-6} c.c. per g. Investigation of the liberation of helium from ferrous meteorites on heating shows that only about 2—6% of the total helium is evolved on heating at 1000° for many hours; the age of such meteorites, therefore, cannot be determined by this method (cf. A., 1930, 1398).

H. F. GILLBE.

Spectro-analytical investigations. IX. Spectro-analytical determination of strontium in calcium. K. RUTHARDT (Z. anorg. Chem., 1931, **195**, 15—23).—The determination of strontium in concentrations of the order of 0·1—0·4 at.-% in calcium salts by the comparative spectroscopic method (Gerlach and Schweitzer, "Die chemische quantitative Emissionsspektralanalyse," Leipzig, 1930, p. 60) is described. Amounts of strontium too small to be detected by ordinary chemical methods may be determined. R. CUTHILL.

Detection of magnesium by means of dyes. J. V. DUBSKY and A. OKAC (Chem. Listy, 1930, **24**, 492—493).—2 : 4 - Dihydroxyphenylazo - *p* - nitro - benzene gives a blue adsorption compound with magnesium salts in alkaline solution; 0·0002 mg. of magnesium can be detected in this way. An identical coloration is given by nickel, and a similar one by cobalt. R. TRUSZKOWSKI.

Indirect determination of magnesium carbonate in the presence of calcium carbonate. G. A. PANTSCHENKO (Ukraine Chem. J., 1930, **5**, [Sci.], 187—196).—The mixture of carbonates is dissolved in a known volume of standardised acid, and excess of acid is titrated back using borax solution, whence the total alkaline-earth alkalinity is calculated. Calcium is precipitated as oxalate from the solution, and the oxalate is titrated, using permanganate, Magnesium is calculated as the difference between total and calcium alkalinity. R. TRUSZKOWSKI.

Determination of magnesium as pyrophosphate. S. S. MIHOLIĆ (Bull. Soc. Chim. Yougoslav., 1930, **1**, 24—16).—Traces of carbon present in the precipitate can be effectually destroyed by heating for 2 hrs. at 480°. This operation can be satisfactorily carried out in a Gooch crucible of Jena glass having pore diameter 20—30 µ. F. L. USHER.

Determination of magnesium with 8-hydroxyquinoline gravimetrically, volumetrically, and colorimetrically. W. A. HOUGH and J. B. FICKLEN (J. Amer. Chem. Soc., 1930, **52**, 4752—4755; cf. Strebinger and Reif, A., 1929, 1258).—1—10 Mg. of magnesium in 50—150 c.c. of solution is precipitated as described (*loc. cit.*) and the precipitate, after being washed with dilute ammonia, is ignited and weighed as magnesium oxide; 0·0001—0·0025 g. of magnesium is best determined volumetrically. The washed precipitate obtained as above is dissolved in 100 c.c. of hot *N*-sulphuric acid and the solution is titrated with potassium permanganate (4·17 g. per litre, 1 c.c.$\equiv$0·0001 g. of magnesium) until, on the addition of 0·5 c.c., the pink colour persists for 2 min. 0·5—5·0 Mg. of magnesium in 70 c.c. of ammoniacal solution may be rapidly determined colorimetrically by addition of 60 c.c. of reagent (0·5 g. of 8-hydroxyquinoline in 100 c.c. of alcohol diluted to 1 litre). The filtrate and ammoniacal washings from the precipitate are made up to 150 c.c. The depth of colour, due to uncombined 8-hydroxyquinoline, is inversely proportional to the weight of magnesium. Of the other metals commonly found in natural waters, calcium alone interferes. J. G. A. GRIFFITHS.

Cyanide method of separating zinc from cadmium. N. A. TANANAEV and N. S. FEDULOV (Ukraine Chem. J., 1930, **5**, [Sci.], 213—216).—Potassium cyanide is added to the solution under examination, containing cobalt, copper, zinc, and cadmium, until the coloration disappears or changes, when sodium sulphide is added in excess, the solution is boiled, and the precipitate of zinc and cadmium sulphides is collected, washed, and extracted with boiling potassium cyanide solution, which dissolves zinc but not cadmium sulphide. Zinc is detected by acidifying the filtrate with acetic acid, when it is precipitated as sulphide. In this way 1 part of cadmium can be detected in the presence of 100 parts of zinc, or of the above other metals. Conversely, 1 part of zinc can be detected in the presence of 100 parts of cadmium, or of 50 parts of copper. Manganese if present should previously be eliminated as dioxide by oxidation with hydrogen peroxide.

R. TRUSZKOWSKI.

Rapid determination of zinc in brass alloys. THEWS and HARBISON.—See B., 1931, 117.

Detection of zinc, copper, and silver. A. SERGEEV (Ukraine Chem. J., 1930, **5**, [Sci.], 227—230).—Sodium hydroxide solution and powdered aluminium are added; the presence of zinc is indicated by a swelling of the grains of metal. Silver is detected by feebly acidifying the solution with nitric acid, and adding a drop of mercury, when grey or silvery needles

separate. Copper is detected by dipping a heated glass rod into a drop of solution and heating in a reducing flame, when an orange coloration appears on the glass; 0·0003 mg. of copper can be detected by this method. R. TRUSZKOWSKI.

Distinction between neutral and basic lead acetate. W. A. MUNDT (Ann. Farm. Bioquim., 1930, **1**, 119—120).—Basic lead acetate (1 in 3000), but not the neutral salt, forms yellow lead peroxide with hydrogen peroxide. CHEMICAL ABSTRACTS.

Iodometric determination of thallium in presence of ferric iron. Determination in cadavers. R. FRIDLI (Deut. Z. ges. gerichtl. Med., 1930, **15**, 478—488; Chem. Zentr., 1930, ii, 1583).—A procedure is described in detail. In a case of fatal poisoning by thallium acetate solution (100 g., 2·5%) the liver contained 3·3 mg., the kidneys 1·6 mg., and the urine 5·0 mg. of thallium per 100 g. (cf. this vol., 56). A. A. ELDRIDGE.

Microchemical detection of certain heavy metals by drop reactions with diphenylthiocarbazide. H. FISCHER (Mikrochem., 1930, **8**, 319—329).—The colour reaction between a carbon tetrachloride solution of diphenylthiocarbazide and aqueous solutions of various heavy metal salts is well adapted to microchemical drop reactions on porcelain or on filter-paper. Copper salts give a yellowish-brown coloration, and in presence of 2% ammonia 0·02 microg. in 0·05 c.c. may be detected; the limit in presence of a 246,000-fold excess of lead or a 144,000-fold excess of cadmium is 0·05 microg. Lead (0·1 microg. in 0·05 c.c.) in presence of 5% potassium cyanide solution yields a completely specific brick-red coloration and the sensitivity is not lowered in presence of 9000—18,000 times the quantity of antimony, zinc, copper, cadmium, or nickel, and is reduced only by one half by a 58,000-fold excess of silver. Silver (0·05 microg. in 0·05 c.c.) in neutral solution yields a violet precipitate which on shaking becomes dispersed throughout the carbon tetrachloride; acids interfere and ammonia greatly reduces the sensitivity. In faintly alkaline solution containing sodium potassium tartrate 0·5 microg. of silver in presence of 4570 microg. of lead, 1000 microg. of zinc, or 900 microg. of antimony may be detected. Although the reaction with zinc is very sensitive, other metals interfere to such an extent as to render the method of little value. An alkaline aqueous solution of diphenylthiocarbazide will detect 0·03 microg. of cobalt; 1·0 microg. may be detected in presence of 1050 microg. of nickel. H. F. GILLBE.

Thio-salts. V. L. MASALSKI (Ukraine Chem. J., 1930, **5**, [Sci.], 129—134).—For the qualitative analysis of mixtures containing copper, silver, mercury, arsenic, antimony, and tin the metals are as usual precipitated as sulphides, which are treated with 20% sodium hydroxide solution. The insoluble residue contains copper, silver, and mercury, which are detected in the usual way. The alkaline solution is acidified, and the reprecipitated sulphides are treated with ammonium carbonate, which dissolves arsenious sulphide, and the antimony is separated from the tin by the action of hydrochloric acid and hydrogen peroxide. R. TRUSZKOWSKI.

Cathode-ray tube in X-ray spectroscopy and quantitative analysis. G. R. FONDA and G. B. COLLINS (J. Amer. Chem. Soc., 1931, **53**, 113—125).—The X-ray spectrum of the substance is excited directly by allowing electrons from a cathode-ray tube to impinge on the material as a target. An ionisation chamber and vacuum-tube amplifier for registering and determining the intensity of the spectral lines are described. Data of the relation between composition and the intensity of the $K\alpha$ radiations from copper–zinc, copper–nickel, iron–nickel, iron–molybdenum, silver–cadmium, and tin–antimony alloys are recorded. 0·5% of an element can be detected, and more than 3% can be determined. J. G. A. GRIFFITHS.

Spectro-analytical determinations in micro-analysis. X. Excitation of spectral lines by high-frequency sparks, and determination of traces of mercury. W. GERLACH and E. SCHWEITZER (Z. anorg. Chem., 1931, **195**, 255—268).—The spectro-analytical determination of mercury by means of the spectrum produced by high-frequency sparks is described. By adding a little copper sulphate to the solution for analysis, then passing hydrogen sulphide and sparking the precipitated mixture of sulphides, amounts of mercury even less than 4γ can be determined with a maximum uncertainty of $\pm 25\%$. If the mercury is deposited electrolytically on tinfoil before being sparked quantities less than $0·07\gamma$ may be determined. Suitable apparatus for the production of high-frequency sparks and for the sparking of solids and liquids is described. R. CUTHILL.

Analytical chemistry of rhenium. II. Determination of rhenium as nitron perrhenate after precipitation as sulphide. W. GEILMANN and F. WEIBKE (Z. anorg. Chem., 1931, **195**, 289—308; cf. A., 1930, 1547).—Rhenium sulphide is precipitated quantitatively from a solution containing 30—35 c.c. of hydrochloric acid (*d* 1·19) per 100 c.c. by heating at 90—95° and then passing in hydrogen sulphide as the solution cools, the current of gas being continued for 2—2·5 hrs. The precipitate is collected on an asbestos filter and the filtrate again boiled and saturated with hydrogen sulphide. After washing the united precipitates with hydrogen sulphide water containing 5% of hydrochloric acid they are suspended in 5% sodium hydroxide solution and oxidised to sodium perrhenate with hydrogen peroxide. The excess of peroxide is then destroyed by boiling and the rhenium is precipitated from the acid solution as nitron perrhenate and determined as such. The maximum error in the above determination is 0·1—0·2 mg. of rhenium and as little as 0·075 mg. of rhenium in 100 c.c. of solution can be detected by precipitation as sulphide. Any molybdenum present in the solution is precipitated by nitron at the same time as the rhenium. Insoluble rhenium compounds should be oxidised to perrhenate by fusion with a mixture of equal parts of sodium peroxide and sodium carbonate. R. CUTHILL.

Diphenylamine as indicator in determination of iron in silicates. C. J. SCHOLLENBERGER (J. Amer. Chem. Soc., 1931, **53**, 88—98; cf. Szebellédy, A., 1930, 1149; Sarver, B., 1927, 557).—The effect of

sulphuric, hydrochloric, phosphoric, hydrofluoric, and fluoroboric acids, and salts, on the electrometric titration curves of ferrous salts with dichromate has been investigated and correlated with the effects of these substances on the sharpness of the diphenylamine end-point and the thiocyanate end-point of the back titration of the ferric iron with titanous chloride. The sharpness of the former end-point in the presence of sulphuric acid with either hydrofluoric or phosphoric acid is related to the lowering of the oxidation potential by the last two acids, which, unlike fluoroboric acid, cause serious errors in the thiocyanate end-point. The ferrous and total iron in silicates is determined by adding to the silicate in a platinum crucible (cf. Sarver, *loc. cit.*) 6 c.c. of water, 6 c.c. of 1 : 1 sulphuric acid, and, after boiling, 6 c.c. of hydrofluoric acid. The cooled liquid is diluted to 25 c.c. and titrated with dichromate, diphenylamine being used as indicator. 4 G. of boric acid are added and the liquid is titrated with titanous chloride, thiocyanate being used as indicator. Organic matter may interfere; manganese does not.

J. G. A. GRIFFITHS.

Detection of cobalt as cæsium cobaltinitrite. H. YAGODA and H. M. PARTRIDGE (J. Amer. Chem. Soc., 1930, **52**, 4857—4858).—The residue obtained by evaporating to dryness the solution of cobalt sulphide in aqua regia is dissolved in 1—2 c.c. of $6M$-acetic acid, and then 2 c.c. of $6M$-potassium nitrite and 0·5 c.c. of $0·5M$-cæsium nitrate are added. 0·01 Mg. of cobaltous ion per c.c. yields a yellow precipitate in about 3 min. Iron, manganese, and nickel do not interfere. J. G. A. GRIFFITHS.

Rapid determination of nickel in plating baths. A. WOGRINZ.—See B., 1931, 162.

Sensitive test for molybdenum. J. V. TAMCHYNA (Chem. Listy, 1930, **24**, 465—466).—Molybdic acid gives a violet coloration with potassium cetylxanthate in dilutions not exceeding 1 : 4,000,000. The presence of excess of tungsten does not interfere with this reaction, which cannot, however, be applied in the presence of copper, iron, nickel, or bismuth.

R. TRUSZKOWSKI.

Detection of zirconium. F. PAVELKA (Mikrochem., 1930, **8**, 345—351).—The limiting concentration for the detection of zirconium by the colour reaction with carminic acid is 1 in 10^5; titanium, phosphate, sulphate, and fluoride interfere, but thorium, cerium, and aluminium are without influence on the reaction if 20% of hydrochloric acid be added to the solution. For the gallocyanine reaction the limiting concentration is 2 in 10^6, and the sensitivity is not greatly reduced by the presence of aluminium, thorium, beryllium, or cerium if 10% of hydrochloric acid be added. The zirconium–gallocyanine complex may be precipitated by addition of 4% sodium arsenate solution to the hot acidified mixture, addition of alcohol to dissolve any excess of gallocyanine, and filtration of the complex arsenate through a filter pencil; 2—3 microg. of zirconium yield a definite blue deposit. The *m*-nitrophenylarsinate may be precipitated by a similar method, and the reaction is then especially useful when large quantities of cerium are present. In all the reactions employing gallocyanine nitrate must be absent, and the reagent should be added in the solid form, as its solutions become less sensitive when kept. When employed as a drop reaction the limiting concentration is about 1 in 2000, and the reaction is applicable in presence of 500 times the quantity of thorium. H. F. GILLBE.

Determination of platinum in platinum ore. W. R. SCHOELLER.—See B., 1931, 117.

Ultra-violet spectrophotometry. G. E. DAVIS and C. SHEARD (J. Opt. Soc. Amer., 1931, **21**, 47—58).—A simple type of container for the under-water spark, with suitable electrical circuits, and a new type of quartz cell to contain liquids under examination are described. Experimental technique, modifications of apparatus, and methods of obtaining data with the quartz spectrograph and Hilger rotating-sector photometer are considered. N. M. BLIGH.

Cathode sputtering. C. H. CARTWRIGHT (Rev. Sci. Instr., 1930, [ii], **1**, 758—763).—The practical technique of sputtering, and a suitable apparatus, are described and discussed with special reference to the deposition of gold and platinum. N. M. BLIGH.

"Star trail" method for spectrographic determination of elements. A. C. SHEAD and G. F. SMITH (J. Amer. Chem. Soc., 1930, **52**, 5295).—The image of a bright line from the spectrum falls on a film moving rapidly at constant speed so that the trace of the line is spread out into a band of uniform density. The density depends on the concentration of the given element in the solution employed. The concentration of the element can be determined by comparison with the bands obtained when solutions of known concentration are used. J. G. A. GRIFFITHS.

Low-vacuum pressure control apparatus. L. A. RICHARDS (Rev. Sci. Instr., 1931, [ii], **2**, 49—52).—An apparatus is described for maintaining any constant vacuum, independent of atmospheric changes, in any number of vacuum tanks, the pressure in each being independently variable. A control vacuum is employed, and is preserved by a pump started automatically by an electrical make and break actuated by variations of external pressure. N. M. BLIGH.

Determination of the reflectivity of metals and reflectors for ultra-violet rays by means of a cadmium cell and electrometer. A. RUTTENAUER (Licht u. Lampe, 1928, **17**, 2 pp.; Chem. Zentr., 1930, ii, 1664).

Effect of various factors in the output of Leclanche cells. V. A. KOSTJEJEV.—See B., 1931, 166.

Filter flasks with interchangeable side-tubes. F. FRIEDRICHS (Chem.-Ztg., 1931, **55**, 31).—The ordinary conical flask for vacuum filtration is provided with a side tubulure into which any type of tube may be fitted by means of rubber or glass stoppers.

A. R. POWELL.

Filter-paper containing iodine. K. SCHERINGA (Pharm. Weekblad, 1930, **67**, 1362).—Filter-papers several years old were found to contain 0·5 mg. of combined iodine. S. I. LEVY.

Electrode containers for rapid p_H measurement. W. KORDATZKI (Chem. Fabr., 1931, 25—

27).—Three electrode containers for the hydrogen or quinhydrone electrode are described. The first consists essentially of a crucible of porcelain, glazed except for its lower extremity. When it is immersed in potassium chloride solution for *E.M.F.* measurement against a calomel electrode the unglazed tip acts as a diaphragm. Several crucibles are used alternately and are kept in saturated potassium chloride solution when not in use. Another design consists of a glass tube narrowed at the bottom and closed by a rod of porous porcelain with rubber connexion. A half-cell suitable for continuous p_H measurement is similarly fitted to a porcelain rod. The tube above this is packed with solid potassium chloride and charged with potassium chloride solution. A side tube communicating with an upper tube in which the solution to be examined is contained enables this to be held in contact with the potassium chloride solution, and, if necessary, run through the apparatus at any desired rate. A series of comparative determinations is given. C. IRWIN.

Luther's calcium electrode of the third order. J. VELISEK and K. SVENCON (Chem. Listy, 1930, **24**, 467—471).—The results obtained for the concentration of calcium ions, using the above electrode, are neither accurate nor reproducible. R. TRUSZKOWSKI.

Vacuum evaporation and distillation. H. N. NAUMANN (Chem. Fabr., 1931, 4—7).—Most vacuum distillation apparatus involves a relatively enormous gas velocity. With liquids which foam the contamination of the distillate can be avoided only by greatly reducing the throughput. A swan-neck connexion between the flask and the condenser minimises this effect as far as possible. When evaporation is to be carried to dryness a flask in two halves is of service. The lower half, of copper, has a central pocket in which the last traces of liquid collect and into which the boiling capillary extends. An apparatus capable of distilling up to 10 litres per hr. at 10—20° is described. This is recommended for the preparation of sera and other sensitive biochemical products. C. IRWIN.

Vacuum fractionation of phlegmatic liquids. K. HICKMAN and W. WEYERTS (J. Amer. Chem. Soc., 1930, **52**, 4714—4728; cf. A., 1930, 567).—Still heads, with special manometric devices, for fractionating liquids under accurately known low pressures are described. In order to obtain correct data, the thermometer should be situated in an expansion of the column where the vapour has a relatively small velocity, and the manometer should operate directly from the wall of this expansion. The methods have been applied to the purification of 1-chloronaphthalene and *n*-butyl benzoate, and the separation of the latter from ethyl phthalate. J. G. A. GRIFFITHS.

Separatory funnel for washing heavy, volatile liquids. H. S. KING (Proc. Nova Scotian Inst. Sci., 1930, **17**, 240—241).—The apparatus is constructed from two separatory funnels, the stem of the first ending in the bulb of the second and the top of the second being joined to the bulb of the first. A heavy liquid in the first funnel can be delivered into the second out of contact with the atmosphere, and after any supernatant liquid has been discarded, is returned for further washing by inverting the apparatus. H. BURTON.

Gas analysis. E. VOSSIECK and A. SCHMITZ (Chem. Fabr., 1930, 529—531).—In the modified apparatus described the combustion and absorption of the gases are conducted in two independent systems so that two analyses can be made side by side. The absorption pipette has the wide part (30 c.c.) at the top and the narrow calibrated part (20 c.c.) at the bottom, whereas in the combustion pipette these positions are reversed. Various minor modifications in the absorption and cooling apparatus are described. A. R. POWELL.

Slow-combustion pipette for gas analysis. H. R. AMBLER (J. Sci. Instr., 1931, **8**, 18—19).—In the apparatus described the slow combustion of gases is ensured without risk of explosion by controlling the rate of supply of oxygen, which is led through a capillary tube under a surface of mercury. The apparatus may also be used as an explosion pipette and for the absorption of gas in liquid reagents. E. S. HEDGES.

Evaporation of large quantities of liquids in the laboratory. C. BLACHER (Chem. Fabr., 1930, 534).—The apparatus previously described by Fuchs (A., 1930, 1549) is modified by inverting the reservoir flask in a beaker from which the liquid is continuously siphoned into the evaporating vessel as the level sinks therein. In this way the reservoir can be repeatedly refilled without disturbing the evaporation. A. R. POWELL.

Physical methods in chemical laboratories. XVI. Action of electrical discharges on gaseous elements and compounds. H. GEHLEN (Z. angew. Chem., 1931, **44**, 30—34).—The preparation, properties, and reactions of active nitrogen and hydrogen are reviewed and a brief account is given of the action of a glow discharge on various organic gases and vapours. A. R. POWELL.

Autographic apparatus for determining inflexion points in magnetic susceptibility curves. J. L. HOUGHTON (J. Sci. Instr., 1931, **8**, 7—14).—The apparatus described enables automatic records of the variation of magnetic susceptibility with temperature to be taken. An alternating current from a valve oscillator is supplied to the magnetising coil of the apparatus and the output from the search coil, amplified and rectified by triode valves and a Westinghouse rectifier, is registered on a thread recorder, together with the temperature of the specimen under examination. E. S. HEDGES.

Adjustable drop-control for burettes. F. HOLLANDER (Science, 1931, **73**, 45—46).—A mechanical drop-control for micro-titrations is decribed. L. S. THEOBALD.

Simple burette without faucet. P. S. TOLCHKOV (J. Chem. Ind., Russia, 1929, 6, 207—208).—Simple arrangements for filling burettes without admittance of air are described. CHEMICAL ABSTRACTS.

Inorganic lubricants. IV. Lubricants for temperatures above and below normal. W. A. BOUGHTON (J. Amer. Chem. Soc., 1930, **52**, 4858—4860).—High b.-p. aqueous solutions of meta- and

ortho-phosphoric acids, sodium metaphosphate alone and mixed with borax, and orthophosphoric acid afford lubricants which may be used within ranges of temperature between 25° and 160°. Fused salts mixed with graphite or kaolin afford lubricants effective within ranges of temperature between 45° and 360°. Solutions of metaphosphoric acid may be used at temperatures between −75° and 0°.

J. G. A. GRIFFITHS.

Manometer for small pressure differentials at high pressures. J. H. BOYD, jun. (J. Amer. Chem. Soc., 1930, 52, 5102—5106).—The instrument is suitably enclosed to permit the use of high pressures and consists of a mercury reservoir of diameter 8·9 cm.; beneath the surface of the mercury projects the lower end of a riser well of 8 mm. bore in which can be moved a screw which permits an electrical circuit through the mercury to be completed or broken. The level of the mercury in the well is measured in terms of the position of the top of the screw when, on slowly raising the screw, the circuit is just broken. Pressure differentials of 1 in. of mercury at a total pressure of 3000 lb. per sq. in. can be determined to within 0·001 in.

J. G. A. GRIFFITHS.

Content of iron soluble in hydrochloric acid of asbestos used for Gooch crucibles. E. CATTELAIN (Bull. Soc. chim., 1930, [iv], 47, 1404—1406).—The iron content of a number of samples of white asbestos fibre "for Gooch crucibles," determined by extraction with hydrochloric acid, varied from 1·187 to 8·553%. Other specimens, *e.g.*, of cord and powder, contained from 0·067 to 12·873%. In all cases traces of manganese also were present. H. F. GILLBE.

Dropping-flask for boiling liquids. E. KRUGER (Chem.-Ztg., 1930, 54, 987).—An Erlenmeyer flask with the side-tube drawn out at the end and slightly bent over is convenient for delivering drops of boiling water, *e.g.*, to precipitates. The neck drawn out a little and bent in the opposite direction will deliver large quantities. L. J. HOOLEY.

Geochemistry.

Iodine content of Latvian waters in relation to the distribution of goitre. J. KUPZIS (Latvij. Univ. Raksti, 1930, 1, 425—453).—Systematic analysis of the water in different parts of Latvia reveals a correlation between iodine deficiency and the incidence of goitre. No effect can be traced to an abnormally large content of calcium, magnesium, iron, or humic substances. Determination of iodine excreted with the urine affords a more satisfactory indication of the adequacy or otherwise of the iodine supply of a district than analysis of the water supply only. The causes of iodine deficiency are discussed.

F. L. USHER.

Radioactivity of Stone Mountain springs. J. A. HOOTMAN and W. S. NELMS (Amer. J. Sci., 1931, [v], 21, 37—38).—The radioactive content of springs at Stone Mountain, Georgia, is due mainly to radium emanation originally dissolved in the water. The values obtained range from 15·60 to 0·12 millimicrocuries per litre. C. W. GIBBY.

Radioactivity of the mineral springs of South Poland. L. WERTENSTEIN, W. BARTNICKA, and J. BICZYK (Spraw. Proc. panst. Inst. farm., 1926; Chem. Zentr., 1930, ii, 29).—The radioactivity of 49 springs did not exceed a few Mache units.

L. S. THEOBALD.

Application of thermo-magnetic analysis to the study of iron minerals and oxides. J. HUGGET and G. CHAUDRON (Korrosion u. Metallschutz, 1930, 6, 79—82; Chem. Zentr., 1930, ii, 1347).—The Curie point of magnetite is near 570°; heating at 330° in air affords an unstable, strongly magnetic compound of composition between Fe_2O_3 and Fe_3O_4. Martite and oligist show instability at 570° and 675°. Goethite, paramagnetic, becomes ferromagnetic when heated in air at 360°. The magnetisability increases in a vacuum owing to removal of water, and at 570° diminishes further. Goethite dehydrated at 600° in a vacuum behaves like magnetite. Lepidocrocite behaves similarly. Pyrite and markasite, at first non-magnetic, undergo oxidation at 400°. Pyrrhotite when heated in air above 250° exhibits at first an increase and then an irregular decrease in magnetisation up to 340°. Rust behaves like goethite or lepidocrocite. A. A. ELDRIDGE.

Mineral collection of the Kongsberg silver works as basis for the study of the origin of the silver deposits. R. STØREN (Tidsskr. Kjemi Berg., 1931, 11, 16—21).—The different forms and modes of occurrence of native silver and argentite in the Kongsberg mining field are described, and the probable modes of formation of the silver minerals are discussed. The mossy variety of native silver invariably contains mercury, in some cases up to 7%, whilst this element is absent from the wire silver; the former kind of silver is also always accompanied by small amounts of nickel and cobalt minerals, thus resembling the occurrence at Temiskaming in Canada. It is suggested that a part of the native silver may have been formed from the reduction of argentite by hydrocarbons; support is afforded to this view by the frequent occurrence of small quantities of anthracite in the lodes. Little attention has hitherto been paid to the presence of mercury in the silver; this element is more abundant than was formerly supposed, although no definite mercury ores occur, and the investigation of the source of this mercury is regarded as being important for determining the mechanism of the origin of the silver deposits. H. F. HARWOOD.

Formation of talc. E. ENK (Kolloid-Z., 1931, 54, 84—86).—The geological formation of talc is further discussed from a colloid-chemical point of view (cf. A., 1930, 732). E. S. HEDGES.

Boleite, pseudoboleite, and cumengeite. G. FRIEDEL (Z. Krist., 1930, 73, 147—158; Chem. Zentr., 1930, ii, 1355).—Boleite, tetragonal, is not

identical with pseudoboleite (cf. Gossner and Arm, A., 1930, 1352). A. A. ELDRIDGE.

Pegmatites of sodalitic syenite from Ruma Island (Los Archipelago, French Guinea). Serandite, a new mineral. A. LACROIX (Compt. rend., 1931, **192**, 189—194).—These pegmatites consist primarily of microperthite, between the plates of which are found (the groups are in approximate order of crystallisation): (1) sodalite, elæolite, and eucolite, with occasionally astrophyllite and arfvedsonite, also leucophanite, fluorspar, serandite, ægyrine, blende, and molybdenite; (2) analcite and mesolite; (3) villiaumite in fine carmine crystals. Eucolite is occasionally replaced by catapleiite, or converted into eudialite. Serandite, leucophanite, and catapleiite are confined to the pegmatites, lavenite being the only silicozirconate in the syenite, which also contains pyrochlore and galena, but no blende or molybdenite. The sodalite fluoresces intensely (orange-yellow) in ultra-violet light, as also do the catapleiite (green), leucophanite (peach), and fluorspar (violet). Serandite is a new mineral, crystallising in monoclinic, peach-coloured crystals sometimes 5 cm. long. *d* 3·215; optically positive, γ 1·688, β 1·660 (approx.), $\gamma-\alpha$ 0·035. Its composition is SiO_2 48·72, Al_2O_3 0·29, Fe_2O_3 0·03, FeO 1·33, MnO 28·99, MgO 0·06, CaO 10·42, Na_2O 7·38, K_2O 0·26, H_2O+ 2·67, H_2O- 0 11, total 100·46%; corresponding with that of an acid manganous sodium calcium metasilicate, $(Mn,Ca)_{7.5},(Na,K)_3,H_2(SiO_3)_{10}$. C. A. SILBERRAD.

Gneisses in Manitoba and Saskatchewan. E. L. BRUCE and A. F. MATHESON (Trans. Roy. Soc. Canada, 1930, [iii], **24**, IV, 119—132).—The Kisseynew gneiss near the ore-body in the Sherritt Gordon mine in northern Manitoba is described. It consists of andesine, amphibole, and garnet, with some magnetite and quartz, and has been derived by the recrystallisation of a sedimentary rock. Chemical analyses are given of the rock and of the contained garnets. Similar gneisses also occur in northern Saskatchewan. L. J. SPENCER.

Hydrargillite and sulphidic bauxite in Istria. T. KORMOS [with GEDEON] (Ban. Kohasz. Lapok, 1903, **63**, 269—277; Chem. Zentr., 1930, ii, 1851).—Analyses are recorded. The mud of the medicinal spring at Santo Stefano contains: Al_2O_3 28·79, SiO_2 41·72, TiO_2 0·40, Fe_2O_3 2·25, Mn_2O_3 trace, CaO 5·16, P_2O_5 0·22, FeS_2 1·18, loss on ignition 20·687%. A. A. ELDRIDGE.

Meliphanite and leucophanite. W. H. ZACHARIASEN (Z. Krist., 1930, **74**, 226—229; Chem. Zentr., 1930, ii, 1964).—Meliphanite has the formula $(Ca,Na)_2Be(Si,Al)_2(O,F)_7$; leucophanite has the formula $(Ca,Na)_2BeSi_2(O,OH,F)_7$. A. A. ELDRIDGE.

Origin of desert varnish. J. D. LAUDERMILK (Amer. J. Sci., 1931, [v], **21**, 51—66). A sample of "desert varnish," the properties of which are described, contained SiO_2 90·00, Al_2O_3 1·20, Fe_2O_3 2·40, CaO 0·60, MgO trace, MnO 4·46, loss on ignition 1·40%. C. W. GIBBY.

Radium in rocks. II. Granites of Eastern North America from Georgia to Greenland. C. S. PIGGOT (Amer. J. Sci., 1931, [v], **21**, 28—36).—Figures given for the radium contents of rocks are revised (cf. A, 1929, 1035). Eleven other rocks have been examined. Granite from Stone Mountain, Georgia, and from North Jay, Maine, contain, respectively, 3·81 and $3{\cdot}39\times10^{-12}$ g. Ra per g. The radium content of the others varies from 2·79 to $0{\cdot}26\times10^{-12}$ g. per g., with an average value of about $0{\cdot}9\times10^{-12}$. C. W. GIBBY.

Chemical reactions of colloidal clay. R. BRADFIELD (J. Physical Chem., 1931, **35**, 360—373).—A general review in which the characteristics of hydrogen clays, the titrable acidity of electrodialysed clays, the distribution of a base between an electrodialysed bentonite and organic acids, and the effect of the exchangeable cations on the physical properties of clays are discussed. L. S. THEOBALD.

Composition of New York soils. J. A. BIZZELL (Cornell Univ. Agric. Exp. Sta. Bull., 1930, No. 513, 25 pp.).—Among numerous soils examined the total calcium content alone is characteristic of soil type. The total contents of nitrogen, phosphorus, sulphur, potassium, and magnesium, whilst in no way associated with type, tended to be higher in more finely textured soils. The nitrogen and sulphur contents were higher and the potassium and magnesium contents lower in surface soils than in subsoils. A. G. POLLARD.

Nature and fate of the meteor crater bolide. H. L. FAIRCHILD (Science, 1930, **72**, 463—467).—Speculative. The nature of the meteor which produced the Meteor Cradle, Arizona, is discussed. L. S. THEOBALD.

Barringer meteorite. D. M. BARRINGER, jun. (Science, 1931, **73**, 66—67).—Polemical (cf. preceding abstract). L. S. THEOBALD.

Chemical aspects of the origin of petroleum. S. C. LIND (Science, 1931, **73**, 19—22).—A presidential address. L. S. THEOBALD.

Organic Chemistry.

Thermal chlorination of methane by a flow method. R. N. PEASE and G. F. WALZ (J. Amer. Chem. Soc., 1931, **53**, 382).—Chlorination (non-catalytic) of methane occurs in pyrex glass tubes above 200° at 1 atm.; the reaction is homogeneous. At 225—300°, the reaction is inhibited by oxygen, but at 375° the rate is not affected. H. BURTON.

Decomposition and synthesis of organic compounds by electrical discharges. I. Electrodeless discharge. W. D. HARKINS and D. M. GANS.—See this vol., 318.

Synthesis and pyrolysis of methylallene and ethylacetylene. C. D. HURD and R. N. MEINERT

(J. Amer. Chem. Soc., 1931, **53**, 289—300).—Methylallene ($\Delta^{\alpha\beta}$-butadiene), b. p. 10·3°, d_4^0 0·676, $n_D^{1.3}$ 1·4205 (tetrabromide, b. p. 97·5°/7 mm., m. p. —2°, d_4^{20} 2·510, n_D^{20} 1·6070), is prepared by the method of Bouis (A., 1928, 1112) by way of $\alpha\beta\gamma$-tribromobutane and *βγ-dibromo-Δ^α-butene*, b. p. 75°/20 mm., d_4^{20} 1·8881, n_D^{20} 1·5464. Methylallene decomposes completely at 500—550° with a contact time of 36 sec.; 75% is polymerised to liquid products which contain a dimeric methylallene, b. p. 110—115°. The gaseous products consist of small amounts of hydrogen, methane, ethane, ethylene, propylene, and allene. Pyrolysis of ethylacetylene (Δ^{α}-butinene), b. p. 8·5° (lit. 8·5° and 14—18°), prepared from sodium acetylide and ethyl sulphate in liquid ammonia, at 580—600° gives about 33% of liquid products similar to those formed from methylallene, allene, and propinene (this vol., 61); hydrogen, paraffin hydrocarbons (main products), ethylene, propylene, and small amounts of allene, acetylene, and propinene are found in the gaseous products. Pyrolyses of allene (*loc. cit.*) and methyallene are very similar.

H. BURTON.

Oxidation of "tri*iso*butylene" by ozone. R. J. McCUBBIN (J. Amer. Chem. Soc., 1931, **53**, 356—359).—Treatment of "tri*iso*butylene" (Butlerov, A., 1880, 230) with ozonised oxygen in acetic acid containing 1·5—2% of acetic anhydride, and subsequent decomposition of the ozonide by the addition of water and zinc dust, affords trimethylacetaldehyde, methyl *tert.*-butylmethyl ketone, di*tert.*-butylmethyl ketone, and methyl $\alpha\alpha$-di*tert.*-butylethyl ketone. To explain the formation of the last-named ketone, it is necessary to assume that a pinacolic rearrangement occurs during ozonolyisis (cf. *loc. cit.*). The original hydrocarbon probably contains $\beta\beta\delta\zeta\zeta$-pentamethyl-$\Delta^{\gamma}$-heptene (2 mols.), $\delta\delta$-dimethyl-β-*tert.*-butylmethyl-Δ^{α}-pentene (1 mol.), and $\beta\delta\delta$-trimethyl-γ-*tert.*-butyl-Δ^{β}-pentene (1 mol.) (which undergoes the rearrangement). H. BURTON.

Synthesis of squalene. P. KARRER and A. HELFENSTEIN (Helv. Chim. Acta, 1931, **14**, 78—85).—Treatment of impure *farnesyl bromide*, b. p. 125—140°/1 mm., prepared from farnesol or nerolidol by Juvala's method (A., 1930, 1401), with potassium at 100—135°, or, better, with magnesium (activated by methyl iodide) in ether, gives a fraction, b. p. 215—240°/1·1—1·2 mm., containing squalene, since it affords a hexahydrochloride, m. p. 144—145°, crystallographically identical with the squalene hexahydrochloride, m. p. 143—145°, described by Heilbron, Kamm, and Owens (A., 1926, 816). Squalene is, therefore, correctly represented as $(CMe_2{:}[CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe]_2{:}CH{\cdot}CH_2{\cdot})_2$ (cf. A., 1930, 1422). The yield of hexahydrochloride is about 7% (on the farnesyl bromide used). H. BURTON.

Preparation of alkyl iodides. H. S. KING (Proc. Nova Scotian Inst. Sci., 1930, **17**, 242—243; cf. *ibid.*, 1924, **16**, 87—91).—Methyl alcohol containing 10% of water can be used in the preparation of methyl iodide by the method previously described (*loc. cit.*). The preparation of an alkyl iodide is expedited by covering the iodine with the alcohol and adding the resultant solution to the mixture of phosphorus and the remainder of the alcohol maintained, in the case of methyl alcohol, at 70—75°. Sufficient alkyl iodide is produced to serve as the solvent for the iodine.

H. BURTON.

Photochemical reactions of gaseous methyl iodide. J. R. BATES and R. SPENCE (J. Amer. Chem. Soc., 1931, **53**, 381).—A study of the photochemical decomposition and oxidation of gaseous methyl iodide supports the initial change $CH_3I \longrightarrow CH_3 + I$ (cf. Iredale and Mills, A., 1930, 1498). Formaldehyde, paraformaldehyde, and methylal are formed during the oxidation. H. BURTON.

Preparation of nitromethane. P. P. PRITZL and H. ADKINS (J. Amer. Chem. Soc., 1931, **53**, 234—237).—In the preparation of nitromethane from equimolecular quantities of sodium chloroacetate and nitrite (Whitmore and Whitmore, Org. Synth., 1923, **3**, 83), approximately 50% of the nitrite is converted into nitromethane. A further 24% affords methazonic acid (by way of nitromethane), whilst the remainder does not react owing to part of the chloroacetate being hydrolysed to glycollate. The yield of nitromethane is increased to 65—70% when an excess of chloroacetate solution is used; this is best added gradually to the nitrite at 100—110°.

H. BURTON.

Preparation of absolute alcohol. E. G. YOUNG (Proc. Nova Scotian Inst. Sci., 1930, **17**, 248—255).—The cheapest method of preparing absolute alcohol is to heat 95% alcohol (1 litre) with calcium oxide (300 g.) for 4 hrs., and then distil; the yield is about 80% (cf. Noyes, A., 1923, i, 433). The method of Lyons and Smith (B., 1926, 384) gives a better yield at a slightly higher cost, but the product often possesses a disagreeable odour. The method of Young (J.C.S., 1902, **81**, 707) is impracticable. H. BURTON.

Configurational relationships of phenylated carbinols. P. A. LEVENE and A. WALTI (J. Biol. Chem., 1931, **90**, 81—88).—Condensation of *d*-propylene oxide with magnesium *n*-propyl bromide gives *l*-methyl-*n*-butylcarbinol, α^{25} —1·75° (*α-naphthylurethane*, m. p. 81—82·5°, $[\alpha]_D^{25}$ —4·28° in alcohol), consequently the Grignard reaction is not accompanied by a Walden inversion (cf. A., 1926, 597; 1928, 1353). Similarly, magnesium phenyl bromide gives *l*-benzylmethylcarbinol, b. p. 114°/25 mm., $[\alpha]_D^{25}$ —19·8° (*α-naphthylurethane*, m. p. 111—113°, $[\alpha]_D$ —31·6°), oxidised by sodium dichromate to benzyl methyl ketone; therefore *l*-benzylmethylcarbinol, *d*-propylene oxide, and *l*-lactic acid are configuratively related. H. A. PIGGOTT.

Preparation of anhydrous pinacol. H. S. KING and W. W. STEWART (Proc. Nova Scotian Inst. Sci., 1930, **17**, 262—267).—Pinacol hydrate is heated with benzene in a flask fitted with a 3 ft. fractionating column, and the benzene in the distillate is separated from water in an automatic separator and returned to the distilling flask. The process is continued until all the water is removed, and the benzene is distilled off, leaving a residue of anhydrous pinacol. The above method is sufficiently accurate to determine the water content of samples of the hydrate. Dehydration by means of calcium carbide in ether gives a product

with a disagreeable odour; the use of anhydrous copper sulphate causes partial decomposition.
H. BURTON.

Homogeneity and polymorphic transformation of pentaerythritol. L. EBERT (Ber., 1931, **64**, [*B*], 114—119; cf. Friederich and Brün, this vol., 62).—The most efficient method for the purification of pentaerythritol is very cautious sublimation in a high vacuum at about 130°; the transparent, thin, quadratic leaflets have m. p. 260·5° (corr.), in agreement with the datum of Friederich and Brün. When heated, tetragonal pentaerythritol passes into a cubic modification; a study of the cooling curve of pentaerythritol fixes the transition temperature at 179·5°.
H. WREN.

High-pressure synthesis of methyl ether and its theoretical basis. E. BIRK and R. NITZSCHMANN (Metallbörse, 1930, **20**, 1295—1296, 1351, 1407; Chem. Zentr., 1930, ii, 1941).—The equilibrium constants for the dehydration of methyl alcohol to methyl ether have been determined for temperatures between 240° and 400°, together with their dependence on the concentration. A mathematical study of the formation of methyl ether, by way of methyl alcohol, from carbon monoxide and hydrogen indicates a yield of 0·892—11·25%.
A. A. ELDRIDGE.

Auto-oxidation reactions. II. Mechanism of the auto-oxidation of ethers. N. A. MILAS (J. Amer. Chem. Soc., 1931, **53**, 221—233).—The rate of absorption of oxygen by dibenzyl ether in absence and presence of various catalysts has been determined at 40±0·05°. Iodine, picric acid, and *p*-benzoquinone are inhibitors, whilst small amounts of copper, silver, gold, iron, and especially mercury are accelerators. Hydroxybenzyl peroxide, benzaldehyde, and benzoic acid are produced during the oxidation. Ultraviolet irradiation of dibenzyl, *benzyl* tert.-*butyl*, b. p. 205·6—208° (corr.; slight decomp.), d_4^{20} 0·9439 (prepared from benzyl chloride and sodium *tert.*-butoxide at the ordinary temperature), ethyl *n*-, *iso*-, *sec.*-, and *tert.*-butyl, *n*-propyl *tert.*-butyl, di-*n*-butyl, and methyl *tert.*-butyl ethers, and dioxan in quartz vessels at about 45° accelerates peroxide formation to varying extents. Hydrogen peroxide is formed in all cases, *tert.*-butyl alcohol is isolated from all the alkyl *tert.*-butyl ethers, and formic acid is obtained in small amount from all ethers containing the methyl or ethyl group; dioxan gives some formic acid and glycollaldehyde. The peroxides from ethyl *tert.*-butyl, *n*-propyl *tert.*-butyl, di-*n*-butyl, and ethyl *iso*butyl ethers are oils which explode violently when heated. Their properties differ from those of mono- and di-hydroxyalkyl peroxides. The views of Wieland and Wingler (A., 1923, i, 650) on the auto-oxidation of ethers are held to be untenable; oxidation is considered to occur through oxonium peroxides (cf. A., 1929, 1019).
H. BURTON.

Reaction between organic sulphur compounds and sodium in liquid ammonia. F. E. WILLIAMS [with E. GEBAUER-FUELNEGG] (J. Amer. Chem. Soc., 1931, **53**, 352—356).—Diethyl, di-*n*-propyl, and di-*n*-heptyl sulphides react with sodium in liquid ammonia forming the corresponding sodium mercaptides and alkanes: $SR_2+2Na+NH_3 \longrightarrow R{\cdot}SNa+NaNH_2+RH$. Diethyl, di-*n*-propyl, and di-*iso*amyl disulphides are converted into the sodium mercaptides: $S_2R_2+2Na \longrightarrow 2R{\cdot}SNa$. Aliphatic mercaptans and liquid ammonia form ammonium mercaptides, converted by sodium into sodium mercaptides and hydrogen: $2R{\cdot}SNH_4+2Na \longrightarrow 2R{\cdot}SNa+2NH_3+H_2$.
H. BURTON.

α-Chloroethane-α-sulphonyl chloride. E. MÜLLER and H. RAUDENBUSCH (Ber., 1931, **64**, [*B*], 94—101; cf. A., 1927, 672).—Complete chlorination of β- or α-trithioacetaldehyde in aqueous suspension gives *α-chloroethane-α-sulphonyl chloride*, b. p. 70—71°/13 mm., in about 50% yield; sulphuric and acetic acids are also formed. The sulphonyl chloride is also produced in glacial acetic acid solution, whereas *heptachlorodiethyl sulphide*, b. p. 35—36°/9 mm., is obtained in presence of carbon tetrachloride. Hypochlorous acid and trithioacetaldehyde give α-chloroethane-α-sulphonyl chloride, but the formation of sulphuric and acetic acids is more marked, in harmony with the observation that the sulphonyl chloride is much more readily oxidised by hypochlorous acid than by chlorine water. *α-Chloroethane-α-sulphonamide*, m. p. 66°, and *α-chloroethane-α-sulphonphenylhydrazide* are described. The chloride is hydrolysed by water to *α-chloroethane-α-sulphonic acid*; the *potassium*, *sodium*, *ammonium*, *barium*, and *silver* salts have been prepared. Treatment of the chloride with anhydrous methyl or ethyl alcohol affords α-chloroethane-α-sulphonic acid in place of the expected ester. *Methyl α-chloroethane-α-sulphonate* can be obtained by use of sodium methoxide, but the simultaneous production of sodium α-chloroethane-α-sulphonate shows that the reaction partly follows the course $CHMeCl{\cdot}SO_2{\cdot}OMe + Me{\cdot}ONa = CHMeCl{\cdot}SO_2{\cdot}ONa + Me_2O$. Phosphorus pentachloride attacks α-chloroethane-α-sulphonyl chloride with difficulty, yielding ethylidene chloride. Treatment of the chloride with zinc dust in alcohol or acetone, but not in completely anhydrous solvents such as benzene or chloroform, affords *potassium ethanesulphonate*, m. p. 285—286°.
H. WREN.

Preparation of carboxylic anhydrides without the use of phosphorus chlorides. T. PYTASZ and T. I. RABEK (Przemysł Chem., 1930, **14**, 529—535).—Pure acetic anhydride may be prepared by allowing sodium chlorosulphonate to react with sodium acetate in acetic anhydride solution, and distilling the product under diminished pressure.
R. TRUSZKOWSKI.

Decomposition of acetic acid in the presence of silica gel. J. A. MITCHELL and E. E. REID (J. Amer. Chem. Soc., 1931, **53**, 338—343).—A maximum yield (about 28% on acid used) of acetone is obtained when acetic acid is passed over silica gel at 430—460°. The rate of decomposition of the acetone produced is appreciable above 400°; the presence of water vapour retards this decomposition (cf. Kultaschev and Kudrjavzeva, A., 1925, ii, 881). It is calculated from the amount of carbon dioxide produced, in conjunction with the acetone isolated, that 40—60% of the acetone originally formed is decomposed. Some decomposition of the acid into methane and carbon dioxide takes place.
H. BURTON.

Drop reactions for acetic and propionic acids. D. KRUGER and E. TSCHIRCH (Mikrochem., 1930, 8, 337—338).—The method previously described (A., 1930, 62) may be employed as a drop reaction by adding to the neutral solution 5% lanthanum nitrate solution, 0·01*N*-alcoholic iodine solution and, after mixing, *N*-ammonia solution. The limit of sensitivity is about 0·05 mg. for both acids. H. F. GILLBE.

Partial hydrogenation of linolenic acid and its esters. T. P. HILDITCH (Chem. Umschau, 1930, **37**, 354—356).—A reply to Bauer and Ermann (A., 1930, 1271). The results of Hilditch and Vidyarthi (A., 1929, 423) are justified, and the discrepancy between these and the results of Bauer is probably ascribable to differences in the conditions of hydrogenation, *e.g.*, temperature, quantity and activity of the catalyst; further, hydrogenation of esters (cf. Bauer) may proceed differently from the hydrogenation of the free acid. E. LEWKOWITSCH.

[Partial hydrogenation of linolenic acid and its esters.] H. K. BAUER (Chem. Umschau, 1930, **37**, 356; cf. preceding abstract).—The experiments (A., 1930, 1271) were made with linolenic esters.
E. LEWKOWITSCH.

Bromides of elæostearic acid. I. Hexabromide. J. VAN LOON (Rec. trav. chim., 1931, **50**, 32—36).—When a solution of either α- or β-elæostearic acid and the theoretical quantity of bromine in carbon tetrachloride is submitted to the action of ultraviolet light, a portion of the solvent evaporated, and the residue cooled to —20°, a crystalline *hexabromide*, m. p. 157°, is obtained, the residue being a liquid hexabromide contaminated with bromine substitution products. The same crystalline hexabromide is similarly obtained from the solid tetrabromide, m. p. 114°. Debromination of either the solid or liquid hexabromide with zinc and alcoholic hydrogen chloride and subsequent hydrolysis of the ester formed affords β-elæostearic acid in quantitative yield.
J. W. BAKER.

αα′-Dimethyl- and αα′-dibromo-αα′-dimethylsuberic acids. C. C. STEELE (J. Amer. Chem. Soc., 1931, **53**, 283—289).—Ethyl methylmalonate (2 mols.), prepared by way of ethyl α-bromo- and α-cyanopropionate, is condensed with tetramethylene bromide (1 mol.), yielding a mixture of ethyl methyl-Δ^{γ}-butenylmalonate and *ethyl αζ-dimethylhexane-ααζζ-tetracarboxylate* (40% yield), b. p. 210—217°/6 mm.. When the corresponding acid is heated, a mixture of *αα′-dimethylsuberic acids*, m. p. 91—92° and 132—133°, is obtained. Bromination of either form in presence of thionyl chloride gives the same *αα′-dibromo-αα′-dimethylsuberic acid*, m. p. 200—201°. When this acid or its *methyl* ester, b. p. 216—219°/30 mm., is treated with copper-bronze or "molecular" silver, ring closure to a *cyclo*hexane derivative does not take place. H. BURTON.

Decomposition of citric acid by sulphuric acid. E. O. WIIG.—See this vol., 315.

Humic acid. J. LUBERTINO (Univ. nac. La Plata fac. agron., 1930, 96 pp.).—A discussion.
CHEMICAL ABSTRACTS.

Propane-αβ-dithiolacetic acid and propane-αβ-disulphonylacetic acid. J. A. REUTERSKIOLD (J. pr. Chem., 1931, [ii], **129**, 121—128).—αβ-Dithiolpropane, prepared by interaction of sodium hydrogen sulphide and αβ-dibromopropane in alcoholic solution and subsequent purification through the lead salt, yields with concentrated aqueous sodium chloroacetate *propane-αβ-dithiolacetic acid*, m. p. 32—35°. Thionyl chloride forms the acid *chloride*, which gives the *dianilide*. The *copper* salts $C_7H_{10}O_4Cu,H_2O$ and $C_{14}H_{23}O_8S_4Cu$ and the *silver* salt have been prepared. The partial resolution of the acid is described. A 15% neutral solution of propane-αβ-dithiolacetic acid saturated with magnesium sulphate is oxidised by solid permanganate at 0° to *propane-αβ-disulphonylacetic acid*, m. p. 185—186°. An excess of alkali decomposes it to sulphinoacetic acid and *Δ^{β}-propenyl-γ-sulphonylacetic acid*. When the sodium salt is brominated in aqueous sodium hydrogen carbonate it splits at the double linking and is oxidised, giving finally *hexabromodimethyl sulphone*, m. p. 131—132·5°, and acetic acid.
E. HOPKINS.

Toluene-*p*-sulphonic acid as catalyst in the preparation of acetals. A. JOHANNISSIAN and E. AKUNIAN (Bull. Univ. Etat. R.S.S. Armenie, 1930, No. 5, 235—244; Chem. Zentr., 1930, ii, 552).—In the preparation of acetals from ketones and aldehydes by Claisen's method toluene-*p*-sulphonic acid is preferable as catalyst to hydrochloric acid, sulphuric acid, or ammonium chloride. A. A. ELDRIDGE.

Gravimetric determination of formaldehyde and hexamethylenetetramine. V. IONESCU and C. BODEA (Bull. Soc. chim., 1930, [iv], **47**, 1408—1419).—In the gravimetric determination of formaldehyde with methone (5 : 5-dimethyldihydroresorcinol) the cold neutral solution free from all other aldehydes is treated with 5—10% excess of methone for 6 hrs. at 20° with occasional agitation. Alternatively the mixture is boiled for 10 min. and then cooled and filtered on a Gooch crucible after ½ hr. and the residue dried at 110—115°. If the boiling is continued beyond 15 min. low results are obtained owing to decomposition of the methylenebisdimethyldihydroresorcinol. In acid solution the reaction is not quantitative. Similarly hexamethylenetetramine can be determined in dilute neutral aqueous solution by agitating and boiling for 10 min. with 5—10% excess of methone, and after cooling and keeping for 30 min., collecting the methylenebisdimethyldihydroresorcinol, and drying at 110—115° for 1—3 hrs. The reaction time depends on the temperature and at 20° is incomplete in 10 hrs. The method is less accurate for amounts of hexamethylenetetramine above 0·5 g. and accurate results are not obtained in acid solution. R. BRIGHTMAN.

β-Methyl-Δ^{α}-butenal. F. G. FISCHER, L. ERTEL, and K. LOWENBERG (Ber., 1931, **64**, [*B*], 30—34).—*iso*Valeraldehyde, prepared from fermentation amyl alcohol, is brominated in chloroform at —25° while irradiated with a powerful Osram lamp, and subsequently treated with ethyl alcohol, thus yielding α-bromo-β-methylbutaldehyde diethylacetal, b. p. 88—89°/13 mm., d_4^{20} 1·1772, n_D^{20} 1·4489, transformed by

potassium hydroxide in an atmosphere of nitrogen at 170° into β-*methyl*-Δ^{α}-*butenal diethylacetal*, b. p. 163—165°/730 mm., d_4^{20} 0·8555, 1·4201. The unsaturated acetal is hydrolysed by aqueous tartaric acid to a mixture of (?) α-*methylene*-n-*butaldehyde*, b. p. 77—80°/atmos. pressure (*semicarbazone*, m. p. 183—184°; p-*nitrophenylhydrazone*, m. p. 141—142°), and β-*methyl*-Δ^{α}-*butenal*, b. p. 132—133°/730 mm., d_4^{20} 0·8722, n_D^{20} 1·4526 (*semicarbazone*, m. p. 221—222°; p-*nitrophenylhydrazone*, m. p. 161—162°), hydrogenated in presence of palladised calcium carbonate to β-methylbutaldehyde (semicarbazone, m. p. 126—127°; *p*-nitrophenylhydrazone, m. p. 116°).
H. WREN.

Hydroxy-aldehydes. IX. Synthesis and properties of an ε-hydroxy-aldehyde. B. HELFERICH and G. SPARMBERG (Ber., 1931, 64, [*B*], 104—109; cf. A., 1925, i, 1039).—(+)-Citronellol, d^{20} 0·8568, n_D^{20} 1·45678, $[\alpha]_D^{20}$ +4·1°, is transformed into its acetate, d^{20} 0·8901, n_D^{20} 1·44383, $[\alpha]_D^{20}$ +2·5°, which is ozonised in glacial acetic acid; reduction of the ozonide with zinc dust leads to the formation of ε-*acetoxy*-γ-*methylhexaldehyde*, b. p. 112—113°/4—5 mm., d^{19} 0·9892, $n_D^{19\cdot1}$ 1·43675, $[\alpha]_D^{18}$ +1·7°, hydrolysed by sodium methoxide in chloroform and methyl alcohol to ε-*hydroxy*-γ-*methylhexaldehyde*, $OH\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot CHO$ or $\begin{matrix}CH_2\cdot CH_2\cdot CH(OH)\\ CHMe\cdot CH_2\text{——}CH_2\end{matrix}\!>\!O$, b. p. 103—106°/3—4 mm., d^{17} 1·0204, $n_D^{18\cdot8}$ 1·46883, $[\alpha]_D^{18\cdot7}$ +14·8° in chloroform. Treatment of the aldehyde with 1% methyl-alcoholic hydrogen chloride affords the *methyl-lactolide*, $\begin{matrix}CH_2\cdot CH_2\cdot CH(OMe)\\ CHMe\cdot CH_2\text{——}CH_2\end{matrix}\!>\!O$, b. p. 35—41°/about 3 mm., d^{17} 0·9370, n_D^{17} 1·43549, $[\alpha]_D^{17}$ +110·6°, which does not reduce Fehling's solution and is readily hydrolysed by aqueous *N*-hydrochloric acid. The aldehyde appears to be a desmotropic mixture of the open and cyclic forms, in which the latter predominates in the liquid and in chloroform, whereas in very dilute aqueous solution the aldehydic form is favoured. The probability of the existence of 1 : 6-lactols and -lactolides among carbohydrates appears greater than previously suspected.
H. WREN.

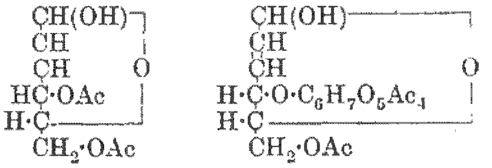
Decomposition of ketones in presence of silica gel. J. A. MITCHELL and E. E. REID (J. Amer. Chem. Soc., 1931, 53, 330—337).—When acetone is passed over silica gel at 430—550°, the main (condensation) product is mesitylene (7·8—17·2% yield); small amounts of mesityl oxide, phorone, *iso*phorone, and xylitone are produced. The primary products of the unimolecular homogeneous decomposition of acetone are keten (optimum yield 4·4%) and methane; the keten subsequently decomposes to ethylene and carbon monoxide. A small amount of propinene is found in the gaseous products, but under the conditions used this is not converted into mesitylene. Under conditions of high temperature and pressure, high-boiling condensation products are formed at the expense of mesitylene. Ketonic condensation products are obtained using methyl ethyl ketone, but acetophenone gives some 1 : 3 : 5-triphenylbenzene.
H. BURTON.

Preparation of water-soluble benzoates of the carbohydrates and their derivatives by the "+—" method. V. V. SAVJALOV (Jahrb. Univ. Sofia Med. Fak., 1928, 7; Chem. Zentr., 1930, ii, 67).—Water-soluble benzoates of sucrose, chondroitin, chondrosin, and of the sodium salts of chondroitin- and mucoitin-sulphuric acids and of nucleic acid have been prepared.
L. S. THEOBALD.

Oxidation of sugars in alkaline solution by gaseous oxygen, and the influence of p_H on the formation of carbon monoxide. M. NICLOUX and H. NEBENZAHL (Compt. rend. Soc. Biol., 1929, 101, 189—192; Chem. Zentr., 1930, ii, 232).—Dextrose is unattacked by oxygen in solutions of 7·38, 7·73, and 8·04 prepared from *M*/15-sodium monohydrogen and potassium dihydrogen phosphate, but in solutions of the same p_H value prepared from 0·67*M*-phosphate dextrose, lævulose, and galactose are attacked with production of carbon monoxide. Carbon monoxide can always be detected in mammalian blood; it may originate from the action of oxygen on dextrose in the presence of blood-phosphate.
A. A. ELDRIDGE.

Preparation of bromoacetyl-sugars and acetoglucals. P. A. LEVENE and A. L. RAYMOND (J. Biol. Chem., 1931, 90, 247—250).—In the preparation of bromoacetyl derivatives of the sugars by the action of hydrogen bromide in acetic anhydride, the reaction product is repeatedly distilled with toluene, which forms an azeotropic mixture with acetic acid, and so readily removes the added reagents, leaving the desired derivative in a crystalline condition. The sugar should be scrupulously dried and finely powdered. The same principle is applied in the reduction of the bromoacetyl compound to the glucal (Fischer and Zach, A., 1913, i, 445), the solution after filtration from excess of zinc being extracted with toluene and the toluene extract treated as above. It is claimed that the products are more readily obtained pure by this procedure.
H. A. PIGGOTT.

Unsaturated reduction products of sugars. XV. Structure of ψ-glucals. M. BERGMANN and W. FREUDENBERG (Ber., 1931, 64, [*B*], 158—161).—Treatment of diacetyl-ψ-glucal (cf. A., 1929, 798) with methyl orthoformate affords the α-*methyl-lactolide*, b. p. 119°/0·3 mm., n_D^{20} 1·4579, $[\alpha]_D^{21}$ +143·0° in benzene, hydrolysed by aqueous barium hydroxide to ψ-*glucal*-α-*methyl-lactolide*, b. p. 118—120°/0·5 mm., n_D^{21} 1·4915, $[\alpha]_D$ +102·3° in water, also obtained by the action of emulsin on ψ-cellobial-α-methyl-lactolide. The unsaturated sugar residue has therefore the same structure in ψ-glucal and ψ-cellobial, and since the glucosido-residue is attached to carbon atom 4 in ψ-cellobial, the pyranoid constitution is established.

(I.)  (II.)

Since glyoxal is obtained by ozonolysis of diacetyl-ψ-glucal, ψ-glucalmethyl-lactolide, or penta-acetyl-ψ-cellobial the structures I and II are established for the ψ-glucial and ψ-cellobial acetates. 2 : 3-Dideoxyglucose and 2 : 3-dideoxycellobiose must likewise be furanoid.
H. WREN.

Acetylmonoses. VI. Ring structure of the mannose penta-acetates. P. A. LEVENE and R. S. TIPSON (J. Biol. Chem., 1931, **90**, 89—98).—1-Bromotetra-acetyl-*d*-mannose, $[\alpha]_D^{23}$ +123·2° in chloroform, prepared from β-mannose penta-acetate, is converted by zinc dust and 50% aqueous acetic acid into triacetylglucal, m. p. 54—55°, $[\alpha]_D^{27}$ —16·3° in alcohol, and by silver acetate in toluene at 95° into α-mannose penta-acetate. The action of silver carbonate in toluene gives a 2 : 3 : 4 : 6-*tetra-acetylmannose*, m. p. 93°, $[\alpha]^{27}$ +26·3° in chloroform, different from the 2 : 3 : 4 : 6-tetra-acetylmannose of Micheel and Micheel (A., 1930, 455); on acetylation this is converted into the original β-mannose penta-acetate. The action of dry sodium methoxide on the bromoacetylmannose in chloroform gives the tetra-acetylmethylmannoside, m. p. 104—105°, $[\alpha]^{27}$ —22·6° in chloroform, of Freudenberg (*ibid.*, 894). Change of structure is unlikely during glucal formation in view of the pyranoside structures of both glucal (Bergmann and Freudenberg, *ibid.*, 70) and bromotetra-acetylglucose; consequently the authors, in contrast to Hudson (*ibid.*, 747), consider that β-*d*-mannose penta-acetate, like the α-compound, has a pyranoside structure. H. A. PIGGOTT.

Methylated tri- and tetra-saccharides from cellulose and starch. K. FREUDENBERG and K. FRIEDRICH (Naturwiss., 1930, **18**, 1114; cf. A., 1930, 1412).—*Tridecamethyl*-β-*methylcellotetraoside*, b. p. 265—275°/0·1 mm., m. p. 139°, $[\alpha]_{578}^{18}$ —14·6° in water, is described. From the decomposition products of acetylated starch are obtained, after methylation, completely corresponding fractions of the same b. p., which are non-crystallisable. The *methylated tri-* and *tetra-saccharide* have $[\alpha]_{578}^{18}$ +133° and +140° in water, respectively. W. R. ANGUS.

Syntheses of a tetrasaccharide acetate. B. HELFERICH and R. GOOTZ (Ber., 1931, **64**, [*B*], 109—114; cf. A., 1928, 1224; 1930, 748).—Gentiobiosido-β-*d*-glucose hendeca-acetate, m. p. 219—220°, prepared in 59% yield from acetobromogentiobiose and 1 : 2 : 3 : 4-β-tetra-acetyl-*d*-glucose in chloroform in presence of silver carbonate, anhydrous calcium chloride, and iodine, is transformed by hydrogen bromide into *acetobromogentiobiosido*-d-*glucose*, m. p. 193—194°, $[\alpha]_D^{17}$ +63·3° in chloroform. 1 : 2 : 3 : 4-β-Tetra-acetyl-*d*-glucose transforms the acetobromotrisaccharide into β-*gentiobiosido*-β-*gentiobiose tetradeca-acetate*, m. p. 207—209° (corr.) after softening at 135°, $[\alpha]^{20}$ —11·1° in chloroform. The free tetrasaccharide shows little tendency to crystallise. The small solubility of the acetate in alcohol is remarkable. The difficulty of obtaining such sugar acetates in a homogeneous state is illustrated by the observation that although analyses and determination of mol. wt. and acetyl groups and of specific rotation give concordant results after 8—12 crystallisations, a constant solubility is attained only after 20 crystallisations. H. WREN.

Constitution of corchorin, the active principle of jute seeds (*Corchorus capsularis*). I. N. K. SEN (J. Indian Chem. Soc., 1930, **7**, 905—911).—Corchorin (A., 1930, 826) [*penta-acetyl* derivative, m. p. 158° (decomp.); *bromo*-derivative *dibromide*, m. p. 100° (decomp.)] is hydrolysed by 10% sulphuric acid to dextrose and *corchogenin*, $C_{16}H_{26}O_3$, m. p. 112—114° (decomp.) after shrinking at 84° [*dibromide*, m. p. 130—132° (decomp.)]. Corchogenin contains a lactone grouping, does not give an oxime or semicarbazone, does not contain an alkoxy-group, affords an amorphous product, m. p. 165—170° (decomp.), when treated with phenylhydrazine, and is oxidised by potassium permanganate in acetone to *corchoric acid*, $C_{15}H_{24}O_5$, m. p. 67—70°, decomp. 94°. Similar oxidation of corchorin affords *glucocorchoric acid*, $C_{21}H_{34}O_{10}$, m. p. 146—148°, hydrolysed by dilute hydrochloric acid to dextrose and corchoric acid. H. BURTON.

Processes taking place when polysaccharides are heated in glycerol. H. PRINGSHEIM (Helv. Chim. Acta, 1931, **14**, 57).—The author's method of depolymerisation of polysaccharide acetates does not involve the use of glycerol. The criticisms of Karrer and von Krauss (A., 1930, 1415) do not, therefore, apply to his results. H. BURTON.

Autohydrolysis of diastatic dextrins. J. EFFRONT (Compt. rend., 1931, **192**, 198—201).—The difficulties experienced in purifying dextrin are due to the formation of maltose by the action of the solvents used. The treatment of dextrin with successive quantities of water increases, particularly when the dilution is high, not only the reducing power of the extract, as measured by its maltose content, but also the reducing power of the residue. The changes which dextrin undergoes on purification were studied by repeated extractions with alcohol followed by an extraction with cold water, evaporating the filtrate to dryness, and again treating with alcohol, the maltose content being measured at the various stages. The reducing power of a dextrin is closely related to its mol. wt. In the saccharification of starch, the reducing dextrin first formed breaks down to give maltose. A. RENFREW.

Amyloid from cellulose. JUSTIN-MUELLER (Bull. Soc. chim., 1930, [iv], **47**, 1400—1404).—When 5·82 parts of cellulose (white filter-paper) are treated with 100 parts of sulphuric acid (*d* 1·58) and poured into a large excess of water, cellulose-amyloid is obtained as a powder. The acid and neutral (washed) pastes are insoluble in ammonia, sodium or potassium carbonate, acetic acid, acetone, or ether–alcohol, and are soluble in ammoniacal copper oxide (Peligot's reagent), but are distinguished from cellulose by their solubility in dilute sodium or potassium hydroxide and blue coloration given with iodine in iodide solution. Unlike hydrocellulose, cellulose-amyloid does not reduce Fehling's solution, and on drying is converted by polymerisation and increased cohesion into a dry product which is not completely soluble in concentrated sodium and potassium hydroxides or in boiling ammoniacal copper oxide. The formation of the amyloid from cellulose thus involves successive dehydration, molecule scission in acid media, hydration in aqueous medium, and finally polymerisation. R. BRIGHTMAN.

Distillation products of cellulose. H. B. ARBUCKLE and H. S. DAVIDSON (J. Elisha Mitchell Sci. Soc., 1929, **45**, 147—149).—Distillation of

cellulose in a vacuum affords formaldehyde, acetone, diacetyl, formic and acetic acids, phenol, *p*-cresol, pyrocatechol, and guaiacol.

CHEMICAL ABSTRACTS.

Structure of cellulose nitrates. DESMAROUX and MATHIEU.—See this vol., 290.

α- and β-Lignosulphonic acids. P. KLASON (Svensk Kem. Tidskr., 1930, **42**, 259—263).—In sulphite waste liquors only 70% of the lignosulphonic acids present can be precipitated by a naphthylamine salt; the unprecipitated acid has been called β-lignosulphonic acid, and the corresponding lignin β-lignin. This latter contains only half the amount of methoxyl found in α-lignin. By precipitation of the β-acid with lead acetate, removal of the lead by hydrogen sulphide, and oxidation with hydrogen peroxide a salt can be obtained on the addition of a naphthylamine salt resembling that of the α-acid, but containing only half as much methoxyl. The β-acid has the formula $C_{19}H_{18}O_6$, that of the corresponding β-lignin being $C_{19}H_{20}O_6$, *i.e.*, a combination of coniferyl alcohol and dihydroxycinnamaldehyde. A solution of the β-acid containing a little hydrochloric acid gives on evaporation to dryness at 60° a dark brown mass, soluble in water to a brown viscous solution which is precipitable by a naphthylamine salt. Analysis of this precipitate gave a formula $C_{46}H_{49}O_{18}NS$ ($=4C_9H_8O_3+H_2SO_3+C_{10}H_9N+3H_2O$). The nature and production of these substances in the cellulose process are discussed.

H. F. HARWOOD.

Phospho- and silico-tungstates of some quaternary bases: analytical applications. L. LEMATTE, G. BOINOT, E. KAHANE, and (MME.) M. KAHANE (Compt. rend., 1930, **191**, 1130—1132).—Analysis of the phospho- and silico-tungstates of choline, acetylcholine, α-methylcholine, α-methylacetylcholine, bromocholine, the ethyl ether of betaine, and trimethylallylammonium show that these compounds are anhydrous, and have the general formulæ $12WO_3,PO_4(NR'R''R''')_3$ and $12WO_3,SiO_2(NR'R''R''')_4$, respectively, thus disagreeing with Drummond's results (cf. A., 1918, i, 336). The purity attained and constancy of composition are sufficient for their use in the determination of these bases with an accuracy of 2—3%.

C. A. SILBERRAD.

Adrenaline as oxidation catalyst. G. BLIX (Skand. Arch. Physiol., 1929, **56**, 131—171; Chem. Zentr., 1930, ii, 903).—Glycine, *d*-alanine, valine, and leucine undergo oxidative deamination by molecular oxygen at 40° in presence of adrenaline. Pyrocatechol, quinol, resorcinol, pyrogallol, and phloroglucinol are also catalytically active. The optimal p_H is 10; amino-acids are measurably oxidised in presence of adrenaline at physiological p_H values. Glycine affords carbon dioxide and formic acid; alanine affords acetaldehyde.

A. A. ELDRIDGE.

Ethyl aminomalonate. Action of alkyl iodides and bromides on ethyl sodioaminomalonate. R. LOCQUIN and V. CERCHEZ (Bull. Soc. chim., 1930, **47**, 1377—1380).—The reactions of ethyl aminomalonate are reviewed. The sodium derivative reacts with alkyl halides, giving the corresponding alkyl derivative in 50% yield.

R. BRIGHTMAN.

Aminoalkylmalonic esters and their derivatives. V. CERCHEZ (Bull. Soc. chim., 1930, [iv], **47**, 1381—1385).—Ethyl sodioaminomalonate is obtained by addition of the ester to a solution of sodium ethoxide, or by addition of sodium to a solution in ether; the reaction is slower in methyl *iso*amyl ether, and does not occur in *n*-butyl ether. With *iso*butyl iodide ethyl sodioaminomalonate gives 55% of *ethyl α-amino-α-isobutylmalonate*, b. p. 136°/14 mm. (*carbamide*, m. p. 194°; *phenylcarbamide*, m. p. 128°; *diamide*, m. p. 153°). *Ethyl-α-amino-α-allylmalonate*, b. p. 134—135°/17 mm. (*carbamide*, m. p. 173—174°; *phenylcarbamide*, m. p. 113°), and *ethyl amino-α-benzylmalonate* (*carbamide*, m. p. 234°; *diamide*, m. p. 156°) are similarly obtained.

R. BRIGHTMAN.

Preparation of α-amino-acids by hydrolysis of aminoalkylmalonic esters. R. LOCQUIN and V. CERCHEZ (Bull. Soc. chim., 1930, [iv], **47**, 1386—1389).—Hydrolysis of aminoalkylmalonic esters with water at 150° or with 10% hydrochloric acid affords α-amino-acids in good yields. Ethyl aminomalonate with water at 150° gives 90% of ethyl aminoacetate and with 10% hydrochloric acid, glycine hydrochloride. Leucine, phenylalanine, and α-amino-Δ^δ-pentenoic acid, decomp. about 250°, are similarly obtained.

R. BRIGHTMAN.

Cystine and its absorption spectrum. D. BARNES (Anal. Fís. Quím., 1930, **28**, 1386—1406).—The different types of cystine crystal obtained by crystallisation from solutions of various p_H are illustrated; the best yield of cystine is obtained at a definite p_H which is dependent on the concentration of the solution, varying from 4 to 6·5 as the cystine concentration changes from 1·5 to 0·5%. The absorption spectra of hydrochloric acid solutions of cystine and of alanine have been examined at wave-lengths from 2300 to 4000 Å. and from 2100 to 3800 Å., respectively. The molecular absorption coefficient–wave-length curves for the two compounds are similar and agree with those obtained by Ward (A., 1924, i, 272); the extinction coefficients increase continuously with decrease of wave-length, and there is no evidence of selective absorption. The structure of cystine is aliphatic, and not cyclic as suggested by Ward. From the wave-length at which absorption commences the heat of dissociation of cystine has been calculated to be 70·8 kg.-cal./mol., and that of alanine 83 kg.-cal./mol. It is suggested that the cystine molecule is easily ruptured at the S·S linking.

H. F. GILLBE.

Crystallised alkali salts of *l*-cystine. G. TOENNIES and T. F. LAVINE (J. Biol. Chem., 1931, **90**, 203—213; cf. Voss and Guttmann, A., 1930, 1170).—The *sodium* ($+1H_2O$), $[\alpha]_D^{25}$ $-89·6°$ in water (calculated on free cystine), $-265°$ in methyl alcohol, *potassium*, $[\alpha]_D^{25}$ $-88·9°$ in water, $-254°$ in methyl alcohol, and *lithium*, $[\alpha]^{29}_r$ $-113·5°$ in water, salts of *l*-cystine are prepared by precipitation of alkaline alcoholic cystine solutions with acetonitrile. They are stable in aqueous solution, and regenerate cystine (determined polarimetrically) completely on acidification, but the sodium and potassium salts decompose in methyl-alcoholic solution with liberation of ammonia.

H. A. PIGGOTT.

Synthesis of cyanic acid and carbamide by the ammoniacal oxidation of carbon. G. Laude (Compt. rend., 1930, **191**, 1135—1137; cf. A., 1921, i, 652).—Carbon derived from (*a*) camphor and (*b*) acetylene, 95·97—97 and 98·2—99·06% C, respectively, has been oxidised in quantities of 0·1 g. at a time by means of 1 g. of copper, 30 c.c. of concentrated ammonia, and 20 g. of potassium permanganate (added in four portions) at 40—45°, the period of oxidation being about 30 hrs. The product from (*a*) gave 11·39% of cyanic acid, that from (*b*) 6·3%.

C. A. Silberrad.

Chlorates and perchlorates of some bases prepared from calcium cyanamide. S. Micewicz (Przemysł Chem., 1926, **10**, 56—58, 136—137; Chem. Zentr., 1930, ii, 379).—Dicyanodiamidine chlorate, $C_2H_7O_4N_4Cl$, decomposes at 129—130°; perchlorate, subl. above 260°, and explodes on continued heating. Guanidine chlorate, $CH_6O_3N_3Cl$, m. p. 100—101°, is less stable than the perchlorate, m. p. 245—246°. Carbamide is soluble in dilute chloric acid, explosive decomposition occurring at 40—50°; the perchlorate, hygroscopic, has m. p. 66—67°. Thiocarbamide is vigorously decomposed by chloric acid; the hygroscopic perchlorate, m. p. 106—107°, explodes when heated.

A. A. Eldridge.

Action of thionyl chloride on anilic acids. W. H. Warren and R. A. Briggs (Ber., 1931, **64**, [*B*], 26—30).—Anilic acids become converted into anils when boiled with eight times their weight of thionyl chloride until evolution of sulphur dioxide and hydrogen chloride ceases. The following examples are cited: oxanilic acid, m. p. 149°, into *oxanil*, not melted below 320°; malonanilic acid into *malonanil*, m. p. 249°; succinanilic acid into succinanil, m. p. 156°; glutaranilic acid, m. p. 126—127°, into *glutaranil*, not molten below 320° [possibly a polymeride of the glutaranil, m. p. 144—145°, obtained by Bodtker (Diss., Leipzig, 1891) from aniline and glutaric acid]; phthalanilic acid, m. p. 158°, into phthalanil, m. p. 203°; camphoranilic acid into camphoranil, m. p. 116°; *diphenanilic acid*, m. p. 176°, from the anhydride and aniline in benzene, into *diphenanil*, m. p. 199°.

H. Wren.

Silica gel as a catalyst in the preparation of nitriles. J. A. Mitchell and E. E. Reid (J. Amer. Chem. Soc., 1931, **53**, 321—330).—When acetic acid and ammonia (excess) are passed over silica gel (activated by heating at 210° in a current of dry air) at about 500° with a contact time of 25 sec., the yield of acetonitrile is almost quantitative. Above 500°, the catalyst is poisoned, the yield diminishes, and ammonium carbonate is produced. The commercial and pure silica gels have the same order of activity. The following nitriles are prepared similarly from the appropriate acids (the figures in parentheses are the percentage yields): propionitrile (85), butyronitrile (90), *n*-valeronitrile (80), *iso*valeronitrile (94), hexonitrile (90), heptonitrile (93), dodeconitrile (55), phenylacetonitrile (87), and β-phenylpropionitrile (81). No nitrile could be obtained from palmitic acid. Acetonitrile, butyronitrile, and benzonitrile are obtained in yields of 87, 75, and 77%, respectively, when *n*-butyl acetate and butyrate, and ethyl benzoate are passed over silica gel with an excess of ammonia. The rates of hydrolysis of benzamide by water and of the formation of acetamide from ammonium acetate are not affected by silica gel; the catalyst is effective only in the dehydration of the amides.

H. Burton.

Catalytic dehydrogenation of dicyclic hydrocarbons. N. D. Zelinski and I. N. Titz (Ber., 1931, **64**, [*B*], 183—188; cf. A., 1926, 277).—*cyclo*Pentyl chloride and benzene in presence of aluminium chloride yield phenyl*cyclo*pentane, b. p. 217°, d_4^{20} 0·9474, n_D^{20} 1·5280, hydrogenated at 220—225° in presence of platinised charcoal to cyclo*hexyl*cyclo*pentane*, b. p. 214°, d_4^{21} 0·8780, n_D^{21} 1·4728; at 300°, the last-named compound is dehydrogenated to phenyl*cyclo*pentane. *Phenyl*cyclo*pentylmethane*, b. p. 233—235°, d_4^{18} 0·9345, n_D^{18} 1·5206, prepared in addition to dibenzyl and a little di*cyclo*pentyl by the action of sodium on benzyl and *cyclo*pentyl chlorides, is stable in presence of platinised charcoal at 300°. When hydrogenated at 220°, it passes into cyclo*hexyl*cyclo*pentylmethane*, b. p. 225—227°, d_4^{19} 0·8789, n_D^{19} 1·4775, dehydrogenated at 300° to phenyl*cyclo*pentylmethane. The pentamethylene ring, even when a component of a dicyclic system, is therefore stable to dehydrogenation.

Repetition of the previous work (*loc. cit.*) shows that the product of the action of magnesium *cyclo*hexyl bromide on *cyclo*pentanone is almost exclusively di*cyclo*hexyl (formed from the halide by the Würtz–Fittig reaction) and that the dehydrogenated product previously described is diphenyl. The expected tertiary alcohol is obtained only in minimal amount from magnesium *cyclo*pentyl chloride and *cyclo*hexanone or from magnesium *cyclo*hexyl bromide and 3-methyl*cyclo*pentanone.

H. Wren.

Alleged electrochemical sulphonation of an aromatic hydrocarbon. F. Fichter, H. E. Suenderhauf, and A. Goldach (Helv. Chim. Acta, 1931, **14**, 249—253).—The sulphur-containing acid produced during the electrochemical oxidation of toluene in presence of alcohol and sulphuric acid is not *p*-sulphobenzoic acid as stated by Puls (A., 1901, i, 318), but is ethylsulphuric acid. The same acid (isolated as the barium salt) is formed from alcohol and sulphuric acid in absence of toluene.

Maleic and fumaric acids are produced during the electrochemical oxidation of acetophenone in presence of *N*-sulphuric acid.

H. Burton.

Decomposition of phenyl iodide dichloride. III. E. V. Zappi and V. Deulofeu (Anal. Asoc. Quím. Argentina, 1930, **18**, 124—132; cf. A., 1930, 79).—A reply to Guglialmelli and others (*ibid.*, 758).

R. K. Callow.

Preparation and properties of some ethyl arylsulphonates and a comparative investigation of their velocities of hydrolysis with those of the corresponding ethyl arylcarboxylates. L. Demény (Rec. trav. chim., 1931, **50**, 60—71).—The following ethyl arylsulphonates have been prepared by the action of sodium ethoxide on the appropriate sulphonyl chloride in dilute alcoholic solution: ethyl benzene-, o-, b. p. 160—163°, m. p. 15°, m-, m. p. 42°, and p-, m. p. 92°, *-nitrobenzene-*, and *p*-toluene-

sulphonates. In general, the velocity of hydrolysis of the sulphonic esters in 30 vol.-% alcohol in $0 \cdot 001N$-alkaline solution is about one tenth that of the corresponding carboxylic ester. With sulphonic esters the effective hydrolysing agent is considered to be water and the velocity depends only slightly on the concentration of alkali used. The mean values for the unimolecular velocity coefficient $k \times 10^4$ in 30% alcohol at 25° for the above sulphonic esters are, respectively, 3·8, 75, 24, 26, and 1·9 (alkalinity 0·001—0·008N), the values of the bimolecular coefficient k for the corresponding carboxylates being 0·46, 1·23, 11·4, 19·0, and —, respectively (alkalinity 0·003—0·005N). Introduction of a nitro-group in the *m*- or *p*-positions has a similar accelerating effect in both series, but in the *o*-position its effect is small in the case of the carboxylic esters, whilst it has a powerfully accelerating influence in the sulphonic ester series.

J. W. BAKER.

Arylsulphonalkylamides. L. DEMENY (Rec. trav. chim., 1931, **50**, 51—59).—By the action of an alcoholic solution of the appropriate amine on various arylsulphonyl chlorides a series of arylsulphonalkylamides has been prepared, the following being new: *benzenesulphon*-n-*hexylamide*, m. p. 17°, and -n-*heptylamide*, m. p. 20°; p-*bromobenzenesulphon*-n-*amylamide*, m. p. 55° (not sharp), -n-*hexylamide*, m. p. 55°, and -n-*heptylamide*, m. p. 65°; p-*toluenesulphon*-n-*butylamide*, m. p. 43°, -n-*amylamide*, a colourless oil, -n-*hexylamide*, m. p. 62°, and -n-*heptylamide*, m. p. 45°; *mesitylenesulphon*-n-*propylamide*, m. p. 54°, -n-*butylamide*, m. p. 44°, -n-*amylamide*, m. p. 42°, -n-*hexylamide*, m. p. 64°, -n-*heptylamide*, m. p. 45°. The m. p. of these derivatives and those previously prepared (A., 1930, 81) are in general agreement with the various laws connecting m. p. and constitution, a minimum value occurring in the case of the *n*-amylamine derivatives. J. W. BAKER.

Ditolyl series. I. A. ANGELETTI [with A. BRAMBILLA] (Gazzetta, 1930, **60**, 967—974).—2-*Iodo*-2′-*nitro*-4 : 4′-*dimethyldiphenyl* (o-*iodo*-o′-*nitroditolyl*), m. p. 83—84°, prepared from 2-nitro-2′-amino-4 : 4′-dimethyldiphenyl (cf. Mascarelli and Gatti, A., 1930, 205) by way of the diazo-compound, is accompanied by a small quantity of ditolyleneiodonium iodide (?) and, as in the preparation of the following compounds, by 4 : 4′-dimethyldiphenylene oxide (cf. Niementowski, A., 1902, i, 21). It seems that decomposition of the diazo-nitro-compound gives first the 2′-nitro-2-hydroxy-compound, which loses nitrous acid to form the dimethyldiphenylene oxide. 2-*Bromo*-, m. p. 73—74°, and 2-*chloro*-2′-*nitro*-4 : 4′-*dimethyldiphenyl*, m. p. 85—86°, were also prepared, but attempts to obtain 2′-nitro-2-hydroxy-4 : 4′-dimethyldiphenyl were unsuccessful. T. H. POPE.

Halogen substitution. II. P. PFEIFFER and P. SCHNEIDER (J. pr. Chem., 1931, [ii], **129**, 129—144).—Coloured unstable carbonium salts, similar to those formed from bromine vapour and auxochrome-substituted αα-diarylethylenes (cf. A., 1928, 633), are also given by the parent hydrocarbons. The following hydrocarbons were examined as to (*a*) colour of solutions in sulphuric acid (formation of a carbonium sulphate) and (*b*) colour produced by bromine vapour (a perbromide), and were converted by the theoretical amount of bromine in solution into the mono- and di-bromo-substitution products, which were examined similarly: diphenyl- and di-*p*-tolyl-ethylene, no reaction; *αα-dinaphthylethylene*, m. p. 107°, from magnesium naphthyl bromide and ethyl acetate and subsequent dehydration of the *carbinol*, m. p. 146°, formed, (*a*) deep malachite-green, (*b*) indistinct red; *β-bromo-αα-dinaphthylethylene*, m. p. 148°, (*a*) bluish-green, (*b*) reddish-brown; *tetrabromo-αα-dinaphthylethylene*, m. p. 69—70°, from the hydrocarbon and excess bromine in chloroform, (*a*) intense grass-green; *p*-diphenylylphenylethylene, m. p. 94—95°, from the corresponding ketone and magnesium methyl iodide (cf. Schlenk and Bergmann, A., 1928, 1031), (*a*) cherry-red, (*b*) grass-green; *β-bromo-αα-*p*-diphenylylphenylethylene*, m. p. 162°, (*a*) reddish-violet, (*b*) dark violet; *ββ-dibromo-αα-*p*-diphenylylphenylethylene*, m. p. 155°, (*a*) reddish-violet; *di-*p*-diphenylylethylene*, m. p. 211°, (*a*) reddish-violet, (*b*) deep green; *β-bromo-αα-di-*p*-diphenylylethylene*, m. p. 187—188°, (*a*) green, changing to bluish-green on warming; with oleum deep blue, and (*b*) reddish-brown; *ββ-dibromo-αα-di-*p*-diphenylylethylene*, m. p. 194—195°, *αα-di-*p*-diphenylyl-Δ$^{\alpha}$-propene*, m. p. 165—166°, (*a*) deep reddish-violet, (*b*) deep green; *β-bromo-αα-di-*p*-diphenylyl-Δ$^{\alpha}$-propene*, m. p. 150—152°, (*a*) bluish-violet on warming, (*b*) greyish-black; *α-phenyl-ββ-di-*p*-diphenylylethylene*, m. p. 192—193°, (*a*) violet, (*b*) grass-green; *α-bromo-α-phenyl-ββ-di-*p*-diphenylylethylene*, m. p. 201—202°, (*a*) deep bluish-green with oleum. An attempt to produce αα-dinaphthyl-β-phenylethylene from phenylethyl acetate and magnesium naphthyl iodide yielded only diphenylacetoacetic ester.

E. HOPKINS.

2-Phenyl-1 : 1-dimethylindene. J. C. EARL and C. A. SMYTHE (J. Proc. Roy. Soc. New South Wales, 1930, **44**, 90—95).—Aluminium bromide can be used in the same way as aluminium chloride for the removal of aromatic hydrogen (cf. Scholl, A., 1913, ii, 56, 734; 1922, i, 258, 261, 331, 336), and can also be used for the removal of aliphatic hydrogen. The interaction of aluminium bromide, trimethylethylene dibromide, and benzene yields 2-*phenyl*-1 : 1-*dimethylindene*, m. p. 51°, b. p. 190—205°/36—38 mm., which, according to conditions, is oxidised to phthalic acid or o-*α-benzoyl-α-methylethylbenzoic acid*, m. p. 198°, converted by acetic anhydride into 3-*acetoxy*-3-*phenyl*-4 : 4-*dimethyl*-3 : 4-*dihydrobenz*iso*pyrone*, m. p. 137°. 3-*Nitro*-2-*phenyl*-1 : 1-*dimethylindene*, m. p. 139—140°, is described. G. DISCOMBE.

Reduction of naphthalene by alkali metals in liquid ammonia. C. B. WOOSTER and F. B. SMITH (J. Amer. Chem. Soc., 1931, **53**, 179—187).—Determinations of the amount of hydrogen (or ethane) evolved when the reaction mixtures from naphthalene and excess of sodium in liquid ammonia are treated with ammonium bromide (or ethyl bromide) indicate that 4 atoms of the metal per 1 mol. of naphthalene are consumed. Hydrolysis of the resultant sodio-derivative gives 1 : 2 : 3 : 4-tetrahydronaphthalene, indicating that the sodium atoms add in the 1 : 2 : 3 : 4-positions. This tetrasodio-derivative is shown to be approximately three quarters ammono-

lysed in solution at −33·5°, by determinations of the amounts of sodium peroxide (from the excess of sodium) and nitrite (from sodamide) formed when the reaction mixture is oxidised with oxygen. Potassium and naphthalene react in essentially the same manner. The results support Willstatter, Seitz, and Bumm's theory (A., 1928, 756) of reductions using sodium amalgam. Those hydrocarbons, including naphthalene, shown by Lebeau and Picon (A., 1914, i, 825, 946) to be reducible by sodium and liquid ammonia, all furnish alkali metal additive compounds.

H. BURTON.

Interaction of *tert*.-butyl chloride and naphthalene. W. GUMP (J. Amer. Chem. Soc., 1931, **53**, 380—381).—When *tert*.-butyl chloride (2 mols.) is heated with naphthalene (1 mol.) in presence of a small amount of aluminium chloride, a mixture of two *ditert.-butylnaphthalenes*, b. p. 319°, m. p. 82—83°, and b. p. 320°, m. p. 145—146°, separable by fractional crystallisation from alcohol, is obtained. These are probably identical with the supposed 1 : 2'- and 1 : 1'-dinaphthyls of Wegscheider (A., 1884, 1185), obtained during the reaction between naphthalene and *iso*butyl chloride. A *tert*.-butylnaphthalene could not be prepared from equimolecular amounts of the reactants.

H. BURTON.

Anthracene derivatives. III. E. DE B. BARNETT and J. A. LOW (Ber., 1931, **64**, [*B*], 49—56).—In spite of the impossibility of a *peri*-co-ordination, the derivatives of 1 : 4-dimethylanthracene resemble the corresponding derivatives of 1 : 4-, 1 : 5-, and 4 : 5-dichloro- and 1 : 5-diphenoxy-anthracene much more closely than those of anthracene itself. Since the assumption that the departure from "normal anthracene properties" is conditioned by different factors in the methyl and chloro-derivatives appears unjustifiable, the hypothesis of a *peri*-co-ordination is considered untenable in spite of the numerous observations in its favour.

o-2 : 5-Dimethylbenzoylbenzoic acid, m. p. 149°, prepared from phthalic anhydride and *p*-xylene in presence of aluminium chloride, is reduced by activated zinc dust, sodium hydroxide, and ammonia to *o-2 : 5-dimethylbenzylbenzoic acid*, m. p. 136°, converted by hot 80% sulphuric acid into 1 : 4-dimethylanthrone, m. p. 116°. 1 : 4-*Dimethylanthranyl acetate*, from the anthrone by pyridine and acetic anhydride, has m. p. 162°. Reduction of 1 : 4-dimethylanthrone with activated zinc dust and ammonia gives 1 : 4-dimethyl-9 : 10-dihydroanthranol, m. p. 134°, from which 1 : 4-dimethylanthracene, m. p. 76°, is derived. Successive treatment of 1 : 4-dimethylanthrone with magnesium methyl iodide and with hydrochloric acid in glacial acetic acid yields 1 : 4 : 9-*trimethylanthracene*, m. p. 9-*Benzyl*-1 : 4-*dimethylanthracene*, m. p. 135°, is converted by bromine in carbon disulphide into 10-*bromo*-9-*benzylidene*-1 : 4-*dimethyl*-9 : 10-*dihydroanthracene*, m. p. 180°, from which the corresponding 10-*piperidino*-, m. p. 150°, 10-*methoxy*-, m. p. 118—119°, and 10-*ethoxy*-, m. p. 130°, -derivatives are obtained. 10-*Bromo*-1 : 4-*dimethylanthrone*, decomp. about 160°, is transformed into 10-*piperidino*-1 : 4-*dimethylanthrone*, m. p. 133°, 10-*anilino*-1 : 4-*dimethylanthrone*, m. p. 192°, 10-*methylanilino*-1 : 4-*dimethylanthrone*, m. p. 179°, 10-p-*dimethylaminophenyl*-1 : 4-*dimethylanthrone*, m. p. 154°, and 10-*methoxy*-1 : 4-*dimethylanthrone*, m. p. 76°. 10-Bromo-1 : 4-dimethylanthrone is converted by benzene and aluminium chloride into 10-*phenyl*-1 : 4-*dimethylanthrone*, m. p. 144°, which when treated successively with magnesium methyl iodide and hydrochloric acid in glacial acetic acid gives 10-*phenyl*-1 : 4-*dimethyl*-9-*methylene*-9 : 10-*dihydroanthracene*, m. p. 129°, oxidised by chromic acid to 10-phenyl-1 : 4-dimethylanthrone. 10-*Phenyl*-9-*benzylidene*-1 : 4-*dimethyl*-9 : 10-*dihydroanthracene*, m. p. 170°, is described. 9 : 10-*Diphenyl*-1 : 4-*dimethylanthracene*, m. p. 189°, is derived from 10-phenyl-1 : 4-dimethylanthrone.

H. WREN.

Fluoranthene. O. KRUBER (Ber., 1931, **64**, [*B*], 84—85).—Treatment of a neutral tar-oil fraction, b. p. 370—390°, with sodium in solvent naphtha at 160° yields a solid sodium derivative from which tetrahydrofluoranthene, m. p. 75°, is obtained after decomposition with water; the filtrate from the sodium compound readily affords pyrene. Oxidation of tetrahydrofluoranthene with sodium dichromate in glacial acetic acid gives (?) *fluorenone-8-propionic acid*, m. p. 137—138°. Tetrahydrofluoranthene unites with sodium and the mixture of compounds is transformed by carbon dioxide into carboxylic acids, from which an *acid*, $C_{17}H_{14}O_2$, m. p. 188° after softening, is obtained; when heated above its m. p. or distilled with lime, it affords tetrahydrofluoranthene. It is unlikely that the tar-oil fraction contains tetrahydrofluoranthene.

H. WREN.

Method of reducing aromatic nitro-compounds. T. E. DE KIEWIET and H. STEPHEN (J.C.S., 1931, 82—84).—Crystalline stannous chloride ($SnCl_2,2H_2O$) is heated with excess of acetic anhydride until completely dehydrated; the resulting solution reduces nitro-compounds to acetamido- or, often where possible (exceptions are *m*-chloronitrobenzene, the nitrobenzoic acids, and *o*-nitrophenol), to *p*-chloroacetamido-compounds. *p*-Chloronitrobenzene gives *p*-chloroacetanilide in absence of free hydrogen chloride, and 2 : 4-dichloroacetanilide in its presence; *o*-, *m*-, and *p*-nitrobenzoic acids give the corresponding aminobenzoic acids; *p*-nitrophenol and its chloro-derivatives give acetamidophenyl acetates, but *o*-nitrophenol and similar derivatives give acetamidophenols, apparently by hydrolysis of intermediately formed 1-methylbenzoxazoles. 3-*Chloro*-4-*nitrophenol*, m. p. 120°, obtained by nitration of *m*-chlorophenol (cf. Uhlemann, Ber., 1869, **2**, 1161; Chem. Fabr. Griesheim-Elektron, G.P. 143,449), gives 3-*chloro*-4-*acetamidophenyl acetate*, m. p. 127°.

H. A. PIGGOTT.

Hydrogenation of aniline under pressure in the presence of cerium and lanthanum as promoters. V. S. SADIKOV and A. J. SCHAGALOV (J. Russ. Phys. Chem. Soc., 1930, **62**, 1635—1642).—The influence of small quantities (1%) of cerium and lanthanum oxides as promoters to the main catalysts (osmium and nickel) in the hydrogenation of aniline under pressure was investigated. With osmium, the addition of cerium oxide does not affect the time of hydrogenation, although the consumption of hydrogen

is decreased. The yield of benzene and *cyclo*hexylamine is much greater, whilst that of di*cyclo*hexylamine is much less, and more aniline is left unreduced, so that cerium oxide appears to act as an inhibitor on osmium. With nickel instead of osmium, the presence of cerium oxide somewhat improves the final yield, but the main factor in the efficiency of the catalyst appears to be the preliminary heat treatment of the latter, which is rendered more sensitive to it by addition of cerium oxide. If lanthanum oxide is used, this sensitiveness is still further increased, whilst the tendency to promote the condensation of the reduction products is diminished, the *cyclo*hexylamine content in the final mixture increasing from 33% in the case of cerium oxide to 71·2% in the case of lanthanum oxide, and that of di*cyclo*hexylamine falling from 52% to 33%. M. ZVEGINTZOV.

Action of alcohols and esters on aniline hydrochloride. S. A. BUSSE and A. I. TRAVIN (J. Russ. Phys. Chem. Soc., 1930, **62**, 1685—1690).—Aniline hydrochloride and benzyl alcohol when heated together gave a 59% yield of phenylbenzylamine, m. p. 35·5°. Using benzyl acetate, the yield was more than 79%. Oxidation with ferric chloride or sulphate gave benzaldehyde; oxidation with nitrosodimethylaniline gave benzaldehyde together with some azoxydimethylaniline, m. p. 241°. With *n*-octyl alcohol aniline gives *phenyloctylamine*, b. p. 158—158·5°/4 mm., *d* 0·9089, n_D^{20} 1·5132, which yielded octaldehyde on oxidation. M. ZVEGINTZOV.

Derivatives of 1-chloro-2-nitronaphthalene. A. P. J. HOOGEVEEN (Rec. trav. chim., 1931, **50**, 37—40).—2-Acetnaphthalide is converted, through the chloroamine, by an excess of bleaching powder solution in dilute acetic acid in alcohol at 16° into 1-chloro-2-acetnaphthalide, which affords 1-chloro-2-nitronaphthalene (Hodgson and Kilner, A., 1926, 279) after hydrolysis, diazotisation, and treatment of the diazo-solution with potassium nitrite in the presence of cuprous–cupric sulphite. It is converted by heating with an alcoholic solution of the appropriate amine in a sealed tube at 180° into 1-amino-, 1-*methylamino-*, m. p. 114°, and 1-*ethylamino-*, m. p. 77°, -2-*nitronaphthalene*, and by alcoholic sodium disulphide into 2 : 2′-*dinitrodinaphthyl disulphide*, m. p. 204°. J. W. BAKER.

Mechanism of chemical reactions. II. Mechanism of the synthesis of secondary and tertiary amines by reduction. K. KINDLER [with W. DEHN and W. PESCHKE] (Annalen, 1931, **485**, 113—126).—Reduction of benzylamine or β-phenylethylamine with palladium-black and hydrogen in boiling alcohol gives, respectively, quantitative and 10% yields of the secondary bases dibenzylamine and di-(β-phenylethyl)amine, the velocity of reduction of benzylamine also being the greater in glacial acetic acid or xylene. Similar reduction of β-phenylethylamine in the presence of benzyl alcohol in xylene affords mainly (90%) *N*-benzyl-β-phenylethylamine (also obtained by catalytic reduction of benzylidene-β-phenylethylamine) and only 6% of di-(β-phenylethyl)amine, determined by the amount of ammonia evolved. Reduction of thiobenzamide with aluminium amalgam and moist ether affords 85% of benzylamine and 8% of dibenzylamine, and proceeds more rapidly than the similar reduction of phenylthioacetamide, which affords 26% and 66% of the primary and secondary bases, respectively. Reduction of the mixture of α-amino-β-phenylethyl alcohol and phenylacetaldimine (obtained by the action of ammonia on phenylacetaldehyde) with aluminium amalgam and water affords di-(β-phenylethyl)amine, in addition to the primary base, similar reduction of α-dimethylamino-β-phenylethyl alcohol yielding β-phenylethyldimethylamine (Decker and Becker, A., 1912, i, 844). Reduction of phenylacetonitrile in acetic acid and ammonium acetate with hydrogen and palladium-black at 65°/2·5 atm. gives, in addition to β-phenylethylamine and the corresponding secondary base, β-phenylethylidene-β-phenylethylamine, reduced to di-(β-phenylethyl)amine in 60% yield. The proportion of primary and secondary bases formed depends on the acid present during the reduction and in aqueous-alcoholic ethyl acetate, glacial acetic acid, and acetic acid containing hydrogen chloride, with hydrogen and palladium-black at 35°/2·5 atm., the proportion of these products is 25, 50, and 90% and 70, 40, and 1%, respectively. The much greater velocity of reduction of benzonitrile compared with that of phenylacetonitrile results in the almost exclusive formation of the primary base in the first case, whilst in the latter a large amount of the secondary amine is also formed. Similar reduction of phenylacetonitrile in the presence of dipropylamine affords β-phenylethyldipropylamine in addition to the normal product di-(β-phenylethyl)amine. These results confirm the following mechanism for the formation of secondary bases:

$CH_2R{\cdot}OH \xrightarrow{-2H} CHR{:}O \xrightarrow{NH_3} CHR{:}NH$ (I) or $CH_2R{\cdot}NH_2 \xleftarrow{2H}$ (I) $\xrightarrow{CH_2R{\cdot}NH_2} CH_2R{\cdot}N{:}CHR \xrightarrow{2H} NH(CH_2R)_2$; and

$RCN \xrightarrow{2H}$ (I) $\xrightarrow{H_2O} CHR(OH){\cdot}NH_2$ (II) $\longrightarrow R{\cdot}CH{:}O + NH_3$; (I) or (II) $\xrightarrow{2H} CH_2R{\cdot}NH_2$ (cf. Kindler, A., 1923, i, 568—572). J. W. BAKER.

Conversion of aldehydes into higher molecular amines. A. SKITA, G. PFEIL, and [in part] H. WINKELER (Annalen, 1930, **485**, 152—173).—The amine, b. p. 110—112°/15 mm., obtained by catalytic reduction of *n*-propylidene*cyclo*hexylamine (Skita and Wulff, A., 1927, 559) with colloidal platinum in alcoholic acetic acid is cyclo*hexyl-(β-methyl-n-amyl)-amine* (III) (*hydrochloride*, m. p. 139°; *phenylurethane*, m. p. 99°), identical with a specimen obtained by similar reduction of *β-methyl-Δ^β-pentenylidene*cyclo*hexylamine* (II), b. p. 118—119·5°/15 mm., obtained by condensation of α-methyl-Δ^α-pentenaldehyde (I) with *cyclo*hexylamine. In the original reduction complete hydrolysis first occurs to give propaldehyde which by an aldol condensation followed by loss of water affords the pentenaldehyde I. This condenses with *cyclo*hexylamine to the Schiff's base II, which is less readily hydrolysed and is reduced to III:

$$2CH_2Me{\cdot}CH{:}N{\cdot}C_6H_{11} \longrightarrow C_6H_{11}{\cdot}NH_2 + CH_2Me{\cdot}CHO \longrightarrow CH_2Me{\cdot}CH{:}CMe{\cdot}CHO \text{ (I)} \xrightarrow{C_6H_{11}{\cdot}NH_2} CH_2Me{\cdot}CH{:}CMe{\cdot}CH{:}N{\cdot}C_6H_{11} \text{ (II)} \longrightarrow CH_2Me{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}NH{\cdot}C_6H_{11} \text{ (III)}.$$

Similar results are obtained with Schiff's bases derived from other aliphatic (but not aromatic) aldehydes and

*cyclo*hexylamine, although the above case is the only one in which hydrolysis is complete. The structure of the reduction products is proved by their identity with the reduction products of the intermediate Schiff's bases synthesised from *cyclo*hexylamine and the appropriate unsaturated aldehyde. Thus ethylidene*cyclo*hexylamine is reduced to *cyclo*hexylethylamine (8%) (*picrate*, m. p. 231°) and *cyclo*hexyl-*n*-butylamine (39%) (also from Δ^{β}-*butenylidene*cyclo*hexylamine*, b. p. 90—91°/15 mm.); *n*-butylidene-, *iso*valerylidene-, *n*-heptylidene-, and γ-phenylpropylidene-*cyclo*hexylamine, by similar reduction, afford, respectively, cyclo*hexyl*-(β-*ethyl*-n-*hexyl*)*amine* (78%), b. p. 140—148°/15 mm. [*hydrochloride*, m. p. 95°; *picrolonate*, m. p. 225—226° (decomp.)] (also from β-*ethyl*-Δ^{β}-*hexylidene*cyclo*hexylamine*, b. p. 139—143°/13 mm.); cyclo*hexyl*-(ε-*methyl*-β-iso*propyl*-n-*hexyl*)-*amine* (15%), b. p. 143—145°/11 mm. (*hydrogen oxalate*, m. p. 193·5—194·5°; *hydrochloride*, m. p. 105°) (also from ε-*methyl*-β-iso*propyl*-Δ^{β}-n-*hexylidene*cyclo*hexylamine*, b. p. 146—152°/16 mm.); cyclo*hexyl*-(β-*amyl*-n-*nonyl*)*amine* (42·3%), b. p. 208—210°/17 mm. (*hydrochloride*, m. p. 90°; *hydrogen oxalate*, m. p. 153°) (also from β-*amyl*-Δ^{β}-n-*nonenylidene*cyclo*hexylamine*, b. p. 208—211°/11 mm.); cyclo*hexyl*-(ε-*phenyl*-β-*benzyl*-n-*amyl*)*amine* (*hydrochloride*, m. p. 169—170°; *hydrogen oxalate*, m. p. 172°) (also from ε-*phenyl*-β-*benzyl*-Δ^{β}-n-*pentenylidene*cyclo*hexylamine*, b. p. 265—270°/16 mm.), together with the normal reduction products, of which cyclo*hexyl*-n-*heptylamine*, b. p. 132—135°/16 mm. (*hydrochloride*, m. p. 211—212°), is new. From *iso*valerylidene-ethylamine is obtained N-(ε-*methyl*-β-iso*propyl*-n-*hexyl*)*ethylamine*, b. p. 213—220° [*picrolonate*, m. p. 221—222° (decomp.)]. When the reduction of the Schiff's base is effected in the presence of another aldehyde this may also undergo an aldol condensation with the aldehyde formed by hydrolysis of the Schiff's base and mixtures of several amines are then formed by the mechanism given above. Thus reduction of propylidene*cyclo*hexylamine in the presence of acetaldehyde affords, in addition to the products obtained above, cyclo*hexyl*-(β-*methylbutyl*)*amine* (29·5%), b. p. 97—99°/15 mm. (*hydrochloride*, m. p. 234°; *phenylurethane*, m. p. 118°) (also from β-*methyl*-Δ^{β}-*butenylidene*cyclo*hexylamine*, b. p. 100—105°/15 mm.), whilst with benzaldehyde as the second component are obtained cyclo*hexyl*-(γ-*phenyl*-β-*methylpropyl*)*amine* (11%), b. p. 164—168°/15 mm. (*hydrochloride*, m. p. 184°; *phenylurethane*, m. p. 116°) (also from γ-*phenyl*-β-*methyl*-Δ^{β}-*propenylidene*cyclo*hexylamine*, b. p. 168—176°/14 mm.), and *cyclo*hexylbenzylamine. Reduction in the presence of furfuraldehyde affords cyclo*hexyl*-(γ-*furyl*-β-*methylpropenyl*)*amine* (8%), b. p. 166—172°/12 mm. (*hydrochloride*, m. p. 180°) (also from γ-*furyl*-β-*methyl*-Δ^{β}-*propenylidene*cyclo*hexylamine*, b. p. 158—162°/12 mm.), together with its *dihydro*- (0·7%), b. p. 155—160°/12 mm., and *tetrahydro*- (8%), b. p. 144—149°/12 mm. (*hydrogen oxalate*, m. p. 165°) -derivatives (the position of the double linking in all three products is undetermined), and cyclo*hexylfurylamine*, b. p. 123—124° (*phenylurethane*, m. p. 113°) (also from *furfurylidene*cyclo*hexylamine*, b. p. 131·5—135·5°/18 mm.). Reduction of *iso*butylidene*cyclo*hexylamine in the presence of formaldehyde affords cyclo*hexyl*-(γ-*hydroxy*-ββ-*dimethylpropyl*)*amine*, b. p. 123—125°/12 mm., m. p. 38° (*hydrochloride*, m. p. 224°; *phenylurethane*, m. p. 150°) (also from γ-*hydroxy*-ββ-*dimethylpropylidene*cyclo*hexylamine*, b. p. 108—110°/12 mm.).

J. W. Baker.

[Possible yellow content of the acidic, red solutions of methyl-yellow.] A. Hantzsch and A. Burawoy (Ber., 1930, 63, [*B*], 3172—3176; cf. A., 1930, 1280).—In reply to Thiel (A., 1930, 1573), reasons are advanced in favour of the view that in salt solutions of *p*-aminoazobenzenes in 2*N*-hydrochloric acid, which in agreement with Thiel contain practically no free base, an equilibrium exists between the yellow azoid and red quinonoid salts. H. Wren.

Azo-dyes and their intermediates. V. Constitution and degree of dispersion of azo-dyes. VI. Relation between molecular size and properties of azo-dyes. P. Ruggli and A. Zimmermann (Helv. Chim. Acta, 1931, 14, 101—126, 127—141).—V. The adsorption of various azo-dyes (all as pure sodium salts) on cotton, in absence and presence of sodium sulphate, has been investigated by the method previously described (cf. A., 1924, ii, 464; B., 1926, 436). Determinations of the viscosity of solutions and their rate of diffusion through 1% gelatin gels (cf. A., 1925, ii, 194) were also made in many cases. The azo-dyes from diazotised dehydrothiotoluidinesulphonic acid and 5-, 6-, and 7-amino-α-naphthol-3-sulphonic, 8-amino-α-naphthol-5-sulphonic, and 6-amino-β-naphthol-4-sulphonic acids show small affinities; these and the rates of diffusion through gelatin are somewhat less than the corresponding values for "Erika B" (prepared from diazotised dehydrothioxylidine and α-naphthol-3 : 8-disulphonic acid). The dyes from diazotised 4-aminoazobenzene-4′-sulphonic acid and the above acids are less substantive and show a higher rate of diffusion than the above. The affinities of the dyes from tetrazotised benzidine and 2 mols. of the above acids are generally higher (much more so in presence of sodium sulphate), but not nearly so good as Congo-red; the dye from 6-amino-β-naphthol-4-sulphonic acid gives a much smaller value than the others, although its rate of diffusion through gelatin is very similar to that of the other members of the series; the difference in the adsorption can be ascribed to the constitution, since coupling takes place, in this case only, in the 1-position.

The bisazo-dye obtained from tetrazotised benzidine and 2 mols. of 6-amino-α-napthol-3-sulphonic acid (J acid) is compared as a typical primary type with those (secondary) prepared by first coupling dehydrothiotoluidine (I) or α-naphthylamine (II) with J acid, and then coupling the resultant azo-compounds (after diazotisation) with a further mol. of the acid. The mol. wt., atom numbers, and degree of sulphonation (=wt. of total SO_3Na groups ×100/mol. wt.) of the three bisazo-dyes are of the same order. The secondary compounds are adsorbed to about three times the extent of the primary dye in absence of sodium sulphate; in presence of the sulphate, the compound from I is adsorbed to a greater extent than Congo-red, whilst its rate of diffusion through gelatin is considerably less than that from II or Congo-red.

The order of coupling does not affect the substantive properties.

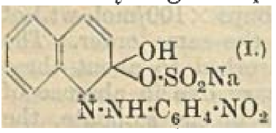
A series of bisazo-dyes of the "Biebrich scarlet" type (cf. Nietzki, A., 1880, 664; 1881, 178) is prepared from diazotised aminoazobenzene, its 4′-sulphonic and 3 : 4′-disulphonic acids with β-naphthol, β-naphthol-6-sulphonic, -3 : 6-disulphonic, and -3 : 6 : 8-trisulphonic acids. The products obtained (all containing 1—3 sulpho-groups) are not substantive except that formed from 4-aminoazobenzene-4′-sulphonic acid and β-naphthol. This is adsorbed to the same extent as a regular substantive dye; the relative viscosity of a 1% solution is much higher than that of any other member of the series examined, and it does not diffuse through gelatin. The colloidal character of the dye is ascribed to association caused by the isolated sulpho-group originating a strong dipole moment. The effect of the number of sulpho-groups on the solubility and colour reaction with sulphuric acid is determined.

VI. Mono-, bis-, tris-, and tetrakis-azo-dyes (*A*, where x=0, 1, 2, and 3, respectively), are prepared by diazotising J acid and coupling with excess of the sodium salt of the same acid, diazotising the purified monoazo-dye, and again coupling as before, and so on. A polyazo-dye of unknown value of x, and in which

(*A*.)

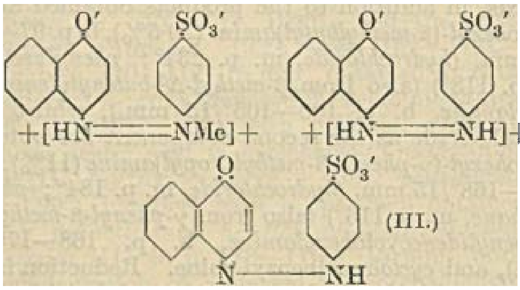
the final NH_2 is probably replaced by OH, is obtained by the action of alkali on diazotised J acid, when self-coupling occurs. The colours given by the dyes in sulphuric acid are not characteristic, but when the solutions are poured into water, orange, red, reddish-violet, violet, and blue precipitates, respectively, are obtained. The shades on cotton and in water show the expected shift towards the blue as the series is ascended, but this is only slight after the bisazo-dye. The affinity for cotton of the monoazo-derivative is much smaller than that of the other compounds (in presence of sodium sulphate), which approximate to those of the substantive type, and are all approximately equal. The rate of diffusion of the monoazo-compound into gelatin is much higher than that of any of the others (the polyazo-derivative does not diffuse); the relative viscosities of the bis- and polyazo-compounds are the same and are higher than those of the other compounds. H. BURTON.

Naphthalene series. III. Action of hydrogen sulphite on *p*-nitrobenzeneazo-α-naphthol. N. N. VOROSCHCOV and P. A. BJELOV (Ber., 1931, **64**, [*B*], 77—83).—*p*-Nitrobenzeneazo-β-naphthol, m. p. 249°, is converted by protracted ebullition with aqueous sodium hydrogen sulphite in presence of chloroform and ethyl alcohol into the yellow additive *compound* (I); it is decomposed with re-generation of the initial material in alkaline solution,



showing that the nitro-group has not suffered reduction. (A similar stability of the nitro-group is observed with *p*-nitrobenzeneazo-α-naphthol.) The corresponding *barium* (anhydrous and monohydrated) and *copper* (anhydrous and octahydrated) salts are described. In aqueous solution the tendency of the sodium salt towards dissociation increases with the dilution. It increases similarly with increasing concentration of hydroxyl ions, whereas hydrochloric acid has a stabilising action which is accentuated up to about 0·5 equivalent of acid but subsequently not considerably enhanced. H. WREN.

Constitution of azo-indicators. I. α-Naphthol-orange. K. H. SLOTTA and W. FRANKE (Ber., 1931, **64**, [*B*], 86—94).—Attempts to determine the acid constant of α-naphthol-orange failed since its conductivity in aqueous solution is so small that it cannot be even approximately determined. Electrometric titration of weighed amounts of the indicator with alkali hydroxide coupled with observations of the colour of the solution shows that the change from yellow to red takes place after addition of exactly one equivalent of hydroxide; a further change of colour is not observed after the addition of a second equivalent of hydroxide. Confirmation of the view that the second hydrogen atom is not connected with the indicator properties is found in the observation that the monoalkyl derivatives behave in a precisely similar manner and are therefore similarly constituted. Treatment of monomethylnaphthol-orange with hydriodic acid does not give methyl iodide, which is obtained by the use of ammonium iodide above 200°. The methyl group is therefore attached to an azo-nitrogen atom, and since fission of the compound with sodium hyposulphite affords 4-amino-α-naphthol the methyl group must be united to the nitrogen vicinal to the benzene nucleus. Treatment of the monomethyl compound with ethereal diazomethane gives a dimethyl compound void of indicator properties; treatment of this with sodium hyposulphite yields 4-methylamino-α-naphthol, and it does not give methyl iodide when treated with phosphorus and hydriodic acid. For the "acid" form of methylnaphthol-orange the constitution I is therefore

(I.)  (II.)

advanced, whereas the structures II and III are ascribed to the yellow "acidic" and the red "alkaline" form of naphthol-orange. Confirmation is found in the direct production of the dimethyl compound from the acidic form and diazomethane in ether.

The following compounds are incidentally described: α-naphthol-orange, decomp. 260°; *methyl-α-naphthol-orange*, decomp. 260°; 4-*methoxyazobenzene*-4′-*sulphonic acid*; 4-p-*nitrobenzamido-α-naphthol*, decomp. 276°; *ethyl*-, decomp. 263—265°; n-*propyl*-, decomp. 268°; n-*butyl*-, decomp. 269—270°; n-*hexyl*-α-

naphthol-orange, decomp. 267°; *dimethylnaphthol-orange*, m. p. 178°; *4-methyl-p-nitrobenzamido-α-naphthol*, m. p. 216°. H. WREN.

Action of ethyl nitrate on phenylhydrazine in presence of sodium ethoxide. E. BAMBERGER and O. BILLETER (Helv. Chim. Acta, 1931, **14**, 219—232).—When a mixture of phenylhydrazine and ethyl nitrate is added gradually with stirring to cold alcoholic sodium ethoxide, a mixture of methylformazyl, m. p. 125—125·3°, sodium nitrite, benzene, aniline, β-acetylphenylhydrazine, and small amounts of phenyl azide, azobenzene, acetic acid, nitrogen, and (probably) diphenyl are produced. The various reactions which probably occur are discussed. Methylformazyl (cf. A., 1903, i, 284) is conveniently prepared by adding benzenediazonium chloride to a cold solution of acetaldehydephenylhydrazone in alcoholic sodium acetate. *Nitromethylformazyl*, NHPh·N:CMe·N:N·C_6H_4·NO_2(+0·5EtOH), m. p. 154°, is obtained similarly using *p*-nitrobenzenediazonium chloride. Much of the work has been published previously (Vierteljahrschr. Naturf. Ges. Zurich, 1903, **48**, 329). H. BURTON.

[Reduction of normal diazo-hydrates.] E. BAMBERGER (Helv. Chim. Acta, 1931, **14**, 242—249).—The formation of β-benzoylhydrazine from benzaldehyde and phenyldi-imide (Angeli, A., 1930, 205) is not considered to be analogous to the production of phenylazohydroxyanilide, O:NPh.NH:NPh, from nitrosobenzene and phenyldi-imide (*loc. cit.*), since the former reaction involves the migration of a hydrogen atom. Angeli's synthesis of benzhydroxamic acid from benzaldehyde and nitrosyl probably results through the intermediate formation of α-nitrosobenzyl alcohol (cf. A., 1902, i, 197). The remainder of the paper has been reviewed previously (A., 1900, i, 193). H. BURTON.

Identification of phenols. C. F. KOELSCH (J. Amer. Chem. Soc., 1931, **53**, 304—305).—The phenol (1 g.) is heated with a 50% solution of chloroacetic acid (2·5 c.c.) and 33% sodium hydroxide solution (3·5 c.c.) at 100° (bath) for 1 hr., the solution acidified, and the resultant aryloxyacetic acid extracted with ether. The following are new: o-, m. p. 143—145°, and m-*chlorophenoxy*-, m. p. 108—110°; m-*bromophenoxy*-, m. p. 107—108·5°; o-, m. p. 134—135°, and m-*iodophenoxy*-, m. p. 114—115·5°, and p-*methoxyphenoxy-acetic acids*, m. p. 110—112°. H. BURTON.

Preparation and properties of tri-, tetra-, and penta-chlorophenols. G. J. TIESSENS (Rec. trav. chim., 1931, **50**, 112—120).—Experimental details are given for the preparation and determination of the electrical conductivity in dilute aqueous solution of various polychlorophenols, a preliminary account of which has already been published (A., 1929, 1173). J. W. BAKER.

Chlorination of iodophenols. III. *o*-Iodophenol. S. BUCHAN and H. McCOMBIE (J.C.S., 1931, 137—144; cf. *ibid.*, 1913, **103**, 1762).—Chlorination of *o*-iodophenol in carbon tetrachloride at 0° gives an unstable iododichloride, which rapidly decomposes to give 4-*chloro*-2-*iodophenol*, m. p. 78°, the constitution of which is proved by its synthesis from the *benzyl ether*, m. p. 84—85°, of 4-chloro-2-nitrophenol, through the amino- and iodo-benzyl ethers. 4-*Chloro*-2-*iodophenyl acetate* (an oil) and *benzyl ether*, m. p. 60°, may be obtained either from 4-chloro-2-iodophenol, or by decomposition of the iododichlorides of o-*iodophenyl acetate* and *benzyl ether* (both oils). o-*Iodophenyl phenylcarbamate*, m. p. 121—122°, and *benzoate*, m. p. 34°, and 4-*chloro*-2-*iodophenyl phenylcarbamate*, m. p. 128°, and *benzoate*, m. p. 88°, form relatively stable *iododichlorides*, m. p. 125°, 98—101°, 146°, and 103—104° (decomp. in every case), respectively; the first of these with acetic acid and aqueous potassium iodide gives o-*iodophenyl* 2 : 4-*dichlorophenylcarbamate*, m. p. 145°, identified by synthesis from *o*-iodophenol and 2 : 4-dichlorophenylcarbimide.

4-Chloro-2-iodophenol on chlorination as above gives an unstable iododichloride, converted by decomposition into 4 : 6-*dichloro*-2-*iodophenol*, m. p. 62°, also obtained by chlorination of *o*-iodophenol; its *acetate*, m. p. 59°, and *benzyl ether*, m. p. 62°, are obtained either from it, or by decomposition of the iododichlorides from corresponding 4-chloro-2-iodophenol derivatives; their iododichlorides decompose in the course of a few days with regeneration of the parent substance. The *benzoate*, m. p. 89°, and *phenylcarbamate*, m. p. 181° (prepared from 4 : 6-dichloro-2-iodophenol only) do not appear to form iododichlorides. A little *trichloro*-o-*iodophenol*, m. p. 52—54°, is formed by decomposition of the iododichloride from 4 : 6-dichloro-2-iodophenol.

2-*Iododiphenyl ether*, m. p. 55—56°, synthesised by standard methods from the 2-nitro-compound, gives an unstable *iododichloride*, m. p. 81—82° (decomp.). The *iododichloride*, m. p. 98° (decomp.), of ω-*o′*-*iodophenoxyacetophenone*, m. p. 123° (from *o*-iodophenol, ω-chloroacetophenone, and sodium ethoxide), is moderately stable. *o*-Iodophenol with carbonyl chloride and pyridine gives the *carbonate*, m. p. 88° [*iododichloride*, stable, m. p. 108° (decomp.)]; with toluene-*p*-sulphonyl chloride the p-*toluenesulphonate*, m. p. 80° [*iododichloride*, stable, m. p. 95—97° (decomp.)]; and with allyl bromide and sodium ethoxide the *allyl ether* (*dibromide*), which with chlorine gives the *iododichloride*, m. p. 84° (decomp.), of *o*-iodophenyl βγ-dichloropropyl ether; the *iododichloride*, m. p. 118° (decomp.), of the dibromide decomposes slowly into 4-*chloro*-2-*iodophenyl βγ-dibromopropyl ether*, m. p. 52°. o-*Iodophenyl ethyl carbonate* (from ethyl chloroformate and the phenol in aqueous sodium hydrogen carbonate) does not give an iododichloride.

Chlorination of *o*-iodophenol in carbon tetrachloride at 60—70° gives hexachloro*cyclo*hexadienone and chloranil. Iodine monochloride and *o*-iodophenol give 4-*chloro*-2 : 6-*di*-*iodophenol*, m. p. 106—107°, which forms an unstable iododichloride. Chlorination of diphenyl carbamate in chloroform at 0° gives 4-*chlorophenyl* 2 : 4-*dichlorophenyl carbamate*, m. p. 157°, identical with the product of interaction of *p*-chlorophenol and 2 : 4-*dichlorophenylcarbimide*, m. p. 61°. The last is prepared from 2 : 4-dichloroaniline and carbonyl chloride at 350—400°. H. A. PIGGOTT.

Chlorination and nitration in methyl-alcoholic solution. E. PŁAŻEK (Rocz. Chem., 1930, **10**, 761—776).—Aromatic hydrocarbons and β-naphthol do not undergo chlorination in methyl-alcoholic solution, the chlorine entering into combination only with the solvent. Phenol, *m*-cresol, and anisole readily yield monochloro-derivatives, quinol yields a mixture of 2 : 3- and 2 : 5-dichloroquinol, with only traces of quinone, whilst pyrocatechol and resorcinol yield uncrystallisable, tarry products. Anthracene is converted into anthraquinone, veratrole gives a dichloro-derivative, guaiacol yields exclusively trichloroguaiacol, m. p. 107°, salicylic acid yields exclusively 5-chloro-2-hydroxybenzoic acid, 3-hydroxybenzoic acid is converted chiefly into 2-chloro-3-hydroxybenzoic acid, with the 6-chloro-derivative as a by-product, whilst 4-hydroxybenzoic acid gives a mixture of products containing 3 : 5-dichloro-4-hydroxybenzoic acid. *p*-Nitrophenol yields 2-chloro-*p*-nitrophenol, *o*-nitrophenol gives a mixture of 6- and 4-chloro-*o*-nitrophenol. Phenol-4-sulphonic acid, aniline, and *o*- and *p*-acetotoluidides yield the same products as in other solvents. *o*-, *m*-, and *p*-Diacetylphenylenediamines give exclusively dichloro-derivatives, *p*-nitroaniline yields 2-chloro-*p*-nitroaniline, with an admixture of 2 : 6-dichloro-*p*-nitroaniline; *o*-nitroaniline yields chiefly 4-chloro-*o*-nitroaniline together with 4 : 6-dichloro-*o*-nitroaniline; *m*-nitroaniline gives a mixture of 4-chloro-*m*-nitroaniline, 4 : 6-dichloro-*m*-nitroaniline, and 2 : 4 : 6-trichloro-*m*-nitroaniline; the last named is the sole product of exhaustive chlorination. *o*-Aminobenzoic acid does not undergo chlorination, whilst the *m*- and *p*-acids yield the same dichloro-derivatives as are obtained using ordinary solvents, together with some trichloroaniline resulting from decarboxylation of the original acid. On the whole, purer products are obtained in greater yield in methyl than in ethyl alcohol. Nitration can be performed in methyl-alcoholic solution only of phenolic substances; phenol gives a mixture of 2- and 4-nitrophenol, anisole yields 2- and 4-nitroanisole, 2- and 4-chlorophenols give respectively a mixture of 2-chloro-4- and -6-nitrophenol and 4-chloro-2-nitrophenol, veratrole yields 4-nitroveratrole, quinol dimethyl ether the 2-nitro-derivative, and *m*-cresol yields 4-nitro-*m*-cresol, together with the 2- and 6-nitro-derivatives. R. TRUSZKOWSKI.

Reaction of *p*-anisidine and ethyl methylacetoacetate. W. O. KERMACK and J. F. SMITH (J.C.S., 1931, 221—222).—The *compound*, m. p. 51° (cf. A., 1930, 1298), isolated from the product of condensation of *p*-anisidine with ethyl methylacetoacetate appears from its nitrogen content to be derived from 2 mols. of base and 1 mol. of ester; this conclusion is supported by the formation of a completely solid product, m. p. 40—46°, by the reagents in these proportions, the yield of aceto-*p*-anisidide obtained on treatment with acetic anhydride, and the mol. wt. in benzene (199, 202), which points to dissociation of a compound of the type $C_{14}H_{19}O_3N,C_7H_9ON$, and is inconsistent with the formula $C_{14}H_{19}O_3N$. H. A. PIGGOTT.

Catalytic preparation of 2 : 4-diaminophenol. W. E. BRADT (J. Physical Chem., 1930, **34**, 2711—2718).—The reduction of 2 : 4-dinitrophenol to the diamine by means of hydrogen in the presence of a nickel catalyst, prepared by the reduction of nickel carbonate in hydrogen at 288°, has been investigated. A maximum yield of 95·1% of 2 : 4-diaminophenol (determined by titration with sodium nitrite) is obtained at 96° with 5 g. of 2 : 4-dinitrophenol in 20 c.c. of absolute alcohol, 2·0 g. of nickel catalyst, at a pressure of 500 lb. per in.^{2} of electrolytic hydrogen. Higher temperatures cause a slight decrease in yield with the formation of ammonia at 125°, and an increased time of reduction beyond 2 hrs. gives only a slight increase. Absolute ethyl alcohol dehydrated over anhydrous copper sulphate at the ordinary temperature is the best solvent. For a given weight of catalyst an optimum concentration of 2 : 4-dinitrophenol exists, and an increase in the ratio of the weight of catalyst to that of the nitrophenol from 0·2 to 0·4 also increases the yield. The maximum yield isolated as crystalline dihydrochloride is 50%. L. S. THEOBALD.

Addition of phenols to the ethylenic linking. Reaction mechanism and synthesis of phenolic ethers. J. B. NIEDERL and S. NATELSON (J. Amer. Chem. Soc., 1931, **53**, 272—277).—When Δ^β-pentene and di*iso*butylene are treated with phenols in presence of sulphuric acid at 0°, and the mixture is kept for a week at the ordinary temperature, phenyl alkyl ethers are obtained. Addition of sulphuric acid to the double linking first occurs; the resultant compound reacts with the phenol, forming the ether and sulphuric acid. A similar mechanism is proposed for the interaction of phenols and unsaturated alcohols, ethers, aldehydes, ketones, acids, and esters; the ethers rearrange in presence of sulphuric acid. The following are prepared: m-*tolyl α-methylbutyl ether*, b. p. 238°, d^{20} 0·920, n_D^{21} 1·500 (also obtained from sodium *m*-tolyloxide and β-bromopentane in alcohol), converted by nitric acid into trinitro-*m*-cresol; o-, b. p. 234°, d^{20} 0·915, 1·493, and p-*tolyl*, b. p. 225°, d^{20} 0·920, n_D^{21} 1·505, *α-methylbutyl ethers*; *phenyl*, b. p. 190°/40 mm., 258°/760 mm., m. p. 12°, d^{20} 0·950, n_D^{21} 1·510, o-*tolyl* (I), b. p. 271°, m. p. 6°, 0·881, 1·472, m-*tolyl*, b. p. 273°, d^{20} 0·895, 1·476, and p-*tolyl*, b. p. 272°, d^{20} 0·889, n^{21} 1·470, *ααγγ-tetramethylbutyl ethers*. When I is heated with zinc and hydrogen chlorides at 200°, rearrangement into *ααγγ-tetramethylbutyl*-o-*cresol*, m. p. 49—50°, occurs. H. BURTON.

Derivatives of dulcin [*p*-ethoxyphenylcarbamide]. E. WERTHEIM (J. Amer. Chem. Soc., 1931, **53**, 200—203).—When a mixture of *p*-ethoxyphenylcarbamide and ethyl chloroformate is heated, first over a free flame until homogeneous and then at 100°, *ethyl* p-*ethoxyphenylallophanate*, m. p. 139—140°, is obtained. This is converted by ammonia at 100° into p-*ethoxyphenylbiuret*, m. p. 185—186°. The carbamide and ethyl chloroformate react at 175°, forming a mixture of *s*-di-*p*-ethoxyphenylcarbamide and s-*di*-p-*ethoxyphenylbiuret*, m. p. 208—209°. p-*Methylthiol*-, m. p. 164—165°, and p-*ethylthiolphenylcarbamides*, m. p. 149—150°, and p-*methylthiol*-, m. p. 198—199°, and p-*ethylthiol-phenylthiocarbamides*, m. p. 136—137°, are prepared by the

usual methods. The last-named thiocarbamides are bitter; the other compounds are tasteless.

H. BURTON.

Detection of β-naphthol. G. DE HAAS (Pharm. Weekblad, 1931, **68**, 29—32).—Addition of glacial acetic acid and concentrated sulphuric acid successively to solutions containing β-naphthol in dilutions up to $1:10^5$ produces a yellowish-green colour at the common surface; on shaking, the mixture becomes fluorescent. Colorations are obtained with other hydroxy-compounds, but no fluorescence.

S. I. LEVY.

Action of bromine on naphthylamine- and aminonaphthol-sulphonic acids. G. HELLER [with H. ARNOLD and J. SCHMIDT] (Z. angew. Chem., 1930, **43**, 1132—1137).—α-Naphthylamine-4-sulphonic acid and bromine (2 mols.) in warm acetic acid give 2:4-dibromo-α-naphthylamine. α-Naphthylamine-5-sulphonic acid and 1 mol. of bromine yield a *bromo*-derivative, which could not be diazotised or coupled with diazotised aniline in acid or alkaline solution; with an excess of bromine in water, 2 : 4-*dibromo-α-naphthylamine-5-sulphonic acid* results. This is converted by heating with water and aniline into a *bromoanilino-α-naphthylamine-5-sulphonic acid*. 2 : 4-*Dibromo-* and *bromoanilino-α-naphthylamine-*8-*sulphonic acids* are prepared similarly. β-Naphthylamine-6-sulphonic acid is brominated in acetic acid to the 1-bromo-derivative (*sodium* salt); the -5- and -7-sulphonic acids also afford 1-*bromo*-derivatives, which when diazotised and coupled with alkaline β-naphthol give red azo-dyes. Definite products could not be isolated from β-naphthylamine-1- and -8-sulphonic acids. *Sodium bromo-β-naphthylamine-*6 : 8-*disulphonate* and a *sodium dibromo-β-naphthylamine-*6(or 8)-*sulphonate* are prepared from β-naphthyl amine-6 : 8-disulphonic acid, whilst the -3 : 6-disulphonic acid affords a *dibromo-β-naphthylamine-*3(or 6)-*sulphonic acid*. In all the above brominations, bromine has no oxidising action on the amino-group (cf. A., 1928, 409).

Treatment of 2-amino-8-naphthol-3 : 6-disulphonic acid with an excess (20 mols.) of bromine in acetic acid at 100° affords 1 : 3 : 6 : 7-*tetrabromo-2-amino-*5 : 8-*naphthaquinone* (I), m. p. 241° [*acetyl* derivative, m. p. 255° (decomp.); *diacetyl* derivative, m. p. 160—161°], reduced by stannous chloride and acetic acid to *tribromo-2-amino-*5 : 8-*dihydroxynaphthalene*, not melted at 300°, and converted by an excess of aniline into *tribromo - 2 - aminoanilino-*5 : 8-*naphthaquinone*, m. p. 215—216° after previous sintering. 2-Amino-5-naphthol-7-sulphonic acid (*dibromo*-derivative, obtained by the action of 2 mols. of bromine in acetic acid) can also be converted into I, also formed when a solution of 2-amino-8-naphthol-6-sulphonic acid in slightly diluted sulphuric acid is treated with an acetic acid solution of bromine at 35°. Bromination of 1-amino-8-naphthol-4-sulphonic and -2 : 4-disulphonic acids in warm aqueous acetic acid gives 2 : 4 : 7-*tribromo-*1-*amino-*5 : 8-*naphthaquinone*, m. p. about 235° after previous sintering. Sodium hydrogen 1-amino-8-naphthol-4 : 6-disulphonate is brominated in acetic acid to 2 : 4 : 5(or 7)-*tribromo-*1-*amino-*8-*naphthol-*6-*sulphonic acid*, whilst in sulphuric acid 1 : 2 : 4 - tribromo - 5 : 8 - naphthaquinone - 6 - sulphonic acid [*potassium* salt ($+2{\cdot}5H_2O$)] results. 2 : 4 : 6 : 7-*Tetrabromo-*1-*amino-*5 : 8-*naphthaquinone*, m. p. 255° after previous sintering, prepared in one experiment from the above sodium salt and an excess of bromine in sulphuric and acetic acids at 40°, is also formed by similar treatment of 1-amino-8-naphthol-5-sulphonic acid. Sodium 1-amino-8-naphthol-3 : 6-disulphonate and bromine in potassium chloride solution afford *potassium* 2 : 4(?)-*dibromo-*1-*amino-*5 : 8-*naphthaquinhydrone-*3 : 6-*disulphonate*, $C_{20}H_8O_{16}N_2Br_4S_4K_4,4H_2O$, deep violet, reduced by stannous chloride to a colourless *substance*, $C_{10}H_7O_8NBr_2S_2$, which with nitrous acid gives first a violet and then a brownish-yellow coloration. 1-Amino-2-naphthol-4-sulphonic acid and bromine in aqueous acetic acid at 100° yield 3 : 4-dibromo-1 : 2-naphthaquinone, m. p. 171°, formed by way of the naphthaquinone-4-sulphonic acid (cf. Boniger, A., 1894, i, 199); when a similar reaction mixture is boiled, 2-*bromo-*3-*hydroxy-*1 : 4-*naphthaquinone*, m. p. 196—198°, results. *Potassium* 4-*bromo-*1 : 2-*naphthaquinone-*6-*sulphonate* ($+H_2O$) is obtained when (sodium) 1-amino-2-naphthol-4 : 6-disulphonate is brominated in boiling aqueous acetic acid and the resulting solution treated with potassium chloride.

H. BURTON.

***cyclo*Hexanediols.** B. ROTHSTEIN (Ann. Chim., 1930, [x], **14**, 461—598).—A detailed account and discussion of results most of which have previously been summarised (A., 1928, 518, 632, 1129, 1130; 1929, 60, 1064, 1441; 1930, 84, 463, 768). The action of organic acids and their derivatives on *cyclo*hexane-1 : 2-diols affords esters of the same configuration as the parent diol, but in the cases of the 1 : 3- and 1 : 4-diols partial stereoisomeric change in the direction *cis*⟶*trans* occurs. The action of hydrogen halides on the 1 : 2-diol yields only resinous products and the 1 : 2-dihalogeno-derivatives can be obtained only by (*cis*-) addition of halogen to *cyclo*hexene. The "pseudo-migration" mechanism suggested in explanation of the identity of the halogeno-derivatives obtained by the action of hydrogen halide (or phosphorus trihalide) on the 1 : 3- or 1 : 4-diols is confirmed by the observation that no migration of the halogen occurs when the halogeno-derivatives are treated with the hydrogen halide under the same reaction conditions. Conversely, acetic acid does not add on to the double linking in *cyclo*hexene derivatives and silver acetate reacts with the dihalogeno-derivatives by direct substitution without stereoisomeric change. Determination of the configuration of the 1 : 3-diols by optical resolution of the *trans*-derivative has so far proved unsuccessful, but configurations are assigned by a comparative study of the m. p. and solubilities of the 1 : 3- and 1 : 4-diols with those of known configuration in the 1 : 2-diol series, the relationships m. p. *cis*<m. p. *trans*, and solubility *cis*>*trans* being general. The following appears to be new. Separation of the product of catalytic reduction of pyrocatechol is effected by conversion of the *cis*-diol into its *iso*propylidene ether, b. p. 75—76°/17 mm. (by the action of acetone and anhydrous hydrogen chloride in the presence of sodium sulphate), which is hydrolysed to the *cis-cyclo*hexane-1 : 2-diol, m. p. 98° (42%) [diacetate, $d_4^{19°}$ 1·0836, $n_D^{19·5}$ 1·4429 (cf. Verkade and others, A., 1930, 337); *cinnamate*,

b. p. 138°/11 mm. (corr.), $d_4^{19.5}$ 1·0648, n_D^{9} 1·5528], leaving the *trans*-diol, m. p. 104° (52%) (*cinnamate*, m. p. 90—91°), the solubility of the two stereoisomerides in dry commercially pure acetone at 20° being 7·195 and 6·595, respectively. *cis-cyclo*Hexane-1 : 3-diol (monobenzoate, $d_4^{22.5}$ 1·1328, n_D^{22} 1·5348) crystallises in three polymorphous forms. The solubility of the *cis*- and *trans*-1 : 3-diols in pure, dry acetone at 17·5° is, respectively, 8·335 and 7·935, and of their di-*p*-nitrobenzoates, m. p. 154·5° and 176·5°, is 2·89 and 1·09, respectively, at 20°. *cis-cyclo*Hexane-1 : 4-diol dicinnamate has d_4^{20} 1·0466, $n_D^{19.5}$ 1·5548; *cis-cyclo*hexane-1 : 3-diol gives *dipropyl*, b. p. 113°/15 mm., d_4^{21} 0·9006, n_D^{22} 1·4430; *diisobutyl*, b. p. 160—162°/16 mm., d_4^{23} 0·9006, n_D^{23} 1·4489; and *dibenzyl*, b. p. 205—207°/1 mm., d_4^{15} 1·0739, n_D^{15} 1·5440, *ethers*. The configuration of *cis*-1 : 2-dibromo*cyclo*hexane, b. p. 101—103°/13 mm., $d_4^{19.5}$ 1·7759, n_D^{19} 1·5445 (by addition of bromine to *cyclo*hexene, above), is proved by its conversion into the *cis*-diol through the *cis*-diacetate. Contrary to Lindemann and Baumann (A., 1930, 209), the dibromo-derivative, m. p. 112°, obtained by the action of hydrogen bromide on the 1 : 3-diol, and to which these authors assigned the *cis*-1 : 3-configuration, is actually the *trans*-1 : 4-dibromo-compound and is accompanied by the *cis*-1 : 4-dibromo-derivative, m. p. 48° (dimorphous), and a liquid *dibromo*cyclo*hexane*, b. p. 114—115°/15 mm., d_4^{20} 1·7834, n_D^{20} 1·5531, which is probably a 1 : 3-derivative. Hydrobromic acid (65%) converts *cyclo*hexane-1 : 4- or -1 : 3-diol di*iso*butyl ether and the 1 : 3-diol dibenzyl ether into a mixture of *trans*-1 : 4-dibromo*cyclo*hexane, m. p. 112°, and its isomeride, m. p. 48°; similar results are obtained with concentrated hydrochloric acid or phosphorus tribromide. J. W. BAKER.

Two stereoisomeric *iso*eugenols. F. BOEDECKER and H. VOLK (Ber., 1931, **64**, [*B*], 61—66).—Technical *iso*eugenol, f. p. about 0°, is converted by dissolution in 15% aqueous sodium hydroxide into the crystalline *sodium* derivative of *iso*eugenol, b. p. 141—142°/13 mm., m. p. 30—33°, d_4^{20} 1·0852, n_D^{20} 1·5782. Treatment of the product obtained from the mother-liquor from the sodium salt with benzoyl chloride and sodium hydroxide yields a *benzoate*, m. p. 59—61°, hydrolysed to the second form of iso*eugenol*, b. p. 134—135°/13 mm., d_4^{20} 1·0851, n_D^{20} 1·5726, which could not be caused to solidify. The isomeric *iso*eugenols (crystalline and liquid) are converted into their respective *methyl ethers*, m. p. 16—17°, b. p. 143—144°/11 mm., d_4^{20} 1·0528, n_D^{20} 1·5692, and b. p. 138—140°/12 mm., d_4^{20} 1·0521, n_D^{20} 1·5616, and *acetates*, m. p. 79°, and b. p. 160—162°/13 mm., n_D^{20} 1·5418. Bromination of *iso*eugenyl acetate, m. p. 79°, affords mainly the dibromide, m. p. 132°, mixed with a smaller amount of the isomeric *dibromide*, m. p. 79°; the relative proportion of the products is reversed when the acetate, b. p. 160—162°/13 mm., is used as initial material. Debromination of either dibromide similarly leads to a mixture of acetates. Conversion of the liquid into the crystalline *iso*eugenol is effected by debromination of the mixed bromide obtained from the liquid acetate, separation of the bulk of the crystalline acetate from the product of repetition of the complete process with the residue, followed finally by hydrolysis of the solid acetate thus obtained. The reverse transformation is effected by debromination and hydrolysis of the small amounts of the bromide, m. p. 79°, obtained by bromination of the acetate of the crystalline *iso*eugenol. Treatment of the product with sodium hydroxide leads to the isolation of the crystalline *iso*eugenol. On grounds of analogy, the *trans*- and *cis*-configurations are ascribed to the crystalline and liquid *iso*eugenols, respectively. H. WREN.

Stereochemistry of diphenylbenzenes. *meso*- and *r*-3 : 6-Dibromo-2 : 5-di-(3-bromo-2 : 4 : 6-trimethylphenyl)quinols and the corresponding quinones. XII. P. R. SHILDNECK and R. ADAMS (J. Amer. Chem. Soc., 1931, **53**, 343—352; cf. A., 1930, 1588).—*p*-Benzoquinone and mesitylene react in presence of aluminium chloride below 5° forming 2 : 5-*di*-(2 : 4 : 6-*trimethylphenyl*)*quinol*, m. p. 225—226° (corr.), which when brominated in chloroform at 50—60° affords two (*meso*- and *r*-) 3 : 6-*dibromo*-2 : 5-*di*-(3-*bromo*-2 : 4 : 6-*trimethylphenyl*)*quinols* (I), m. p. 334—335° (corr.; slight decomp.), and (II), m. p. 294—295° [corresponding *diacetates*, m. p. 285—286° (corr.) and 237—238° (corr.), respectively]. Oxidation of I and II with *p*-benzoquinone in alcohol gives the corresponding orange-coloured 3 : 6-*dibromo*-2 : 5-*di*-(3-*bromo*-2 : 4 : 6-*trimethylphenyl*)-p-*benzoquinones*, m. p. 295—296° (decomp.) and 284—285° (decomp.), respectively. These are reduced by stannous chloride in pyridine to the respective quinols and are oxidised by alkaline hydrogen peroxide to 3-*bromo*-2 : 4 : 6-*trimethylbenzoic acid*, m. p. 168° (corr.), also prepared by brominating 2 : 4 : 6-trimethylbenzoic acid in carbon tetrachloride in presence of iron filings at 120—130° (bath). Treatment of I or II with liquid bromine gives the same 3 : 6-*dibromo*-2 : 5-*di*-(3 : 5-*dibromo*-2 : 4 : 6-*trimethylphenyl*)*quinol*, m. p. (block) 395—398° [*diacetate*, m. p. 297° (corr.)], oxidised by *p*-benzoquinone in alcohol to 3 : 6-*dibromo*-2 : 5-*di*-(3 : 5-*dibromo*-2 : 4 : 6-*trimethylphenyl*)-p-*benzoquinone*, m. p. (block) 390—393°. This is reducible to the original quinol and is oxidised by alkaline hydrogen peroxide to 3 : 5-*dibromo*-2 : 4 : 6-*trimethylphenylbenzoic acid*, m. p. 210—211° (corr.), also formed by the action of liquid bromine on 3-bromo-2 : 4 : 6-trimethylbenzoic acid at the ordinary temperature. H. BURTON.

Migration of acyl from sulphur to nitrogen. H. P. LANKELMA and A. E. KNAUF (J. Amer. Chem. Soc., 1931, **53**, 309—312).—Treatment of the hydrochloride (I) of 4-chloro-2-aminothiophenol, m. p. 198—201° (decomp.; lit. 120°), prepared by reduction of 4 : 4'-dichloro-2 : 2'-dinitrodiphenyl disulphide with tin and alcoholic hydrochloric acid, with benzoyl chloride in boiling dimethylaniline gives 5-*chloro*-2-*phenylbenzthiazole*, m. p. 139°; 5-*chloro*-2-*methylbenzthiazole*, m. p. 68—69°, is prepared similarly, using acetic anhydride. When I is heated with benzoyl chloride in dimethylaniline at 100°, 4-*chloro*-2-*benzamidophenyl thiobenzoate*, m. p. 158—159°, is formed. This is hydrolysed by alcoholic potassium hydroxide at the ordinary temperature to 4-*chloro*-2-*benzamidothiophenol*, m. p. 105—106° (*acetate*, m. p. 129—130°, hydrolysed to the original thiophenol), which when

crystallised from alcohol passes into 5-chloro-2-phenylbenzthiazole. Treatment of I with acetic anhydride in dimethylaniline at 100° gives 4-*chloro-2-acetamidophenyl thioacetate*, m. p. 150—151°, hydrolysed to 4-*chloro-2-acetamidothiophenol*, m. p. 92—94°, which when crystallised from alcohol passes into 5-chloro-2-methylbenzthiazole. Hydrolysis of 4-*chloro-2-acetamidophenyl thiobenzoate*, m. p. 141—142°, gives 5-chloro-2-phenylbenzthiazole, showing that the benzoyl group migrates from sulphur to nitrogen. H. BURTON.

Determination of constitution by changing the order in which groups are introduced into the benzene nucleus. J. W. DIENSKE (Rec. trav. chim., 1931, **50**, 21—31).—Mainly experimental details of results previously described (this vol., 78; Challenger and Collins, A., 1924, i, 953) on the conversion of *p*-halogenoaniline and *p*-thiocyanoaniline into identical *p*-halogenocyanobenzene. Improved yields are obtained by using a solution of cuprous thiocyanate in the Sandmeyer reaction (Thurnauer, A., 1890, 749). The formation of di-iododiphenyl disulphide observed by Challenger and Collins (*loc. cit.*) when cuprous thiocyanate acts on diazotised *p*-iodoaniline was not confirmed, a *substance*, m. p. 88—100°, being obtained. By similar reactions are obtained: p-*thiocyanobenzonitrile*, m. p. 127·5°, and *p*-dithiocyanobenzene, m. p. 108·5° (Challenger and Peters, A., 1928, 750, give m. p. 106°), nitrated by absolute nitric acid at 0° to its 2-nitro-derivative, m. p. 146·5° (*loc. cit.*, m. p. 143—144°). The use of potassium hydrosulphide for hydrolysis of aromatic thiocyano-derivatives to thiophenols and disulphides is unnecessary, since these products are readily obtained by hydrolysis with boiling 10% potassium hydroxide or moderately concentrated sulphuric acid and thus from *p*-bromo- and *p*-iodo-thiocyanobenzene are obtained mixtures of *p*-bromo- or *p*-iodo-thiophenol and 4 : 4′-dibromo- or 4 : 4′-di-iodo-diphenyl disulphides, respectively. J. W. BAKER.

Condensation of benzyl alcohol with *cyclo*hexene in the presence of phosphorus pentoxide. D. N. KURSANOV (J. Russ. Phys. Chem. Soc., 1930, **62**, 1691—1695).—The condensation of benzyl alcohol and *cyclo*hexene in the presence of phosphorus pentoxide takes place readily with the formation of much tarry matter which cannot be purified, and benzyl-Δ^1-*cyclo*hexene, b. p. 127·2—128·4°/15 mm., d^{20} 0·9634, n_D^{20} 1·5400, which on oxidation with alkaline potassium permanganate yielded benzoic acid and a neutral compound, m. p. 105—106°, which could not be identified. M. ZVEGINTZOV.

Conjugated systems. VI. Preparation of the geometrical isomerides of styrylmethylcarbinol and phenylbutadiene. VII. Reactions of the geometrical isomerides of styrylmethylcarbinol. I. E. MUSKAT and M. HERRMAN (J. Amer. Chem. Soc., 1931, **53**, 252—260, 260—271).—VI. When the reaction product (*A*) from magnesium methyl bromide and cinnamaldehyde is decomposed with dilute acid and the residue from the completely acid-free ethereal extract distilled, trans-*styrylmethylcarbinol*, b. p. 117°/4 mm., n^{31} 1·5550, is obtained. When this is distilled in presence of a trace of acid, *cis*-styrylmethylcarbinol, b. p. 144°/21 mm., n^{31} 1·5536, is isolated. The *cis*- and *trans*-carbinols are also formed from magnesium methyl iodide and cinnamaldehyde; the reaction product is decomposed with sulphurous acid, and the resulting acid-free extract contains the *trans*-form. The *cis*-carbinol eliminates water very readily, even on keeping, forming *cis*-α-phenylbutadiene, b. p. 86°/11 mm. (cf. Klages, A., 1906, i, 661). Decomposition of *A* with 50% sulphuric acid affords trans-*α-phenylbutadiene*, b. p. 76°/11 mm., n^{28} 1·5920, also formed when the *cis*-isomeride is kept in presence of a trace of acid and then distilled, or when trans-*α-methylcinnamyl chloride*, b. p. 104°/6 mm., is heated with pyridine.

VII. *trans*-Styrylmethylcarbinol furnishes a phenylcarbimide derivative, m. p. 94°, identical with that described by Klages (*loc. cit.*), and an acetate, b. p. 141—144°/15 mm., previously prepared by Burton (A., 1929, 554). When the carbinol is heated to 180°, the main product formed is a *compound*, $C_{20}H_{22}O$, b. p. 200°/6 mm. (*tetrabromide*, m. p. 179°). *cis*-Styrylmethylcarbinol does not give a phenylcarbimide derivative; it is dehydrated by acetic anhydride, forming mainly dimeric α-phenylbutadiene, but it yields with ethereal hydrogen chloride cis-*α-methylcinnamyl chloride*, b. p. 108°/6 mm. Catalytic reduction of both carbinols by Adams' method shows that the *cis*-form is reduced more readily; *γ-phenyl-α-methylpropyl alcohol*, b. p. 105°/6 mm. (*phenylcarbimide* derivative, m. p. 113°), is produced in each case. The *cis*-carbinol (oxide, b. p. 117°/3·5 mm.) is oxidised more rapidly by perbenzoic acid than is the *trans*-isomeride (oxide, b. p. 118°/4 mm.). When the *trans*-oxide is heated with 2*N*-sulphuric acid, a compound, b. p. 200°/4 mm., is formed by elimination of 1 mol. of water from 2 mols. of the oxide. The styrylmethylcarbinol of Klages (*loc. cit.*) is probably a mixture of *cis*- and *trans*-forms; that prepared by Burton (*loc. cit.*) appears to be the *trans*-modification. H. BURTON.

Constitution of colourless and coloured triphenylmethane derivatives. I. LIFSCHITZ (Ber., 1931, **64**, [*B*], 161—182).—Reply is made to the criticism of Hantzsch and Burawoy (A., 1930, 901) of the work of the author and Girbes (A., 1928, 1001). The properties of colourless and coloured triphenylmethyl derivatives are explained on the basis that in the great majority of compounds Ar_3CX the C·X linking is heteropolar. Whether isomeric, truly homopolar compounds exist is not immediately material. In conformity with Werner's theories, these compounds by intrusion of suitable groups can yield true, complex salts, $[Ar_3C \cdots R]^{\cdot}X'$, the ions of which may be stable or undergo further transformation either by solvatisation or addition of neutral molecules to the anion or by isomerisation of the cation to the quinonoid form 

the actual parent of the halochromic carbonium ions. The homopolar compounds (*e.g.*, triphenylmethane, triphenylcarbinol esters, tetraphenylmethane), provided they do not contain special chromophores, are colourless and yield non-characteristic absorption spectra. The heteropolar derivatives, $Ar_3C \cdots X$ (triphenylmethyl halides, thiocyanates, perchlorates)

and [Ar_3C · · · in so far as absorption is not caused by the group R, are colourless and do not give more characteristic absorption spectra than the homopolar compound, whereas the quinonoid derivatives are coloured and show powerful selective absorption of the short waves of the visible region. A review of the literature shows that these theories are not at variance with recorded data as far as mol. wt. and behaviour in connexion with Beer's law are concerned. The halochromic compounds are structural analogues of Wurster's dyes, the quinhydrones and related compounds, the additive products of ketones, and the triphenylmethane dyes. It is not valid to assume that solutions of a particular triphenylmethylcarbinol invariably contain the same complex or that, for example, solutions of a perchlorate in chloroform or *s*-tetrachloroethane are comparable with that of the carbinol in anhydrous sulphuric acid. The quinonoid nature of the halochromic compounds is illustrated by comparison of their behaviour with that of the fuchsones, dibromofuchsone, and diphenylquinonedi-imine particularly towards *NN'*-diphenyl-*p*-phenylenediamine.

H. Wren.

Naphthalene series. II. Diaryl- and triarylmethane derivatives of dimethyl-α-naphthylamine. B. Gokhle and F. A. Mason (J.C.S., 1931, 118—126).—4 : 4'-*Tetramethyldiamino*-1 : 1'-*dinaphthylcarbinol*, m. p. 184—186° (rapidly heated), is formed in minute yield by oxidation of the corresponding methane base (Morgan, *ibid.*, 1900, **77**, 283) by chloranil in acetic acid, but not by other oxidising agents commonly employed in such cases. Methylal may be used in place of formaldehyde in the preparation of the methane. The *chloride* and *anilide* of 4-dimethylamino-1-naphthoic acid (cf. A., 1889, 150) were prepared; attempts to synthesise 4 : 4'-tetramethyldiamino-1 : 1'-dinaphthyl ketone from the former and dimethyl-α-naphthylamine, or by oxidation of the corresponding methane, failed. Interaction of the acid chloride with dimethylaniline in presence of aluminium chloride in the cold, however, gives p-*dimethylaminophenyl 4-dimethylamino-1-naphthyl ketone*, m. p. 128·5—129°, and this condenses further with dimethylaniline under the influence of phosphoryl chloride, with apparent formation of "Naphthoblau" (Noelting and Philipp, A., 1908, i, 295); reduction of the ketone with sodium amalgam and alcohol gives the corresponding *carbinol*, m. p. 62—63°. *Hexamethyltriaminotrinaphthylmethane*, m. p. 266—267·5°, is obtained by condensation of dimethyl-α-naphthylamine with ethyl orthoformate and aluminium chloride at 70°; the condensation could not be effected by means of zinc chloride. 4-Aminodimethyl-α-naphthylamine (*benzoyl* derivative, m. p. 195°) is obtained by reduction of the corresponding nitroso-compound by zinc dust and acid; it is not converted into a dye of the methylene-blue type by oxidation in presence of dimethyl-α-naphthylamine and sodium thiosulphate.

The absorption maxima of the blue solutions in acetic acid of *pp'*-tetramethyldiaminodiphenylcarbinol and the two carbinols described above agree with those calculated on Moir's theory.

H. A. Piggott.

Heteropolar carbon compounds. XII. New dyes of the aniline-blue series, and perchlorates of important triphenylmethane dyes. W. Dilthey and R. Dinklage (J. pr. Chem., 1931, [ii], **129**, 24—30).—*Tri*-p-*diphenylene*-, decomp. about 225°, 4 : 4' : 4''-*tri*-(p-*phenoxyphenyl*)-, decomp. about 230°, and 4 : 4' : 4''-*tri*-(p-*phenylthiolphenyl*)-*pararosaniline*, decomp. 220—230° (as *hydrochlorides*), are prepared by interaction of *p*-aminodiphenyl, *p*-aminodiphenyl ether, and *p*-aminodiphenyl sulphide, respectively, and pararosaniline base at 120—180° in presence of benzoic acid. It is found that the bathochromic effects of these substituents are little, if at all, greater than that of the phenyl nucleus (aniline-blue), a fact which is considered to support the "carbenium" formula for these dyes (cf. A., 1929, 1067).

The following m. p. of dye perchlorates, obtained by rapidly heating the carefully dried substances, are regarded as comparative (*ibid.*, 1293): malachite-green, m. p. about 200°; brilliant-green, m. p. 183°; rhodamine 3B, m. p. 167°; crystal-violet, m. p. 239—240°; methylene-blue, m. p. 231—232°; Victoria-blue, decomp. 320°; pararosaniline, m. p. 317° (decomp.).

H. A. Piggott.

Synthetic bases closely related to ephedrine. E. Cherbuliez, F. Neumeier, and H. Lozeron (Helv. Chim. Acta, 1931, **14**, 186—200).—Treatment of cinnamyl acetate with iodine and mercuric oxide in moist ether gives an iodohydrin, converted by methylamine in alcohol at 100° into β-*methylamino*-α-*phenylpropane*-αγ-*diol* [dl-ω-*hydroxyephedrine*], b. p. 175—178°/14 mm., m. p. 110° (*hydrochloride*, m. p. 159·5°), also prepared by the same method from cinnamyl alcohol and benzoate. The following β-*methylamino*-γ-*alkoxy*-α-*phenylpropyl alcohols* [*alkoxyephedrines*] are prepared similarly from the appropriate cinnamyl alkyl ethers: γ-*methoxy*-, b. p. 148°/12 mm. (*hydrochloride*, m. p. 151—153°); γ-*ethoxy*-, b. p. 148—150°/10 mm. (hygroscopic hydrochloride); γ-*propoxy*-, b. p. 151—153°/12 mm.; γ-*butoxy*-, b. p. 155—157°/13 mm., and γ-*allyloxy*-, b. p. 155—157°/12 mm. *Cinnamyl ethyl ether*, b. p. 125—126°/11 mm., is prepared from cinnamyl alcohol and ethyl sulphate in presence of alkali; *cinnamyl propyl*, b. p. 131—132°/13 mm., *butyl*, b. p. 138°/13 mm., and *allyl ethers*, b. p. 131—132°/12 mm., are obtained from sodium cinnamoxide and the requisite alkyl iodide in benzene. When cinnamyl alcohol is treated with iodine and mercuric oxide in methyl alcohol and the resultant product heated with alcoholic methylamine, β-*methylamino*-γ-*methoxy*-γ-*phenylpropyl alcohol*, b. p. 143°/11 mm., m. p. 83·5° (hygroscopic hydrochloride; *hydrogen oxalate*, m. p. 143°), is obtained in 31% yield. The yields of the above substances, for which pharmacological data are given, vary from 5 to 40%.

H. Burton.

Nickelic compound of benzamidoxime. J. V. Dubsky and M. Kuraš (Chem. Listy, 1930, **24**, 464).—The salt $(NH_2\cdot CPh{:}NO)_3Ni$ is produced by the oxidation of an ammoniacal solution of a nickelous salt containing benzamidoxime.

R. Truszkowski.

Action of ozone on benzoic acid and phenylated fatty acids. H. Rupe and H. Hirschmann (Helv.

Chim. Acta, 1931, **14**, 49—56).—Treatment of phenylacetic acid with ozone (10—12%) in carbon tetrachloride for 24 hrs. at 0—15°, and subsequent decomposition of the triozonide produced with water, gives small amounts of unchanged acid, formic and malonic acids, and glyoxal. β-Phenylpropionic and benzoic acids afford small amounts of succinic and oxalic acids, respectively, in addition to glyoxal and formic acid. Benzoic acid is the most stable of the three acids to ozone; its triozonide, which is the most unstable, is, however, obtained in the largest amount. A considerable part of the phenylacetic and β-phenylpropionic acids is completely oxidised (cf. A., 1916, i, 409). H. BURTON.

α-Benzyl-δ-methyl-Δ^{γ}-hexenoic acid and the lactone of γ-hydroxy-α-benzyl-δ-methyl-*n*-hexoic acid. G. DARZENS and A. LEVY (Compt. rend., 1930, **191**, 1455—1457).—Dry hydrogen bromide at 130—140° converts γ-methyl-Δ^{β}-buten-α-ol into the corresponding *bromide*, b. p. 120° (95% yield), which reacts with ethyl sodiobenzylmalonate to give *ethyl benzyl-(γ-methyl-Δ^{β}-butenyl)malonate*, b. p. 184—187°/9 mm. This is hydrolysed by alcoholic potassium hydroxide to give the corresponding *malonic acid*, decomp. at 160—170° in a vacuum into a mixture of *α-benzyl-δ-methyl-Δ^{γ}-hexenoic acid*, b. p. 157—160°/7 mm., m. p. 49·5° (80%), and the *lactone*

$CH_2Ph\cdot CH<\begin{matrix}CH_2\cdot CHPr^{\beta}\\ CO-O\end{matrix}$, b. p. 148—150°/6 mm., m. p. 25° (20%). All attempts to cyclise the acid or the lactone to the corresponding tetrahydronaphthalene derivative (A., 1926, 1239) were unsuccessful. J. W. BAKER.

3-Iodo-β-naphthoic acid. H. GOLDSTEIN and E. CORNAMUSAZ (Helv. Chim. Acta, 1931, **14**, 200—203).—*3-Iodo-β-naphthoic acid*, m. p. 214° (*methyl* ester, m. p. 55°; *ethyl* ester, m. p. 78°; *amide*, m. p. 241°; *anilide*, m. p. 205°), is prepared by the usual method from 3-amino-β-naphthoic acid.

H. BURTON.

Catalytic effect of magnesium alcoholates on the reaction of Grignard reagents with carbon dioxide. C. R. KINNEY and M. L. MAYHUE (J. Amer. Chem. Soc., 1931, **53**, 190—199).—The amount of triphenylacetic acid obtained when magnesium triphenylmethyl chloride is treated with carbon dioxide is diminished by the addition of small amounts of triphenylcarbinol; when the amount of carbinol is 15·3 mol.-%, the yield of the acid, under the usual experimental conditions, is zero. Addition of benzaldehyde also causes a marked diminution in the yield. The yields of phenylacetic, benzoic, and valeric acids from magnesium benzyl chloride, phenyl bromide, and butyl bromide are also depressed by the addition of benzyl alcohol, phenol, and butyl alcohol, respectively. In these cases, the addition of more than 6 mol.-% does not cause such a pronounced diminution in the amount of the respective acid as with magnesium triphenylmethyl chloride.

Cleavage of tetraphenylethane could not be accomplished with magnesous iodide at 300° in an atmosphere of carbon dioxide. H. BURTON.

Reaction of phenyl *o*-acetoxybenzoate. H. SZANCER (Pharm. Zentr., 1931, **72**, 68—69).—Phenyl *o*-acetoxybenzoate (Phennin) (0·02 g.), sodium nitrite (0·002 g.), and water (0·5 c.c.), superposed on sulphuric acid (1 c.c.), give a red ring and, after mixing, a green solution which becomes lemon-yellow (distinction from salol; Ekkert, this vol., 88) when made alkaline. H. E. F. NOTTON.

Two modifications of methyl *p*-hydroxybenzoate. L. KOFLER and A. KOFLER (Mikrochem., 1931, **9**, 45—51).—Two modifications of methyl *p*-hydroxybenzoate, m. p. 110° and 126°, respectively, are described. The first is formed by rapid cooling of the sublimate and the second by slow cooling. The former is transformed into the latter on recrystallisation. The two forms are readily distinguishable under the polarising microscope. E. S. HEDGES.

Preparation of 4-nitrophthalimide and derivatives. L. F. LEVY and H. STEPHEN (J.C.S., 1931, 79—82).—A 78% yield of 4-nitrophthalimide, unaccompanied by 3-nitrophthalimide, is obtained by the action of nitric acid on phthalimide dissolved in sulphuric acid containing 10% of free sulphur trioxide. Nitration under similar conditions of *N*-phenylphthalimide gives *p*-nitroaniline and phthalic acid, and of phthalic anhydride 4-nitrophthalic acid only. 4-Aminophthalimide (A., 1908 i, 651) [*acetyl* derivative, m. p. 331° (decomp.)] gives with phthalic anhydride at 180° *4-phthalimidophthalimide*, m. p. 319° (decomp.), and is converted by standard methods into 4-chloro- and 4-hydroxy-phthalimides (Graebe and Rée, J.C.S., 1886, **49**, 524, 529).

H. A. PIGGOTT.

Preparation of ellagic acid. F. ZETZSCHE and M. GRAEF (Helv. Chim. Acta, 1931, **14**, 240—242).—Crystalline sodium sulphite is added to an aqueous extract of Turkish tannin and the mixture boiled for 1 hr., whereby sodium ellagate (4% of original tannin) separates; carbon dioxide is evolved during the process owing to the decomposition of gallic acid. Ellagic acid (*tetra-acetyl* derivative, m. p. 317—319°) is best purified by crystallisation from pyridine and then decomposing the resulting pyridine salt with dilute hydrochloric acid. Pyrogallol is extracted from the mother-liquors after separation of the above sodium salt; subsequent evaporation of the residual solution affords sodium gallate. H. BURTON.

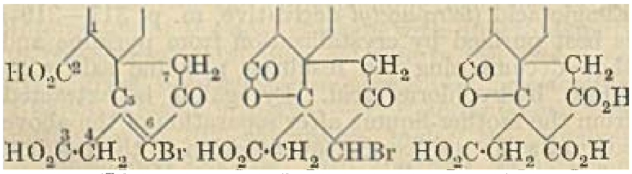
Action of potassium hydroxide on tetracarboxylic esters of the dimalonic series. Preparation of ethylphenylpropionic acids. H. T. LO (Bull. Chem. Soc. Japan, 1930, **5**, 326—333).—Ethyl *o*-xylylenedimalonate yields on hydrolysis with alcoholic potassium hydroxide and subsequent decarboxylation at 150—155°, besides *o*-phenylenedipropionic acid (Perkin, J.C.S., 1888, **53**, 18), *o-ethylphenylpropionic acid*, m. p. 103° (*silver* salt; *ethyl* ester, b. p. 131°/10 mm.), the yield of the latter increasing with the concentration of the alkali hydroxide used for hydrolysis. *o*-Phenylenedipropionic acid does not lose carbon dioxide when distilled in a vacuum or when boiled with alcoholic potassium hydroxide. p-*Ethylphenylpropionic acid*, m. p. 114—115° (*silver* salt; *ethyl* ester, b. p. 141°/15 mm.), is similarly formed when ethyl *p*-xylylenedimalonate (Kipping, *ibid.*, 35) is hydrolysed. Ethyl *m*-xylylenedimalonate

(Kipping, *loc. cit.*) affords under similar conditions almost exclusively *m*-phenylenedipropionic acid.

R. CHILD.

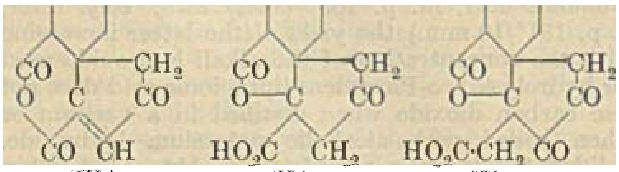
Bile acids. XXXI. Constitution of ψ-choloidanic acid. H. WIELAND, L. ERTEL, and E. DANE. **XXXII. New degradation of deoxybilianic acid.** E. DANE and H. WIELAND (Z. physiol. Chem., 1930, **194**, 107—118, 119—123).—XXXI. When ψ-choloidanic acid, $[\alpha]_D^{20}$ +14·6° in alcohol (tetramethyl ester, m. p. 132°, $[\alpha]_D^{20}$ +8·27° in alcohol) (cf. A., 1923, i, 41), is heated, a mixture of 15% of pyro-ψ-choloidanic acid [the *methyl* ester, m. p. 192°, is identical with the compound formed when dimethyl ψ-choloidanate is heated (cf. *loc. cit.*)], and an acid, $C_{22}H_{32}O_5$, m. p. 199°, which is not affected by sodium hydroxide solution or reducing agents, is produced. When pyro-ψ-choloidanic acid is treated with *N*-sodium hydroxide, three equivalents are consumed, and a tricarboxylic *acid*, $C_{23}H_{32}O_7$, m. p. 212° (*dimethyl* ester), is produced; an anhydride ring is opened. The last-named acid is stable to permanganate, but is oxidised by chromic and acetic acids to a small amount of an *acid*, $C_{23}H_{32}O_{10}$, m. p. 180—182° (decomp.). It is concluded from these results that ψ-choloidanic acid is a lactonic tetracarboxylic acid; one of the carboxyl groups is in the side-chain, and the loss of carbon dioxide is accompanied by the formation of a cyclic ketone, since the pyro-acid reacts with bromine.

Bromination of deoxybilianic acid in acetic acid containing a little iodine at 75° affords a *dibromo*-derivative, m. p. 215° (decomp.), converted by methyl-alcoholic potassium hydroxide into *bromodeoxybilienic acid*, $C_{24}H_{33}O_7Br$, m. p. 218° (decomp.) (*trimethyl* ester, m. p. 93°), represented by the partial structure I. This is reduced by zinc and hydrochloric acid to deoxybilianic acid and oxidised by nitric acid (*d* 1·4) to ψ-choloidanic acid (as III), probably by way of the lactone (II). The formation



(I.) (II.) (III.)

of ψ-choloidanic during the oxidation of deoxybilianic acid (cf. *loc. cit.*) is explained by the formation of a hydroxyl group on C_5, subsequent lactonisation, and fission of the ring between C_6 and C_7. Pyro-ψ-choloidanic acid is formulated as IV: the production of only a dimethyl ester from IV is explained by the spontaneous lactonisation of the corresponding free acid to V.



(IV.) (V.) (VI.)

XXXII. Oxidation of bromodeoxybilienic acid with alkaline potassium permanganate at 30° gives 6-*keto-5-hydroxydeoxybilianic acid*, m. p. 223—225° (*oxime*, m. p. 200°); the following changes occur:

>C:CBr· ⟶ >C(OH)·CBr(OH)· ⟶ >C(OH)·CO·.

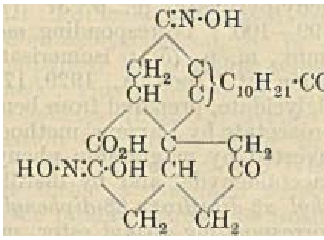
Esterification of this with diazomethane affords a *trimethyl* ester, m. p. 154°, whilst with methyl-alcoholic hydrogen chloride, a *trimethyl* ester, m. p. 178°, results. The ketohydroxy-acid is converted by hydrochloric and acetic acids into the *diketo-lactonic acid* (VI), m. p. 258—260° (slight decomp.), also formed as the main product of the attempted oxidation of the hydroxy-acid with nitric acid (*d* 1·4), reduced by hydrogen in presence of platinum oxide and acetic acid to 6-*ketodeoxybilianic acid*, m. p. 255° after previous sintering (*trimethyl* ester, m. p. 108°). Oxidation of the hydroxy-acid with nitric acid (*d* 1·51) yields a small amount of a *pentacarboxylic acid*, $C_{24}H_{36}O_{11}$, m. p. 180° (decomp.).

H. BURTON.

Bile acids. XXXIII. Bromination of dehydrocholic and dehydrodeoxycholic acids. H. WIELAND and T. NOGUCHI (Z. physiol. Chem., 1931, **194**, 248—259).—Dehydrocholic acid and bromine (1 mol.) in acetic acid at about 15° give a bromo-derivative, m. p. 182—183° (decomp.) [*ethyl* ester, m. p. 192° (decomp.), prepared by similar bromination of ethyl dehydrocholate], converted by cold 0·1*N*-potassium hydroxide into a *hydroxydehydrocholic acid* (+H_2O), m. p. 187° (decomp.). With 2 mols. of bromine at 15—20°, α-*dibromodehydrocholic acid* (+Ac·OH), m. p. 200° (decomp.), (+EtOH) decomp. 206°, (+0·5Et_2O) decomp. 174°, results. This is converted by 0·5*N*-potassium hydroxide into a *dihydroxydehydrocholic acid* (+Et_2O), m. p. 198° (decomp.), and an *isomeride* (?), m. p. 212—213° (decomp.), whilst treatment with barium hydroxide solution affords a *hydroxytriketocholenic acid* (+0·5Ac·OH), m. p. 257° (decomp.). When dehydrocholic acid is treated with an excess of bromine in acetic acid at 50—65°, β-*dibromodehydrocholic acid* (+Ac·OH), m. p. 265—266° (decomp.), is obtained. This results from the action of the evolved hydrogen bromide on higher bromo-derivatives. Dehydrocholic acid and 5 mols. of bromine in acetic acid below 30° give a *tetrabromodehydrocholic acid*, m. p. 213° with blackening, and an impure *tribromo*-derivative, m. p. 202—203° (decomp.) (recrystallisation of this from acetic acid gives a product approximating to a tetrabromo-derivative, but the m. p. is unaltered); with 8 mols. of bromine at the ordinary temperature, an impure *pentabromodehydrocholic acid*, m. p. 192° with blackening, results. Bromination of dehydrodeoxycholic acid (improved method of preparation given) with 3 mols. of bromine at 50° furnishes a mixture of two *tribromo*-derivatives, (*a*), (+0·5Ac·OH), m. p. 212—213° (decomp.), m. p. (solvent-free) 184° (decomp.), and (*b*), (+0·5Ac·OH), m. p. 215° (also formed when dehydrodeoxycholic acid is treated with 6 mols. of bromine in the cold). Not more than three atoms of bromine could be introduced into dehydrodeoxycholic acid. H. BURTON.

Bile acids. XXIX. M. SCHENCK (Z. physiol. Chem., 1931, **194**, 33—42; cf. Schenck and Kirchhof, A., 1930, 1435).—Nitric acid (*d* 1·4) converts the oximes of *iso*deoxybilianic and cilianic acids, $C_{24}H_{37}O_7N$ and $C_{24}H_{35}O_{10}N$, respectively, into the

corresponding keto-acids. Although there appears to be transitory formation of a nitroso-compound by the action of nitric acid on *iso*bilianic acid oximelactam, the product isolated is the keto-lactamtricarboxylic acid, $C_{24}H_{35}O_8N$ (A., 1929, 1070). Under the same conditions, *iso*bilianic acid dioxime affords in small yield a nitroso-compound, $C_{24}H_{33}O_9N$, decomp. 220—222°, probably identical with that obtained from bilianic acid dioxime (A., 1928, 1007).



(I.)

Neither the nitrohydroxamic acid, $C_{24}H_{34}O_9N_2$ (A., 1929, 558), nor its oximino-derivative (I) undergoes the Beckmann–Wallach change when treated with sulphuric acid. A. COHEN.

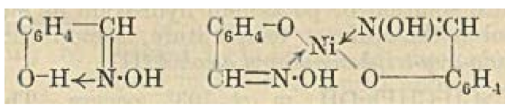
Production of benzaldehyde from benzyl chloride. P. SCHORIGIN, I. KIZBER, and E. SMOLIANINOVA (J. Appl. Chem., Russia, 1930, 3, 721—726).—When boiled with aqueous calcium nitrate, benzyl chloride affords benzaldehyde (60—65%) and benzoic acid (10%). The presence of aluminium or copper retards oxidation by the nitric acid which is liberated. Free nitric acid may be employed. CHEMICAL ABSTRACTS.

Formation of thioamides from acylated aldehydecyanohydrins. VII. J. F. OLIN and T. B. JOHNSON (Rec. trav. chim., 1931, **50**, 72—76).—Acyl derivatives of aliphatic aldehydecyanohydrins are best prepared by shaking together molecular proportions of the aldehyde, the acyl chloride, and powdered sodium or potassium cyanide with crushed ice until the odour of the acyl chloride disappears. Conversion of these derivatives into the corresponding thioamides is best effected by saturating a solution of the acylated cyanohydrin and triethanolamine in alcoholic solution with hydrogen sulphide. Unlike pyridine, the triethanolamine does not cause dissociation of the thioamide into hydrogen sulphide and the parent nitrile. Thus from the appropriate acylated cyanohydrin are prepared (80—90% yield): *α-benzoyloxy-*, $CHPh(OBz)\cdot CS\cdot NH_2$, m. p. 139°, and *α-acetoxy-*, m. p. 104°, *-phenylacetothioamide*; *benzoyloxyacetothioamide*, m. p. 103°, *α-benzoyloxypropionthioamide*, m. p. 104°, and *α benzoyloxy-*n*-butyrthioamide*, m. p. 106°. All these derivatives are destroyed by hydrolysis with mineral acids or alkalis. J. W. BAKER.

Isomerisation of hydroxyaldehydes. IV. Transformation of α-bromo-β-phenylpropaldehyde and α-hydroxy-β-phenylpropaldehyde. S. DANILOV and E. VENUS-DANILOVA (J. Russ. Phys. Chem. Soc., 1930, **62**, 1697—1711).—α-Bromo-β-phenylpropaldehyde, obtained by direct bromination of hydrocinnamaldehyde, gives a stable *monohydrate*, m. p. 87·5—88°, and a *semicarbazone*, m. p. 136·5°. When heated with an aqueous suspension of barium carbonate, the bromoaldehyde is converted into α-hydroxy-β-phenylpropaldehyde, m. p. 51·5—52°, b. p. 120—121°/4 mm. (oxime, m. p. 123°; semicarbazone, m. p. 136·5°; osazone, m. p. 137°; benzoyl derivative, m. p. 70°), together with some hydrocinnamic acid. If silver oxide is used instead of barium carbonate, α-hydroxy-β-phenylpropionic acid, m. p. 98°, is also formed. On oxidation, the aldehyde yielded a variety of products, among them phenylacetaldehyde, b. p. 88—89°/12 mm. (semicarbazone, m. p. 155°), and α-hydroxy-β-phenylpropionic acid. When heated in alcoholic sulphuric acid solution in a sealed tube, the aldehyde isomerises with the formation of acetylphenylcarbinol, b. p. 130—132°/13 mm. (semicarbazone, m. p. 194°), and the corresponding α-diketone, benzoylacetyl, b. p. 113—115°/13 mm.; dioxime, m. p. 238—239°. The carbinol, on treatment by Grignard's method with magnesium phenyl bromide, yielded βγ-dihydroxy-βγ-diphenylpropane, m. p. 103—104°, which gave acetophenone on oxidation. M. ZVEGINTZOV.

Acetylation of *o*-hydroxy-aldehydes. T. MALKIN and M. NIERENSTEIN (J. Amer. Chem. Soc., 1931, **53**, 239—242).—Treatment of salicylaldehyde, β-resorcylaldehyde, and phloroglucinaldehyde with acetic anhydride in presence of ether and potassium carbonate gives the corresponding *O*-acetyl, *diacetyl*, m. p. 69°, and *triacetyl*, m. p. 101°, derivatives. In absence of ether, formation of benzylidene acetate occurs. The triacetylphloroglucinaldehyde of Pratt and Robinson (A., 1925, i, 826; cf. Robertson and Robinson, A., 1927, 974) is 2 : 4 : 6-triacetoxybenzylidene acetate (Herzig and Wenzel, A., 1904, i, 251). H. BURTON.

Co-ordination compounds of oximes. II. Nickel and cobalt compounds of *o*-hydroxybenzaldoxime. O. L. BRADY (J.C.S., 1931, 105—107).—*Nickel* and *cobalt* complexes of salicylaldoxime are described. To account for the attack of its oximino- and not its phenolic hydroxyl group on acetylation, the formula (I) is suggested for the oxime, which has

(I.) 

the physical properties of a co-ordination compound. The corresponding structure (II) is advanced for the nickel (and cobalt) complexes. H. A. PIGGOTT.

2-Hydroxy-4-methoxy- and 4-hydroxy-2-methoxy-benzaldehydes. T. E. DE KIEWIET and H. STEPHEN (J.C.S., 1931, 84—85; cf. A., 1898, i, 581; 1922, i, 555).—*m*-Methoxyphenol is condensed with hydrogen cyanide and hydrogen chloride in dry ether in the cold, the resulting aldimide hydrochlorides (after 24 hrs.) hydrolysed by a large excess of water, and the aldehydes separated by distillation in steam in which 2-hydroxy-4-methoxybenzaldehyde alone is volatile. The *phenylhydrazone*, m. p. 158°, p-*nitrophenylhydrazone*, m. p. 255° (decomp.), and *semioxamazone*, m. p. 242°, of 4-hydroxy-2-methoxybenzaldehyde, and the p-*nitrophenylhydrazone*, m. p. 226·5°, *semioxamazone*, m. p. 247°, and *semicarbazone*, m. p. 230°, of 2-hydroxy-4-methoxybenzalbehyde are described. H. A. PIGGOTT.

Catalytic production of acetophenone. I. G. Lakomkin (J. Appl. Chem., Russia, 1930, 3, 555—572).—Acetophenone is obtained by interaction of acetic and benzoic acids in presence of thorium dioxide or preferably manganous oxide. The quantity of catalyst used affects the yield only if the acid vapours are not preheated. The yield is maximal at 600°; preheating of the reacting vapours is recommended.

Chemical Abstracts.

Action of organic magnesium compounds on αβ-oxido-ketones and -esters. E. P. Kohler, N. K. Richtmyer, and W. F. Hester (J. Amer. Chem. Soc., 1931, 53, 205—221).—α-Benzoyl-β-phenylethylene oxide, prepared by a modification of Weitz and Scheffer's method (A., 1921, i, 868), is converted by an excess of magnesium phenyl bromide at the ordinary temperature into triphenylcarbinol (phenyldiethylcarbinol is produced similarly using magnesium ethyl bromide) and resinous material. The reaction involves the intermediate formation of benzophenone, since triphenylcarbinol is also obtained from magnesium phenyl bromide and α-benzoyl-β-anisylethylene oxide, whilst magnesium mesityl bromide and α-acetyl-β-phenylethylene oxide give acetylmesitylene. When α-benzoyl-β-phenylethylene oxide is treated with 1 mol. of magnesium phenyl bromide at −10°, and the mixture decomposed with ice-cold acid, *βγ-oxido-αγγ-triphenylpropyl alcohol* (I), $\begin{matrix}CHPh\\O\end{matrix}\!\!>CH\cdot CPh_2\cdot OH$, m. p. 129—130°, is produced. This is unaffected by magnesium phenyl bromide at −10°, but is converted at the ordinary temperature into triphenylcarbinol. Treatment of I with methyl alcohol containing a little hydrochloric acid gives *αβ-dihydroxy-γ-methoxy-αγγ-triphenylpropane*, m. p. 154—155° (oxidised by chromic and acetic acids to methyl benzoate and benzophenone), also prepared by the action of magnesium phenyl bromide on phenyl α-hydroxy-β-methoxy-β-phenylethyl ketone (*dimethylacetal*, m. p. 122°, obtained from phenyl αβ-dibromo-β-phenylethyl ketone and methyl-alcoholic sodium methoxide). When I is treated with a dilute solution of potassium hydroxide in methyl alcohol at the ordinary temperature, isomerisation to *βγ-oxido-αγγ-triphenylpropyl alcohol* (II), $\begin{matrix}CHPh\\O\end{matrix}\!\!>CH\cdot CHPh\cdot OH$, m. p. 103°, occurs. This is oxidised by chromic and acetic acids to *α-benzoyl-ββ-diphenylethylene oxide*, m. p. 124—125°, and with magnesium phenyl bromide yields diphenylacetaldehyde and benzhydrol: (II)+Ph·MgBr⟶CPh_2:CH·OMgBr +Ph·CHO; Ph·CHO+Ph·MgBr⟶$CHPh_2$·OMgBr. Treatment of II with magnesium methyl iodide gives diphenylacetaldehyde, benzaldehyde, and a small amount of probably *diphenylacetylphenylcarbinol*, m. p. 128°. When II is exposed to air, autoxidation occurs and the main product formed is the *peroxide*, $\begin{matrix}CHPh\\O\end{matrix}\!\!>CH\cdot O\cdot O\cdot CHPh\cdot OH$, which decomposes at about 160° into benzaldehyde, formic acid, and benzophenone, and reacts with magnesium methyl iodide, forming *αα-diphenylpropylene glycol*, m. p. 94—95°, also prepared from ethyl lactate and an excess of magnesium phenyl bromide, and α-phenylethyl alcohol. Dibromodibenzoylmethane reacts with magnesium phenyl bromide, forming *phenyl α-bromo-β-hydroxy-ββ-diphenylethyl ketone*, m. p. about 180° (decomp.), converted by methyl-alcoholic sodium methoxide into α-benzoyl-ββ-diphenylethylene oxide. This reacts with magnesium phenyl bromide and ethyl iodide, yielding diphenylacetaldehyde in each case: $\begin{matrix}CPh_2\\CHBz\end{matrix}\!\!>O$+R·MgX⟶$CPh_2$:CH·OMgX+Bz·R.

The ethyl diphenylglycidate of Pointet (A., 1909, i, 234) and of Bardon and Ramart (A., 1926, 950) is ethyl ββ-diphenylpyruvate, m. p. 37° (*phenylhydrazone*, m. p. 99—100°; corresponding *methyl* ester, b. p. 175°/5 mm., m. p. 75°); isomerisation occurs during distillation (cf. Troell, A., 1929, 171). Crude ethyl diphenylglycidate, prepared from benzophenone and ethyl chloroacetate by Darzens' method (A., 1905, i, 116), is converted by magnesium phenyl bromide into diphenylacetaldehyde, and by distillation with steam into *ethyl αβ-dihydroxy-ββ-diphenylpropionate*, m. p. 130° (corresponding *methyl* ester, m. p. 130—131°). ββ-Diphenylpyruvic acid phenylhydrazone has m. p. (block) 245° (decomp.; lit. 189°). Triphenylcarbinol is also obtained when ethyl ββ-dimethylglycidate and α-phenyl-β-nitrophenylglycidate are treated with magnesium phenyl bromide. There is no evidence that oxido-compounds form 1 : 4-additive products with Grignard reagents (cf. Bardon and Ramart, *loc. cit.*)

The initial product of the reaction between ethyl ββ-diphenylpyruvate and magnesium phenyl bromide is *ethyl α-hydroxy-αββ-triphenylpropionate*, m. p. 118—120°. The further reaction products are *phenyl α-hydroxy-αββ-triphenylethyl ketone*, m. p. 123°, and *αβ-dihydroxy-ααβγγ-pentaphenylpropane*, m. p. about 190° (decomp.). When the last-named compound is heated in acetic acid a mixture of benzhydrol and phenyl benzhydryl ketone is obtained; in absence of the acid small amounts of benzophenone and αββ-triphenylethyl alcohol are produced also.

H. Burton.

Benzoin condensation. Influence of the nature of radicals on the formation of mixed benzoins. M. Tiffeneau and (Mlle.) J. Levy (Compt. rend., 1931, 192, 287—290).—By the ordinary benzoin condensation benzaldehyde with *o*-methoxybenzaldehyde, anisaldehyde, piperonal, and furfuraldehyde, and anisaldehyde with *o*-methoxybenzaldehyde afford (>50% yield) only one benzoin, namely, benzoyl-*o*-methoxyphenyl- (*semicarbazone*, m. p. 178—179°); p-*methoxybenzoylphenyl-*, m. p. 105·5—106·5°; 3 : 4-*methylenedioxybenzoylphenyl-*, m. p. 120° (*semicarbazone*, m. p. 180—182°); *furfuroylphenyl-*, m. p. 135—136° (*semicarbazone*, m. p. 192—193°); and p-*methoxybenzoyl-*o-*methoxyphenyl-*, m. p. 101—102° (*semicarbazone*, m. p. 204°), *-carbinol*, respectively. Benzaldehyde and *m*-methoxybenzaldehyde afford m-*methoxybenzoylphenyl-* and *benzoyl-*m-*methoxyphenylcarbinol*, whilst anisaldehyde and piperonal give p-*anisoyl-3 : 4-methylenedioxyphenyl-* and *3 : 4-methylenedioxybenzoyl-*p-*anisyl-*, m. p. 98—99° (*semicarbazone*, m. p. 191°), *-carbinol*. Mixtures of isomeric benzoins are thus obtained when the affinities of the two aryl groups are approximately equal.

J. W. Baker.

Reactivity of substituents in the five-carbon ring. V. Jacobi (J. pr. Chem., 1931, [ii], 129,

55—96).—Interaction of equimolecular quantities of 1 : 3-diketohydrindene and terephthalaldehyde at 110—120° gives 1 : 3-*diketo*-2-p-*aldehydobenzylidenehydrindene*, m. p. 173°; excess of the former gives 2 : 2′-*terephthalylidenebis*-1 : 3-*diketohydrindene*, m. p. 293°. In each case a yellow substance of high m. p. is also formed. The action of magnesium methyl iodide on 1 : 3-diketohydrindene leads to enolisation, and only by use of a large excess of the Grignard reagent is 1 : 3-*dihydroxy*-3-*methylindene* (or 3-*hydroxy*-1-*keto*-3-*methylhydrindene*), b. p. 126°/10 mm., again accompanied by a yellow substance of high m. p., formed. This is dehydrated when heated to 3-*keto*-1-*methylindene* (no m. p. given).

The isolation of 5-bromoindene in a crystalline form, m. p. 36°, is described. With magnesium in ether it forms a Grignard reagent only with difficulty; the product cannot be isolated in a state of purity, but its formation is proved by regeneration of indene on decomposition with water or dilute acids.

1 : 2 : 5-*Tribromohydrindene* is obtained as an unstable oil by addition of bromine to 5-bromoindene in light petroleum. With 10% alcohol it gives 1 : 5-*dibromo*-2-*hydroxyhydrindene*, m. p. 80·5—81·5°. Interaction of indene dibromide with absolute alcohol gives 1-*bromo*-2-*ethoxyhydrindene*, and with methyl alcohol 1-*bromo*-2-*methoxyhydrindene*. Distillation of the former under reduced pressure gives 1-*bromoindene*, b. p. 135·5—136°, oxidised by dilute nitric acid to phthalic acid; its constitution is proved by its conversion by magnesium, followed by carbon dioxide, in dry ether into *indene*-1-*carboxylic acid*, m. p. about 70°, identified by difference. Bromination of 1-bromoindene resulted in a small amount of substitution only, no direct addition being observed.

Distillation of indene dibromide at atmospheric pressure gives 3-*bromoindene*, b. p. 110—120°/11 mm., oxidation of which with dilute nitric acid gives phthalic acid. Action of magnesium in ether precipitates the magnesium indyl bromide, converted by carbon dioxide into *indene*-3-*carboxylic acid*, m. p. about 160°, 3 : 3′-*di-indyl ketone*, m. p. 235°, and indene. Unlike the 1-bromo-compound, 3-bromoindene readily adds bromine to give 1 : 2 : 3-*tribromohydrindene*, converted by 10% alcohol into 1 : 3-*dibromo*-2-*hydroxyhydrindene*, m. p. 90°.

Bromination of indene in a hot, dilute aqueous suspension gives a *tribromoindene*, m. p. 133·5—134°, which, from its oxidation by dilute nitric acid to a *dibromophthalic acid*, m. p. 135°, must be dibrominated in the benzene nucleus. H. A. PIGGOTT.

Polymerisation and pyrogenic decomposition of phenylacetic anhydride. I. *cyclo*Butane-α-diones. P. KALNIN (Latvij. Univ. Raksti, 1930, **1**, 468).—A preliminary note. During the fractionation of phenylacetic anhydride in a vacuum considerable decomposition occurs, with the production of phenylacetic acid and a residue of a red substance which gives the reactions of an α-diketone. The red substance is considered to be diphenyl*cyclo*butane-α-dione, formed by unsymmetrical polymerisation of the enolic form of the anhydride and elimination of 2 mols. of phenylacetic acid. F. L. USHER.

B B

Sulphonic acid derivatives of naphthaquinone chloroimines and di-imines. W. SWIENTOSŁAWSKI, A. PILTZ, and F. KRACZKIEWICZ (Rocz. Chem., 1931, **11**, 40—48).—*Potassium* β-*naphthaquinone*-1-*chloroimine*-4-*sulphonate*, the corresponding 1-*bromo*-derivative, *potassium* β-*naphthaquinone*-2-*chloroimine*-4-*sulphonate*, and α-*naphthaquinonedichloroimine*-6-*sulphonate* are prepared by halogenating the appropriate aminonaphthol- or naphthylenediamine-sulphonic acid and salting out the product with potassium chloride as formed at a low temperature. R. TRUSZKOWSKI.

New compound of benzaldehyde and anthrahydroquinone. H. A. BEATTY (J. Amer. Chem. Soc., 1931, **53**, 378—380).—A solution of anthrahydroquinone in benzaldehyde containing a trace of hydrochloric acid gradually deposits (in absence of oxygen) a *compound*, $C_{28}H_{20}O_3$, m. p. 211—212° (corr.), probably formed by elimination of 1 mol. of water between 2 mols. of benzaldehyde and 1 mol. of oxanthrone (the tautomeric form of anthrahydroquinone). The compound is conveniently obtained when a mixture of anthraquinone, benzoic acid, alcohol, and benzaldehyde is exposed to sunlight in absence of oxygen, whereby photo-reduction of the quinone occurs; the volatile products are distilled with steam, and the residue is treated successively with alcohol and sodium hyposulphite to remove resinous material and unchanged anthraquinone, respectively. The compound is hydrolysed by alcoholic hydrochloric acid to benzaldehyde and anthrahydroquinone. H. BURTON.

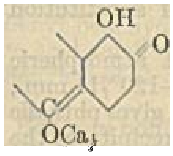
Reduction products of the hydroxyanthraquinones. XII. G. F. ATTREE and A. G. PERKIN (J.C.S., 1931, 144—173; cf. A., 1930, 607).—The hydroxy- and methoxy-9-anthrones (-anthranols) described below are prepared by reduction of the corresponding hydroxy- or methoxy-anthraquinones with stannous chloride and hydrochloric acid (cf. Goodall and Perkin, A., 1924, i, 527).

Demethylation of a methoxyanthraquinone may generally be avoided by addition of the reducing agent to a solution in hot acetic acid and allowing to cool; partial demethylation may be effected during reduction by boiling for a limited time. Prolonged boiling may lead to the reduction of both carbonyl groups. In the majority of cases the anthrone is readily oxidised by ferric chloride in alcohol and acetic acid to the corresponding dianthrone, which is formed in varying yield, often accompanied by the anthraquinone; it is suggested that the latter is formed by reaction in the anthranol form. In comparatively few cases could further oxidation to the corresponding dianthraquinones, helianthrones, and naphthadianthrones be effected (cf. A., 1924, i, 300; 1925, i, 1160). The following are described: 3-*methoxy*-9-*anthrone*, m. p. 108—109° (by reduction of 2-methoxyanthraquinone with copper and sulphuric acid at 140°: purified through the *anthranyl acetate*, m. p. 152—154°); 3 : 3′-*dimethoxy*-9 : 9′-*dianthrone*, m. p. 215—217°; the *dianthranyl diacetate*, m. p. 228—230°, is oxidised by iodine in pyridine to 3 : 3′-dimethoxydianthraquinone (A., 1925, i, 1160), further oxidised by insol-

ation in pyridine to 2 : 2′-dimethoxynaphthadianthrone (*loc. cit.*); 3 : 6-dihydroxyanthrone, m. p. 183—184° (A., 1882, 975) 3 : 3′ : 6 : 6′-*tetrahydroxydianthrone*, decomp. indef. 270—300° (*hexa-acetyl* derivative, m. p. 280—282°); 3 : 6-*dimethoxyanthrone*, m. p. 158—160° (*acetyl* derivative, m. p. 180—181°) [by reduction of the *dimethyl ether*, m. p. 215—217°, of *iso*anthraflavic acid (methyl sulphate and alkali) by copper and sulphuric acid]; 3 : 3′ : 6 : 6′-*tetramethoxydianthrone*, m. p. 242—243° (*diacetyl* derivative, m. p. 255—256°); 6-*hydroxy*-3-*methoxyanthrone*, m. p. 234—236° (*diacetyl* derivative, m. p. 197—199°); 6 : 6′-*dihydroxy*-3 : 3′-*dimethoxydianthrone*, m. p. 292—295° (*tetra-acetyl* derivative, m. p. 229—231°); 3 : 7-dihydroxyanthrone; 3 : 3′ : 7 : 7′-*tetrahydroxydianthrone*, m. p. 315—318° (*hexa-acetyl* derivative, darkens 290°); 2 : 3-dihydroxyanthrone (A., 1903, i, 840); 2 : 2′ : 3 : 3′-tetrahydroxydianthrone [*tetra-acetoxy*-compound, m. p. 274—277° (acetic anhydride); 2 : 2′ : 3 : 3′-*tetra-acetoxy*-9 : 9′-*dianthranyl diacetate*, m. p. 293—295° (acetic anhydride and pyridine)]; 2 : 3-*dimethoxyanthrone*, m. p. 143—146° (*acetyl* compound, m. p. 169—171°); 2 : 2′ : 3 : 3′-*tetramethoxydianthrone*, m. p. 243—245° (*diacetyl* derivative, m. p. 194—196°), readily oxidised by alkaline persulphate to 2 : 2′ : 3 : 3′-*tetramethoxydianthraquinone*, m. p. 290—291°, which is converted by insolation in a mixture of benzene and alcohol into 2 : 2′ : 3 : 3′-*tetramethoxy-helianthrone*, m. p. 287—288°, and -*naphthadianthrone*, the last being the sole product if the action of light is prolonged; 4 : 4′-*dihydroxydianthrone*, m. p. 256—258° (*tetra-acetyl* derivative, m. p. 265—267°); 1 : 5-dihydroxyanthrone (cf. A., 1902, i, 773); 1 : 5-*dimethoxyanthrone*, m. p. 181—182° (*acetyl* compound, m. p. 169—171°); 1 : 1′ : 5 : 5′-*tetramethoxydianthrone*, m. p. 305—307°: 1-*hydroxy*-5-*methoxyanthrone*, m. p. 131—133° (*diacetyl* derivative, m. p. 161—163°); 1 : 1′-*dihydroxy*-5 : 5′-*dimethoxydianthrone*, m. p. 287—289° (*tetra-acetyl* derivative, m. p. 250—252°); 1 : 8-*dimethoxyanthrone*, m. p. 196—197° (by reduction of chrysazin dimethyl ether by zinc and ammonia); 1 : 1′ : 8 : 8′-*tetramethoxydianthrone*, m. p. above 340°; 1-*hydroxy*-8-*methoxyanthrone*, m. p. 183—185° (*diacetyl* derivative, m. p. 164—165°); 1 : 1′-*dihydroxy*-8 : 8′-*dimethoxydianthrone*, m. p. above 330° (*acetyl* derivative, m. p. 284—287); 3 : 4-dimethoxyanthrone, m. p. 162° [*acetyl* derivative, m. p. 146—148°; *methyl ether*, m. p. 116—118° (by methylation of 3 : 4-dihydroxyanthrone with methyl sulphate and alkali; cf. Graebe and Thode, A., 1906, i, 863; preparation of the dimethoxyanthrone by these authors' method is improved by use of pyridine as solvent)].

1-Hydroxyanthrone is not affected by ferric chloride at 100°. 1-*Methoxyanthrone*, m. p. 129—131°, prepared by use of copper and sulphuric acid, differs in m. p. from the "1-methoxyanthrone" of Graebe and Bernhard (A., 1906, i, 865), which is probably its methyl ether; it is not acetylated by acetic anhydride and pyridine, a property that appears characteristic of α-hydroxy- and α-methoxy-anthrones.

1 : 1′-*Dimethoxydianthrone* (*diacetyl* derivative, m. p. 290—291°) is best prepared by air oxidation in alkaline methyl alcohol; if much alcohol is employed 1 : 1′-*dimethoxydianthraquinone*, m. p. 315—316°, is formed, also produced by oxidation of the dianthrone with iodine in pyridine at 60°; it is oxidised by insolation in acetone to 4 : 4′-*dimethoxynaphthadianthrone* and -*helianthrone*, hydrolysed by 40% hydrobromic acid at 180° to 4 : 4′-*dihydroxynaphthadianthrone*, scarlet, and -*helianthrone*, orange-red, all melting above 360°. An improved method of preparation of 1-hydroxy-2-methoxyanthrone (Miller and Perkin, A., 1926, 174) is described. It is oxidised to 1 : 1′-*dihydroxy*-2 : 2′-*dimethoxydianthrone* (*tetra-acetyl* derivative, m. p. 242—245°) by the methods already described, and also by boiling its solution in nitrobenzene, or by the action of alkali hypoiodite in alcohol, or diazomethane in acetone. 4 : 4′-*Dihydroxy*-3 : 3′-*dimethoxyhelianthrone*, m. p. above 330°, is formed from the anthrone by the action of iodine or arsenic acid in pyridine, or by continued boiling of its nitrobenzene solution, and to some extent by attempted acetylation of the dianthrone at the b. p.; it cannot be acetylated or reduced, but is demethylated by hydrochloric and acetic acids at 180° to 3 : 3′ : 4 : 4′-*tetrahydroxyhelianthrone*, m. p. above 360° (3 : -*diacetoxy*-compound, m. p. about 325°), which possesses poor affinity as a mordant dye, but is sulphonated by 20% fuming sulphuric acid at 100° to a product (isolated as crude sodium salt) with marked affinity for wool, which it dyes in deep reddish-brown to slate-blue shades. As causes of the low tinctorial power of this hydroxyhelianthrone the marked chelation of the α-hydroxyl groups, which prevents the formation of a tetra-acetyl derivative. and the absence of an hydroxyl group in the *p*-position to the carbonyl group, are suggested, tinctorial power being regarded as due to a quinonoid type of metallic complex (annexed formula). Oxidation of 1 : 2-dihydroxyanthrone with ferric chloride or the minimum quantity of nitrobenzene gives 1 : 1′ : 2 : 2′-*tetrahydroxydianthrone* [*tetra-acetyl* derivative, m. p. 245—247° (acetic anhydride and pyridine)]; excess of the latter, or iodine in pyridine, gives 3 : 3′ : 4 : 4′-tetrahydroxyhelianthrone, converted by sulphuric acid at 160° into a substance isolated in small amount as *acetyl* derivative (probably 4 : 4′-dihydroxy-3 : 3′-diacetoxynaphthadianthrone).



Attempted reduction of 1 : 3-dimethoxyanthraquinone with copper and sulphuric acid fails, but zinc and ammonia in water or pyridine gives (probably) 10-*hydroxy*-1 : 3-*dimethoxyanthranol*, m. p. 156—158°, and stannous chloride gives (after acetylation) 1 : 3-*diacetoxyanthranyl acetate*, m. p. 154—155°, identified by hydrolysis to 1 : 3-dihydroxyanthrone, also obtained by reduction of purpuroxanthin with stannous chloride. A stannous chloride reduction of anthrarufin dimethyl ether at 65° for 3 hrs. gives 10-*hydroxy*-1 : 5-*dimethoxyanthrone*, m. p. 153—155°. Oxidation of 6-acetoxy-3-methoxyanthranyl acetate (above) with chromic and acetic acids gives the *acetyl* derivative, m. p. 194—196°, of iso*anthraflavic acid monomethyl ether*, m. p. 283—285°; the last-named is also obtained by oxidation of the anthrone, and in minute amount by methylation of *iso*anthraflavic acid. 2 : 2′ : 3 : 3′-*Tetrahydroxy-helianthrone* (*tetra-

acetyl derivative, m. p. 295—297°) and *-naphtha-dianthrone* (*tetra-acetyl* derivative, m. p. above 360°) are obtained by demethylation of the corresponding methoxy-derivatives with hydrochloric and acetic acids at 190° and 215°, respectively. The former readily dyes mordanted calico and wool, for which the latter has little affinity; its acetyl derivative is oxidised by chromic acid to 2 : 2′ : 3 : 3′-*tetra-acetoxy-1 : 1′-dianthraquinonyl*, m. p. 200° with subsequent re-solidification and re-melting at 268—270° (*tetra-hydroxy*-compound, m. p. above 360°).

H. A. PIGGOTT.

Reaction of aromatic 1 : 4-diketonemonoximes occurring in place of the Beckmann transformation. I. R. SCHOLL, H. SEMP, and E. STIX [with, in part, W. MESSE] (Ber., 1931, 64, [B], 71—77).—The poor yield of anthraquinone-1-carboxyxylidide obtained by the action of alcoholic hydrogen chloride on *m*-xylyl 1-anthraquinonyl ketoxime (cf. A., 1927, 885) has led to examination of the behaviour of glacial acetic and sulphuric acids, which leads to the formation in good yield of an *anhydride*, $C_{23}H_{15}O_2N$, m. p. 240°. The theoretically possible products of the Beckmann transformation of the oxime, anthraquinone-1-carboxy-*m*-xylidide and 1-m-*xylamido-anthraquinone*, m. p. 261—262°, are converted by the reagents into anthraquinone-1-carboxylic acid and 1-aminoanthraquinone, respectively. Anhydride formation does not take place between the oxime hydroxyl and a hydrogen atom of the *ortho*-methyl group, since, although p-*xylyl 1-anthraquinonyl ketoxime*, m. p. 223° after softening and becoming yellow at 218°, is transformed into an *anhydride*, $C_{23}H_{1?}O_2N$, m. p. 265—266° after darkening at 255°; similar behaviour is exhibited by *p*-tolyl 1-anthraquinonyl ketoxime (*anhydride*, $C_{22}H_{13}O_2N$, m. p. 236—237°) and phenyl 1-anthraquinonyl ketoxime (*anhydride*, $C_{21}H_{11}O_2N$, m. p. 291°), whereas phenyl *m*-xylyl ketoxime could not be caused to yield an anhydride, but affords only the products of the Beckmann transformation. The possibility that anhydride formation involves a hydrogen atom in aromatic union is examined at the instances of phenyl, *m*-xylyl, and *p*-xylyl 2-methylanthraquinonyl 1-ketoximes, which are unchanged by short treatment with the reagent, but transformed under more drastic conditions into 2-methylanthraquinone-1-carboxylic acid and black, ill-defined products, and mesityl 1-anthraquinonyl ketoxime, which decomposes in a different direction. The possibility that the anhydride is an acridine derivative is negatived by the observation that anthraquinone-1 : 2-acridone is converted by distillation with zinc dust into 2-*anilino-anthracene*, m. p. 197—198° (*picrate*) (also derived from --anilinoanthraquinone), whereas the anhydride affords a sublimate from which a homogeneous product could not be isolated.

p-*Xylyl 1-anthraquinolyl ketone*, m. p. 205°, *anthraquinone-1-carboxyanilide*, m. p. 288—289°, and --*methylanthraquinone-1-carboxyanilide*, m. p. 287—288°, are incidentally described. H. WREN.

Deguelin. I. Preparation, purification, and properties of deguelin, a constituent of tropical fish-poisoning plants. E. P. CLARK (J. Amer. Chem. Soc., 1931, 53, 313—317).—Details are given for the isolation of the compound, m. p. 171° (A., 1930, 967) (now termed *deguelin*), from derris and cube roots. Deguelin, $C_{23}H_{22}O_6$, is oxidised by alkaline potassium ferricyanide to *dehydrodeguelin*, $C_{23}H_{20}O_6$, m. p. 233°, oxidised by chromic and acetic acids to *dehydrodeguelone*, $C_{23}H_{18}O_7$, m. p. 292° (corr.) after darkening at about 280°. Treatment of dehydrodeguelin with alcoholic potassium hydroxide and zinc dust affords *deguelic acid*, $C_{23}H_{24}O_8$, m. p. 189° (corr.), converted by acetic anhydride and sodium acetate into dehydrodeguelin. Deguelin is a dimethoxylactone; it occurs also in the leaves of *Cracca* (*Tephrosia*) *vogelii* and the roots of *C. toxicaria*.

H. BURTON.

Relation between rotenone, deguelin, and tephrosin. E. P. CLARK (Science, 1931, 73, 17—18).—Oxidation of deguelic acid with hydrogen peroxide yields derric acid. Tephrosin with sulphuric and acetic acids or with acetic anhydride forms dehydrodeguelin. Derric acid constitutes one half of the molecule of rotenone, deguelin, and tephrosin.

L. S. THEOBALD.

Senegin and its fission products. O. DAFERT and E. KALMAN (Pharm. Acta Helv., 1930, 5, 71—77; Chem. Zentr., 1930, ii, 1999).—Senegin, a saponin extracted from senega root by means of alcohol, m. p. 240°, contains C 52·29, H 7·17%. It is hæmolytic at a dilution of 1 in 6×10^4. Treatment with sulphuric acid affords dextrose 41·09, methylpentose 11·12, and arabinose 11·06%, and Wedekind and Krecke's compound having m. p. 270° (A., 1924, i, 976).

A. A. ELDRIDGE.

Action of Beckmann's mixture on monocyclic terpenes. II. Terpinolene and "origanene." T. A. HENRY and H. PAGET (J.C.S., 1931, 25—32).—Terpinolene on oxidation with Beckmann's mixture gives, in addition to the principal products lævulic and acetic acids, a small quantity of an unsaturated keto-lactone (I), to which the constitution of β-*thuja-keto-lactone*, m. p. 48—50° [*semicarbazone*, m. p. 222—223° (corr., decomp.)], is given, since on catalytic reduction it yields homoterpenyl methyl ketone. With permanganate I yields lævulic acid, but prolonged treatment with Beckmann's mixture at 60° yields terebilic acid, catalytically reduced to terebic acid. Hydrolysis of I by warm alkali gave an unsaturated acid (II), m. p. 130°, considered to be β-iso*propenyl-ε-keto-Δ^{α}-heptenoic acid*, since on reduction it gives ε-keto-β-*iso*propylheptoic acid. It is considered that these reactions are best explained by the assumption that the first step in the oxidation is the formation of a tetrahydric alcohol by addition of four hydroxyl groups to the two double linkings. The presence of "origanene" in Cyprus origanum oil is confirmed (cf. Pickles, J.C.S., 1908, 93, 866). Crystallographic data are given for two terpinolene tetrabromides, the new *tetrabromide* having m. p. 119°. Both yield terpinolene on debromination.

J. D. A. JOHNSON.

Natural and synthetic rubber. VI. Pyrolysis of natural rubber in presence of metallic oxides. T. MIDGLEY, jun., and A. L. HENNE (J. Amer. Chem. Soc., 1931, 53, 203—204).—Pyrolysis of pale crepe rubber in presence of magnesium or zinc oxides gives

the same products as are obtained in their absence (A., 1929, 702), but in different proportions. Zinc oxide has approximately the same effect as magnesium (*loc. cit.*). H. BURTON.

Menthone series. IX. Resolution of *dl*-menthol and *dl*-camphor-10-sulphonic acid. J. READ and W. J. GRUBB (J.C.S., 1931, 188—195).—*dl*-Menthol may be resolved by fractional crystallisation of its *d*(or *l*)-camphor-10-sulphonate, obtained by the action of *d*(or *l*)-camphor-10-sulphonyl chloride in quinoline. The esters are pure (40%) after four crystallisations (twice from light petroleum and twice from ethyl acetate), but hydrolysis, which is best carried out with hot 50% aqueous oxalic acid, gives only 10% of pure *d*(or *l*)-menthol together with *d*(or *l*)-camphor-10-sulphonic acid and *d*(or *l*)-Δ^3-menthene. Similarly *dl*-camphor-10-sulphonic acid may be resolved, using *d*- and *l*-menthols, since *d*-menthol is thus made readily accessible. The menthol esters of camphor-10-sulphonic acid when heated at 153° decompose smoothly into the menthols and the Δ^3-menthenes. Crystallographic data are given for *l*-menthyl *d*-camphor-10-sulphonate. J. D. A. JOHNSON.

Optically active diazo-compounds. Diazocamphane. U. HEUBAUM and W. A. NOYES (J. Amer. Chem. Soc., 1930, **52**, 5070—5078).—Treatment of *s*-dibornylcarbamide with nitrogen trioxide in ether at −15° gives the *mononitroso*-derivative, m. p. 73—75° (decomp.), which decomposes slowly at the ordinary temperature to the original carbamide. Nitrosobornylurethane, $[\alpha]_D$ +11° in ether, and nitroso*neo*bornylurethane, $[\alpha]_D$ −18·5° in ether, prepared similarly from the corresponding urethanes, are converted by 2% methyl-alcoholic sodium methoxide in ether at −20° into diazocamphane and diazo*neo*camphane, respectively. Rotatory powers for ethereal solutions of these are given for various wavelengths; the dispersion curve for each compound has its maximum at about 5750 Å., this anomaly being due to an absorption band situated at about 5650 Å. The difference in shape of the dispersion curves, the isolation of a small amount of *l*-bornyl chloride, $[\alpha]_D$ −33·2° in ether, from the decomposition products of diazocamphane by treatment with ethereal hydrogen chloride, and the formation of *d*-bornyl chloride by similar decomposition of diazo*neo*camphane indicate that the diazo-compounds possess different structures. The main product of decomposition of both diazo-compounds is, however, tricyclene, thus indicating that they possess (in part) the same structure. It is suggested that the diazo-compounds may exist as equilibrium mixtures of much cyclic and little chain forms (cf. Lindemann, Wolter, and Groger, A., 1930, 586). H. BURTON.

Addition of hydrogen to acetylene derivatives. XVIII. Synthesis and hydrogenation of di-(hydroxybornyl)acetylene. J. S. SALKIND and W. O. MOCHNATSCH (J. Russ. Phys. Chem. Soc., 1930, **62**, 1643—1647).—*s*-Di(hydroxybornyl)acetylene, m. p. 201—202°, which gives an intense red coloration with sulphuric acid, was obtained by Grignard's method by warming camphor with the magnesium derivative of acetylene dibromide for 20 hrs. Hydrogenation in the presence of even considerable quantities of colloidal palladium as catalyst was very slow, but with palladium-black s-*di(hydroxybornyl)ethylene*, m. p. 165—167°, giving a yellow coloration with sulphuric acid, was rapidly obtained, whilst complete reduction to s-*di(hydroxybornyl)ethane*, m. p. 204°, required about 5½ hrs. M. ZVEGINTZOV.

Oxidation of 5-hydroxycamphor from campherol. Y. ASAHINA and M. ISHIDATE (Ber., 1931, **64**, [*B*], 188—192; cf. A., 1928, 526; 1929, 72).—Repeated crystallisation of crude campherol from light petroleum, hydrolysis of 5-acetoxycamphor, or treatment of crude hydroxycamphor with 10% potassium hydroxide followed by crystallisation from light petroleum gives 5-hydroxycamphor, m. p. 222°, $[\alpha]_D^{25}$ +43·8° in ethyl alcohol. 5-*Acetoxycamphorsemicarbazone*, m. p. 180—185°, is hydrolysed by sodium carbonate to 5-hydroxycamphorsemicarbazone, m. p. 233°. Cautious oxidation of 5-hydroxycamphor affords a *labile* 5-*ketocamphor*, m. p. 195—200°, $[\alpha]_D^{20}$ +70·6° in alcohol, which decolorises permanganate in water or acetone and bromine in chloroform. Repeated crystallisation from glacial acetic acid converts it into *p*-diketocamphane, stable towards permanganate. With semicarbazide it gives *p*-diketocamphanedisemicarbazone, m. p. 295°. Oxidation of labile 5-ketocamphor with aqueous potassium permanganate at 0° gives stable 5-ketocamphor, m. p. 210°, $[\alpha]_D^{21}$ +103°, and 1 : 5 : 5-*tri-methyl*cyclo*pentane*-2 : 4-*dione*-1-*acetic acid*, m. p. 251° (*disemicarbazone*, m. p. 251°), also formed by autoxidation of the labile compound, the enolic content of which increases during preservation. H. WREN.

Camphor and terpenes. V. So-called camphorcyanohydrins. J. HOUBEN and E. PFANKUCH (Annalen, 1930, **483**, 271—304; cf. A., 1927, 364).—In view of the suggestions of Lapworth and others (A., 1927, 1080) the nature of the compounds described by Passerini (A., 1925, i, 1290) and by Houben and Pfankuch (A., 1927, 364) has been investigated. Passerini's compound is identified with camphene-1-carboxylamide (Houben and Willfroth, A., 1913, i, 970, 1196). Thus, the three forms prepared from the optical varieties of camphor, viz., a racemic form, a *l*-form (sample described of $[\alpha]_D$ −47·8°), and a *d*-form, prepared by the action of potassium cyanide on pernitrosocamphor from pure *d*-camphor in presence of triethylamine ($[\alpha]_D$ +78·5°), all melt at 209—210°, not depressed by camphene-1-carboxylamide prepared from bornyl chloride, for which a value $[\alpha]_D$ +32° has been recorded (*loc. cit.*). The observations of Passerini on the acid hydrolysis of the compound could not be confirmed, the action of hydrochloric acid leading to a chlorocamphanecarboxylamide. No formation of an imino-ether takes place with dry alcoholic hydrogen chloride; alkaline hydrolysis of the *dl*-"cyanohydrin" affords (90% yield) *dl*-camphene-1-carboxylic acid, m. p. 109—110°. d-*Camphene-1-carboxylic acid*,

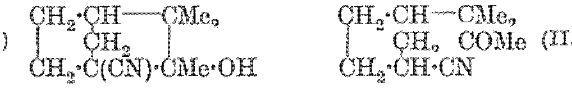
$$\begin{array}{l} CH_2\cdot CH\text{———}CMe_2 \\ |\qquad CH_2 \qquad\quad | \\ CH_2\cdot C(CO\cdot NH_2)\cdot C{:}CH_2 \end{array}$$

(similarly from the *d*-"cyanohydrin"), m. p. 83—84°, $[\alpha]_D^{18}$ +95·5°, gives with *l*-camphene-1-carboxylic acid from *l*-bornyl

chloride, the above racemate. The acid so obtained by hydrolysis is further characterised by oxidation with ozone to camphenonic acid (new m. p. 134°; oxime, m. p. 171—172°) (*d*-acid, m. p. 106°, $[\alpha]_D^{20}$ +75°). Similar ozonisation of the *d*-" cyanohydrin " affords *d*-camphenonamide, m. p. 152—153°, $[\alpha]^{20}$ +55°. Further, the acid from the *d*-cyanohydrin is hydrogenated to D-l-*dihydrocamphene*-1-*carboxylic acid*, m. p. 56—57° (*amide*, through the chloride, m. p. 174—175°, $[\alpha]_D^{18}$ −16·7°); direct hydrogenation of the *d*-" cyanohydrin " affords the last-mentioned amide, whilst the *dl*-compound gives quantitatively the dihydrocamphene-1-carboxylamide, m. p. 189—190°, described by Houben and Willfroth (*loc. cit.*). *d*-Camphene-1-carboxylic acid, m. p. 83—84°, is readily converted through the chloride into the original *d*-" camphorcyanohydrin," m. p. 208—210°, which with acetic anhydride gives d-*camphene*-1-*nitrile*, b. p. 108—110°, m. p. 38—40°, $[\alpha]_D^{18}$ +40·5° (no iminoether formation with alcoholic hydrogen chloride). Treatment of either active form of the cyanohydrin with alcoholic hydrogen chloride causes the rotation gradually to approach zero, the formation of an intermediate *compound*, $C_{11}H_{17}ON,2HCl$, being postulated; on treatment with water the original compound is re-formed, and inversion of the rotation may occur.

The mechanism of the formation of camphene-1-carboxylamide from pernitrosocamphor is discussed; in this connexion the *silver* salt and *methyl* ester, m. p. 102°, of Passerini's intermediate compound are described.

To Houben and Pfankuch's compound is ascribed the constitution I. Hydrolysis of I cannot be



(I) (II.)

effected without other alteration of the molecule; the action of sodium methoxide causes isomerisation to 3-(αα-*dimethylacetonyl*)cyclo*pentamethylene*-1-*nitrile* (II), b. p. 172—174°/17 mm., the corresponding ketonic *acid* (III), b. p. 186—188°/10 mm., $[\alpha]_D^{18}$ −2·6° (*dl*-acid also prepared) (*semicarbazone*, m. p. 200—202°), resulting on hydrolysis with methyl-alcoholic potassium hydroxide. *dl*-III is broken down to *dl*-camphene-camphoric acid, m. p. 134—135°, by the action of hypobromite, *l*-III similarly giving a mixture of active and inactive acids from which *l*-camphene-camphoric acid, m. p. 142—143°, $[\alpha]_D$ −1·0°, is isolated.

D-l-6-*Bromocamphane*-1-*carboxylic acid*, m. p. 118—120° (efferv.), $[\alpha]_D^{18}$ −15·5° (by addition of hydrogen bromide to *d*-camphene-1-carboxylic acid), on treatment with dilute alkali is converted into a mixture of the original acid and D-l-6-*hydroxycamphane*-1-*carboxylic acid*, m. p. 142—143°, $[\alpha]_D^{17}$ −17°, which is stable to alkaline hydrolysis, but readily passes into *d*-camphene-1-carboxylic acid, m. p. 83°, on treatment with dilute acids; the corresponding *methyl* ester, m. p. 59—60°, $[\alpha]_D^{18}$ −19·5°, is converted by sodium methoxide into the *methyl* ester of III, b. p. 154—155°/17 mm., $[\alpha]_D$ −3° (*semicarbazone*, m. p. 86—87°), and by methyl-alcoholic alkali into III, $[\alpha]_D$ −6·6°; like the free acid, it is sensitive to mineral acids, readily yielding methyl camphene-1-carboxylate.

6-Hydroxycamphane-2-carboxylic acid (A., 1926, 1251), m. p. 221°, $[\alpha]_D$ +12·2°, and its *methyl* ester, m. p. 61—62°, $[\alpha]_D^{18}$ +24·5°, are not converted into a ketonic acid by methyl-alcoholic alkali; they are very sensitive to mineral acids, yielding camphene-2-carboxylic acid.

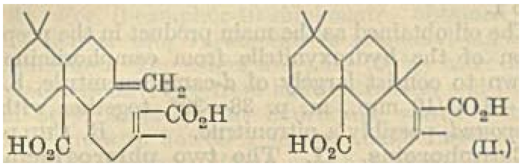
It has not been found possible to convert dl-*bromocamphane*-1-*nitrile*, m. p. 150—151° (by addition of hydrogen bromide to 2-camphene-1-nitrile; see above), into I.

The oil obtained as the main product in the preparation of the hydroxynitrile from camphorimine is shown to consist largely of *d*-camphenenitrile, b. p. 108—112°/10 mm., m. p. 38—39°, together with a *compound*, possibly a nitronitrile. R. CHILD.

Camphoreins. II. The two phloroglucinol-camphoreins. V. DEULOFEU (Anal. Asoc. Quim. Argentina, 1930, **18**, 164—171; cf. A., 1930, 783).—The isomerism of α-phloroglucinolcamphorein, m. p. above 290° (Sircar and Dutt, J.C.S., 1922, **121**, 1283) and β-phloroglucinolcamphorein, m. p. 214—218° (Singh, Rai, and Lal, *ibid.*, 1421), may be attributed to condensation with different carbonyl groups of camphoric anhydride. Neither is convertible into the other by way of the acyl derivatives. α-Phloroglucinolcamphorein yields deeply-coloured *sodium* and *disodium* salts of quinonoid structure, and a colourless *tetra-acetyl* derivative, m. p. 136° (decomp.), and pale yellow *tetrabenzoyl* derivarive, m. p. 205° (decomp.), of lactone structure. β-Phloroglucinolcamphorein yields deeply-coloured *sodium* and *disodium* salts and a colourless *tetra-acetyl* derivative, m. p. 152° (decomp.). R. K. CALLOW.

Higher terpene compounds. XLIII. Bouveault reduction of the esters of agathic- and *iso*-agathic-dicarboxylic acids. Conversion of the last-named ester into a new methylpimanthrene. L. RUZICKA and J. R. HOSKING (Helv. Chim. Acta, 1931, **14**, 203—219).—Dimethyl agathicdicarboxylate (one ester group only is hydrolysed by short treatment with alcoholic sodium hydroxide) is treated with sodium and alcohol, the resultant product hydrolysed and separated into neutral (30%) and acidic (70%) fractions. The neutral part consists mainly of *methyl hydroxydihydroagathate*, $C_{18}H_{30}(CH_2{\cdot}OH){\cdot}CO_2Me$, b. p. 193—195°/0·2 mm., d_4^{15} 1·026, n_D^{1} 1·5076, together with a small amount of *dihydroxydihydroagathene*, $C_{18}H_{30}(CH_2{\cdot}OH)_2$, m. p. 112—113°, which is reduced catalytically (Adams) in ethyl acetate to *dihydroxytetrahydroagathene*, m. p. 107—108°. Distillation of the acidic fraction in a high vacuum causes elimination of carbon dioxide with the production of methyl noragathate, b. p. 146—148°/0·1 mm., d_4^{11} 1·002, n_D^{11} 1·5082 (cf. A., 1929, 572), which is practically unaffected by treatment with sodium and alcohol; *methyl hydrogen dihydroagathicdicarboxylate*, b. p. 210—212°/0·1 mm., is also isolated from the distillate. Reduction of dimethyl *iso*agathicdicarboxylate (this vol., 232) with sodium and alcohol gives a mixture of *methyl hydroxyisoagathate*, b. p. 203—205°/0·3 mm., m. p. 125—126°, and *dihydroxyisoagathene*, $C_{18}H_{28}(CH_2{\cdot}OH)_2$, m. p. 172—173°, both of which are unsaturated (yellow colorations with tetranitromethane). The former of these is converted by hot 99% formic acid into a mixture of (probably) methyl dehydro*iso*agathate and *iso*agathate, dehydrogenated

by selenium at 260—340° to a *methylpimanthrene*, m. p. 142—143° [*picrate*, m. p. 161—163°; *quinone*, m. p. 194° (*quinoxaline*, m. p. 131—132°, from o-phenylenediamine)]. Crystallographic data [by NANNINGA] are given for tetrahydronoragathic acid (A., 1929, 572). The various transformations of agathicdicarboxylic acid are readily explicable when the acid is formulated as I (evidence for this from

(I.)  (II.)

ozonolysis experiments to be published later). *iso*-Agathicdicarboxylic acid is represented as II. The building of the carbon skeleton (I) from four isoprene units is discussed. H. BURTON.

Higher terpene compounds. XLIV. Constitution of pimanthrene. L. RUZICKA, G. B. R. DE GRAAFF, and J. R. HOSKING (Helv. Chim. Acta, 1931, **14**, 233—239).—Oxidation of retenequinone (1-methyl-7-*iso*propylphenanthraquinone) with potassium permanganate in aqueous pyridine (cf. Bucher, A., 1910, i, 239) affords a mixture of 4-β-hydroxy*iso*propyldiphenyl-2 : 2′ : 3′-tricarboxylic acid, m. p. 188° (cf. *loc. cit.*), and amorphous products, separable owing to the ready solubility of the latter in acetone. The tricarboxylic acid is oxidised by chromic and acetic acids to diphenyl-2 : 4 : 2′ : 3′-tetracarboxylic acid (*methyl* ester, m. p. 153—154°), whilst the amorphous products are oxidised by nitric acid (*d* 1·5) to hemimellitic and trimellitic acids. Oxidation of retene with alkaline potassium ferricyanide gives a mixture of the above tetracarboxylic acid and phenanthrene-1 : 7-dicarboxylic acid (*methyl* ester, m. p. 151—152°), separable owing to their differing solubilities in methyl alcohol. The dicarboxylic acid is also formed by similar oxidation of pimanthrene. Pimanthrenequinone is oxidised as retenequinone to the above tetracarboxylic acid and amorphous products (oxidised by nitric acid to hemimellitic acid and the tetracarboxylic acid). Pimanthrene is 1 : 7-dimethylphenanthrene.

The formation of a dimethylphenanthrene, m. p. 45°, from retene by Meyer's method (Z. angew. Chem., 1924, **37**, 796) could not be confirmed.

H. BURTON.

Fokienol, a new monocyclic sesquiterpene alcohol. L. S. GLICHITCH (Compt. rend., 1930, **191**, 1457—1460).—From the essential oil, d^{15} 0·909—0·938, $[\alpha]_D$ +10·75° to 15°, n_D^{20} 1·495—1·505, obtained by distillation of the stems of *Fokienia Hodginsii*, a new tertiary, monocyclic sesquiterpene alcohol, *fokienol*, $C_{15}H_{26}O$, b. p. 125—126°/2 mm. (corr.), d^{23} 0·9236, $[\alpha]_D$ +18·6°, n_D^{23} 1·4975, is isolated and purified through its *formate*, b. p. 126(?166)—170°/2 mm. (corr.), $d^{21.5}$ 0·9785, $[\alpha]_D$ +16·5°, $n_D^{21.5}$ 1·4970, some racemisation probably occurring during isolation. The corresponding acetate and benzoate decompose on distillation even under reduced pressure. Fokienol contains two double linkings and is readily dehydrated by the usual acid reagents to a dicyclic sesquiterpene *isofokienene*, b. p. 96—99°/3 mm., d^{23} 0·9076, $[\alpha]_D^{23}$ +14·6°, n_D 1·5055 (the constants varying slightly with the conditions of dehydration), but dehydration with metaphosphoric acid gives the monocyclic sesquiterpene *fokienene*, b. p. 112—114°/7 mm., d^{15} 0·8802, $[\alpha]_D^{15}$ +16·9°, n_D^{15} 1·49594, in 15—20% yield. All these compounds yield cadalene on catalytic dehydrogenation with sulphur. J. W. BAKER.

Bitter substances from the elecampane root. K. F. W. HANSEN (Ber., 1931, **64**, [*B*], 67—71).—Technical " helenin " is distilled in a high vacuum and the solution of the distillate in alcohol is saturated with ammonia whereby a mixture of iso*alantolamide*, m. p. 235—240°, and *alantolamide* is precipitated, whereas *dihydro*iso*alantolactone*, $C_{15}H_{22}O_2$, m. p. 174°, remains unaffected. When heated at 210° or 240° and then distilled the amides lose ammonia and pass into *iso*alantolactone, m. p. 112°, and alantolactone, m. p. 76°, respectively. Reduction of *iso*alantolactone with sodium amalgam and water gives dihydro*iso*alantolactone identical with the natural product. Dehydrogenation of the three lactones by selenium at 260—320° gives 1-methyl-7-ethylnaphthalene, identified as the picrate, m. p. 101°, and styphnate, m. p. 126°, and oxidised by potassium ferricyanide to naphthalene-1 : 7-dicarboxylic acid. Complete hydrogenation of the lactones in presence of glacial acetic acid and spongy platinum followed by dehydrogenation of the product with selenium affords 1-methyl-7-ethylnaphthalene in considerably better yield, so that it is very improbable that the second carbon atom removed under the action of selenium is present in a methylene group. The lactones belong to the sesquiterpene series and are of the same type as eudesmol. H. WREN.

Velocity measurements on the opening of the furan ring in hydroxymethylfurfuraldehyde. II. H. P. TEUNISSEN.—See this vol., 316.

γ-Nitro-β-furylbutyrophenones. N. L. DRAKE and H. W. GILBERT (J. Amer. Chem. Soc., 1930, **52**, 4965—4967).—Furfurylideneacetophenone, b. p. 176°/17 mm., m. p. 26°, reacts with sodionitromethane in methyl alcohol forming *γ-nitro-β-furylbutyrophenone*, m. p. 49·5—50° ; *γ-nitro-γ-phenyl-β-furylbutyrophenone*, m. p. 153—153·5°, is prepared similarly, using phenylnitromethane. *Furfurylidene*-p-*bromoacetophenone*, m. p. 80—81°, gives similarly p-*bromo-γ-nitro-β-furyl-* and p-*bromo-γ-nitro-γ-phenyl-β-furylbutyrophenones*, m. p. 72—73° and 87—88·5°, respectively. H. BURTON.

Absorption spectra of γ-pyrones and pyroxonium salts. R. C. GIBBS, J. R. JOHNSON, and E. C. HUGHES (J. Amer. Chem. Soc., 1930, **52**, 4895—4904).—The ultra-violet absorption spectra of γ-pyrone, 2 : 6-dimethyl-γ-pyrone, benzo-γ-pyrone, and xanthone in alcoholic hydrogen chloride are similar to the spectra in alcoholic solution; there is a slight shift of the bands towards the red in the acid solutions. The formation of the oxonium salts does not appear to cause any appreciable change in the structure of the pyrone ring. The absorption spectrum of the dimethylpyrone in alcoholic sodium ethoxide is the same as in alcohol (cf. Baly, Collie, and Watson, J.C.S., 1909, **95**, 144); the pyrone does not exist in

benzenoid–quinonoid equilibrium in solution (cf. Heilbron, Barnes, and Morton, J.C.S., 1923, **123**, 2559). The spectrum of the dimethylpyrone also resembles that of 1 : 2 : 6-trimethyl-4-pyridone, but differs from that of 4-methoxy-2 : 6-dimethylpyridine. The absorption spectrum of xanthhydrol in alcoholic hydrogen chloride is identical with that of xanthene in alcohol (or alcoholic hydrogen chloride), but differs from that of xanthone; xanthhydrol exhibits a different spectrum in sulphuric acid. The salts of pyrones are best represented as $\left\{O<\begin{matrix}CH:CH\\CH:CH\end{matrix}>C:\overset{\oplus}{O}H\right\}\overset{\ominus}{X}$; such a formula explains the failure of Gibson and Simonsen to resolve pyrone salts (A., 1928, 1254). The coloured compounds obtained from dimethylpyrone and organic acids by Kendall (A., 1914, i, 858) cannot be prepared with the pure pyrone.

H. Burton.

Brazilin and hæmatoxylin. XI. Hydroxybenzylchromanones. P. Pfeiffer, E. Breith, and H. Hoyer (J. pr. Chem., 1931, [ii], **129**, 31—54; cf. A., 1930, 1041).—By interaction of appropriate derivatives of benzaldehyde with chromanone and 7-methoxy-, 7-hydroxy-, and 7 : 8-dihydroxy-chromanones in absolute alcohol under the influence of hydrogen chloride, the following are prepared: 4′-*methoxy-*, m. p. 134°; 3′ : 4′ *dimethoxy-*, m. p. 117°; 3′ : 4′-*methylenedioxy-*, m. p. 134·5—137°; 4′-*hydroxy-3′-methoxy-*, m. p. 126—129° (*acetyl* derivative, m. p. 160°); 3′ : 4′-*dihydroxy-*, m. p. 224—225° (sinters 205°) (*diacetyl* derivative, m. p. 166°); 3′-*hydroxy-7 : 4′-dimethoxy-*, m. p. 153—154° (*acetyl* derivative, m. p. 139—140°); 7-hydroxy-4′-methoxy- (cf. A., 1925, i, 1303); 7-*hydroxy-3′ : 4′-dimethoxy-*, m. p. 245—249° (*acetyl* derivative, m. p. 151—152°); 7-*hydroxy-3′ : 4′-methylenedioxy-*, m. p. 234—236° (*acetyl* derivative, m. p. 132·5—134°); 7 : 4′-*dihydroxy-3′-methoxy-*, m. p. 230—231·5° (sinters at 215°) (purified through the *diacetyl* derivative, m. p. 151—152·5°); 7 : 3′ : 4′-*trihydroxy-*, m. p. 250—253° (sinters 215—217°) (purified through *triacetyl* derivative, m. p. 132—134°); 7 : 8-*dihydroxy-4′-methoxy-*, m. p. 192° (*diacetyl* derivative, m. p. 140°); 7 : 8-*dihydroxy-3′ : 4′-dimethoxy-*, m. p. 174—175° (+1H_2O), m. p. 123—126° (*diacetyl* derivative, m. p. 183°); 7 : 8 : 4′-*trihydroxy-3′-methoxy-* (+1H_2O), m. p. 206—207° (*triacetyl* derivative, m. p. 180—181°), and 7 : 8 : 3′ : 4′-*tetrahydroxy-benzylidenechromanone*, decomp. 220—265° (*tetra-acetyl* derivative, m. p. 166—167°). 7 : 8-*Dihydroxychromanone*, m. p. 188—188·5° (+1H_2O, lost at 110—120°) [*diacetyl* derivative, m. p. 111°; *semicarbazone*, m. p. 224—225° (decomp.)], is obtained by demethylation of 7 : 8-dimethoxychromanone (*loc. cit.*) by aluminium bromide in boiling benzene or, better, by boiling, concentrated, aqueous hydrobromic acid. 7-Hydroxychromanone (*loc. cit.*) is also obtained by demethylation of the methoxy-compound by the first method. By hydrogenation in presence of platinum of acetoxy-derivatives of the corresponding benzylidenechromanones 3′-*hydroxy-7 : 4′-dimethoxy-*, m. p. 123—124° [*acetyl* derivative, m. p. 90—91° (*oxime*, m. p. 160—161°)], 7 : 3′ : 4′-*trihydroxy-*, m. p. 201—202° (*triacetyl* derivative, m. p. 117°), 7 : 8-*dihydroxy-3′ : 4′-dimethoxy-*, m. p. 177° (*dibenzoyl* derivative, m. p. 177·5—178°), and 7 : 8 : 3′ : 4′-*tetrahydroxy-benzylchromanone*, decomp. above 200° (*tetra-acetyl* derivative, m. p. 107—108°), are obtained. The colours of the solutions of these substances in concentrated sulphuric acid are described.

H. A. Piggott.

Condensation of benzilic and anisilic acids and xanthhydrol with thiophen and thionaphthen. J. Ancízar-Sordo and A. Bistrzycki (Helv. Chim. Acta, 1931, **14**, 141—153).—Benzilic acid and thiophen condense in presence of acetic and sulphuric acids at the ordinary temperature giving *diphenylthienylacetic acid*, m. p. 217—218° (*silver* salt; *methyl* ester, m. p. 149—150°), brominated in acetic acid to a *diphenyldibromothienylacetic acid*, m. p. 213—214° (decomp.). Treatment of the acid with sulphuric acid containing a little acetic acid below 35° affords diphenylthienylcarbinol, m. p. 129—130° (lit. 125—131°), whilst potassium hydroxide solution at 180° converts it into diphenylthienylmethane, m. p. 63—64°. Pure products could not be obtained from anisilic acid and thiophen. Xanthhydrol and thiophen react in presence of phosphoric oxide and ether forming 9-*thienylxanthen*, m. p. 150—151°. Benzilic acid and thionaphthen afford *diphenylthionaphthenylacetic acid*, m. p. 244—245° (decomp.) (*sodium* salt; *methyl* ester, m. p. 151—152°), convertible as above into *diphenylbromothionaphthenylacetic acid*, m. p. 223—224° (slight decomp.) (also converted into *diphenylbromothionaphthenylcarbinol*, m. p. 166—167°), *diphenylthionaphthenylcarbinol*, m. p. 125—126°, and *diphenylthionaphthenylmethane*, m. p. 104—105°. Anisilic acid and thionaphthen give *dianisylthionaphthenylacetic acid*, m. p. 245—246° (decomp.) (*barium* salt; *methyl* ester, m. p. 166—167°). 9-*Thionaphthenylxanthen*, m. p. 172—173°, is prepared similarly to the thienyl analogue.

H. Burton.

Behaviour of pyrrolidine during catalytic dehydrogenation. N. D. Zelinski and J. K. Jurjev (Ber., 1931, **64**, [*B*], 101—103; cf. A., 1929, 1461).—Pyrrole is hydrogenated in presence of palladised asbestos at 160° or, preferably, of rhodium on asbestos at 100° to pyrrolidine, also obtained from pyrroline in presence of palladised asbestos at 135°. The constants, b. p. 85·5—86·5°/741 mm., $d_4^{23.5}$ 0·8533, $n_D^{23.5}$ 1·4423, are recorded. At 300°, pyrrolidine is readily dehydrogenated to pyrrole in presence of palladised asbestos.

H. Wren.

Synthesis of compounds in the pyrrole and pyrrolidine series. L. C. Craig [with R. M. Hixon] (J. Amer. Chem. Soc., 1931, **53**, 187—190).—1-*n*-Butylpyrrole, obtained together with 1-*n*-butylpyrrole-2-carboxy-*n*-butylamide, m. p. 57° [free *acid*, an oil (*amide*, m. p. 108°)], when mucic acid is treated with *n*-butylamine (cf. Reichstein, A., 1927, 573), is reduced smoothly to 1-*n*-butylpyrrolidine (*chloroaurate*, m. p. 78°) by hydrogen in presence of platinum oxide and an equivalent amount of alcoholic hydrochloric acid. 1-Methylpyrrolidine is prepared by similar reduction of 1-methylpyrrole. Tetramethylene chloride and *p*-toluidine react at 100°, forming 1-p-*tolylpyrrolidine*, b. p. 120°/8 mm., m. p. 42·5° (*chloroplatinate*, decomp. 175°).

H. Burton.

Preparation of hydroxyproline. H. K. Klabunde (J. Biol. Chem., 1931, **90**, 293—295).—In

the isolation of proline from the hydrolysis products of gelatin by fractionation of their copper salts (cf. Town, A., 1928, 1148), *l*-hydroxyproline is found in the fraction containing proline, and may be separated by extraction with absolute alcohol, in which it is insoluble, and purified by means of its picrate (cf. Cox and King, A., 1930, 73). H. A. PIGGOTT.

Pyrrole-2-aldehyde. B. EMMERT and K. DIEHL (Ber., 1931, 64, [*B*], 130—132).—The hypothesis that pyrrole-2-aldehyde is in equilibrium dependent on the solvent with a more complex form (cf. A., 1929, 1083) is supported by the observation that it is transformed by benzoyl chloride and powdered potassium hydroxide in light petroleum into a mixture of 1-*benzoylpyrrole-2-aldehyde*, m. p. 90° (also derived from the sodium derivative of pyrrole-2-aldehyde and benzoyl chloride; *phenylhydrazone*, m. p. 154°), and the dimeric *benzoyl* derivative,

$$CH<\begin{matrix}CH{:}C\cdot CH(OBz)\cdot N\cdot CH\\ CH\cdot N\cdot CH(OBz)\cdot C{:}CH\end{matrix}>CH,$$ m. p. 178°.

p-*Toluoylpyrrole-2-aldehyde*, m. p. 79—80° (*phenylhydrazone*, m. p. 146°), and the dimeric *product*, $C_{26}H_{22}O_4N_2$, m. p. 167—168°, are analogously prepared. H. WREN.

Stereochemistry of *N*-phenylpyrroles. Preparation and resolution of *N*-*o*-carboxyphenyl-2 : 5-dimethylpyrrole-3-carboxylic acid. XIII. L. H. BOCK and R. ADAMS (J. Amer. Chem. Soc., 1931, 53, 374—376).—Ethyl acetonylacetoacetate and anthranilic acid in alcohol give, after alkaline hydrolysis, N-o-*carboxyphenyl*-2 : 5-*dimethylpyrrole*-3-*carboxylic acid*, m. p. 224·5—225·5°, resolved by brucine into the d-, $[\alpha]_D$ +27° in alcohol [*brucine* salt, m. p. 175—180° (decomp.), $[\alpha]_D$ +13·5° in chloroform], and l-*isomerides*, $[\alpha]_D$ −27·2° in alcohol [*brucine* salt, m. p. 231—232° (decomp.), $[\alpha]_D$ −44·9° in chloroform]. The active acids racemise when boiled with 0·1*N*-sodium hydroxide for 24 hrs. H. BURTON.

Resolution of 1-α-piperidinobenzyl-β-naphthol. W. R. BRODE and J. B. LITTMAN (J. Amer. Chem. Soc., 1930, 52, 5056—5058).—*dl*-1-α-Piperidinobenzyl-β-naphthol (A., 1930, 775) is resolved by *d*-camphorsulphonic acid into the d-, m. p. 199—200°, $[\alpha]_D$ +189° in benzene, and *forms*, m. p. 201—202°, $[\alpha]_D$ −211° in benzene [d-*camphorsulphonate*, m. p. 184—185° (decomp.), $[\alpha]_D$ +4·7° in chloroform]. All m. p. are corr. H. BURTON.

Hydrogenation of pyridine with hydrogen under pressure by the Bergius process. H. THATE (Rec. trav. chim., 1931, 50, 77—90).—The products obtained by hydrogenation of pyridine at 500°/50—100 atm. have been investigated qualitatively and quantitatively. In the absence of a catalyst absorption of hydrogen begins at 450°. Analysis of the gaseous products after removal of ammonia shows the presence of hydrogen (67·9%), carbon monoxide (1·2%), nitrogen (1·2%), methane (13·8%), ethane (7·4%), propane (4·7%), butane (2·0%), butane+pentane (1·0%), ethylene+propylene (0·5%), and propylene+butylene (0·4%), the hydrocarbons being formed by cracking of the pentane originally formed. Steam-distillation from an acid solution of the liquid products (1·2%) affords pentane, valeronitrile, an unsaturated hydrocarbon $C_{10}H_{11}$ (formed only when 1% of aluminium or ferric chloride is added as catalyst), and nitriles, b. p. 220—260°. Steam-distillation from an alkaline medium affords primary amines (containing *n*-amylamine), unchanged pyridine, 3- and 3 : 5-alkylated piperidines, 2 : 2′-dipyridyl, and, probably, 2 : 4-dipyridyl. The solid product consists of carbon and ammonium cyanide. The relative proportions of (1) hydrocarbons, (2) nitriles, and (3) secondary and tertiary amines formed varies with the conditions of hydrogenation. Thus at 500°/50 atm. for 1 and 4 hrs., proportions are, respectively, (1) 16, (2) + (3), 2·5%; and (1) 29, (2) + (3), 2·5%, whilst at 500°/100 atm. for 1 hr. they are (1) 25%, (2) 4·6%, and (3) traces only. Since similar products are obtained by hydrogenation of piperidine, the mechanism of the hydrogenation of pyridine is considered to be primarily reduction to piperidine which subsequently breaks down to the products enumerated above, and a scheme of the formation of these is given. A summary of investigations on the hydrogenation of both aromatic and aliphatic compounds is given. J. W. BAKER.

2 : 4-Substituted derivatives of pyridine. R. GRAF [with E. LEDERER-PONZER and L. FREIBERG] (Ber., 1931, 64, [*B*], 21—26).—Pyridine-2-carboxylic acid is converted by protracted treatment with boiling thionyl chloride into 4-chloropyridine-2-carboxyl chloride hydrochloride, transformed by water into 4-chloropyridine-2-carboxylic acid, m. p. 180—181°, in 50—55% yield. When treated with hydrazine hydrate in benzene it affords *di-4-chloropyridine-2-carboxyhydrazide*, $C_{12}H_8N_6Cl_2$, m. p. 269—271° (decomp.). 4 - *Chloropyridine* - 2 - *carboxyl chloride* is converted into the methyl ester hydrochloride, which is treated successively with sodium methoxide and hydrazine hydrate, thereby giving 4-*chloropyridine-2-carboxyhydrazide*, m. p. 167—168° (*benzylidene* derivative, m. p. 178°). Treatment of the hydrazide in *N*-hydrochloric acid with potassium nitrite affords the *azide*, m. p. 92°, converted by warm, dilute acetic acid into nitrogen, carbon dioxide, and 4-*chloro-2-aminopyridine*, m. p. 130—131° (*picrate*, m. p. 243—244°). 4-*Chloro-2-carbethoxyaminopyridine*, m. p. 161°, from the azide and boiling ethyl alcohol, is transformed by boiling hydriodic acid into 4-*chloro-2-aminopyridine hydriodide*, m. p. 206—207° (decomp.). Treatment of the amine with an excess of benzoyl chloride and potassium hydroxide yields 4-*chloro-2-dibenzoylaminopyridine*, m. p. 165—166°, converted by boiling ethyl alcohol into ethyl benzoate and 4-*chloro-2-benzamidopyridine*, m. p. 120—121°. 4-*Chloro-2-acetamidopyridine*, m. p. 115—116°, is described. 4 - *Chloro* - 2 - *hydroxypyridine* has m. p. 184°. 2 : 4-*Dichloropyridine*, b. p. 184°, m. p. 0° (additive *compound* with mercuric chloride), is prepared in the usual manner. 4-Iodopyridine-2-carboxylic acid, m. p. 169° (decomp.), prepared from the chloro-acid, hydriodic acid (*d* 1·7), and red phosphorus, is converted by methyl alcohol and sulphuric acid (1 : 1) into the methyl ester, from which the corresponding *amide*, m. p. 158°, and *hydrazide*, m. p. 160—161° (*benzylidene* derivative, m. p. 207—208°), are obtained. The hydrazide is converted

successively into the *azide*, m. p. 89° (decomp.), and 4-*iodo-2-aminopyridine*, m. p. 163—164° (*picrate*, m. p. 253—254°). 4-*Iodo-2-carbethoxyaminopyridine*, m. p. 167°, very slowly hydrolysed by boiling hydriodic acid, 4-*iodo-2-dibenzoylaminopyridine*, m. p. 176—177°, 4-*iodo-2-benzamidopyridine*, m. p. 167—168°, 4-*iodo-2-acetamidopyridine*, m. p. 150°, and 4-*iodo-2-hydroxypyridine*, m. p. 195°, are described.
H. WREN.

Condensation of pyridine- and quinoline-carboxylic acids with amino-acids. H. MEYER and R. GRAF (Biochem. Z., 1930, **229**, 154—163).—Molecular proportions of the chlorides (or, less satisfactorily, of the anhydrides) of the pyridinemonocarboxylic acids as well as of those of quinaldinic and cinchonic acids and of that of 2-phenylquinoline-4-carboxylic acid react in chloroform solution with aliphatic and aromatic amino-acids to give esters of *N*-substituted amino-acids. The free acids, obtained from the esters by alkaline hydrolysis, are sparingly soluble in water but readily soluble in dilute acids and alkalis. The following substances were prepared: picolinuric acid, m. p. 184—185° (cf. Cohn, A., 1893, ii, 544); nicotinuric acid, m. p. 237—238° (cf. Ackermann, A., 1912, ii, 967) (*methyl* ester, m. p. 67—68°; *amide*, m. p. 193—195°); iso*nicotinuric acid*, m. p. 221—222° (*ethyl* ester, m. p. 89—90°; *amide*, m. p. 227—228°); *quinaldinic acid*, m. p. 183—184° (*methyl* ester, m. p. 100°; *amide*, m. p. 231—232°); *cinchonuric acid*, m. p. 244—246° (*ethyl* ester, m. p. about 120°; *amide*, m. p. 226—227°); N-2-*phenyl-4-quinolylglycine*, m. p. 216° (*ethyl* ester, m. p. 140—141°; *amide*, m. p. 213°); N-*nicotinylglycylglycine*, m. p. 232° (*ethyl* ester, m. p. 144—145°); N-*nicotinylanthranilic acid*, m. p. 258—259° (*methyl* ester, m. p. 127°); N-*picolinylanthranilic acid*, m. p. 171—172° (*methyl* ester, m. p. 84—85°); N-*nicotinylanthranilanthranilic acid* (cf. Meyer, A., 1907, i, 317), m. p. 222° (*methyl* ester, m. p. 181°).
W. MCCARTNEY.

Anhydrides of pyridine- and quinoline-monocarboxylic acids. R. GRAF (Biochem. Z., 1930, **229**, 164—168; cf. A., 1928, 1379).—The anhydrides can be prepared by the action of a benzene solution of the acid chloride on the sodium salt. The method cannot be used, however, for the preparation of the 2-carboxylic acids. The anhydrides behave like those of the aromatic acids. They are stable towards moisture, have m. p. lower than those of the corresponding acids, and do not sublime. Their b. p. are higher than those of the corresponding acids. Substances previously described (A., 1925, i, 836) contained only traces of the anhydrides. *Nicotinic anhydride*, m. p. 122—124°, b. p. 200°/1 mm., iso*nicotinic anhydride*, m. p. 103—104°, and cinchonic anhydride, m. p. 215°, b. p. 240—250°/1 mm. (corresponding *amide*, m. p. 178—179°), were prepared.
W. MCCARTNEY.

Preparation of isatin from oximinoacetanilide by Sandmeyer's method. J. P. WIBAUT and M. C. GEERLING (Rec. trav. chim., 1931, **50**, 41—43).—Oximinoacetanilide is hydrolysed at the ordinary temperature by dilute sulphuric acid to aniline, formaldehyde, and hydroxylamine: $NHPh\cdot CO\cdot CH{:}N\cdot OH + H_2O \longrightarrow NH_2\cdot OH + NHPh\cdot CO\cdot CHO \longrightarrow NH_2Ph + CO_2 + CH_2O$. Such hydrolysis explains the observed separation of isatinmonoxime from the acidic mother-liquor in the preparation of isatin by Sandmeyer's method (A., 1919, i, 318), the hydroxylamine formed from the unchanged anilide reacting with the isatin remaining in solution.
J. W. BAKER.

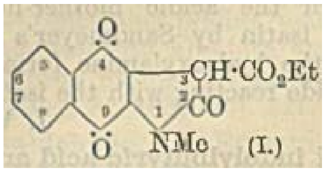
Synthesis of indolylbutyric acid and its derivatives. R. W. JACKSON and R. H. MANSKE (J. Amer. Chem. Soc. 1930, **52**, 5029—5035).—Ethyl *cyclo*hexanone-2-carboxylate and benzenediazonium chloride react in presence of ice and alkali hydroxide, forming the phenylhydrazone, m. p. 142—143° (all m. p. are corr.), of ethyl hydrogen α-ketopimelate. Treatment of this with alcoholic sulphuric acid gives *ethyl γ-2-carbethoxy-3-indolylbutyrate*, b. p. 235°/7 mm., m. p. 76° (corresponding *dimethyl* ester, m. p. 64°); a small amount of *s*-diphenylcarbamide is isolated during the distillation of these esters. The corresponding *dicarboxylic acid*, m. p. 193—194° (decomp.), is decomposed by heat to a mixture of 1-keto-1 : 2 : 3 : 4-tetrahydrocarbazole (small amount) and *γ-3-indolylbutyric acid*, m. p. 124°, when purified through its *methyl* ester, m. p. 73—74°. *γ-3-Indolylbutyrhydrazide*, m. p. 112°, is converted by the usual method into the azide and thence, by treatment with water or methyl alcohol, into *s-di-(γ-3-indolylpropyl)-carbamide*, m. p. 124°, or *methyl γ-3-indolylpropylcarbamate*, respectively. Both these compounds react with phthalic anhydride at 230°, forming *γ-3-indolylpropylphthalimide*, m. p. 132°, hydrolysed by aqueous-alcoholic hydrazine to γ-3-indolylpropylamine.

Reduction of methyl β-3-indolylpropionate with sodium and alcohol gives *γ-3-indolylpropyl alcohol*, solidifies at 0° (*picrate*, m. p. 101°; *phenylcarbimide* derivative, m. p. 94°). *δ-3-Indolylbutyl alcohol*, m. p. 32—33° (*picrate*, m. p. 192°; *phenylcarbimide* derivative, m. p. 88°), is prepared similarly from methyl γ-3-indolylbutyrate. When γ-3-indolylbutyrazide is first decomposed in warm benzene and the resultant product treated with hydrogen chloride, about 5% of 2-*keto-2 : 3 : 4 : 5-tetrahydrohomo-3-carboline*, m. p. 220°, is produced (cf. A., 1927, 256). *δ-3-Indolylbutylmalonic acid*, m. p. 177°, is produced together with much tetrahydrocarbazole from ethyl sodiomalonate and δ-3-indolylbutyl *p*-toluenesulphonate (cf. Peacock and Tha, A., 1928, 1115).

The formation of the above carbazole derivatives emphasises the reactivity of the 2-hydrogen atom in indole.
H. BURTON.

Synthesis of hydroxy-*N*-methylnaphthindolequinone and *N*-methylnaphthisatinquinone. Z. KITASATO and C. SONE (Bull. Chem. Soc. Japan, 1930, **5**, 348—354).—Ethyl 3-bromo-1 : 4-naphthaquinonyl-3-malonate (Liebermann, A., 1899, i, 373, 522) and alcoholic methylamine give a mixture of 3-*bromo-1 : 4-naphthaquinonyl-2-acetmethylamide*, m. p. 165°, and *ethyl 2-keto-1-methyl-2 : 3-dihydronaphthindole-4 : 9-quinone-3-carboxylate* (I), yellow, decomp. about 220° after turning bluish-violet at 190°. When I is boiled with alkali in air, 2-*hydroxy-1-methylnaphthindole-4 : 9-quinone*, deep blue, not melted at 300°, is produced. This is oxidised by nitric and sulphuric acids to 1-*methylnaphthisatin-4 : 9-quinone*, m. p. 268°.

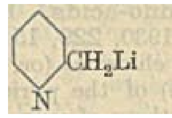
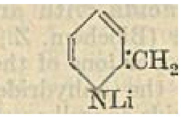
Various reactions of indigotin, nandazurin (cf. A., 1927, 1094), and the above hydroxyindole are compared.


(I.)

Ethyl 6-*bromo*-3 : 4-*dimethoxycinnamate*, m. p. 114—115° (the free *acid*, m. p. 244°, is prepared by the usual method from 6-bromoveratraldehyde), and *ethyl* 3-*bromo*-1 : 4-*naphthaquinone*-2-*carboxylate*, m. p. 119°, prepared from 2 : 3-dibromo-1 : 4-naphthaquinone and ethyl formate in presence of alcoholic sodium ethoxide, are converted by alcoholic methylamine into 6-*bromo*-3 : 4-*dimethoxycinnam-methylamide*, m. p. 183°, and 3-*bromo*-1 : 4-*naphthaquinone*-2-*carboxylamide*, m. p. 164—165°, respectively.

H. BURTON.

Organo-alkali compounds. VIII. Reactions between lithium alkyls, pyridine, and condensed pyridine systems. K. ZIEGLER and H. ZEISER (Annalen, 1930, **485**, 174—192).—The preparation of pyridine derivatives by the primary addition of lithium alkyls and aryls (A., 1930, 1191) has been extended to various substituted pyridines and condensed pyridine systems such as quinoline, *iso*quinoline, and acridine. Decomposition of the additive product of quinoline and lithium butyl (in benzene solution) with water affords a 90% yield of 2-*butyl*-1 : 2-*dihydroquinoline*, b. p. 160—162°/14 mm., 128°/0·06 mm., $d_4^{20\cdot 6}$ 0·9961, $n^{20\cdot 6}$ 1·56959, converted by heating in nitrobenzene into 2-*butylquinoline*, b. p. 153°/14 mm., $d_4^{21\cdot 2}$ 1·0018, $n^{21\cdot 2}$ 1·56932 (*picrate*, m. p. 162—163°). The latter is also obtained (50—60% yield) by thermal decomposition of the *N*-lithium 2-butyldihydroquinoline in an atmosphere of nitrogen, and in this case fractional crystallisation of the picrate affords a small quantity of an isomeric *picrate*, m. p. 145°, indicating that a small amount of 1 : 4-addition of the lithium butyl occurs. Thermal decomposition of the crystalline additive compound of lithium phenyl and quinoline causes decomposition of the expected product, but decomposition with water affords a mixture of 2-phenylquinoline and its 1 : 2-dihydro-derivative, converted completely into the former by heating in nitrobenzene. The lithium derivatives obtained with *iso*quinoline are more stable to heat; that from lithium butyl is decomposed by water in an atmosphere of nitrogen to 1-*butyldihydro*iso*quinoline*, b. p. about 135°/0·4 mm., which is autoxidisable and is converted directly by heating in nitrobenzene into 1-*butyl*iso*quinoline*, b. p. 154—157°/14 mm. (*picrate*, m. p. 185·5°). Decomposition of the product obtained from *iso*quinoline and lithium phenyl with water causes a large amount of dehydrogenation of the dihydro-compound, and heating with nitrobenzene gives 1-phenyl*iso*quinoline, m. p. 97° (lit. m. p. 87—88°: the specimen, m. p. 80°, obtained by Bergmann and others, A., 1930, 1596, is impure). 9-Butyl-9 : 10-dihydroacridine, obtained similarly, has m. p. 105° (lit. m. p. 98—100°). Dehydrogenation of alkyldihydroacridines to the acridine derivative occurs smoothly when they are heated with a slight excess of mercuric oxide in boiling alcohol. Thermal decomposition, in a sealed tube at 100°, of the product obtained by the action of lithium butyl in benzene on 2-butylpyridine affords, mainly, 2 : 5(?)-*dibutylpyridine*, b. p. 243—244° [*chloroplatinate*, m. p. 192·5—193° (decomp.)]. The reaction between lithium alkyls and 2-substituted pyridine or quinoline derivatives yields lithium derivatives of these substances, the structure of which may be either type I or II. With alkyl halides they behave as if they

(I.)   (II.)

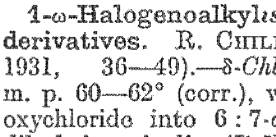
possessed structure I. Thus the lithium compound obtained from lithium phenyl and quinaldine reacts with propyl bromide, benzyl chloride, and allyl chloride to give, respectively, 2-butylquinoline, 2-β-phenylethylquinoline, m. p. 28° (lit. m. p. about 30°), and 2-Δ^{γ}-*butenylquinoline*, b. p. 152·5—154°/14 mm., $d_4^{17\cdot 4}$ 1·0255, $n_\alpha^{17\cdot 4}$ 1·58647 (*picrate*, m. p. 143°), whilst with benzophenone is obtained αα-*diphenyl*-β-(2-*quinolyl*)-*ethyl alcohol*, $C_9H_6N{\cdot}CH_2{\cdot}CPh_2{\cdot}OH$, m. p. 165°, dehydrated by concentrated sulphuric and acetic acids to 2-(β-*phenylstyryl*)*quinoline*, m. p. 103—103·5°. Similarly, lithium methyl converts α-picoline, with evolution of methane, into its lithium derivative, which reacts with benzyl chloride to give 2-(β-phenylethyl)quinoline (*picrate*, m. p. 127°). On the other hand, with carbon dioxide these lithium derivatives react according to the structure II, the products being the parent bases, presumably derived from an intermediate *N*-carboxylic acid. Decomposition of the reaction product of 9-methylacridine and lithium phenyl with water affords only the original base.

J. W. BAKER.

Synthesis of quinoline compounds. VI. Preparation of acylamido-derivatives of 8-hydroxyquinoline. K. MATSUMURA and C. SONE (J. Amer. Chem. Soc., 1931, **53**, 177—179).—The following acetamidohydroxyquinolines are obtained when the appropriate aminohydroxyquinolines (1 mol.) are treated with acetic anhydride (1·1 mols.) in presence of ether and sodium acetate at the ordinary temperature for 3 days: 7-*iodo*-5-*acetamido*-8-*hydroxy*-, m. p. 212° [*hydrochloride*, m. p. 196° (decomp.)]; 5-*acetamido*-8-*hydroxy*-, m. p. 218—219° [*hydrogen sulphate*, m. p. 263° (decomp.)]; 5-*acetamido*-6-*hydroxy*-, m. p. 278° (decomp.) (*hydrogen sulphate*); 7-*acetamido*-8-*hydroxy*-5-*methyl*-, m. p. 203—204° (*sulphate*, m. p. 180°). 7-*Amino*-8-*hydroxy*-5-*methylquinoline*, m. p. 141—142° [*picrate*, decomp. 215—220°; ON-*diacetyl* derivative, m. p. 222° (*hydrogen sulphate*, m. p. 183°); ON-*dibenzoyl* derivative, m. p. 181°, prepared by a method similar to the above using benzoyl chloride in place of acetic anhydride], is obtained when 7-nitroso-8-hydroxy-5-methylquinoline is reduced with stannous chloride and hydrochloric and acetic acids. 5-*Benzamido*-8-*hydroxyquinoline*, m. p. 237—238° [*hydrogen sulphate*, m. p. 225—227° (decomp.)], is prepared by the pyridine method in the cold. Methylation of 8-hydroxy-5-methylquinoline with methyl iodide and methyl-alcoholic potassium hydroxide gives 8-*methoxy*-5-*methylquinoline*, b. p. 298—302°/773

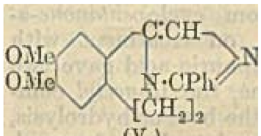
mm. [*picrate*, m. p. 180—181°; *chloroplatinate*, m. p. 224° (decomp.)]. H. Burton.

1-ω-Halogenoalkyl*iso*quinolines and their derivatives. R. Child and F. L. Pyman (J.C.S., 1931, 36—49).—*δ-Chlorovalero-β-veratrylethylamide*, m. p. 60—62° (corr.), was converted by phosphorus oxychloride into 6 : 7-*dimethoxy*-1-*δ-chlorobutyl*-3 : 4-*dihydro*isoquinoline (I) [*hydrochloride*, m. p. 172—173° (corr.)], isolated as its *picrate*, m. p. 156—157° (corr.). The same substance was also obtained together with a little of the picrate of II from *δ-bromovalero-β-veratrylethylamide*, m. p. 70—72° (corr.). Cyclisation of I to 5 : 14-*dehydro*-10 : 11-*dimethoxy*-1 : 2 : 3 : 4 : 6 : 7-*hexahydrobenzpyridocolinium chloride*,



(II), m. p. 197—198° (corr.) (air-dried *salt*, $+HCl,2H_2O$, effervesces at 103° after softening at 90°), isolated as the *picrate*, m. p. 185—186° (corr.), was effected by warming. The iodide has m. p. 210—212°. Reduction of II gave 10 : 11-*dimethoxy*-1 : 2 : 3 : 4 : 6 : 7-*hexahydrobenzpyridocoline*, m. p. 54°, b. p. 225°/15 mm. [*hydrochloride*, m. p. 235—237° (corr., decomp.); picrate, m. p. 172—174° (corr.); *α-methiodide*, m. p. 228° (corr.); *β-methiodide*, m. p. 244—245° (corr.). Partial conversion α——→β at 250°]. *γ-Bromobutyro-β-veratrylethylamide*, m. p. 65° (corr.), which readily decomposes into butyrolactone and *β-veratrylethylamine hydrobromide*, m. p. 179—180° (corr.), with phosphorus oxychloride gave, after treatment of the product with picric acid, a mixture of 6 : 7-dimethoxy-1-γ-chloropropyl-3 : 4-dihydro*iso*quinoline picrate (crude), m. p. 163—164°, and 4 : 13-*dihydro*-9 : 10-*dimethoxy*-1 : 2 : 3 : 5 : 6 : 13-*hexahydrobenzpyrrocolinium picrate*, m. p. 201—202° (corr.). The corresponding *chloride* (III), m. p. 120—122° (corr.) ($+2H_2O$), m. p. of anhydrous material 204—205°, on reduction with tin and hydrochloric acid in alcohol gave 9 : 10-*dimethoxy*-1 : 2 : 3 : 5 : 6 : 13-*hexahydrobenzpyrrocoline*, m. p. 88—89° (corr.) [*hydrobromide*, m. p. 186° (corr.); *picrate*, m. p. 187° (corr., decomp.)]. The relatively greater tendency to form the five-membered ring in III than the six-membered ring in II is emphasised. By similar reactions, *chloroaceto-β-veratrylethylamide*, m. p. 96° (corr.), and *bromoaceto-β-veratrylethylamide*, m. p. 115° (corr.), with phosphorus oxychloride gave 6 : 7-*dimethoxy*-1-*chloromethyl*-3 : 4-*dihydro*isoquinoline *hydrochloride*, darkens at 210°, effervesces at 217° [*picrate*, m. p. 196° (corr., decomp.)], which with aqueous potassium cyanide yielded 1-*cyano*-6 : 7-*dimethoxy*-1-*chloromethyltetrahydro*isoquinoline, softens at 122°, m. p. 125° (corr., decomp.). With aqueous-alcoholic potassium cyanide the latter yielded 6 : 7-*dimethoxy*-1-*cyanomethyl*-3 : 4-*dihydro*isoquinoline (IV), m. p. 173° (corr.) [*hydrochloride*, m. p. 205—206° (corr.); *picrate*, m. p. 225° (decomp.)], also obtained from *cyanoaceto-β-veratrylethylamide*, m. p. 115° (corr.), 127—128° after resolidification, and phosphorus oxy-chloride. Reduction of IV with sodium and alcohol gave, after treatment of the crude base with picric acid, 6 : 7-*dimethoxy*-1-*β-aminoethyltetrahydro*isoquinoline *dipicrate* (40% yield), m. p. 205° (corr.); it crystallises from alcohol with EtOH [dihydrochloride $+H_2O$, m. p. 276—277° with effervescence (corr.)]. Bromoaceto-β-veratrylethylamide with phosphorus pentoxide in xylene led to 6 : 7-*dimethoxy*-1-*bromomethyl*-3 : 4-*dihydro*isoquinoline *picrate*, m. p. 190—191° (decomp., corr.), *chloroaceto-β-m-methoxyphenylethylamide*, m. p. 56—57° (corr.), with phosphorus oxychloride gave 6-*methoxy*-1-*chloromethyl*-3 : 4-*dihydro*isoquinoline *picrate*, m. p. 169—170° (uncorr.), and *chloroaceto-β-piperonylethylamide*, m. p. 72° (corr.), with the same reagent gave 6 : 7-*methylenedioxy*-1-*chloromethyl*-3 : 4-*dihydro*isoquinoline *picrate*, m. p. 179—180° (corr., decomp.), but with *β-chloropropiono-β-veratrylethylamide*, m. p. 102—103° (corr.), it gave no isolable product.

An attempt to prepare 6 : 7-dimethoxy-1-aminomethyl-3 : 4-dihydro*iso*quinoline from *hippuro-β-veratrylethylamide* ($+H_2O$), m. p. 85—95°, by dehydration with phosphorus oxychloride followed by hydrolysis, led unexpectedly to what is considered to be 9 : 10-*dimethoxy*-3-*phenyl*-5 : 6-*dihydrobenzglyoxalocoline* (V), m. p. 187° (corr.) [*hydrochloride*, m. p. 286—287° (corr., decomp.); *hydrobromide*, m. p. 293° (corr.); *methiodide*, m. p. 255° (corr.); *picrate*, m. p. 226—227° (corr.); *mononitro*-derivative, m. p. 202° (corr.)].



(V.)

Demethylation of V yielded 9 : 10-*dihydroxy*-3-*phenyl*-5 : 6-*dihydrobenzylgoxalocoline hydrochloride* ($+3H_2O$), m. p. 293° (corr.). *Hippuro-β-phenylethylamide* has m. p. 161° (corr.).

None of a number of these substances possessed marked amœbicidal, antimalarial, or trypanocidal activity. J. D. A. Johnson.

Preparation of brominated cinchophens [2-phenylcinchoninic acids]. H. G. Lindwall, J. Bandes, and I. Weinberg (J. Amer. Chem. Soc., 1931, **53**, 317—319).—Isatin reacts with *p*-methoxy- and *p*-bromo-acetophenones in aqueous-alcoholic potassium hydroxide forming 2-anisyl-, m. p. 216°, and 2-p-*bromophenyl-cinchoninic acids*, m. p. 293°, respectively. Similarly, 5 : 7-dibromoisatin (conveniently prepared by brominating isatin in 95% alcohol) reacts with acetophenone and *p*-methoxyacetophenone to give 6 : 8-*dibromo-2-phenyl-*, m. p. 270—271°, and 6 : 8-*dibromo-2-anisyl-cinchoninic acids*, m. p. 263—264°, respectively. H. Burton.

Derivatives of pyrrole. I. Synthesis of 3-keto-4 : 5-dihydrodi-(1 : 2)-pyrrole and 8-keto-5 : 6 : 7 : 8-tetrahydropyrrocoline. G. R. Clemo and G. R. Ramage (J.C.S., 1931, 49—55).—Potassium pyrrole and ethyl chloroacetate in benzene gave *ethyl 1-pyrrylacetate*, b. p. 112°/20 mm., hydrolysed to 1-*pyrrylacetic acid*, m. p. 91° (*amide*, m. p. 169°). *Ethyl β-1-pyrrylpropionate*, b. p. 122°/23 mm., and *β-1-pyrrylpropionic acid*, m. p. 62° (*amide*, m. p. 81°), were prepared similarly. Cyclisation of *succino-n-butylimide*, b. p. 140°/17 mm. (from potassium succinimide and *n*-butyl bromide; 80% yield), to a derivative of 5 : 6 : 7 : 8-tetrahydropyrrocoline could not be effected. Potassium pyrrole with β-chloroethyl, β-cyanoethyl, and γ-chloropropyl toluene-*p*-sulphonates yielded 1-*β-chloroethylpyrrole*, b. p. 84°/20 mm., 1-*β-cyanoethylpyrrole*, b. p. 140°/20 mm., and 1-*γ-chloropropylpyrrole*, b. p. 87°/15 mm., respectively.

Cyclisation of 1-β-cyanoethylpyrrole to 3-*keto*-4 : 5-*dihydrodi*-(1 : 2)-*pyrrole*, m. p. 54° (*piperonylidene* derivative, m. p. 194°), was effected by treatment with hydrogen chloride in dry ether in presence of zinc chloride, the product being isolated as its *semicarbazone*, m. p. 211°. γ-Bromobutyronitrile and potassium pyrrole gave γ-1-*pyrrylbutyronitrile*, b. p. 152°/23 mm., cyclised to 8-*keto*-5 : 6 : 7 : 8-*tetrahydropyrrocoline*, m. p. 34° (*semicarbazone*, m. p. 193°; *piperonylidene* derivative, m. p. 136°). *Ethyl* β-1-*pyrroylpropionate*, m. p. 50°, b. p. 162°/22 mm., and β-1-*pyrroylethyl methyl ketone*, b. p. 148°/16 mm. (*phenylhydrazone*, m. p. 131°; *semicarbazone*, m. p. 190°), are also described. J. D. A JOHNSON.

Action of nitric acid on polycyclic indole derivatives. IX. S. A. BRYANT and S. G. P. PLANT (J.C.S., 1931, 93—105).—7 : 8-*Dihydro*-αβ-*naphthapentindole* (I), m. p. 167° [picrate, m. p. 167° (decomp.)], prepared from cyclo*pentanone*-α-*naphthylhydrazone*, m. p. 95°, on treatment with acetic anhydride containing sulphuric acid gave two isomeric acetyl derivatives; one, the 10-*acetyl* compound, m. p. 157°, reverted to the base on hydrolysis, the other (m. p. 215°) is presumed to be 1(?)-*acetyl*-7 : 8-*dihydro*-αβ-*naphthapentindole*, since it cannot be hydrolysed, and it forms an *oxime*, m. p. 236° (decomp.). cyclo*Pentanone*- β - *naphthylhydrazone*, m. p. 77°, similarly gave 9 : 10-*dihydro*-α′ -*naphthapentindole* (II), m.p. 103° [picrate, m.p. 189° (decomp.); *benzoyl* derivative, m. p. 196°; *carbethoxy*-derivative, m. p. 160°]. This product could also be an isomeric substance the formation of which would involve fusion of the indole and naphthalene nuclei through the ββ′-positions of the latter. This constitution is considered improbable, since the analogous cyclisation of *cyclo*hexanone-β-naphthylhydrazone has been shown to lead to the αβ-derivative (Oakeshott and Plant, A., 1928, 1023). Acetylation of II with acetyl chloride in acetone in presence of alkali gave 7-*acetyl*-9 : 10-*dihydro*-α′ -*naphthapentindole*, m. p. 170° (readily hydrolysed to the base), which with acetic anhydride in presence of concentrated sulphuric acid gave 5(?) : 7-*diacetyl*-9 : 10-*dihydro*-α′ -*naphthapentindole* (III), m. p. 234°. Hydrolysis of the latter gave 5(?)-*acetyl*-9 : 10-*dihydro*-α′β′-*naphthapentindole*, m. p. 239°, which could be reacetylated to III and gave a *benzoyl* derivative, m. p. 163°. Nitration of the 7-*acetyl*, 7-*benzoyl*, and 7-*carbethoxy*-derivatives of II gave 5(?)-*nitro*-7-*acetyl*-, m. p. 247°, 5-(?)-*nitro*-7-*benzoyl*-, m. p. 259°, and 5(?)-*nitro*-7-*carbethoxy*- m. p. 202°, -9 : 10-*dihydro*-α′β′-*naphthapentindoles*, each of which on hydrolysis yielded 5(?)-*nitro*-9 : 10-*dihydro*-α′ -*naphthapentindole*, m. p. 228°. From the carbethoxy-derivative a *dinitro*-compound, m. p. 220° (decomp.), was also obtained.

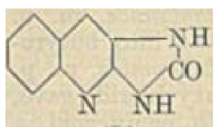
Cyclisation of 2-methyl*cyclo*hexanone-β-naphthylhydrazone gave two products, IV, m. p. 115° [picrate, m. p. 201° (decomp.)], and V, m. p. 92° (picrate, m. p. 166°), the former of which was shown to be 8-*methyl*-8 : 9 : 10 : 11-*tetrahydro*-α′β′-*naphthacarbazole*, since dehydrogenation led to 8-*methyl*-α′β′-*naphthacarbazole*, m. p. 144°, rationally synthesised from 2-hydroxy-3-naphthoic acid and *o*-tolylhydrazine through 8-methyl-α′β′-naphthacarbazole-6-carboxylic acid, m. p. 320°, by decarboxylation of the latter. By analogy, to product V the constitution of 12-*methyl*-8 : 9 : 10 : 11-*tetrahydro*-α′β′-*naphthacarbazolenine* is assigned. The constitutions given to IV and V by Cecchetti and Ghigi (A., 1930, 787) are therefore incorrect.

Treatment of 5 : 6-dihydro-αβ-naphthacarbazole with acetic anhydride containing a little sulphuric acid gave the 1(?)-*acetyl* derivative, m. p. 253°, b. p. about 370°/40 mm., not hydrolysed by alcoholic potassium hydroxide, and forming an *oxime*, m.p. 292° (decomp.).

Benzoylation of benzopentindole gave the 7-*benzoyl* derivative, m. p. 187°, which, treated in acetic acid with nitric acid, gave 14-*nitro*-6-*hydroxy*-7-*benzoyl*-6 : 14-*dihydrobenzopentindole*, m. p. 169° (decomp.), hydrolysed by aqueous potassium hydroxide to 14-*nitro*-6-*hydroxy*-6 : 14-*dihydrobenzopentindole* [not pure, m. p. 200° (decomp.)].

J. D. A. JOHNSON.

Condensation of hydantoin with *o*-nitrobenzaldehyde. J. KOZAK and L. MUSIAŁ (Bull. Acad. Polonaise, 1930, A, 432—438).—Hydantoin and *o*-nitrobenzaldehyde condense in presence of zinc chloride at 100—110°, forming 5-*o*-*nitrobenzylidenehydantoin*, m. p. 278—280° (decomp.), reduced by red phosphorus and hydriodic acid to the quinoline *derivative* (I), m. p. 348—349°.



(I.)

Nitration of 5-*o*-nitrobenzylidenehydantoin affords the 1-*nitro*-derivative, m. p. 224—226° (decomp.), whilst bromination and chlorination in acetic acid gives the 1-*bromo*-, m. p. 247—248°, and the 1 : 3-*dichloro*-derivatives, m. p. 180—182° (decomp.), respectively. Oxidation of the nitrobenzylidenehydantoin with ozone in acetic acid affords *o*-nitrobenzaldehyde and parabanic acid, whilst oxidation of its 1-nitro- and halogeno-derivatives with alkaline potassium permanganate gives *o*-nitrobenzoic acid. H. BURTON.

New product derived from pyramidone. R. CHARONNAT and R. DELABY (Bull. Sci. pharmacol., 1930, 37, 7—27, 75—89; Chem. Zentr., 1930, ii, 1988—1989; cf. A., 1930, 223, 329, 351).—The preparation of dioxypyramidone, and its solubility relationships with pyramidone and antipyrine, are described. Colour reactions for distinguishing the substances are described. Dioxypyramidone is stable towards oxidising agents, halogens, acid dyes, tannin, mercury and silver compounds, alkaloidal salts, and phenols. Partial hydrolysis affords α-acetyl-β-phenyl-α-methylhydrazine and (with barium hydroxide) barium dimethyloxamate. A. A. ELDRIDGE.

Relation of quinoxaline to the ammonia system. F. W. BERGSTROM and R. A. OGG, jun., (J. Amer. Chem. Soc., 1931, 53, 245—251).—Quinoxaline [additive *compound* (1 : 2) with sodium hydrogen sulphite] reacts with ethereal magnesium phenyl bromide in nitrogen forming *dl*-2 : 3-diphenyl-1 : 2 : 3 : 4-tetrahydroquinoxaline (the corresponding 2 : 3-dimethyl derivative is prepared similarly, using magnesium methyl iodide), and with alcoholic hydrogen cyanide at 100° giving about 30% of 2 : 3-*dicyano*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, m. p. 168·5° (corr.)

[*diacetyl* derivative, m. p. 93·5° (corr.)]. Oxidation of quinoxaline with aqueous ammonium persulphate affords 2 : 3-dihydroxyquinoxaline, whilst treatment with two equivalents of potassamide in liquid ammonia gives the dipotassium salt of fluorubin (Hinsberg and Schwantes, A., 1904, i, 198) and tar. The above reactions are in accordance with the behaviour of quinoxaline as an ammonoglyoxal. Pyrazine does not undergo any of the above reactions.

H. BURTON.

ψ-Bases. I. N-Methylpyrazinium salts and their corresponding bases. J. G. ASTON (J. Amer. Chem. Soc., 1930, **52**, 5254—5262).—Mainly a more detailed account of work previously reviewed (A., 1930, 1597). The following is new. 6-*Hydroxy*-1 : 2 : 2 : 5 : ψ-*pentamethyltetrahydropyrazine chloroplatinate* has m. p. 282° (decomp.). The same *chloroplatinate*, m. p. about 285° (decomp.), is obtained from 1 : 2 : 2 : 3 : 5 : 5 - hexamethyl-6 - methylenetetrahydropyrazine and 1 : 2 : 2 : 3 : 5 : 5 : 6-heptamethyldihydropyrazinium iodide (after treatment with silver chloride).

H. BURTON.

Spectrochemical study of amino-acid anhydrides. IV. Light absorption of azlactones, diketopiperazines, hydantoins, and thiohydantoins. T. ASAHINA (Bull. Chem. Soc. Japan, 1930, **5**, 354—365).—In continuance of previous work (A., 1926, 659; 1928, 218; 1929, 1362), solutions (usually alcoholic) of the following substances were examined spectroscopically: the azlactones of *o*-, m. p. 158·6° (lit. 137—138°), *m*-, and *p*-acetoxy-, m. p. 177·5° (lit. 172—173°), and o-, m. p. 161°, *m*-, and *p*-methoxybenzylidenehippuric acids; α-benzamidocinnamic acid; α-benzamido-*o*-, m. p. 199·5° (decomp.; lit. 185·5°), and -*p*-hydroxycinnamic acids; α-benzamido-*o*-, m. p. 208°, -*m*-, and -*p*-methoxycinnamic acids; 3 : 6-dibenzylidene- and 3 : 6-difurfurylidene-2 : 5-diketopiperazines; 5-benzylidene- and 5-furfurylidene-hydantoins; 2-thiohydantoin [1-acetyl, 1-benzoyl, 5-benzylidene, and 5-*furfurylidene*, m. p. 255° (decomp.), derivatives]; 2-thio-5-benzylhydantoin (1-acetyl derivative), and 2-thio-5-*p*-hydroxybenzylhydantoin. The α-benzamido-acids are less bathochromic than the corresponding azlactones, whilst the thiohydantoins are more bathochromic than the corresponding hydantoins.

H. BURTON.

Pyrimidines. CXIX. Determination of constitution of alkylation products of phenyluracil and phenylhydrouracil. J. EVANS and T. B. JOHNSON (J. Amer. Chem. Soc., 1930, **52**, 4993—5005).—Treatment of 6-phenyluracil with methyl iodide in methyl-alcoholic sodium methoxide gives a mixture of 6-*phenyl*-3-*methyl*-, m. p. 228—230°, and -*phenyl*-1 : 3-*dimethyl-uracil*, m. p. 122—122·5°; the former of these is also obtained when its 5 : 6-dihydro-derivative is heated with bromine in acetic acid. Ethyl chloroacetate and 6-phenyluracil (*potassium* salt, not melted at 300°) in alcoholic sodium ethoxide affords *ethyl* 6-*phenyluracil*-3-*acetate*, m. p. 205—206° [free *acid*, m. p. 304—305°, converted by methyl sulphate into 6-*phenyl*-1-*methyluracil*-3-*acetic acid*, m. p. 261—263° (*methyl* ester, m. p. 157—157·5°; *ethyl* ester, m. p. 109—110°), which could not be reduced]. Benzaldehyde, malonic acid, and ammonium acetate react in boiling alcohol to give cinnamic and β-amino-β-phenylpropionic acids, m. p. 215—216° (lit. 228—231°). The amino-acid and potassium cyanate afford the corresponding carbamide, which when heated with 10% hydrochloric acid, passes into 6-phenyl-5 : 6-dihydrouracil. Treatment of the sodium derivative of this with methyl iodide in alcohol gives 6-*phenyl*-3-*methyl*-5 : 6-*dihydrouracil*, m. p. 149—150·5°, hydrolysed by barium hydroxide and aqueous methyl alcohol to β-(γ′-*methylcarbamido*)-β-*phenylpropionic acid*, m. p. 178° (decomp.). The sodium salt of the phenyldihydrouracil and ethyl chloroacetate afford mainly *ethyl* 6 *phenyl*-5 : 6-*dihydrouracil*-3-*acetate*, m. p. 154·5—156° [5-*bromo*-derivative, m. p. 259—261° (decomp.)], hydrolysed to a mixture of the corresponding *acid*, m. p. 228—231°, and an acid, m. p. 170—180° (ethyl ester, m. p. 132—135°).

Benzylidenemethylamine reacts with malonic acid in alcohol, forming, by way of α-*methylaminobenzylmalonic acid*, decomp. 147°, a mixture of cinnamic and β-*methylamino*-β-*phenylpropionic acids*, m. p. 168·5—169°. The amino-acid and potassium cyanate give β-(α-*methylcarbamido*)-β-*phenylpropionic acid*, m. p. 165—167°, converted by hot 10% hydrochloric acid into 6-*phenyl*-1-*methyl*-5 : 6-*dihydrouracil*, m. p. 158—159·5° [5-*bromo*-derivative, m. p. 214—215° (decomp.), which when heated passes into 6-phenyl-1-methyluracil]. Treatment of the sodium derivatives of 6-phenyl-1-methyluracil and its 5 : 6-dihydro-derivative with ethyl chloroacetate gives ethyl 6-phenyl-1-methyluracil-3-acetate and its 5 : 6-*dihydro*-derivative, m. p. 70—71°, respectively.

H. BURTON.

Azo-compounds from ketotrimethylmethylenepyrazine. VII. E. PRINCIVALLE (Gazzetta, 1930, **60**, 963—966; cf. A., 1928, 1027; 1929, 196, 197; 1930, 223, 929).—6-Keto-1 : 2 : 4-trimethyl-5-methylene-1 : 4 : 5 : 6-tetrahydropyrazine (1 mol.) reacts with (1) phenylhydrazine (1 mol.) or benzenediazonium chloride, giving 6-*keto*-1 : 2 : 4-*trimethyl*-ψ-*benzeneazomethylene*-1 : 4 : 5 : 6-*tetrahydropyrazine*,

$NPh{:}N{\cdot}CH{:}C{<}{\genfrac{}{}{0pt}{}{CO{\cdot}NMe}{NMe{\cdot}CH}}{>}CMe$, m. p. 201° (decomp.),

which forms a *hydriodide*, m. p. 228° (decomp.), and (2) *p*-toluenediazonium chloride, giving 6-*keto*-1 : 2 : 4-*trimethyl* - 5 - p - *tolueneazomethylene* - 1 : 4 : 5 : 6 - *tetrahydropyrazine*, m. p. 214° (decomp.), which forms a *hydrochloride*, m. p. 205° (decomp.), and a *hydriodide*, m. p. 226° (decomp.).

T. H. POPE.

***neo*Nicotine and isomeric pyridylpiperidines.** C. R. SMITH (J. Amer. Chem. Soc., 1931, **53**, 277—283).—neo*Nicotine* [2-(3′-*pyridyl*)*piperidine*], b. p. 280—281°/775 mm. [*picrate*, m. p. 213° (corr.)], is also formed when pyridine is treated with sodium under the conditions previously described (A., 1924, i, 558); it is reduced catalytically (Adams) to 2 : 3′-dipiperidyl. Reduction of 2 : 3′-dipyridyl with tin and hydrochloric acid gives isoneo*nicotine* [3-(2′-*pyridyl*)*piperidine*], b. p. 282° (slight decomp.)/760 mm. [*picrate*, m. p. 217—218° (corr.)]. Similar reduction of 2 : 2′-, 4 : 4′-, 3 : 3′-, and 3 : 4′-dipyridyls affords varying amounts of 2-(2′-*pyridyl*)-*piperidine*, b. p. 265—266°/756 mm. (*picrate*, m. p. 187°), 4-(4′-pyridyl)piperidine [*iso*nicotine], 3-(3′-

pyridyl)piperidine [nicotidine], and 4-(3'-*pyridyl*)-*piperidine* (*picrate*, m. p. 240° with slight darkening). Nicotimine (Pictet and Rotschy, A., 1901, i, 339) is probably not 2-(3'-pyridyl)piperidine.

H. BURTON.

γ-Triazines: synthesis of thiolamino-ethyl- and -propyl-triazines and new data on thiolimino-methyltriazine. A. OSTROGOVICH and V. GALEA (Atti R. Accad. Lincei, 1930, [vi], **11**, 1012—1019; cf. A., 1912, i, 320).—2-*Amino*-6-*thiol*-4-*ethyl*-1 : 3 : 5-*triazine*, m. p. 257—258° (decomp.), forms a *picrate*, m. p. 188—189° (decomp.), and a *silver* salt. 2-*Amino*-6-*thiol*-4-*propyl*-1 : 2 : 3-*triazine*, m. p. 262—263° (decomp.), forms a *picrate*, m. p. 153° (decomp.), and a *silver* salt. 2-Amino-6-thiol-4-methyl-1 : 2 : 3-triazine (*loc. cit.*) forms anhydrous crystals from hot solutions and hydrated ($1H_2O$) from cold solutions, and gives a *picrate*, m. p. 196—197° (decomp.), and a *silver* salt.

T. H. POPE.

γ-Triazines: synthesis of two aralkylamino-thioltriazines. A. OSTROGOVICH and V. GALEA (Atti R. Accad. Lincei, 1931, [vi], **12**, 162—165; cf. A , 1930, 1449; this vol., 239).—2-*Amino*-4-*thiol*-6-*benzyl*-1 : 3 : 5-*triazine*, m. p. 270—271° (decomp.), prepared under the conditions employed for obtaining the corresponding alkyl derivatives, forms *silver* and *copper* ($+0{\cdot}5H_2O$) salts and a *picrate*, m. p. 187—188° (decomp.). 2-*Amino*-4-*thiol*-6-*styryl*-1 : 3 : 5-*triazine*, m. p. 284—285° (decomp.), prepared in the cold, forms a *copper* salt and a *picrate*, m. p. 221—222° (decomp.).

T. H. POPE.

Pyrrole compounds with amino-groups and unsaturated side-chains. H. FISCHER and K. ZEILE (Annalen, 1930, **483**, 251—271; cf. A., 1930, 1298).—Ethyl 3-amino-2 : 4-dimethylpyrrole-5-carboxylate (I) (*acetyl* compound, m. p. 201°) is better prepared by nitrosation of ethyl 2 : 4-dimethylpyrrole-5-carboxylate, followed by reduction, than by reduction of the nitropyrrole (cf. Fischer and Stern, A., 1926, 303); the *diazonium chloride* (from I and *iso*amyl nitrite), decomp. 175°, is not convertible in the usual way into a hydroxy-compound, nitrogen being eliminated with formation of ethyl 2 : 4-dimethyl-pyrrole-5-carboxylate, m. p. 125°. 3-*Amino*-2 : 4-*dimethylpyrrole*-5-*carboxylic acid* (by hydrolysis of I) (*acetyl* derivative, m. p. 203°) is converted at 75°, with loss of carbon dioxide, into 3-*amino*-2 : 4-*dimethylpyrrole*, m. p. 127° (*acetyl* derivative, m. p. 205°); the last-named is unstable, readily losing ammonia, and cannot be diazotised. Attempts to obtain a pyrrole substituted by an $NH{\cdot}CH_2{\cdot}CO_2H$ grouping by interaction of I and chloroacetic acid were unsuccessful.

The action of hydrobromic and formic acids on I (the corresponding acid or its acetyl compound) affords (3-*amino*-2 : 4-*dimethylpyrryl*)-(3'-*amino*-2' : 4'-*dimethylpyrrolenyl*)*methene hydrobromide* (II), decomp. above 280°; sodium acetate causes elimination of 2 mols. of hydrogen bromide from II, yielding the *monohydrobromide*, m. p. 234°; the free methene could not be crystallised. Attempts to synthesise porphyrins from II by the succinic acid fusion method (cf. A., 1928, 1384) were successful.

Bromination of the acetyl derivative of I gives an unstable bromo-compound, converted by boiling water into *ethyl di* (3-*acetamido*-4-*methyl*-2-*pyrryl*)*methane*-5 : 5'-*dicarboxylate*, m. p. 251° (after sintering) (corresponding 5 : 5'-*dicarboxylic acid*, m. p. 214°). The latter, when boiled with formic acid in the presence of iron powder, affords traces of impure 1 : 4 : 5 : 8-*tetramethyl*-2 : 3 : 6 : 7-*tetra-acetylaminoporphin*, which shows absorption bands at 598·9, 578·4, and 552·8 μμ.

Bromination of ethyl 2 : 4-dimethyl-3-(β-dicyano-vinyl)pyrrole-5-carboxylate (III) (A., 1924, i, 543) affords a perbromide, converted by hydrogen sulphites into a monobromo-derivative, probably *ethyl* 2-*bromomethyl*-4-*methyl*-3-(β-*dicyanovinyl*)*pyrrole*-5-*carboxylate*, m. p. 258°, which, like the bromo-derivative of ethyl 3-chloroacetyl-2 : 4-dimethylpyrrole-5-carboxylate (A., 1930, 1298), is unreactive. Bromination of the same compound in methyl alcohol yields *ethyl* 2-*carbomethoxy*-4-*methyl*-3-(β-*dicyanovinyl*)-*pyrrole*-5-*carboxylate*, m. p. 187°, hydrolysed to 4-*methylpyrrole*-3-*aldehyde*-2 : 5-*dicarboxylic acid*, m. p. above 360°; the *methyl* ester of the latter has m. p. 180° (*oxime*, m. p. 221°; *semicarbazone*, m. p. 247°). 5-*Carbethoxy*-4-*methyl*-3-(β-*dicyanovinyl*)*pyrrole*-2-*carboxylic acid*, m. p. above 360°, results from the action of sulphuryl chloride on III.

Hydrolysis of III affords *ethyl* 2 : 4-*dimethyl*-3-(β-*carboxyvinyl*)*pyrrole*-5-*carboxylate* (*methyl* ester, m. p. 150°); carbon dioxide could not be eliminated from this compound without loss of the vinyl and carbethoxyl side-chains, the products obtained by vacuum distillation being 2 : 4-dimethylpyrrole and the corresponding methene (hydrobromide; picrate, m. p. 215°). The action of sulphuryl chloride on the acrylic acid above yields 5-*carbethoxy*-4-*methyl*-3-*chlorovinylpyrrole*-2-*carboxylic acid*, m. p. 241° (corresponding 2 : 5-*dicarboxylic acid*, does not melt); the same reagent converts ethyl 2 : 4-dimethylpyrrole-3-aldehyde-5-carboxylate into 3-*chloro*-5-*carbethoxy*-4-*methylpyrrole*-2-*carboxylic acid*, m. p. 260°.

Condensation of 2 : 4-dimethylpyrrole-3 : 5-dialdehyde with cryptopyrrole and 2 : 4-dimethyl-3-pyrryl methyl ketone, respectively, in presence of hydrobromic acid affords 4'-*aldehydo*-3 : 3' : 5 : 5'-*tetramethyl*-4-*ethylpyrromethene hydrobromide* and (3-*aldehydo*-2:4-*dimethylpyrryl*)-(3'-*acetyl*-2' : 4'-*dimethylpyrrolenyl*)*methene hydrobromide*, m. p. 210°.

A molecular *compound* of ethyl 2 : 4-dimethyl-3-β-nitrovinylpyrrole-5-carboxylate (A., 1924, i, 543) with nitromethane is described.

[With G. LECHNER.] The action of sulphuryl chloride on ethyl 2 : 4-dimethylpyrrole-3-thioaldehyde-5-carboxylate (A., 1926, 303), an improved preparation of which is described, leads to 5-*carbethoxy*-4-*methylpyrrole*-3-*aldehyde*-2-*carboxylic acid*, m. p. 169° (*anil*, m. p. 225°; *phenylhydrazone*, m. p. 235°).

R. CHILD.

Chlorophyll series. IV. Degradation of chlorophyll and allomerised chlorophyll to simple chlorins. J. B. CONANT, J. F. HYDE, W. W. MOYER, and E. M. DIETZ (J. Amer. Chem. Soc., 1931, **53**, 359—373).—Pyrochlorin *e*, $C_{32}H_{36}O_2N_4,H_2O$ (cf. A., 1930, 225), obtained in improved yield when a 1% solution in diphenyl is boiled for 5 min., affords a *methyl* ester, m. p. 184° (*copper* salt), apparently isomeric with phylloporphy-

rin methyl ester. Reduction of pyrochlorin *e*, catalytically or with hydriodic acid in acetic acid, and oxidation of the resultant product with air gives phylloporphyrin in good yield; a phyllochlorin is also produced which affords a *methyl* ester, $C_{32}H_{40}O_2N_4$, m. p. 150°, differing from the phyllochlorin ester of Treibs and Wiedemann (A., 1929, 941). Pyrochlorin *e* is considered to be a normal degradation product of chlorophyll. "Pyrochlorin *e*-porphyrin" (*loc. cit.*), identical with the chloroporphyrin e_3 of Fischer and Moldenhauer (A., 1930, 482), is separable by fractionation with ether and hydrochloric acid into phylloporphyrin and *pyrochloroporphyrin* (*methyl* ester, $C_{33}H_{38}O_2N_4$, m. p. 226—237°). The last-named porphyrin is converted into phylloporphyrin by reduction and re-oxidation as above.

Treatment of crude phæophytin ($a+b$) with propyl-alcoholic potassium hydroxide in ethereal pyridine, and methylation of the resultant product with ethereal diazomethane gives the dimethyl derivative of phæopurpurin 7 (A., 1930, 1299). When phæopurpurin 7 is heated with diphenyl, carbon monoxide and dioxide are evolved and a mixture of small amounts of pyroporphyrins (acid numbers 6 and 8) and 15—16% of *chlorin* f *monomethyl* ester [methylated further to the *dimethyl* ester, m. p. (block) 182°] is produced. Hydrolysis of phæopurpurin 7 with propyl-alcoholic potassium hydroxide gives potassium oxalate, porphyrins, and *chlorin* f, $C_{32}H_{38}O_4N_4$, indicating that it is an α-keto-acid. When chlorin *f* is heated, a considerable amount of pyrroporphyrin is produced. Rhodoporphyrin is formed when chlorin *f* methyl ester is treated with alcoholic potassium hydroxide in presence of pyridine and magnesium oxide and when the dimethyl ester is reduced with hydriodic and acetic acids.

When chlorophyll *a* is allomerised by keeping in alcohol for 24—48 hrs. and the resultant product hydrolysed with alcoholic potassium hydroxide, phæopurpurin 7 (isolated as its dimethyl derivative after treatment with diazomethane) is obtained. Formulæ are suggested for chlorin *f* and pyrochlorin *e*.

H. BURTON.

ψ-Bases in the *iso*oxazole series. III. E. P. KOHLER and C. L. BICKEL (J. Amer. Chem. Soc., 1930, **52**, 4943—4949).—5-*p*-Chlorobenzoyl-3 : 4-diphenyl*iso*oxazole, m. p. 165—166° (A., 1930, 786) (improved preparation given), is treated with ethyl sulphate at 125—130°, the product hydrolysed with diluted (1 : 1) hydrochloric acid, and the solution treated with ferric chloride whereby 5-p-*chlorobenzoyl*-3 : 4-*diphenyl*-2-*ethyl*isoo*xazolinium ferrichloride*, two forms, m. p. 130·5° and 139° (the corresponding *hydrogen sulphate*, m. p. 192—193°, separates from the hydrolysed solution), is produced. Treatment of the ferrichloride with aqueous sodium hydrogen carbonate in ether gives the *ψ-base*,

$$\begin{matrix}CPh\text{———}C(OH)\cdot CO\cdot C_6H_4Cl\\ CPh\cdot NEt\cdot O\end{matrix}$$

m. p. about 128° (decomp.), which when kept decomposes to *p*-chlorobenzoic acid and 3 : 4-*diphenyl*-2-*ethyl*isoo*xazolone*, m. p. 145—146°; the *iso*oxazolone is also prepared by Kohler and Blatt's method (A., 1928, 430). Attempted preparation of the methyl ether of the ψ-base results in the formation of *p*-chlorobenzoic acid and *methyl* β-*ethylamino*-α-*phenylcinnamate*, m. p. 101—102° (ozonolysis products benzoic acid and benzethylamide). Hydrolysis of this ester with hydrochloric acid at the ordinary temperature gives methyl benzoylphenylacetate and deoxybenzoin. 3 : 4-*Diphenyl*-2-*ethyl*isoo*xazolinium ferrichloride*, m. p. 75—76°, is converted by aqueous alkali into the *ether*, $\left(\begin{matrix}CPh\text{——}CH\cdot\\ CPh\cdot NEt\cdot O\end{matrix}\right)_2O$, m. p. 148°, which with methyl-alcoholic sodium hydroxide affords the above cinnamate.

H. BURTON.

Constitution of indophenine. G. HELLER (Chem.-Ztg., 1930, **55**, 985).—In support of his own quinonoid formula (Z. angew. Chem., 1924, **37**, 1017) for indophenine and criticism of the more recent one of Steinkopf and Roch (this vol., 104) the author briefly reviews previous work and refers *inter alia* to Schotten's isatin-blue, which must be quinonoid, and to the inability of the formula of Steinkopf and Roch to explain the colour of mesoxyphenine.

L. J. HOOLEY.

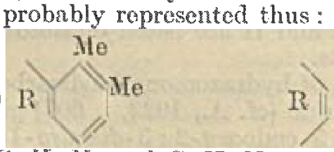
Constitution of the so-called dithiourazole of Freund. IV. Isomerism of hydrazodithiodicarbonamides, iminothiolthiodiazoles, and iminothiodiazolones. S. L. JANNIAH and P. C. GUHA (J. Amer. Chem. Soc., 1930, 52, 4860—4866).—Short treatment of hydrazodithiodicarbonamide, $NH_2\cdot CS\cdot NH\cdot NH\cdot C(:NH)\cdot SH$, m. p. 223° (absorption curve shows one band), with boiling 2*N*-hydrochloric acid gives an *isomeride*, $[SH\cdot C(:NH)\cdot NH\cdot]_2$, m. p. 203° (absorption curve shows two bands), also obtained when the original substance is dissolved in 2*N*-sodium hydroxide, the solution kept for 24 hrs., and then acidified. When the more fusible form is heated at 120° for 24 hrs., it passes into the less fusible modification. Both isomerides give the same derivatives and are converted by short treatment with hydrochloric acid (*d* 1·19) into 2-*imino*-5-*thiol*-2 : 3-*dihydro*-1 : 3 : 4-*thiodiazole* (I), m. p. 234°. The acetyl derivative, m. p. 303°, obtained from this is hydrolysed by 2*N*-hydrochloric acid to 2 : 5-endo*imino*-2-*thiol*-2 : 3-*dihydro*-1 : 3 : 4-*thiodiazole* (II), m. p. 244° (also acetylated to the acetyl derivative of m. p. 303°), also formed when I and the isomeric hydrazodithiodicarbonamides are heated with 5*N*-hydrochloric acid; II is identical with the dithiourazole of Freund (A., 1895, i, 400). The structures assigned to I and II are based on absorption spectra measurements.

Treatment of hydrazomonothiodicarbonamide with acetic anhydride (cf. A., 1923, i, 607) gives probably 2-*amino*-2 : 5-endo*oxy*-2 : 3-*dihydro*-1 : 3 : 4-*thiodiazole*, m. p. 235°.

H. BURTON.

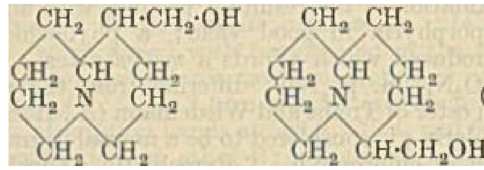
Yohimbine. II. F. MENDIK and J. P. WIBAUT (Rec. trav. chim., 1931, 50, 91—111; cf. A., 1929, 335).—Dehydrogenation of yohimbine or yohimboaic acid with selenium at 300° affords *yobyrine*, $C_{19}H_{18}N_2$, m. p. 217° (*loc. cit.* described as a substance $C_{18}H_{16}N_2$, m. p. 212—213°) (*hydrochloride*, m. p. 300°; *methiodide*), *dihydroyobyrine*, $C_{19}H_{20}N_2$, m. p. 170° (*methiodide*), and *ketoyobyrine*, $C_{20}H_{16}ON_2$, m. p. 328° (*loc. cit.*, m. p. 326°), the nomenclature being based on the hypothetical substance yobine, $C_{19}H_{24}N_2$, derived from yohimbine, $C_{19}H_{22}N_2(OH)\cdot CO_2Me$, by replace-

ment of the hydroxyl and carbomethoxy-groups by hydrogen. Yobyrine is probably identical with the substance, m. p. 211°, obtained by Hahn and Schuch (A., 1930, 1194) by heating yohimboaic acid with selenium and soda-lime in a high vacuum at 300—350°, but the ether structure, $(C_{18}H_{12}N_2)O_2$, assigned by these investigators is considered improbable. Similar dehydrogenation of diacetylyohimbine (Hahn and Schuch, *loc. cit.*; cf. Schomer, A., 1927, 1097) affords yobyrine and dihydroyobyrine, but no ketoyobyrine, whilst a small quantity of an oil, b. p. 135° (approximately), possibly selenoacetic acid, AcSeH, was also isolated. When the *methosulphate* of yobyrine is treated with potassium hydroxide in boiling aqueous solution, a *substance*, m. p. 192—195°, is obtained which, although the analytical data agree best with $C_{20}H_{18}ON_2$, is probably the methoxy-compound, $C_{20}H_{20}ON_2$, obtained by simultaneous oxidation and reduction in accordance with the known behaviour of quinolinium and acridinium bases. Fusion of ketoyobyrine with potassium hydroxide at 345—350° affords a basic *substance*, $C_{11}H_{10}O_2N_2$, m. p. 258°, and 1 : 2-dimethylbenzoic acid (hemellitic acid), m. p. 142—144°, identical with a specimen synthesised by the action of mercury fulminate on *o*-xylene in carbon disulphide in the presence of aluminium chloride and separation of the resulting 2 : 3- and 3 : 4-dimethylbenzonitriles or of the benzoic acids obtained on hydrolysis. The solubility of the calcium salt of hemellitic acid decreases with rise of temperature. By the usual Fischer indole synthesis from the *o*-, *m*-, and *p*-tolylhydrazones of propaldehyde are obtained, respectively, 3 : 7-, b. p. 281—282° (*picrate*, m. p. 142—143°), 3 : 6-, m. p. 116—117° (*picrate*, m. p. 179—180°), and 3 : 5-, b. p. 277—278°, m. p. 74·5° (*picrate*, m. p. 179—180°), *-dimethylindole*, but none of these is identical with the supposed dimethylindole (picrate, m. p. 156—157°) obtained by heating yohimbine hydrochloride with alkali and superheated steam or by distillation of yohimbine with zinc dust (Winterstein and Walter, A., 1927, 1208). If the latter is a dimethylindole it can only be the 3 : 4-derivative. The significance of these results and others in the literature in relation to the structure of yohimbine is discussed, and it is suggested that the relationship of yobyrine, $C_{19}H_{18}N_2$ (I), to the base $C_{13}H_{12}N_2$ (II) obtained by Winterstein and Walter (*loc. cit.*) is probably represented thus :

(I.)  (II.)

The bases $C_{13}H_{12}N_2$ and $C_{12}H_{10}N_2$ (1 methyl group lost by reduction) probably contain the benzene ring which is isolated as *iso*quinoline (Winterstein and Walter, *loc. cit.*) and not as the dimethylindole, that in the latter being the one isolated as 1 : 2-dimethylbenzoic acid. On this hypothesis yohimbine contains a reduced benzene nucleus and not a tetrahydro*iso*quinoline or a tetrahydroquinoline ring as suggested by Hahn and Schuch (*loc. cit.*) and by Schomer (*loc. cit*), respectively. J. W. Baker.

Constitution of lupinine. I. K. Winterfeld and F. W. Holschneider (Ber., 1931, 64, [*B*], 137—150; cf. Schöpf, A., 1928, 1144).—Examination of lupinine confirms the structure I suggested by Karrer

(I.)  (II.)

and others (A., 1929, 200) and shows the presence of a structural isomeride (II), for which the name allo*lupinine* is suggested.

Lupinine, m. p. 68—69°, is converted by treatment with acetic and sulphuric acids at 180° into anhydrolupinine, which is hydrogenated in presence of palladised calcium carbonate to lupinane, $C_{10}H_{19}N$, b. p. 82—83°/13 mm. Treatment of the last-named compound with cyanogen bromide in boiling benzene produces *bromolupinanecyanoamide*, $C_{11}H_{19}N_2Br$, which does not yield crystalline salts. Replacement of the bromine atom by hydrogen is effected with difficulty, but *lupinanecyanoamide*, $C_{11}H_{20}N_2$, is obtained in 85% yield by treatment with potassium hydroxide in methyl alcohol and then with hydrogen in presence of palladised calcium carbonate. As by-product, a base, $C_{11}H_{21}N_2$, is isolated as the *chloroplatinate*, $(C_{11}H_{21}N_2)_2,H_2PtCl_6$, m. p. 217—218° (decomp.), and *mercury* salt. Hydrolysis of lupinanecyanoamide with aqueous-alcoholic hydrochloric acid at 95—98° give a secondary *base*, $C_{10}H_{21}N$, b. p. 101—102°/11 mm. (*hydrochloride*, m. p. 151—153°; *hydriodide*; *hydrobromide*, m. p. 168—170°; non-crystalline *benzoyl*, p-*nitrobenzoyl*, and *acetyl* derivatives; β-*naphthalenesulphonyl* compound, m. p. 86—87°). Treatment of the hydrochloride with potassium cyanate affords a viscous oil transformed by benzoyl chloride into a *dibenzoyl* derivative of half-hydrolysed lupinanecyanoamide, $C_{10}H_{20}N{\cdot}CO{\cdot}NBz_2$, m. p. 169—170°; this compound can also be isolated from the product of the moderated hydrolysis of lupinanecyanoamide with alcoholic hydrochloric acid at 85°. An acid, b. p. 130—132°/9 mm., is obtained by hydrolysis of lupinanecyanoamide with aqueous sulphuric acid. Hydrogenation of lupinanecyanoamide in presence of palladised calcium carbonate gives the base $C_{11}H_{21}N_2$, yielding a chloroplatinate, m. p. 216—217° (decomp.), identical with that described above.

Treatment of the secondary base with silver acetate in acetic acid at 180° gives the tertiary pyridine base, $C_{10}H_{15}N$, b. p. 110—112°/39—40 mm. (*chloroplatinate*, long, orange-red crystal aggregates or coarse, yellowish-red crystals, m. p. 190—191°, decomp. 192—194°; *chloroaurate*, m. p. 46—47°). The base $C_{10}H_{15}N$ is shown to be a mixture of 3-methyl- and 6-methyl-2-*n*-butylpyridine, since when oxidised by potassium permanganate under varied conditions it affords the four pyridinecarboxylic acids : 2-*n*-butylpyridine-6-carboxylic acid, isolated as the *copper* salt and *chloroplatinate*, $(C_{10}H_{13}O_2N)_2PtCl_4$, m. p. 154—155° (decomp.); 2-*methylpyridine*-6-*carboxylic acid*, m. p. 95—96°, isolated as the *copper* salt, m. p. 253—255° (decomp.) [yielding 2-methylpyridine when subjected to dry distillation], and *hydrochloride*, m. p. 202·5—203·5° (decomp.) (also

prepared by oxidation of 2 : 6-dimethylpyridine); pyridine-2 : 3-dicarboxylic acid; 3-methylpyridine-2-carboxylic acid. H. WREN.

Lupanine. K. WINTERFELD and A. KNEUER (Ber., 1931, **64**, [*B*], 150—158).—Lupanine is converted by hydriodic acid (*d* 2·0) and red phosphorus at 240—245° into β-lupinane, b. p. 85—86°/15 mm. (*chloroaurate*, m. p. 143—144°; picrate, m. p. 165—166°; chloroplatinate, decomp. 217°) [identical with the product obtained by Schopf (A., 1928, 1144) and with that derived from matrine by Kondo and Sato (A., 1921, i, 882)], and a fraction, b. p. 145—147°/12—13 mm., from which crystalline salts could not be obtained but gives a well-marked pyrrole reaction. It is suggested that lupanine is constituted by the union of a lupinane ring with a pyrrolidine complex. Treatment of lupanine with cyanogen bromide in boiling benzene in the absence of moisture affords *bromolupaninecyanoamide*, $C_{15}H_{21}ON_2$,CNBr, $[\alpha]_D^{18}$ +82·86° in 90% alcohol, which does not yield salts and is reduced by zinc dust in boiling 80—85% acetic acid to the non-crystalline *lupaninecyanoamide*. The last-named compound is hydrolysed by sulphuric acid to a non-crystalline, secondary *base*, $C_{15}H_{26}ON_2$, characterised by the *chloroaurate*, m. p. 153°, *picrate*, m. p. 93—94°, *hexahydrated chloroplatinate*, and *benzoyl* derivative, m. p. 195° (*chloroaurate*, m. p. 206°). Fission of the benzoyl compound could not be effected with phosphorus pentabromide or pentachloride. The base is transformed by methyl iodide into a *methiodide*, m. p. 277—278° from which N-*methyl-lupanine* [*chloroaurate*, m. p. 140° (decomp.)] is derived. Attempts to degrade *N*-methyl-lupanine are impeded by the poor yields. H. WREN.

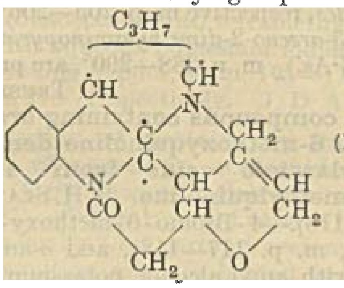
Optical rotation of quinine alkaloids. R. DIETZEL and K. SOLLNER (Arch. Pharm., 1930, **268**, 629—636).—The values of $[\alpha]^{25\cdot5}$ for 0·0285*M*-aqueous solutions of the monohydrochlorides of quinine, quinidine, and cinchonidine are changed by the addition of 1 equivalent of hydrochloric acid from —175·4°, +224·2°, and +213·2° to —277·9°, +312·3°, and +271·4°, respectively, and by a further 0·4 equivalent of acid to —280·7°, +310·0°, and +271·1°. The changes are connected with the passage of the quinoline nitrogen atom into the ionised state. Similarly, $[\alpha]^{22\cdot5}$ for 0·25*M*-aqueous sodium tartrate is changed from +34·1° to +13·1° by the addition 1 equivalent of sulphuric acid and to +10·2° by 3·2 equivalents, and $[\alpha]^{22\cdot5}$ for 0·25*M*-aqueous tartaric acid is changed from +15·1° to +13·5° by 0·80 equivalent of sulphuric acid and to +41·2° by 1·6 equivalents of sodium hydroxide.

H. E. F. NOTTON.

Cinchona alkaloids. VII. Sulphonation of quinine and hydroquinine. G. GIEMSA and M. OESTERLIN (Ber., 1931, **64**, [*B*], 57—61; cf. A., 1925, i, 291).—The readiness of reaction between hydroquinine and sulphuric acid and the easy hydrolysis of the product appear to indicate that the supposed sulphonic acids are hydrogen sulphates. Reaction does not take place unless an alcoholic hydroxyl group is present. If the latter group is acetylated either hydrolysis and "sulphonation" take place or there is no change. Hydroquinine chloride and deoxyhydroquinine do not yield "sulphonic acids," whereas acetyl- and benzoyl-hydroquinine undergo exchange esterification. It is not possible to obtain the corresponding "acylsulphonic acids" from "hydroquininesulphonic acid" and acetyl chloride or chloroformic esters. Diazotised 5-aminohydroquininesulphonic acid, like diazotised 5-aminohydroquinine, is reduced to methylhydrocuprean. In consequence of the possibility of isomerisation to the *iso*-base, quinine does not afford a homogeneous reaction product with concentrated sulphuric acid. Isomerisation is avoided by the use of acetic anhydride as solvent, whereby *quininesulphonic acid*, decomp. 237° after darkening at 230°, $[\alpha]_D^{20}$ +88·86° in *N*-sodium hydroxide [*hydrochloride* (+$5H_2O$), m. p. 205°], is produced. It is quantitatively hydrolysed by 25% hydrochloric acid to quinine and, with bromine in glacial acetic acid, gives *quininesulphonic acid dibromide*, m. p. 232° after darkening at 218°, hydrolysed to quinine dibromide, m. p. 218—220°. Potassium permanganate oxidises quininesulphonic acid to *chiteninesulphonic acid*, m. p. 221—225°, hydrolysed by boiling hydrochloric acid to chitenine, m. p. 280°. Acetylquinine in acetic anhydride is scarcely affected by sulphuric acid. Treatment of quinine with concentrated sulphuric acid at 0° yields mainly hydroxyhydroquininesulphonic acid, which is almost certainly a mixture of isomerides; small amounts of *iso*quininesulphonic acid and niquinesulphonic acid are also produced.

H. WREN.

Molecular structure of strychnine and brucine. R. ROBINSON (Proc. Roy. Soc., 1931, **A**, **130**, 431—452).—The Bakerian lecture for 1930. The work of Tafel, Leuchs, Perkin, and Robinson is summarised and the partial structure I assigned to strychnine. Brucine contains methoxyl groups in the 6- and



(I.)

7-positions of the quinoline fragment. Methyl-ψ-strychnidine has been found to be isomeric with strychnidine; it is re-named *neo*strychnidine.

H. BURTON.

Determination of morphine in aqueous solution. H. BAGGESGAARD-RASMUSSEN and S. A. SCHOU (Arch. Pharm., 1930, **268**, 673—680).—A mixture of chloroform (3 vols.) and *iso*propyl alcohol (1 vol.) is superior to the solvents previously suggested for the extraction of morphine (solubility, 0·785% wt./vol.) from its aqueous suspension. The aqueous solution, concentrated, if necessary, to contain 0·1—0·2 g. of morphine in 20 c.c., is treated with 5 c.c. of 4% sodium carbonate solution and extracted as rapidly as possible with four quantities of 25 c.c. of solvent. The extract is filtered through a small dry paper, evaporated to dryness, and the residual morphine determined acidimetrically. The application of the

method to micro-determinations and to more dilute solutions is described. H. E. F. NOTTON.

Germanochlorides of alkaloids. A. TCHAKIRIAN.—See this vol., 322.

Arseno-organic compounds. I. Phenyl-α-naphthylarsine derivatives. J. KLIPPEL (Rocz. Chem., 1930, **10**, 777—783).—*Phenyl-α-naphthylcyanoarsine*, m. p. 99·5—100°, is prepared by treating phenyl-α-naphthylmethylarsine with cyanogen bromide, and the corresponding *chloroarsine*, m. p. 46—46·5°, by the action of chlorine. Both products yield *phenyl-α-naphthylarsine oxide*, m. p. 116·5—117·5°, on alkaline hydrolysis, and this oxide gives, on further hydrolysis, *phenyl-α-naphthylarsinic acid*, m. p. 189—189·5°. R. TRUSZKOWSKI.

Arsenopyridine compounds. E. PŁAZEK (Rocz. Chem., 1930, **10**, 751—760).—*3-Arsinopyridine-2-carboxylic acid* (I), m. p. 280—300° (decomp.), is prepared by the action of arsenious oxide on 3-diazopyridine-2-carboxylic acid; decarboxylation of this acid cannot be effected by any of the reactions ordinarily used for this purpose. Its *oxide*, m. p. 316° (decomp.), is prepared by the action of sulphur dioxide on its aqueous solution, and this oxide is converted by hot hydrochloric acid into *3-dichloroarsinopyridine-2-carboxylic acid hydrochloride*. The acid I reacts with sodium hypophosphite and potassium iodide to yield *bis-3-arsenopyridine-2-carboxylic acid* $(CO_2H{\cdot}C_5H_3N{\cdot}As{:})_2$. The *mono-* and *di-sulphides* of acid I (decomp. 250° and 231°) are prepared by the action of hydrogen sulphide respectively on the oxide and the acid. *2-Dimethylaminopyridine-5-arsinic acid*, m. p. above 300° (decomp.), is prepared by the action of arsenic trichloride on 2-dimethylaminopyridine. The corresponding *oxide*, m. p. 265°, *mono-* and *di-sulphides*, respective m. p. 205—206° and 118—120°, and *bis-5-arseno-2-dimethylaminopyridine*, $(NMe_2{\cdot}C_5H_3N{\cdot}As{:})_2$, m. p. 288—290°, are prepared. R. TRUSZKOWSKI.

Quinoline compounds containing arsenic. II. Synthesis of 6-methoxyquinoline derivatives of aminophenylarsinic acids from 4-bromo-6-methoxy-2-methylquinoline. R. H. SLATER (J.C.S., 1931, 107—118).—4-Bromo-6-methoxy-2-methylquinoline (I), m. p. 117—118°, and *o*-aminophenylarsinic acid with amyl alcohol, potassium carbonate, and traces of copper bronze and iodine furnish in moderate yield o-*6'-methoxy-2'-methyl-4'-quinolylaminophenylarsinic acid* (II), m. p. 302—303° (decomp.) (*salts* described), which on reduction in alcoholic hydrochloric acid solution containing a trace of iodine, by means of sulphur dioxide, gives *12-chloro-7-methoxy-11-methyl-5 : 12-dihydroquinbenzarsazine*, darkens 235°, m. p. 245—247° (decomp.), oxidised by hydrogen peroxide in acetic acid solution to *7-methoxy-11-methylquinbenzarsazinic acid*, unmelted at 310° (*salts* described). With phosphorus oxychloride II furnishes *7-methoxy-11-methylquinbenzarsazinyl chloride*, darkens 150°, m. p. 165—167°. *o*-Tolidine and I when heated at 140—150° for 9 hrs. give *4-o-tolidino-6-methoxy-2-methylquinoline*, m. p. 199—200° (*acetyl* derivative, m. p. 182—183°), which by the Bart reaction yields *4' : 6''-methoxy-2''-methyl-4''-quinolylamino-3 : 3'-dimethyldiphenylylarsinic acid*, m. p. 304—305° (decomp.) (*salts* described). *o*-Dianisidine and I similarly yield *4-o-dianisidino-6-methoxy-2-methylquinoline*, m. p. 195—196° [*acetyl* derivative, m. p. 140° (loss of water), m. p. 200—201°], from which *4' : 6''-methoxy-2''-methyl-4''-quinolylamino-3 : 3'-dimethoxydiphenylylarsinic acid*, m. p. 243—245° (decomp.) (*salts* described), is obtained by the Bart reaction. From I and *pp'*-diaminodiphenylmethane, p-*6-methoxy-2-methyl-4-quinolylamino*-p'-*aminodiphenylmethane*, m. p. 135—145° (loss of water), and p-*6-methoxy-2-methyl-4-quinolylaminodiphenylmethane*-p-'*arsinic acid*, chars at 300° after darkening, are prepared in an analogous manner. From aniline and 4-chloro-6-methoxy-2-methylquinoline, *4-anilino-6-methoxy-2-methylquinoline*, m. p. 208—209° (*hydrochloride*, unmelted at 310°), was obtained. J. D. A. JOHNSON.

Constitution of phenarsazine chloride. C. P. A. KAPPELMEIER (Rec. trav. chim., 1931, **50**, 44—50).—Polemical against Gibson, Johnson, and Vining (A., 1930, 1601). J. W. BAKER.

Reaction between dichloroarsines and secondary aromatic arsines. C. S. GIBSON (J. Amer. Chem. Soc., 1931, **53**, 376—377).—Lewis and Stiegler's observation (A., 1930, 1601) that 6-β-chlorovinylphenarsazine and 7-β-chlorovinyl-7 : 12-dihydrobenzophenarsazine are 10-chloro-5 : 10-dihydrophenarsazine and 7-chloro-7 : 12-dihydrobenzophenarsazine, respectively, was first shown by Burton and Gibson (A., 1926, 419) and confirmed by Seide and Gorski (A., 1929, 1321). H. BURTON.

Oxidation of heterocyclic arsenic compounds by iodine. G. A. RAZUBAIEV and V. S. MALINOVSKI (Ber., 1931, **64**, [*B*], 120—130).—The oxidation of alkyl and aryl derivatives of dihydrophenarsazine by iodine in aqueous-alcoholic solution takes place according to the scheme $NH{<}{}^{C_6H_4}_{C_6H_4}{>}AsR+I_2+2H_2O\rightarrow 2HI+NH{<}{}^{C_6H_4}_{C_6H_4}{>}AsR(OH)_2$, whereas with the chloro-derivatives and oxides the equations are $NH{<}{}^{C_6H_4}_{C_6H_4}{>}AsCl+I_2+2H_2O=NH{<}{}^{C_6H_4}_{C_6H_4}{>}AsO{\cdot}OH+2HI+HCl$ and $(NH{<}{}^{C_6H_4}_{C_6H_4}{>}As)_2O+2I_2+3H_2O=2NH{<}{}^{C_6H_4}_{C_6H_4}{>}AsO{\cdot}OH+4HI$. The compound under investigation is dissolved in alcohol and the solution is diluted with water until a turbidity is produced. Alcoholic iodine is added until a bright yellow colour is produced. In course of the titration water is added in two or three portions. Initially the colour of the iodine disappears immediately on shaking, but towards the end of the titration 10—30 seconds are required. The yellow colour caused by a slight excess of iodine should persist for 24—48 hrs. In certain cases it is preferable to add immediately about three fourths of the necessary iodine and, after the precipitated oxide has dissolved, to treat the mixture with sufficient aqueous sodium hydrogen carbonate to neutralise the liberated hydrogen iodide. The titration is subsequently finished in the usual manner. For the isolation of the products of the reactions it is necessary to neutralise the liberated hydrogen iodide either by titration with standard

sodium hydroxide or by addition of an excess of freshly-precipitated silver oxide. In the majority of cases the oxides and dihydroxides separate from the concentrated solutions with hygroscopic moisture or water of crystallisation, which is readily lost in a vacuum over phosphoric oxide at the ordinary temperature. Transition of dihydroxide to oxide occurs at a higher temperature.

The following new compounds are incidentally described: 10-*methyl*-5 : 10-*dihydrophenarsazine dihydroxide*, m. p. (indef.) 201—205°, and the corresponding *oxide*, decomp. 256—257°; 10-*ethyl*-5 : 10-*dihydrophenarsazine dihydroxide*, m. p. (hydrated) 141—143°, (anhydrous) 141—183° (indef.), and the *oxide*, m. p. 239°; 10-*propyl*-5 : 10-*dihydrophenarsazine*, m. p. 81—82°, from the 10-chloro-compound and magnesium propyl iodide, its *dihydroxide*, m. p. 93°, and *oxide*, m. p. 111—112°; 10-iso*amyl*-5 : 10-*dihydrophenarsazine*, m. p. 76—78° (*dihydroxide*, m. p. 95—96°; *oxide*, m. p. 101—102°); 10-*phenyl*-5 : 10-*dihydrophenarsazine oxide*, decomp. 280—300°.

H. WREN.

Preparation of aromatic mercuric chlorides from aromatic diazonium chlorides. R. E. McCLURE and A. LOWY (J. Amer. Chem. Soc., 1931, **53**, 319—321).—When benzenediazonium chloride is treated with mercury (in a finely-divided state produced by stirring), mercury phenyl chloride is obtained in 45% yield: $Ph{\cdot}N_2Cl + Hg \longrightarrow Ph{\cdot}HgCl + N_2$. Mercury *o*-tolyl (72%), *p*-tolyl (52%), *p*-xylyl (64%), and α-naphthyl chlorides (20%) are prepared similarly (percentage yields given in parentheses) from the appropriate amines.

H. BURTON.

Influence of acid chlorides and pyrrole on the colour test for reactive organometallic compounds. Constitution of magnesium pyrryl halides. H. GILMAN and L. L. HECK (J. Amer. Chem. Soc., 1930, **52**, 4949—4954).—The colour test for the detection of an excess of a Grignard reagent (A., 1925, ii, 1011; 1928, 160; 1930, 778) in a reaction mixture is interfered with by acetyl, benzoyl, carbonyl, and oxalyl chlorides, phosphorus pentachloride, and thionyl chloride, but is unaffected by the presence of many other chlorides. When pyrrole is treated with magnesium methyl iodide in di-*n*-butyl ether at 29°, only 1 mol. of methane is evolved, indicating the presence of one active hydrogen atom. It is concluded from this that magnesium pyrryl halides contain the group $\vdots N{\cdot}MgX$.

H. BURTON.

Heterocyclic systems containing selenium. IV. *cyclo*Selenohexane. G. T. MORGAN and F. H. BURSTALL (J.C.S., 1931, 173—180; cf. A., 1930, 1051).—αζ-Hexamethylene dibromide and alcoholic sodium selenide yield cyclo*selenohexane* (I), b. p. 106°/68 mm., 188—190°/756 mm., n_D^{18} 1·5470, p_{18} 1·353, parachor 302·1, in small yield, together with a *dimeride* (II), m. p. 92°, and a *polymeride* (III), m. p. 36—37°. With bromine I, II, and III furnish *dibromides*, m. p. 118—119°, 145° (decomp.), and 94—95° (decomp.), respectively, reducible to the selenohydrocarbons. The *dichloride*, m. p. 48°, *di-iodide*, m. p. 82°, *methiodide*, decomp. 149—, and *mercurichloride*, m. p. 193—194° (decomp.), of I are described. Depolymerisation of II and III at 220° yields 2-*methyl*cyclo*selenopentane* (IV), b. p. 90°/65 mm., 169—171°/764 mm., n_D^{18} 1·5205, d_4^{22} 1·287 [*mercurichloride*, m. p. 112°; *methiodide*, m. p. 164° (decomp.)], the *dibromide* (dichloride, dibromide, and di-iodide are gums) of which on distillation under diminished pressure gives β-methylpentamethylene dibromide. *Hexamethylene-αζ-diselenocyanate* (V) (an oil), from potassium selenocyanate and αζ-hexamethylene dibromide, on alkaline hydrolysis gives cyclo*hexamethylene* 1 : 8-*diselenide* (VI), m. p. indef. about 40°, which at 250° decomposes into selenium and IV. *Hexamethylenediselenious acid*, decomp. 147°, is formed by oxidising V and VI with nitric acid.

J. D. A. JOHNSON.

***cyclo*Tellurobutane (tetrahydrotellurophen).** G. T. MORGAN and F. H. BURSTALL (J.C.S., 1931, 180—184).—Amorphous tellurium dissolves in αδ-tetramethylene di-iodide at 130° to give cyclo*telluributane* 1 : 1-*di-iodide* (two forms; both m. p. 149—150°), which is reduced in aqueous suspension by sulphur dioxide to cyclo*tellurobutane* (I), b. p. 105—106°/122 mm., 166—167°/761 mm. (Siwoloboff method), n_D^{18} 1·6175 (*mercurichloride*, m. p. 146—147° after sintering at 140°; a *methiodide*, darkens 200°, unmelted at 240°). The *dibromide*, m. p. 130°, and *dichloride*, m. p. 111—112°, are obtained from I and the appropriate halogen. cyclo*Telluributane* 1-*oxide*, m. p. 241° (decomp.), from the dihalides and alkali, or aerial oxidation of I, reacts with the dibromide to give *bis*cyclo*telluributane* 1 : 1′-*oxydibromide*, m. p. 207° (decomp.). Tetramethylene bromide and aluminium telluride at 125° yield 1-δ-*bromobutyl*cyclo*telluributane* 1-*bromide*, m. p. 152—153°, and *tetramethylene - αδ - bis*cyclo*telluributane* 1 : 1′ - *dibromide*, m. p. 225° (dissociation into tetramethylene bromide and I). With aqueous potassium iodide, these yield the corresponding iodides, m. p. 175—176° (decomp.) and decomp. 215°, respectively.

J. D. A. JOHNSON.

Disintegration of proteins by amides. Disintegration of casein in acetamide. E. CHERBULIEZ and G. DE MANDROT (Helv. Chim. Acta, 1931, **14**, 163—183).—When 1 part of casein (Hammarsten) is added gradually to 5 parts of acetamide at 100—110°, the resulting mixture heated to 200° during several min., and the acetamide removed by distillation at 100—110°/1 mm. and subsequent extraction with acetone, a residue is obtained which is largely soluble in hot water, readily soluble in ammonia or alkali carbonate, gives most of the usual protein colour reactions, and contains slightly less nitrogen than casein. Extraction of the product with alcohol, and purification of the dissolved material by twofold precipitation with copper acetate and removal of copper as the sulphide, gives a fraction which when analysed by the method previously described (this vol., 245) shows values for the nitrogen distribution and acetylated esters similar to those for casein. Mol. wt. determinations of various products obtained under different conditions of heating show that they all possess approximately the same value of 350 (mean); fractionation with alcohol gives products of the same mol. wt. Determinations of the equivalents of the same products by dissolution in dilute

alkali hydroxide and titrating the excess also show that all the fractions have a similar value (provided the titrations are carried out immediately). Polymerisation occurs under the influence of alkali; this is most marked with the products prepared by short heating with acetamide. Polymerisation does not occur to any appreciable extent in neutral solution. Cyclisation probably occurs during the disintegration.
H. BURTON.

Separation of the digestion products of proteins by the method of differential analysis. S. V. DESAI (Biochem. J., 1930, **24**, 1897—1904).—Peptic digests of gelatin, egg-albumin, blood-fibrin, glutelin, and caseinogen and a tryptic digest of gelatin and "bactopeptone" were dialysed through membranes of graded permeability prepared by Pierce's method (A., 1928, 233). Fractions of increasing molecular complexity as shown by determination of free amino- and peptide-nitrogen were obtained. S. S. ZILVA.

Mol. wt. of egg-albumin. II. In presence of electrolytes. J. B. NICHOLS (J. Amer. Chem. Soc., 1930, **52**, 5176—5187; cf. A., 1927, 99).—The partial specific volume of crystalline egg-albumin, purified by electrodialysis, does not vary appreciably with p_H (3·6—7·3), except in strongly acid solution. The sedimentation constant in the isoelectric region of the protein has a mean value of $4·06\times10^{-13}$ cm. per sec. at 30°; the diffusion constant is abnormal. The mol. wt. of the protein is approximately 34,500. The molecule is spherical and has a radius of 2·17 mμ. The depression of the sedimentation constant, due to the Donnan effect, is found to be a maximum at about p_H 3 in unbuffered solutions, for the acid side of the isoelectric point. In buffered solutions, the constant has approximately the same value at p_H 3—7. At p_H 1·16, denaturation of the protein occurs; sedimentation is rapid owing to the aggregation of the formed gel into particles containing approximately seven molecules. H. BURTON.

p_H-Stability region of egg-albumin. B. SJÖGREN and T. SVEDBERG (J. Amer. Chem. Soc., 1930, **52**, 5187—5192; cf. preceding abstract).—The ultraviolet absorption curve of pure egg-albumin shows a maximum at about 280 mμ and a minimum at about 254 mμ for solutions at p_H 2·2, 5·5, and 11·2; the value of the extinction coefficient is lowest at p_H 5·5. Decomposition of the protein into non-centrifugable material occurs above p_H 9 and below p_H 4. The sedimentation constant is independent of p_H in the range 3—11, and has a mean value of $3·54\times10^{-13}$ at 20° as compared with the value of $3·31\times10^{-13}$ calculated from Nichols' results (*loc. cit.*). The mol. wt., sedimentation constant, molar frictional constant, and molecular radius of egg-albumin are identical with the corresponding values for Bence-Jones protein (A., 1930, 233); the isoelectric points of the two proteins differ. H. BURTON.

Denaturation of proteins. VII. N. BOOTH.—See this vol., 316.

Effect of light and salts on gelatin. A. GALINSKY.—See this vol., 319.

Micro-determination of carbon and hydrogen by Pregl's method. A. FRIEDRICH (Mikrochem., 1931, 9, 20—26).—Errors in carbon determination are generally due to varying composition of the oxygen used and are eliminated by purification of the oxygen. The essential features ensuring correct results for hydrogen are constancy of temperature of the lead peroxide layer and constant conditions of the absorption apparatus. E. S. HEDGES.

Micro-determination of carbon and hydrogen in organic mercury compounds. M. FURTER (Mikrochem., 1931, 9, 27—30).—In the micro-determination of carbon and hydrogen by Pregl's method the presence of mercury compounds causes a high value for hydrogen and a low value for carbon, due to the distillation of small quantities of mercury into the calcium chloride tube and to some reaction between mercury vapour and the lead peroxide-asbestos used for filling, which probably causes incomplete oxidation of the carbon.
E. S. HEDGES.

Micro-analytical determination of methoxyl groups. (MISS) G. M. WARE (Mikrochem., 1930, 8, 352—355).—Micro-Zeisel determinations with compounds containing from one to five methoxyl groups in presence of acetic anhydride and phenol yield results which, after application of the Friedrich correction, are in good agreement with the theoretical values for mono- and di-methoxy-compounds, but are low when a greater number of methoxyl groups are present. In all cases the method is satisfactory if pellets of the substance and hydriodic acid (*d* 1·96) are employed; the carbon dioxide used should be washed with silver nitrate solution, sulphuric acid, and, finally, with a suspension of red phosphorus in 10% cadmium sulphate solution. H. F. GILLBE.

Determination of fatty acids. II. Determination of mixtures of two fatty acids by partition between ethyl ether and water. C. H. WERKMAN (Iowa State Coll. J. Sci., 1930, 4, 459—464; cf. A., 1930, 1161).—The solution (0·1*N*, 30 c.c.) is shaken with ether (20 c.c.), and the aqueous phase (25 c.c.) is titrated with 0·1*N*-alkali. Values of the partition constant have been determined for the pairs of acids: butyric–acetic, –propionic, –lactic; acetic–propionic, –lactic. The composition of mixtures may be determined by reference to the graph.
CHEMICAL ABSTRACTS.

Potentiometric determination of cystine and cysteine. K. YAMAZAKI (J. Biochem., Japan, 1930, **12**, 207—222).—Pure cystine and cysteine solutions can be accurately titrated with sodium bromate in presence or absence of bromide ions, but in the presence of other amino-acids titration with sodium iodate in the presence of iodine is more accurate. Temperature and acidity, which determine the extent to which cysteine is oxidised to cystine or cysteinic acid, are important, as also is the rate of titration with iodine. Tryptophan is the only amino-acid which affects the titration of cysteine by sodium iodate, probably owing to its own oxidation in presence of cysteine. CHEMICAL ABSTRACTS.

Effect of hydrogen-ion concentration on precipitation of certain basic substances by phosphotungstic acid. R. A. PETERS (Biochem. J.,

1930, **24**, 1852—1855).—The hydrogen-ion concentration at which phosphotungstate precipitates of certain bases appear depends largely on the constitution of the base. With most of the bases studied the precipitation appears with decreasing alkalinity; with guanidine compounds, this is reversed.

S. S. ZILVA.

Colour reactions of benzene, naphthalene, anthracene, phenanthrene, *p*-benzoquinone, anthraquinone, and quinoline. L. EKKERT (Pharm. Zentr., 1931, **72**, 51—53).—Each of the above substances gives brilliant colour reactions when 0·01 g. in ethyl alcohol (1 c.c.) is treated with a 10% solution of *p*-dimethylaminobenzaldehyde in sulphuric acid (5 drops), or with nitroso-β-naphthol (0·001 g.), and first superposed upon, then mixed with sulphuric acid (1 c.c.). The ultra-violet fluorescence colours of the products and of the original alcoholic solutions are also given.

H. E. F. NOTTON.

Determination of cresols. P. DUMONT (J. Pharm. Belg., 1930, **12**, 1—4, 21—27, 41—45, 65—67, 87—92; Chem. Zentr., 1930, ii, 98).—By interaction with bromine *o*- and *p*-cresol can be converted into dibromo-derivatives and *m*-cresol into the tribromo-derivative; bromometric titration cannot be used for analysis of the isomerides in solution, but *m*-cresol can thus be determined in a mixture. A colorimetric method for the determination of *o*-cresol in a mixture of isomerides is described. Iodometric titration is not applicable, but *m*-cresol can be determined iodocolorimetrically in the absence of its isomerides. The determination of *m*-cresol by Qvist's modification of Raschig's method (gravimetric determination as trinitro-*m*-cresol) is satisfactory. Methods based on distillation with steam or extraction by means of a solvent give good results.

A. A. ELDRIDGE.

Differentiation of cyclic monophenols and monoamines from polyphenols and polyamines. A. MARENZI (Ann. Farm. Bioquim., 1930, **1**, 99—105).—Differentiation is effected by means of phosphotungstic and phosphomolybdic reagents.

CHEMICAL ABSTRACTS.

Determination of piperidine in a mixture with pyridine and its homologues. A. TRAVERS and FRANQUIN (Compt. rend., 1930, **191**, 1340—1343).—The piperidine in a mixture with pyridine, α-picoline, -:6-lutidine, and collidine can be determined by electrometric titration of the mixture using the hydrogen or quinhydrone electrode.

P. G. MARSHALL.

Detection and determination of cocaine in admixture with novocaine. F. WEISS (Apoth.-Ztg., 1930, **45**, 724—726; Chem. Zentr., 1930, ii, 1897).—In dilute alcoholic ethereal (1:2) solution novocaine, but not cocaine, is precipitated by picric acid. Cocaine hydrochloride in 5% admixture with novocaine hydrochloride can be extracted with hot benzene. Determination of methoxyl leads to the determination of cocaine in presence of novocaine.

A. A. ELDRIDGE.

Specificity of the phenol reagent in the determination of tyrosine in proteins. V. CIOCALTEU (Compt. rend. Soc. Biol., 1929, **101**, 198—199; Chem. Zentr., 1930, ii, 99).

Effect of precipitates on the proportionality and the development of colour in colorimetric determinations. C. CIOCALTEU (Compt. rend. Soc. Biol., 1929, **101**, 216—218; Chem. Zentr., 1930, ii, 99).—The addition of lithium sulphate prevents the formation of disturbing precipitates in the determination of tyrosine according to the Folin–Looney method.

L. S. THEOBALD.

Potentiometric determination of alkaloids by means of potassium mercuri-iodide. II. L. MARICQ (Bull. Soc. chim. Belg., 1930, **39**, 496—502).—Atropine, hyoscyamine, pilocarpine, cinchonine, and sparteine can be determined gravimetrically (to within 1—2%) as their mercuri-iodides, by adding potassium mercuri-iodide solution to their dilute acid solutions. Low results obtained with pilocarpine may be remedied by also adding mercuric iodide.

J. D. A. JOHNSON.

Sodium alizarinsulphonate as reagent for alkaloids. L. ROSENTHALER (Apoth.-Ztg., 1930, **45**, 638—640; Chem. Zentr., 1930, ii, 1742).—Limiting concentrations for the micro-precipitation of alkaloids by sodium alizarinsulphonate are recorded. The reagent is specially suitable for the detection of atropine.

A. A. ELDRIDGE.

Potentiometric titration of alkaloids with bi-metallic electrodes. M. L. HOLT and L. KAHLENBERG (J. Amer. Pharm. Assoc., 1931, **20**, 11—15).—Potentiometric methods for the determination of brucine, strychnine, codeine, cocaine, morphine, and cinchonine using various metallic couples are described.

E. H. SHARPLES.

Biochemistry.

Deep respiration tetany. F. HOLTZ (Z. physiol. Chem., 1931, **194**, 76—80).—The reactions of a resting human subject to electrical stimuli during deep respiration are described. During this condition, the serum-phosphorus falls to one third of its normal value.

A. COHEN.

Changes in blood-chloride during asphyxiation. I. T. SASO (J. Biochem., Japan, 1930, **12**, 161—185).—During acute asphyxia the whole blood- and plasma-chloride diminishes continuously; in slow asphyxia the whole blood-chloride increases despite diminution in the plasma-chloride. In prolonged asphyxia the plasma-chloride at first decreases, then increases, and finally decreases again. The hæmoglobin content of the blood is unchanged.

CHEMICAL ABSTRACTS.

Peripheral leucocytosis and erythrocytosis. I. Influence of pulmonary ventilation and of p_H of blood. P. A. ASHMARIN and I. A. ALEXEEV-BERKMAN. **II. Pulmonary ventilation and erythrocytosis.** P. A. ASHMARIN and E. A. VLADIMIROVA. **III. Effect of the activity of the**

gastrointestinal tract on peripheral leucocytosis and erythrocytosis. P. A. Ashmarin, I. A. Alexeev-Berkman, and E. A. Vladimirova. **IV. Relation of urinary acidity to changes in peripheral leucocytosis.** P. A. Ashmarin and I. A. Alexeev-Berkman. **V. Effect of local cooling and warming on morphological composition of the blood.** P. A. Ashmarin, I. A. Alexeev-Berkman, and E. A. Vladimirova (Arkh. Biol. Nauk, 1929, **29**, 273—282, 283—287, 289—298, 299—302, 303—314). Chemical Abstracts.

Fœtal blood. I. Oxygen relationships of umbilical cord blood at birth. N. J. Eastman (Bull. Johns Hopkins Hosp., 1930, **47**, 221—230).—Fœtal blood exhibits high oxygen capacity and high capillary unsaturation. Chemical Abstracts.

Isolation by cataphoresis of two different oxyhæmoglobins from the blood of some animals. A. Geiger (Proc. Roy. Soc., 1931, **B**, **107**, 368—380).—By the cataphoresis of oxyhæmoglobin of certain animals such as sheep and ox at a p_H in the neighbourhood of the commonly accepted isoelectric point (6·5—7·0) and in presence of sufficiently low concentrations of phosphate buffer the oxyhæmoglobin from one animal has been separated into two fractions, one migrating to the cathode and the other to the anode. These two oxyhæmoglobins when again subjected to cataphoresis cannot be further fractionated but behaved as homogeneous proteins, the isoelectric points of which differed by 0·3—0·4 p_H unit. The two oxyhæmoglobins from the same blood gave different oxygen dissociation curves, confirming the view that the two fractions represent distinct substances. Sometimes at least, human blood also contains two different oxyhæmoglobins, but their isoelectric points appear to be close together, so that separation is more difficult. Preliminary electro-dialysis of the hæmoglobin solutions facilitates separation. W. O. Kermack.

Variation of hæmoglobin content [of blood] and blood-forming function of the liver. S. Tatuzawa (Sei-i-kwai Med. J., 1930, **49**, No. 5, 37—62).—The hourly variation for the normal resting rabbit is less than 1%; short exercise reduces the value by 1%. Subcutaneous injection of oxygen increases, and of carbon dioxide decreases, the hæmoglobin content. Liver-juice increases blood formation. Chemical Abstracts.

Blood pigments. XIII. Preparation of methæmoglobin; fluoro[met]hæmoglobin, fission of hæmoglobin by papain, and the hæmoglobin in pernicious anæmia. F. Haurowitz (Z. physiol. Chem., 1931, **194**, 98—106).—The method previously described (A., 1924, i, 1127) for the preparation of methæmoglobin is untrustworthy; a more convenient procedure is to suspend oxyhæmoglobin in 5% alcohol and keep the mixture for 6—10 days at 37—40°. The conversion of methæmoglobin into its fluoro-derivative (cf. *loc. cit.*), which shows an absorption maximum at about 606 mμ, is complete only after 30 min. The action of papain–hydrogen cyanide on hæmoglobin at p_H 5 is similar to that of trypsin (A., 1930, 942); the hæmin-proteose produced has properties similar to those of the compound obtained by the action of sodium hydroxide on hæmoglobin (Waelsch, A., 1927, 893). The hæmoglobin of pernicious and secondary anæmia has the same resistance to sodium hydroxide as that from normal blood. H. Burton.

Determination from the optical density and viscosity of a suspension of the number and volume of dispersed particles. (Mme.) G. Achard (Compt. rend., 1931, **192**, 242—244).—The viscosity of a suspension of red blood-corpuscles is related to their number by the formula $\eta/\eta_0=1+0{\cdot}0486N^{1{\cdot}67}$, where η and η_0 are the viscosities of the suspension and excipient, respectively, and N, the number of particles per mm.$^3\times10^{-6}$, lies between 0·2 and 10·0. Exponential and hyperbolic equations similar to those of Vles express the relationship between opacity and number of red blood-corpuscles. A. Renfrew.

Proteolytic enzymes in human leucocytes. E. Husfeldt (Z. physiol. Chem., 1931, **194**, 137—165).—Extraction of the leucocytes from the blood of a patient suffering from myeloid leucæmia, which are essentially those from bone-marrow, with 87% glycerol gives an extract containing two proteinases, a cathepsin and a tryptase. The former of these shows hydrolytic action at p_H 3—7; optimum fission of caseinogen and edestin occurs at p_H 4·3 and 5·3, respectively. The activity of the tryptase towards caseinogen increases (from p_H 4) with rise in alkalinity of the medium. The amount of the tryptase isolated from the cells increases with their destruction (by autolysis with chloroform at 37°). Autolysis of the leucocytes (essentially polymorphonuclear) from the exudate of an acute empyema gives a suspension containing mainly tryptase. The fission of caseinogen by this suspension is similar to the hydrolysis by glycerol extracts of the leucocytes from the blood of the horse and dog (Willstätter, Bamann, and Rohdewald, A., 1930, 234). A glycerol extract of the leucocytes from normal blood contains peptidases. The extract hydrolyses alanylglycylglycine readily at p_H 7·3; the rate of fission of alanylglycine (optimum at p_H 7·2) is three times that of leucylglycine (optimum p_H 8·1). The above enzymes are also found in glycerol extracts of granulocytes. H. Burton.

Phase-rule equilibria of horse serum-globulin. J. W. McBain and E. Jameson (Trans. Faraday Soc., 1930, **26**, 768—769).—Observations have been made on horse serum-globulin to ascertain the various states which it can assume and the conditions under which they can exist. The results obtained have been analysed in a phase diagram. There is great similarity to soap both in respect of the forms of globulin and soap which separate and the shapes of the areas representing the solutions of the two substances. It appears that globulin solution, euglobulin, and pseudoglobulin are three phases of the same substance, dehydrated globulin. A solution of globulin is the ordinary isotropic solution, whilst euglobulin and pseudoglobulin are liquid crystalline phases, or a liquid and glass which are slightly doubly refracting. W. O. Kermack.

Action of alcohols on the coagulation by heat of protein solutions buffered with acetate. F. Teorell (Biochem. Z., 1930, **229**, 1—15).—Whether

ethyl alcohol is present or not, serum-albumin (horse) is coagulated by heat only between p_H 4·7 and 6·2. Methyl, ethyl, and propyl alcohols, in this order, have increasing inhibitory effects on coagulation by heat provided acetate is present. The effects are more pronounced when the concentration of the acetate is high than when it is low. When the concentration of the alcohol exceeds about 20% (by volume) the coagulated material wholly or partly dissolves when hot, but is re-precipitated on cooling. Coagulation in the cold is promoted in increasing degree by the alcohols in the following order : propyl, ethyl, methyl. Human plasma and horse plasma are affected in the same way as is horse serum, but the coagulation of ovalbumin by heat is not influenced by alcohol–acetate mixtures. W. McCartney.

Composition of ox blood. A. Anderson, H. E. Gayley, and A. D. Pratt (J. Dairy Sci., 1930, **13**, 336—348).—Determinations of hæmoglobin, non-protein-nitrogen, urea-nitrogen, creatinine, sugar, chlorides, phosphorus, calcium, and carbon dioxide-binding capacity have been made.

Chemical Abstracts.

Acetylcholine in ox-blood. F. Wrede and W. Keil (Z. physiol. Chem., 1931, **194**, 229—231).—When ox-blood is treated with alcohol, trichloroacetic acid, and ether as described by Kapfhammer and Bischoff (A., 1930, 1464), the resulting extract contains no acetylcholine. A similar extract from blood to which acetylcholine has been added shows none of the characteristic activity of acetylcholine. H. Burton.

Determination of cholesterol, phosphorus, and inorganic calcium in one sample of blood-serum. G. H. Baril and J. Labarre (Trans. Roy. Soc. Canada, 1930, [iii], **24**, V, 185—187).—To 1 c.c. of serum are added 1 c.c. of distilled water and 1 c.c. of potassium oxalate (2%). The calcium oxalate is separated by centrifuging and after washing determined with permanganate in the usual way. The cholesterol in the mother-liquor is extracted with ether after the addition of alcoholic potassium hydroxide and determined by Grigaut's method. The phosphorus is then determined by the method of Benedict and Theis (A., 1924, ii, 700).

W. O. Kermack.

Precipitation in the determination of unfermentable substances in blood. R. Ege and J. Roche (Compt. rend. Soc. Biol., 1929, **102**, 703—706; Chem. Zentr., 1930, ii, 100).—Fermentation should not proceed longer than 1—2 hrs. at 37°, the yeast must be practically free from reducing substances, and its amount should not exceed 3—4 mg. of dry substance for 1 c.c. of blood. If 100 mg. are employed the filtrate after precipitation with zinc hydroxide is richer in nitrogen than that obtained after precipitation with sodium tungstate; such a filtrate is unsuitable for the determination of sugar.

A. A. Eldridge.

Colorimetric method of investigating the carbohydrate metabolism of blood and organs. I. Occurrence of hexoses in addition to dextrose in human blood : their production *in vitro*. Z. Dische (Biochem. Z., 1930, **229**, 169—195).—Differences between the results obtained when the sugar in a sample of blood is determined by two different methods (diphenylamine–hydrochloric acid and indole–sulphuric acid methods) indicate that, in addition to dextrose, human blood contains two other hexoses, a ketose and an aldose. The amount of these two hexoses in the blood is not increased in alimentary hyperglycæmia. In hypoglycæmia produced by administration of insulin the two hexoses are more rapidly eliminated than is dextrose. In blood kept at 38° for 2 hrs. the greater part of the two hexoses disappears, but when blood is kept at the ordinary temperature, a ketose, probably a constituent of a phosphoric ester and identical with the ketose already mentioned, is produced. This ketose, which disappears from the blood when kept at 37° much more rapidly than does dextrose, is found in the red corpuscles only, whereas the preformed hexoses are about equally distributed between plasma and corpuscles. Both the hexoses are produced from dextrose when this is added to blood.

W. McCartney.

Protein-sugar in the blood-plasma of the horse. H. Bierry (Compt. rend., 1931, **192**, 240—241).—In the products of hydrolysis of the protein-sugar obtained from the purified albumin of horse plasma, *d*-mannose, *d*-galactose, and *d*-glucosamine have been detected and determined. The galactose linking is the weakest. The reducing power of the glucosamine is about a quarter of the reducing power of the total protein-sugar. A. Renfrew.

Blood-sugar level of the ox. E. A. Hewitt (J. Amer. Vet. Med. Assoc., 1930, **77**, 362—367).—The blood-sugar of heifers and non-lactating cows is higher than that of lactating cows. A high value may be correlated with œstrus in heifers. Variations in pathogenic conditions are recorded.

Chemical Abstracts.

Distribution of sugar in the blood of fishes. J. E. Gray and F. G. Hall (J. Elisha Mitchell Sci. Soc., 1929, **45**, 142—146).—Whole blood of normal fishes contains about 75 mg. of sugar per 100 c.c. The average ratio of plasma- to corpuscle-sugar is : menhaden 2·12, pickerel 1·75, scup 1·47, silver hake 3·60, shad 3·80, dogfish 1—1·03.

Chemical Abstracts.

Alimentary blood-sugar curve. Changes in the blood-sugar curve during blood-circulation. W. W. Oppel (Arch. exp. Path. Pharm., 1930, **158**, 348—367; cf. A., 1929, 462).—Arterial and venous lævulose and total blood-sugar of dogs are determined at intervals over a period of 3 hrs. after intestinal administration of sucrose (3 g. per kg. body-wt.). The parallel changes exhibited by the lævulose and blood-sugar curves are explained by inversion of sucrose, and it is concluded that absorption of sugar from the intestine, and not glycogen utilisation, is responsible for alimentary blood-sugar.

A. Cohen.

[Determination of] sugar in 0·02 c.c. of blood by the method of Folin and Malmros. J. F. McClendon (Proc. Soc. Exp. Biol. Med., 1930, **27**, 773—775).—The blood (0·02 c.c.) is blown into tungstic acid solution (2 c.c.), the pipette is rinsed, and the mixture is stirred for 1 min. and centrifuged.

Potassium ferrocyanide solution (0·4 c.c.) and cyanide-carbonate solution (0·2 c.c.) are added to 1 c.c. of the clear liquid and to the standard sugar solution (5 c.c.). The test mixture is boiled for 8 min., cooled in water for 1 min., treated with 1 c.c. of ferric iron-ghatti solution, shaken, kept for 1 min., and then diluted to 5 c.c. Ten colorimetric comparisons are made as rapidly as possible.

CHEMICAL ABSTRACTS.

Micro-determination of blood-sugar. R. B. GIBSON (Proc. Soc. Exp. Biol. Med., 1930, **27**, 480—483).—Protein and non-sugar reducing substances are precipitated from 0·2 c.c. of blood with 2·5 times as much sodium tungstate and sulphuric acid as would be required by the original Folin and Wu procedure. The colour developed by the arsenotungstate reagent with formaldehyde (Benedict) is permanent. Venous blood contains 66—122 (average 91) mg. of sugar per 100 c.c. CHEMICAL ABSTRACTS.

Glycolysis of blood. I. H. K. BARRENSCHEEN and K. HÜBNER (Biochem. Z., 1930, **229**, 329—342; cf. A., 1928, 912).—The mathematical equations proposed for representing the mechanism of glycolysis of blood are unsatisfactory and, in particular, fail to allow for the fact that a 15—30 mm. period of induction exists. This period can be suppressed by the addition of sulphate, phosphate, or arsenate ions. Since during glycolysis inorganic phosphate disappears and since this disappearance is accelerated by sulphate ions, the action of the latter may be regarded as an activation of phosphorylation. Administration of large doses of dextrose to fasting persons also suppresses the induction period of the glycolysis and accelerates the disappearance of the inorganic phosphate of their blood. When hexosediphosphate (but not hexosemonophosphate) is added to blood the induction period disappears and glycolysis is accelerated. These results indicate analogy between fermentation by yeast and glycolysis.

W. MCCARTNEY.

Determination of uric acid in blood. R. A. TRELLES and R. FERRAMOLA (Chemia, 1929, **6**, 175—180; Chem. Zentr., 1930, ii, 100).—The method of Benedict (A., 1922, ii, 405) is recommended for determining uric acid in blood (plasma and corpuscles), but that of Flatow (A., 1926, 1283) is preferred for plasma or serum alone. L. S. THEOBALD.

Determination of uric acid in blood. V. V. SAVJALOV and A. VALKOVITSCH (Jahrb. Univ. Sofia Med. Fak., 1928, **7**; Chem. Zentr., 1930, ii, 100).—One c.c. of 10% sodium hydroxide solution and 1 c.c. of 5% ammoniacal silver nitrate are covered with the serum (0·5 c.c. in 250 c.c. of water), and after 1 min. a brown ring appears when the blood contains 0·002—0·0025% of uric acid. In a modification of the method, 2 c.c. of sodium hydroxide and ammoniacal silver nitrate are mixed with 1 c.c. of serum and 5 c.c. of water, and the colour obtained is compared with that given by 5 c.c. of a standard solution of uric acid and 1 c.c. of sheep's serum with the same reagents. L. S. THEOBALD.

Calcium and phosphorus content of blood and the creatinine coefficient of the urine of some inhabitants of Malaya. F. E. BYRON (Bull. Inst. Med. Res. Malay, 1930, No. 4, 1—4).—The serum-calcium and phosphorus content of the blood of normal tropical inhabitants does not appear to vary from the usual standards, but in natives suffering from tropical ulcers and anæmia the serum-calcium content is sub-normal, whilst the phosphorus determinations are within the normal limits. The urinary excretion of creatinine in native males is comparable with that observed in Europeans, but the values for normal females are lower. The excretion of creatinine in the urine in tropical ulceration and anæmia is considerably reduced. C. C. N. VASS.

Determination of blood-calcium. C. O. GUILLAUMIN (J. Pharm. Chim., 1931, [viii], **13**, 65—76).—Plasma or serum (5 c.c.) is digested with 15 c.c. of "nitroperchloric" acid (100 c.c. of perchloric acid, d 1·61; 250 c.c. of nitric acid, d 1·39), heating gently at first and then vigorously to take to dryness. The colourless residue is dissolved in 5 c.c. of water acidified with hydrochloric acid and washed into a centrifuge tube. After heating for 2—3 min. on the water-bath, 2 c.c. of saturated ammonium oxalate solution are added, followed by ammonia, drop by drop, to give p_H 5·0, using methyl-red or cresol-green as indicator. The calcium may then be determined by igniting the oxalate, dissolving in hydrochloric or sulphuric acid, and titrating the excess with carbonate-free sodium hydroxide. Alternatively, the oxalate may be determined by hot permanganate. For the red cells the blood is centrifuged and the cells are treated with 20% trichloroacetic acid. A volume of liquid equivalent to 5 c.c. of original erythrocytes should be evaporated to 3—4 c.c., when ammonium oxalate is added and the determination continued as above. T. MCLACHLAN.

Micro-determination of copper in blood. F. GRENDEL (Pharm. Weekblad, 1930, **67**, 1345—1351).—Improvements in the author's method of micro-determination of copper in foods (B., 1930, 1089), which result in greatly increased delicacy, are described. The method permits determination of $3—5\times10^{-3}$ mg. Cu in 3—5 c.c. of blood with an accuracy of 2×10^{-4} mg. S. I. LEVY.

Silicic acid content of human blood and its variation after ingestion of silicic acid. H. KRAUT (Z. physiol. Chem., 1931, **194**, 81—97).—The silica content of the ash from 23 samples of normal blood varies from 1·16 to 3·02%; the average value is about 1·7%. The mean value for 55 samples of blood from subjects with pulmonary tuberculosis is 1·99% (limiting values 1·07 and 4·02%). Administration of "silistren" (a glycol silicate), equivalent to 10 g. of SiO_2 during 4 weeks, to tubercular subjects causes, in about 80% of the cases, an increase in the silica content of the blood; the normal value is reached after 4 weeks. Inhalation of a solution of low-molecular silicic acid (Willstatter, Kraut, and Lobinger, A., 1929, 1251) during 4 weeks (=400 mg. of SiO_2) causes a considerable increase in the silica content of the blood, which is, in many cases, greater than the amount inhaled.

The silica content of the ash (from 5 c.c. of blood) is determined by repeated treatment of the ash with nitric and sulphuric acids, evaporation to dryness, and

incineration of the residue; the difference in weight when this is heated with hydrofluoric and sulphuric acids is determined. H. BURTON.

Toxicity of blood which has been frozen. W. A. OSBORNE (Austral. J. Exp. Biol., 1930, 7, 223—225).—Defibrinated blood taken from a dog produces toxic effects when injected into the same animal after having been twice frozen and thawed. The action is probably due to a protein liberated from the corpuscles and possibly denatured as the result of freezing and thawing. W. O. KERMACK.

Antitrypsin. I. Determination in serum. F. CHROMETZKA and W. KNOKE. **II. Nature.** F. CHROMETZKA (Z. ges. exp. Med., 1930, 69, 656—664, 665—678; Chem. Zentr., 1930, ii, 2143).—The viscosimetric and Willstätter's titration methods are equally good. The effects of reaction time, concentration of enzyme and substrate, and the p_H on the antitryptic action of serum have been investigated. The p_H curve shows in acid as well as in alkaline solutions an antitrypsin decomposition maximum which is independent of the isoelectric point of the serum-colloids, but coincides with a maximal increase in viscosity of the serum. The irreversible decomposition of antitrypsin is regarded as "swelling-denaturation." No change in solubility of the serum components was observed. A. A. ELDRIDGE.

Agglutination of cell suspensions. N. BEUMÉE-NIEUWLAND (Chem. Weekblad, 1930, 27, 658—663). S. I. LEVY.

Antigenic properties of collagen and their variations under the influence of radium emanation. J. LOISELEUR and A. URBAIN (Compt. rend. Soc. Biol., 1930, 103, 776—778; Chem. Zentr., 1930, ii, 80).—Collagen from rats' tails, dissolved in dilute acetic acid, shows towards rabbits certain antigenic properties which are weakened by heating or by the action of radon. L. S. THEOBALD.

Toxicity of lungs in fœtal life and its accelerating influence on blood coagulation. K. SAKURAI (Sei-i-kwai Med. J., 1930, 49, No. 1, 23—24).—The toxicity to rabbits and the coagulant power for dog's oxalated blood-plasma of a saline extract of fœtal dog's lung are parallel, but the toxicity is only one eighth of that of adult lung. CHEMICAL ABSTRACTS.

Influence of human placental extract on the blood coagulation of the rabbit. E. HORI and K. SAKURAI (Sei-i-kwai Med. J., 1930, 49, No. 2, 21—29).—Changes in the coagulability and composition of rabbit's blood after injection of different quantities of human placental extract are recorded. CHEMICAL ABSTRACTS.

Toxicity of human placenta for rabbits, and its accelerating influence on coagulation of blood. Chemical nature. K. SAKURAI (Sei-i-kwai Med. J., 1929, 48, No. 12, 52—89).—The toxicity of the placental extract is parallel with its blood-coagulating power. Both activities are weakened or destroyed by oxidation, heat, proteolytic enzymes, and long exposure to air. The active principle is globulin-like in nature, but contains 1·226% P; it is not a nucleo- or phospho-protein, and is considered to be tissue fibrinogen. CHEMICAL ABSTRACTS.

Determination of the time of coagulation of blood. H. LAMBERT (Münch. med. Woch., 1930, 77, 586—588; Chem. Zentr., 1930, ii, 80)—An alkali-free substance, "Athrombit," which strongly hinders coagulation and is suitable for the manufacture of instruments, is described. L. S. THEOBALD.

Sodium polyanetholesulphonate, a new preventive of blood-coagulation. V. DEMOLE and M. REINERT (Arch. exp. Path. Pharm., 1930, 158, 211—218).—The effect of sodium polyanetholesulphonate on blood-coagulation, blood-pressure, and respiration is described. Blood taken from a rabbit 1 hr. after injection of 15 mg. per kg. body-wt. does not coagulate in 24 hrs. It is suggested that prevention of coagulation is associated with the molecular size rather than with the chemical constitution of the preventive. A. COHEN.

Double refraction of myosin and its relation to the structure of the muscle fibre. A. L. VON MURALT and J. T. EDSALL (Trans. Faraday Soc., 1930, 26, 837—851).—Optical observations on a solution of muscle-globulin undergoing a shearing movement between crossed Nicols indicate that it consists of a monodisperse system of myosin particles of an ellipsoid or rod-like form. Denaturation causes disappearance of double refraction. The extract of muscle-globulin may also be obtained as a thixotropic gel. W. O. KERMACK.

Constituents of muscle extract of aquatic animals. III. Oyster. K. YOSHIMURA and K. NISHIDA (J. Agric. Chem. Soc. Japan, 1930, 6, 618—622).—Fresh oyster contained: water 84·27, crude protein 8·19, protein 5·33, water-soluble crude protein 3·16, water-soluble protein 0·31, crude fat 1·43, crude ash 1·71%. The following nitrogen compounds were isolated from 13 kg. of fresh muscle: trimethylamine chloroaurate 1·40, adenine picrate 0·15, arginine nitrate 1·90, betaine hydrochloride 30·70, leucine 4·70, taurine 17·30, ammonium chloride 10·92 g. CHEMICAL ABSTRACTS.

Choline in the uterus and its relation to labour. E. STRACK and A. LOESCHKE (Z. physiol. Chem., 1931, 194, 269—276).—Non-pregnant human uterus contains 47 mg. of choline per kg. of fresh organ. The uterus of the pig and cow contains about 160 mg. per kg. whether pregnant or non-pregnant. The placenta of the cow, after 5—6 months, contains only 90 mg. per kg. (cf. A., 1929, 1191). There appears to be no relation between the choline content of the uterus and labour. H. BURTON.

Protein sulphuric ester from the mucous membrane of the stomach. H. MATHIS (Biochem. Z., 1930, 229, 263—264; cf. A., 1930, 945).—The constitution of protein sulphuric esters varies according to the organ from which they are derived. The compound obtained from the anterior part of the pituitary gland has the properties of a globulin, and of the nine sulphur atoms which it contains seven are present in sulphuric acid radicals and none in cystine radicals. None of the properties of a globulin is exhibited by the substance obtained from the liver,

and in this substance two of the three sulphur atoms occur in sulphuric acid radicals, whilst the third is not in a cystine radical. The ester extracted from the mucous membrane of the stomach contains 1·67—1·77% S, all of which forms part of sulphuric acid radicals. W. McCartney.

Kephalin from human brain. II. Oxidation and purification of kephalin. I. H. Page and M. Bulow (Z. physiol. Chem., 1931, **194**, 166—190).—Purification of kephalin by Frankel and Neubauer's method (A., 1909, i, 870) gives an ash-free product; the yield is, however, only 50%. Ether–alcohol precipitation gives a product with a low iodine value, whilst precipitation of an aqueous emulsion with alcohol affords a sample with a higher iodine value. When kephalin is exposed to air for about 30 days, decreases in the carbon, hydrogen, and nitrogen content and the iodine value are found; the neutralisation value increases. These changes are largely obviated when the kephalin is kept under alcohol. The oxidation of solutions or suspensions of kephalin by air is accelerated by the addition of ferrous or ferric salts; the presence of acetic acid is not essential, as is the case with lecithin (cf. Warburg, A., 1913, i, 698). H. Burton.

Oxycholesterol and intermediary cholesterol metabolism. G. Bischoff (Z. ges. exp. Med., 1930, **70**, 83—99; Chem. Zentr., 1930, ii, 2005).—Cholesterol and sitosterol, when heated in air above the m. p., give Lifschütz's oxycholesterol reaction. Cholesteryl oleate gives the reaction without previous hydrolysis. Oxycholesterol is formed when aqueous-alcoholic cholesterol is evaporated in air on a water-bath. Oxycholesterol was not obtained in absence of air from brain, blood, or egg-yolk.
A. A. Eldridge.

Bromides of the highly unsaturated acids of cod-liver oil. I. Denisov (Masloboino Zhir. Delo, 1929, No. 6, 31—34).—Determinations of the solubility and bromine content of the bromo-compounds indicate that the compounds insoluble in ether probably represent terapinic acid as octabromo-derivative. Linolenic acid is probably not present.
Chemical Abstracts.

Nature of the highly-unsaturated fatty acids in lard from pigs fed on menhaden oil. J. B. Brown (J. Biol. Chem., 1931, **90**, 133—139).—Feeding of pigs on a diet containing about 14% of menhaden oil results in an increase in unsaturation of the lipins and fatty acids of the livers, and the storage of 2·7% of highly-unsaturated acids in the lard. These highly-unsaturated acids, isolated as the polybromides of their methyl esters, are of approximately the same mol. wt., but are less unsaturated than those isolated in a similar manner from the original menhaden oil; the m. p. range of the methyl ester polybromides is similar in the two cases. H. A. Piggott.

Cystine and cysteine content of human hair. T. Tadokoro and H. Ugami (J. Biochem., Japan, 1930, **12**, 187—193).—The cystine content of the terminal portion of human hair is lower than that of other portions; it diminishes with age, although the cystine : nitrogen ratio remains constant. Black hair contains more melanin than white; it also has a high cystine and low nitrogen content. The hair of young men contains more glutathione and has a higher cysteine : cystine ratio than that of old men.
Chemical Abstracts.

Occurrence of lead in hen's eggs. W. B. S. Bishop and T. Cooksey (Med. J. Austral., 1929, **2**, 660—662).—Lead (0·052—0·114 mg. per egg) was detected. Chemical Abstracts.

Geographic location and iodine content of the thyroid gland. F. Fenger, R. H. Andrew, and J. J. Vollertsen (J. Amer. Chem. Soc., 1931, **53**, 237—239).—The (yearly) average iodine content of desiccated, fat-free, pig-thyroid glands from N. Dakota is 0·32% (limits 0·13 and 0·53%), whilst for glands from Texas it is 0·60% (limits 0·44 and 0·78%).
H. Burton.

Relative amounts of lysozyme present in the tissues of some mammals. H. Florey (Brit. J. Exp. Path., 1930, **11**, 251—261).—In general the spleen, kidneys, and lungs are rich in lysozyme; skeletal muscle contains little or none. The amount present in the testis and brain is small. Rat tissue has a low content of the enzyme.
Chemical Abstracts.

Chemical nature of protein substances of living cells. O. Loew (Protoplasma, 1930, **11**, 196—209).—Evidence is advanced in support of the theory that protoplasm is built up from labile protein molecules which represent the initial stage of protein synthesis in plants. The labile form may be coagulated and yield the normal reserve protein of the tissues. A. G. Pollard.

Isoelectric point of cells and tissues. H. Pfeiffer (Trans. Faraday Soc., 1930, **26**, 822—834).—A discussion of the conception of the isoelectric point of cell contents, with a review of methods used for its determination. W. O. Kermack.

Osmotic properties of living cells (eggs of *Arbacia punctulata*). M. McCutcheon, B. Lucké, and H. K. Hartline (J. Gen. Physiol., 1931, **14**, 393—403).—The Boyle–van 't Hoff law is followed reasonably accurately over wide variations in osmotic pressure by eggs of *Arbacia punctulata*, if allowance is made for osmotically inactive constituents, and the membrane is truly semipermeable.
P. G. Marshall.

Kinetics of osmosis in living cells. B. Lucké, H. K. Hartline, and M. McCutcheon (J. Gen. Physiol., 1931, **14**, 405—419).—The permeability of unfertilised eggs of *Arbacia punctulata* is independent of the osmotic pressure of the solution and is greater during exosmosis than during endosmosis at 15—21°.
P. G. Marshall.

"Hyrax," a new mounting medium for diatoms. G. D. Hanna (J. Roy. Microscop. Soc. 1930, **50**, 424—426).—The properties of "hyrax," a synthetic naphthalene resin, n 1·82248, are described. F. O. Howitt.

The mucus of the gastric juice and its variations. D. R. Webster (Trans. Roy. Soc. Canada, [iii], 1930, V, **24**, 199—200).—Gastric juice obtained from dogs with a gastric fistula and œsophagotomy

was neutralised with sodium hydroxide, acidified with acetic acid, and 1—2 volumes of acetone were added, when a precipitate was obtained from which a substance was separated, apparently a monosodium salt of mucoitinmonosulphonic acid. The content of the mucin-like substance in the gastric juice varied inversely with the acidity, but directly with the concentration of total base and neutral chlorides. It was very scanty in histamine juice, but greatly increased by pilocarpine stimulation.

W. O. KERMACK.

Variations in the composition of the gastric juice under different conditions. B. P. BABKIN (Trans. Roy. Soc. Canada, 1930, [iii], **24**, V, 201—205).—Experiments on dogs with a Heidenhain pouch (in which the parasympathetic nerves have been cut) show that "hormonal" stimulation (caused by the presence of food in the stomach and independent of nervous impulse) causes increase in the quantity and acidity of the juice, but not in content of organic substance (mucin-like material) or of enzyme, whilst injection of pilocarpine, which stimulates the parasympathetic, causes the formation of a juice rich in enzymes and organic substance. The quantity and acid content are in this latter case increased only in a minor degree.

W. O. KERMACK.

Gastric secretion in infants and children. A. V. NEALE (Arch. Dis. Childhood, 1930, 5, 137—145).—The effect of injection of histamine on the acidity is described. CHEMICAL ABSTRACTS.

Acidity and chloride content of gastric juice. G. V. RUDD (Brit. J. Exp. Path., 1930, **11**, 240—244).—Responses to meals of gruel and cream have been compared. Variations in composition of the gastric juice are due to changes in the amounts of hydrochloric acid and neutral chloride being secreted; the total chloride content remains approximately constant. CHEMICAL ABSTRACTS.

Changes in composition of parotid saliva in the dog after section of the sympathetic nerve in the neck and after extirpation of the superior cervical sympathetic ganglion. H. BAXTER (Trans. Roy. Soc. Canada, 1930, [iii], **24**, V, 207—211).

Digestive secretions of the larva of the Japanese beetle (*Popillia japonica*, Newm.). C. SWINGLE (J. Econ. Entom., 1930, **23**, 956—958).—The presence of iron (ferrous), aluminium, calcium, magnesium, potassium, sodium, ammonium, carbonate, chloride, nitrite, and phosphate is recorded.

A. G. POLLARD.

Iron content of milks (human, cow, donkey, and goat). E. LESNÉ, R. CLEMENT, and P. ZIZINE (Bull. Soc. Chim. biol., 1930, **12**, 1410—1413).—The milk (500 c.c.) is evaporated to a paste and then incinerated. The iron in the ash is determined by dissolving in hydrochloric acid, adding potassium permanganate solution until pink, and making alkaline with sodium hydroxide solution. After warming to remove traces of ammonia, the solution is made exactly neutral with hydrochloric acid and diluted to 40 c.c. The coloration produced by adding 5 c.c. of a 1% solution of alloxantin is compared with that produced by a standard solution of iron. It is shown that the iron content is approximately the same in the milks of woman, cow, goat, and donkey.

B. LEVIN.

Determination of acids in urine. F. MAINZER and M. BRUHN (Biochem. Z., 1930, **229**, 216—232).—A method is described by which the titratable acidity of urine can be determined while its content of carbon dioxide is kept constant. Although the magnitude of the titratable acidity of the urine is dependent on the pressure of carbon dioxide prevailing during the titration, this method gives satisfactory results with acid urines, and the errors arising in the case of alkaline urines can be corrected by calculation if the carbon dioxide content and its pressure are known. If the titratable acidity and the total carbon dioxide content are determined at the same pressure of carbon dioxide the value (titratable acidity+ammonia−hydrogen carbonate) is independent of the absolute value of the carbon dioxide pressure. W. MCCARTNEY.

Detection of acetone and acetoacetic acid in urine. H. KAISER and E. WETZEL (Süddeut. Apoth.-Ztg., 1930, **70**, 175—180; Chem. Zentr., 1930, ii, 2018—2019).—Normal urine is free from ketonic substances; when present, acetone and acetoacetic acid occur together. The nitroprusside reaction detects both. The Lorber–Fischer–Horkheimer iodoform reaction is the most trustworthy. Gerhardt's ferric chloride reaction is characteristic but insensitive. For the detection of acetoacetic acid Arreguine's improved method is free from objection. Colorimetric methods for the determination of acetone substances are inaccurate. A. A. ELDRIDGE.

Acetoacetic acid in the organism. H. KAISER, E. WETZEL, and D. BEISCHER (Süddeut. Apoth.-Ztg., 1930, **70**, 152—153; Chem. Zentr., 1930, ii, 2018).—Saturation of a solution of sodium acetoacetate (Emden and Michaud) with sodium chloride affords the solid salt, which in solution is much more stable than the free acid. Methods of detection are discussed. A. A. ELDRIDGE.

Origin of urobilinogen. I. M. RABINOWITCH (Arch. Int. Med., 1930, **46**, 1014—1017).—Removal of blood from a human ovarian cyst caused an excessive urobilinogen content of the urine to become normal. Since this blood was sterile, it is suggested that urobilinogen may be formed not only extra-intestinally, but also in the absence of reducing bacteria. A. COHEN.

Urine containing bile pigment. H. SZANCER (Süddeut. Apoth.-Ztg., 1930, **70**, 262; Chem. Zentr., 1930, ii, 1895).—The reactions of an icterous urine containing bile pigment and 3% of dextrose are described. Bilirubin appears to be easily oxidisable, a fact which may lead to error owing to the production of a green colour with reagents for protein or aldehyde.

A. A. ELDRIDGE.

Determination of bile acids. Cholaluria. C. L. DUCO and P. T. PANZA (Semana med., 1930, **37**, 1193—1198; Chem. Zentr., 1930, ii, 1893).—The surface tension of a solution, brought to the iso-electric point with 1% phosphoric acid, is determined before and after removal of the bile acids by means

of animal charcoal. The depressant effect on the surface tension of balsamic substances is independent of the acidity; hence these can be distinguished from bile acids by determination of the surface tension before and after acidification. Determinations of bile acids in urine and duodenal juice were made. Salts of bile acids are normally excreted in the urine, which contains 0·10—0·25 g. per litre, calculated as sodium glycocholate. A. A. ELDRIDGE.

Microscopical studies in pernicious anæmia. I. W. E. COOKE and C. F. HILL (J. Roy. Micros. Soc., 1930, **50**, 427—432).—An investigation of the histology of the erythroblasts and erythrocytes in pernicious anæmia. F. O. HOWITT.

Effect of muscular exercise in beriberi. III. Oxygen debt, oxygen requirement, and changes in respiratory quotient, respiratory volume, and carbon dioxide output. E. HAYASAKA and R. INAWASHIRO. **IV. Intermediate water exchange. V. Lactic acid metabolism.** E. HAYASAKA (Tohoku J. Exp. Med., 1930, **14**, 53—71, 72—84, 85—92). CHEMICAL ABSTRACTS.

Relation of vitamins to carcinogenesis. W. NAKAHARA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, **15**, 32—36).—There is no satisfactory evidence supporting the view that vitamin-*A* deficiency or excessive administration of vitamin-*D* is conducive to the development of cancer. W. O. KERMACK.

Effect of testicle extract and normal serum on the growth of a transplantable epithelial tumour of the rabbit. F. D. REYNALS (Science, 1930, **72**, 608—609).—Testicle extract inhibited, whilst normal rabbit serum promoted, growth. L. S. THEOBALD.

Mechanism of enhancement of infections by testicle extract. D. C. HOFFMAN and F. D. REYNALS (Science, 1930, **72**, 508).—An inert substance such as India ink spreads to a greater extent in the skin of rabbits when mixed with testicle extract and intracutaneously injected. Kidney and spleen extracts also increase spreading, but rat and rabbit sera are without effect on the diffusion of the ink. An increased permeability of the host cells also appears to be an effect of the enhancing extract. The enhancing activity of testicle extract is destroyed by heating at 60° for 30 min. L. S. THEOBALD.

Increase of the blood-phenol and -phenol derivatives and the appearance of free phenol in the blood in cirrhosis of the liver. E. BECHNER (Munch. med. Woch., 1930, 77, 751—752; Chem. Zentr., 1930, ii, 79).—A moderate increase in blood-phenol could be detected in many cases of cirrhosis; the appearance of free phenol is also noteworthy. Disturbances in the detoxication of intestinal poison must take place accordingly in cirrhosis.
L. S. THEOBALD.

Acceleration of blood coagulation by eclampsia urine. K. SAKURAI (Sei-i-kwai Med. J., 1930, **49**, No. 4, 27—37).—Urea, uric acid, creatinine, and hippuric acid do not accelerate blood coagulation. Urine of eclampsia accelerates coagulation, whilst that of pregnant women excreting a large amount of albumin does not contain a coagulant.
CHEMICAL ABSTRACTS.

Urobilin and bilirubin in the blood and urine in leprosy. E. A. MOLINELLI and M. ROYER (Compt. rend. Soc. Biol., 1929, **102**, 873; Chem. Zentr., 1930, ii, 79).—Urinary urobilin is normal in leprosy. Blood bilirubin is not increased; urobilin is not present in the blood. L. S. THEOBALD.

Post-operative blood chemistry. E. ANDREWS and K. REUTERSKIOLD (Ann. Surg., 1930, **92**, 786—799).—After operation no significant changes were found in the blood-sugar, -water, -chloride, or -carbon dioxide. The permeability of the skin was increased. Profound changes occur in the mineral salt balance, the potassium : calcium ratio often falling below unity. CHEMICAL ABSTRACTS.

Acid–base equilibrium in man after removal of the stomach. P. A. ASHMARIN and E. E. MARTINSON (Arkh. Biol. Nauk, 1928, **28**, 399—417).—Abrupt and relatively great changes in the p_H of the urine with changes in the acidity of the diet were observed; they are attributed to retention of bases and to excretion of bases through the intestinal tract. For low p_H values, urinary $A-B=NH_3+F-K$; for all p_H values $A-B-NH_3$ where A=inorganic acid, B=inorganic bases, total titratable acidity, K=organic acids with correction for amino-acids and creatinine, and R=titratable acids less hydrogen carbonate and free carbon dioxide.
CHEMICAL ABSTRACTS.

Acid–base equilibrium of peptic ulcer. R. STERN (Arch. exp. Path. Pharm., 1930, **158**, 108—115).—Peptic ulcer was treated (orally) with an alkaline preparation on a protein-deficient diet. In a small proportion of cases the urine was readily alkalised. In most cases, however, a p_H of 7·0 was only temporarily observed after several days of continuous treatment, the response resembling that of cases of acid urine without ulcer. A. COHEN.

Effect of parathyroidectomy on the formation of ethereal sulphates in dogs. V. E. STEFANOVICH (Arkh. Biol. Nauk, 1928, **28**, 291—295).—Extirpation of parathyroid or thyroid of dogs with gastric fistula resulted in augmented ethereal sulphate conjugation, whilst complete thyroparathyroidectomy caused great diminution in this synthesis. Administration of calcium stimulated indirectly the activity of the liver. Lowering of the blood-calcium did not always diminish ethereal sulphate synthesis. Complete extirpation did not disturb the synthesis in dogs which fasted before and after the operation.
CHEMICAL ABSTRACTS.

Parathyroid and fluoro-hypocalcæmia. R. GERSCHMANN (Compt. rend. Soc. Biol., 1930, **104**, 411—412; Ann. farm. bioquim., 1930, **1**, 77—84; Chem. Zentr., 1930, ii, 1870).—With thyroparathyrectomised dogs the hypocalcæmia following intravenous injection of sodium fluoride sets in more rapidly and remains at the minimal value; with normal dogs the original value was not reached after 24 hrs.
A. A. ELDRIDGE.

Parathyroid and hypocalcæmia. R. GERSCHMANN (Compt. rend. Soc. Biol., 1930, **104**, 413—414; Ann. farm. bioquim., 1930, **1**, 85—88; Chem. Zentr., 1930, ii, 1870).—The blood-calcium curve of thyroparathyrectomised dogs after intravenous injection

of calcium chloride is similar to, but at a lower level than, that of normal dogs given a similar injection.

A. A. ELDRIDGE.

Derangement, during disease, of the mechanism regulating the mineral metabolism of cattle. B. SJOLLEMA and L. SEEKLES (Biochem. Z., 1930, **229**, 358—380; cf. A., 1928, 1395).—The mineral content of the blood-serum of cows suffering from parturient paresis or grass staggers has been examined. It has been found that, especially as regards the quantities of magnesium, total calcium, diffusible calcium, and inorganic phosphorus, great differences are exhibited between the diseased and healthy animals and between animals suffering from one disease and those suffering from the other. Differences were also found in the ratios between the different mineral constituents as well as between the different forms in which they were present. Generalisations regarding the connexion between the mineral contents of the blood and the symptoms of the diseases cannot be given, although from knowledge of these contents diagnoses can be made.

W. McCARTNEY.

Serum-calcium in pneumonoconiosis. M. J. SOKOLOFF and A. CANTAROW (Amer. Rev. Tuberculosis, 1930, **22**, 449—454).—The serum-calcium (7·98—14·81 mg. per 100 c.c.) was high in 26 of 31 cases; the value is not related to the incidence or activity of the complicating tuberculous process.

CHEMICAL ABSTRACTS.

Serum-proteins in the toxæmias of pregnancy. N. J. EASTMAN (Amer. J. Obstet. Gyn., 1930, **19**, 343—351).—Variations in the serum-protein during gestation and the toxæmias of pregnancy tend towards a decrease in total protein, associated with a slight relative increase in globulin in normal pregnancy and a more marked increase in pre-eclampsia and eclampsia. The average albumin : globulin ratio is: normal 1·7, pregnant 1·6, eclampsia and pre-eclampsia 1·3. CHEMICAL ABSTRACTS.

Gastric juice in pregnancy. F. ARZT (Amer. J. Obstet. Gyn., 1930, **20**, 382—385).—In pregnancy the free hydrochloric acid and total acidity of the stomach are low. CHEMICAL ABSTRACTS.

Relation between phosphorus, chloride, and hydrogen carbonate in the serum of rachitic and normal rabbits. B. HAMILTON, L. KAJDI, and D. MEEKER (Bull. Johns Hopkins Hosp., 1930, **47**, 215—220).—In both cases the serum-phosphorus varies in the opposite direction to the sum of chloride and hydrogen carbonate. CHEMICAL ABSTRACTS.

Absorption spectrum of blood and its relation to rickets. R. SUHRMANN and W. KOLLATH (Naturwiss., 1931, **19**, 65—66).—The failure to confirm the work of the authors on a difference in absorption between blood-cell solutions of normal and rachitic rats by Gibbs, Johnson, and Shapiro (A., 1930, 1311) is explained as due to the use of a different diet either normally or during the breeding period. F. O. HOWITT.

Maize component of a rachitogenic diet. R. S. HARRIS and J. W. M. BUNKER (Science, 1931, **73**, 95). Storage of ground maize meal for six months ensures the development of a definite rachitic condition in white rats, without unduly restricting growth. L. S. THEOBALD.

Chloride and water content of striped muscle, liver, and kidney tissue in experimental scurvy. L. RANDOIN and A. MICHAUX (Compt. rend., 1931, **192**, 108—110).—The rise in percentage of chloride and water in the liver and kidney tissue of guinea-pigs deprived of vitamin-*C*, minimal at first, increases as death approaches, although the total amounts of both these constituents remain constant. On the other hand, muscle-chloride may rise from 0·50 g. to 1·67 g. per kg. on a completely vitamin-free diet and may exceed 1 g. per kg. even when the latter is devoid of chloride. P. G. MARSHALL.

Artificial toothache in rabbits. I. Influence on blood-sugar. T. NAGIRA and S. NOGUCHI. **II. Sedative action of reagents on the pulp.** T. NAGIRA and T. YAO (Folia Pharmacol. Japon., 1930, **9**, No. 4, 262—272, 273—281).—Moderate electrical stimulus of the pulp produced an increase in blood-sugar which decreased after double splanchnectomy. Secretion of adrenaline was increased. Sedative action was exhibited, in decreasing degree, by phenol, clove oil, menthol, and cineole.

CHEMICAL ABSTRACTS.

Chemical alterations in the blood of rats infected with pathogenic and non-pathogenic trypanosomes. R. W. LINTON (J. Exp. Med., 1930, **52**, 695—700).—Blood of rats infected with *Trypanosoma Lewisi* gives normal values for lipoid phosphorus, lecithin, and carbon dioxide-combining capacity; the liver-glycogen also is normal. *T. equiperdum* is injurious to the host. CHEMICAL ABSTRACTS.

Effect of oral administration of irradiated ergosterol on blood serum-calcium in pulmonary tuberculosis. J. KAMINSKY and D. L. DAVIDSON (Amer. Rev. Tuberculosis, 1930, **22**, 48—52).—Ingestion of "viosterol" was followed by a considerable, and sometimes persistent, rise in serum-calcium.

CHEMICAL ABSTRACTS.

Blood-phosphorus in health and disease. V. Composition of the reticulocyte. H. D. KAY (Brit. J. Exp. Path., 1930, **11**, 148—152).—In diseases involving a high percentage of reticulocytes small quantities of nucleic acid-phosphorus, approximately proportional to the reticulocytosis, have been detected. CHEMICAL ABSTRACTS.

Action of ultra-violet radiation on the protein fraction of blood-plasma *in vitro*. L. KOSTYAL (Biochem. Z., 1930, **229**, 100—108).—When blood-plasma taken from persons suffering from various diseases is irradiated with a quartz lamp, alterations, which vary according to the nature of the disease, take place in the rate at which red corpuscles sink in such plasma. An explanation of the changes is suggested. W. McCARTNEY.

Structure, behaviour, and physiological characteristics of vertebrate cells cultivated *in vitro*. H. B. FELL and E. N. WILLMER (Trans. Faraday Soc., 1930, **26**, 772—778).—A review of the factors determining the uncontrolled growth of tissues *in vitro*. W. O. KERMACK.

Surface structure in the integration of cell activity. R. A. Peters (Trans. Faraday Soc., 1930, **26**, 797—807).—A general theory of the structure and activity in the living cell is sketched, emphasis being laid on the importance of the molecular constitution and orientation of interfaces.

W. O. Kermack.

Membrane-phenomena in living matter: equilibrium or steady state. A. V. Hill (Trans. Faraday Soc., 1930, **26**, 667—673).—The osmotic pressure of the white and yolk of the hen's egg has been determined by the thermo-vapour pressure method of the author (cf. A., 1930, 1211). The difference of osmotic pressure between the white and the yolk in the one-day-old egg corresponds with 0·26—0·29% sodium chloride and on keeping in air it gradually declines, in agreement with the results of Straub (A., 1929, 264). Very similar results are obtained when the eggs are kept in an atmosphere of hydrogen, so that the energy which is required for the maintenance of the difference of osmotic pressure is presumably not derived from oxidation processes. It is argued that the concentration differences inside and outside living cells and the electric potentials which exist across cell membranes are not equilibrium conditions, but are presumably sustained by chemical reactions proceeding in the cell or at its membrane.

W. O. Kermack.

Kinetics of living matter. E. Fauré-Fremiet (Trans. Faraday Soc., 1930, **26**, 779—793).—A discussion of the formation of pseudopodia and the motility of cells and the relation of these to the physico-chemical properties of the protoplasm.

W. O. Kermack.

Oxidative nature of the nerve impulse. F. O. Schmitt (Science, 1930, **72**, 583—584).—Sodium cyanide can completely inhibit nerve respiration; in 0·001*N*-sodium cyanide inhibition is complete for only an hour or so, and then falls to a residual amount, whilst in 0·1*N*-solution inhibition is practically constant at 80—95%. Nerve respiration can also be inhibited more or less completely by carbon monoxide in the dark, but illumination of the nerve weakens inhibition of the resting metabolism. Action potential is produced by an oxidation of a substance or substances in nerve and a respiratory enzyme containing iron appears to be essential. L. S. Theobald.

Conditions of metabolism affecting change of sex. P. Joyet-Lavergne (Compt. rend., 1931, **192**, 180—182).—When the germinal cells of the male are subjected to an environment where their fat metabolism is higher, they give rise to ova. Conversely, when female germinal cells are subjected to conditions producing a rise in general metabolism and a lowering of the reducing power of the tissues, they give rise to spermatozoa. P. G. Marshall.

Relationship between electrical differences of potential in the skin and normal basal metabolism. C. Purdy, A. F. Johnson, and C. Sheard (Science, 1931, **73**, 46—49).—Electrical potential in the skin of normal persons has been correlated with basal metabolism. Higher basal metabolic rates are accompanied by smaller *P.D.* and *vice versa*.

L. S. Theobald.

Relation of the calcium : phosphorus ratio to calcification. R. M. Bethke, C. H. Kick, and O. H. M. Wilder (Ohio Agric. Exp. Sta. Bull., 1930, No. 446, 147).—Experiments with rats indicate that, within certain limits, the ratio of calcium to phosphorus in the ration is of greater significance in calcification than the concentration of these elements. The degree of calcification is directly proportional to the Ca : P ratio. Wider Ca : P ratios are associated with greater requirements for vitamin-*D*.

A. G. Pollard.

Relationship in the hen between the development of ova, blood-calcium, and the antirachitic factor. W. C. Russell, C. H. Howard, and A. F. Hess (Science, 1930, **72**, 506—507).—The presence of large ova and high blood-calcium does not always indicate active egg production. The antirachitic factor may not be the essential factor in the development of ova or in causing high blood-calcium.

L. S. Theobald.

Utilisation of milk and inorganic calcium and phosphorus. M. T. Potter and M. M. Kramer (J. Home Econ., 1930, **22**, 923—924).—In periods in which milk furnished most of the calcium, or in which chiefly inorganic calcium and phosphorus were administered, the calcium and phosphorus were retained equally well. Chemical Abstracts.

Relation between ovarian function and mineral content of blood. A. Schepetinsky and M. Kafitin (Arch. Gynäk., 1929, **136**, 397—406; Chem. Zentr., 1930, ii, 1387).—During menstruation the blood-calcium of normal women varies only between 11 and 14 mg. per 100 c.c.; in the premenstrual period the value is slightly high. The blood-potassium, -sodium, and -chlorine diminish during menstruation, whilst the -inorganic phosphorus shows little change. A. A. Eldridge.

Ovarian function and lipoid metabolism. I. Relation between cholesterol metabolism and ovarian function. II. Relation between lecithin metabolism and ovarian function. III. Distribution of blood-cholesterol between free and esterified cholesterol in various functional phases of the generative gland. Total blood-fatty acid in regular, irregular, and absence of, ovarian function. C. Kaufmann and O. Muhlbock (Arch. Gynäk., 1928, **134**, 603—625; 1929, **136**, 478—502; 1929, **139**, 254—277; Chem. Zentr., 1930, ii, 1386—1387).—I. Women's blood-serum normally contains 125 mg. of cholesterol per 100 c.c. During menstruation values down to 41% of the average are observed; this fall is preceded by an increase which may reach 50%. In disturbance of the ovarian function a fall was also observed; it was independent of the loss of blood.

II. The lecithin content is 234 mg. per 100 c.c., and is normally not subject to regular variation during various periods of the cycle.

III. The fall in blood-cholesterol during menstruation is due to a fall in free cholesterol; 85—90% of the cholesterol is then esterified, instead of about 70%. An increase in blood-total fatty acid was observed during normal menstruation.

A. A. Eldridge.

Auriculo-ventricular junctional system of the heart. II. Metabolic activity. III. Phosphatide and cholesterol content. IV. Anaerobic oxidation. K. YAMAZAKI (J. Biochem., Japan, 1930, **12**, 223—234).—The junction has a higher dehydrogenase and oxidase activity, but a lower sulphydryl content, than the rest of the heart muscle. The Tawara bundle of the ox heart contains less phosphatide than the heart muscle. It is resistant to cyanide, still consuming oxygen when poisoned with 0·0004*M*-potassium cyanide.

CHEMICAL ABSTRACTS.

Role of the spleen in genesis of bilirubin and cholesterol. D. ANTIĆ and D. BORIC (Z. ges. exp. Med., 1930, **70**, 658—665; Chem. Zentr., 1930, ii, 2153).—With rabbits extirpation of the spleen caused a fall in bilirubin and a rise in cholesterol and erythrocyte number. Similar results were obtained in a case of hæmolytic icterus after splenectomy.

A. A. ELDRIDGE.

Effect of consumption of various foods on the amount of multiply unsaturated acids in the blood. N. BEREND (Biochem. Z., 1930, **229**, 323—328).—The amount of multiply unsaturated acids in the blood of dogs first decreases then increases if they are fed on fat. If carbohydrate is given with the fat the initial decrease does not occur. No change takes place in the content of multiply unsaturated acids as a result of feeding with carbohydrate alone or with protein alone. W. MCCARTNEY.

Protein [feeding] studies. A. E. PERKINS (Ohio Agric. Exp. Sta. Bull., 1930, No. 446, 115—116).—Comparison is made of the composition of the blood, milk, and urine of cows receiving high-protein and low-protein rations. The urea contents of blood and urine during high-protein feeding averaged respectively 15 and 300 times those during low-protein feeding. Little difference was apparent in routine tests of milk in the two cases, but a closer examination of the non-protein-nitrogen showed a close agreement between the proportions of these constituents in the blood and milk of the respective animals. Of the non-protein-nitrogen group of substances only the proportions of urea and ammonia were markedly and consistently affected by differences in the ration.

A. G. POLLARD.

Nutritive value of blood-meal protein for growth. A. R. WINTER (Ohio Agric. Exp. Sta. Bull., 1929, No. 436, 42 pp.).—The palatability of blood-meal is low and in general controls its nutritive value. The digestibility of blood-meal decreases with fall of temperature used in preparation. The biological value of the protein is low. The basic amino-acids occur in approximately the same amounts as in caseinogen. Pig's blood has a greater nutritive value than sheep's blood and the serum a higher value than the clot. Blood-meal is not toxic, and is satisfactorily supplemented by caseinogen or maize gluten. A. G. POLLARD.

Nutritive value of benniseed (*Sesamum indicum*). W. E. MCCULLOCH (Nature, 1931, **127**, 199—200).—Analyses of seed grown in the Benue Province gave the following relative percentages: oil 52·6, protein 23·4, ash 4·0, CaO 1·2, P_2O_5 1·39. The plant appears to exercise a strong selective absorptive power for calcium. L. S. THEOBALD.

Increase of hepatic proteins with a diet of a mixture of amino-acids, butter-fat, and dextrose. C. GAUTIER (Bull. Soc. Chim. biol., 1930, **12**, 1382—1391; cf. A., 1928, 792).—By comparing the weight of the right lobes of the livers removed from frogs with the weight of the left lobes and remaining portions of the liver after feeding the same animals for some weeks on a diet composed of a mixture of amino-acids, butter-fat, dextrose, vitamins, and saline mixture, it is found that the weight of the liver is greatly increased, and the total amount of protein is increased, although the proportion of protein is less. The weight of the liver is increased twice in proportion to that of the total amount of protein.

B. LEVIN.

Tryptophan and histidine are anabolic substances. G. FONTÈS and L. THIVOLLE (Compt. rend., 1931, **192**, 63—65).—Subcutaneous injection of 100 mg. of tryptophan per day into dogs fed on a constant diet causes a marked increase in weight. Histidine (200 mg. per day) is without effect, but simultaneous injection of the same quantities of these amino-acids causes a greater increase in weight than tryptophan alone, and a distinct decrease in urinary nitrogen. It is concluded that these amino-acids aid assimilatory processes, particularly those affecting nitrogen metabolism. A. COHEN.

New function of the stomach. Role of this organ in the metabolism of carbamide. R. VLADESCO, D. SIMICI, and M. POPESCO (Compt. rend., 1931, **192**, 308—310).—In normal metabolism the stomach removes a portion of the carbamide from the blood and passes this into its contents in the form of ammonia. Carbamide (60 c.c. of a 2·5% solution) was injected into the jugular vein of a dog, previously anæsthetised with chloralose, followed by a histamine injection to increase gastric secretion, and the amount of carbamide in the blood, and of ammonia in the gastric juice, determined at intervals. The former rapidly decreases, a corresponding increase in the ammonia content being observed. Similar results are obtained when a carbamide solution is kept with gastric juice (dog) *in vitro* at 37°. J. W. BAKER.

Nitrogen metabolism of children. J. P. PARSONS (Amer. J. Dis. Children, 1930, **39**, 1221—1239).—Normal children, 4—8 yrs. old, and diabetic children receiving insulin may maintain a positive nitrogen balance on 1·1 or 2·2 g. of protein per kg., respectively. An isodynamic equivalent of carbohydrate or fat must replace the protein withdrawn in order to maintain nitrogen balance on a minimum protein intake. CHEMICAL ABSTRACTS.

Sulphur compounds in the organism of the dog. I. Action and fate of thiophen in the metabolism of the dog. A. A. CHRISTOMANOS (Biochem. Z., 1930, **229**, 248—254).—Of the total amount of thiophen subcutaneously administered to dogs up to 12% is excreted in the combined form in the urine and part of the remainder may be converted in the organism into ethyl sulphide. Thiophen has no inhibitory effect on the nitrogen metabolism.

A modification of the process of Fletcher and Hopkins for the determination of lactic acid (A., 1907, ii, 373) can be used for the colorimetric determination of 0·07—7·0 mg. of thiophen. W. McCartney.

Elimination of phosphoric acid from adenylic acid in muscular contraction. G. Embden and M. Lehnartz (Klin. Woch., 1930, **9**, 937; Chem. Zentr., 1930, ii, 2154).—At the moment of contraction adenylic acid liberates phosphoric acid. The increase in the non-pentose-phosphoric acid observed immediately after fatiguing stimulation is followed by a much greater increase in this pentose fraction after 2 hrs. A. A. Eldridge.

Caloric quotient of lactic acid in muscle. O. Meyerhof, R. McCullagh, and W. Schulz (Pflüger's Archiv, 1930, **224**, 230—248; Chem. Zentr., 1930, ii, 1722).—The following new determinations ($\pm 10\%$) of the caloric quotient (g.-cal. per g. of lactic acid formed anaerobically in muscle) are recorded: up to the beginning of fatigue 360—395; in progressive anaërobiosis without effusion of lactic acid from muscle 345; during effusion 300; in caffeine rigor 280; in minced muscle up to the formation of 0·5—0·7% of lactic acid 300; with passage of lactic acid into phosphate solution 240. A. A. Eldridge.

Toxicity of *dl*-lactic acid and extent to which it can be assimilated. O. Fürth and P. Engel (Biochem. Z., 1930, **229**, 381—396).—The most satisfactory method for the determination of lactic acid in urine is that of Ishihara (A., 1913, ii, 536). In man, when *dl*-lactic acid is administered 20—30% of it is excreted in the urine. In rabbits, the toxic effect of the acid, especially when orally administered, is high. The toxicity to mice is not so pronounced, and rats tolerate very large doses. Neither the assimilation of the acid nor its toxic effects are affected by administration of sodium carbonate, adrenaline, phloridzin, or dextrose. In rabbits non-fatal phosphorus poisoning causes excessive excretion of lactic acid, but after recovery the power to assimilate the acid is temporarily increased. In rats to which over-doses of lactate are administered no storage of lactic acid or of its precursors takes place. As regards their catalytic oxidation with active charcoal, there is no difference between *d*- and *l*-lactic acids. It is concluded that *dl*-lactic acid is not a completely assimilable or useful food. W. McCartney.

Lactacidogen in intermediary metabolism. A. Y. Kharit (Arch. Biol. Nauk, 1929, **29**, 443—454).—The blood-lactacidogen of man, dog, and rabbit is of the same order of magnitude as the muscle-lactacidogen. Evidence of lactacidogen synthesis in the intestinal wall and lungs is adduced. Carbohydrate feeding and increased blood-sugar do not raise the blood-lactacidogen. The lactacidogen-phosphorus is found in the acid-soluble fraction of the blood-phosphorus. Chemical Abstracts.

Glycogen storage in the white rat when fed on the roots of *Arctium lappa*. J. C. Krantz, jun., and C. J. Carr (J. Pharm. Exp. Ther., 1931, **41**, 83—87).—The addition of the dry powdered root of *A. lappa* (containing 50—70% of carbohydrate yielding lævulose on hydrolysis) to the basal diet (cacao butter) of white rats results in an increase of glycogen in the liver to 5—6 times the amount found in controls. An increase is also caused by the addition to the basal diet of the pure carbohydrate isolated from the roots. W. O. Kermack.

Action of maltose on the metabolism and anabolism of infants. M. Steuber and A. Seifert (Arch. Kinderheilkunde, 1930, **87**, 192—207; Chem. Zentr., 1930, ii, 85).—The increase in weight of children was always less with successive increased administration of dextrose and equicaloric lowering of fat. The effect of the increased carbohydrate dose on digestion manifested itself only in a slightly lower consumption of nitrogen and mineral substances. The retention of nitrogen and of inorganic material was essentially less, but the heat production per unit area was unaffected. Fat synthesis from dextrose was not detectable. L. S. Theobald.

Significance of bile acids in carbohydrate metabolism. VIII. Mechanism of the hypoglycæmic action of bile acids. K. Tsuji (J. Biochem., Japan, 1930, **12**, 139—160).—The hypoglycæmic effect of the administration to rabbits of bile acids is probably due to paralysis of the sympathetic. The effect is increased by potassium ions. Chemical Abstracts.

Morphological basis for certain tissue resistance. W. deB. MacNider (Science, 1931, **73**, 103—105).—Subcutaneous injection of a solution of uranium nitrate (2—4 mg. per kg.) results in an initial increase in the formation of urine, which is albuminous, a decrease in elimination of phenolsulphonephthalein, a reduction in reserve alkali of the blood, and an initial retention of blood-carbamide and -non-protein-nitrogen followed by retention of creatinine. The morphological changes are described. L. S. Theobald.

Action of magnesium chloride on the respiration and contractility of the frog ventricle. J. Leibowitz and A. Schweitzer (Biochem. Z., 1930, **229**, 291—295; A., 1930, 1613).—At the end of the season of the year at which the frog's heart exhibits hypersensitivity towards the action of magnesium salts the gradually decreasing inhibitory effect which these have on the contractility of the organ runs parallel with their inhibitory effect on the respiration of the tissues. The inhibitory effect of low concentrations of magnesium chloride on biological oxidation in the frog can be observed, in summer, in the heart tissue but not in the liver tissue. W. McCartney.

Action of intracerebral injection of calcium, magnesium, strontium, barium, potassium, and sodium ions. M. Cloetta and H. Fischer (Arch. exp. Path. Pharm., 1930, **158**, 254—281).—Typical phenomena of sleep may be induced in rats, cats, dogs, and rabbits by injecting 0·05—1·5 mg. of calcium chloride into a sharply-defined area of the infundibular region of the brain. The effect of magnesium is indefinite, but, in higher doses, is similar to that of calcium. Strontium produces non-characteristic symptoms of paralysis and stimulation associated with toxic effects. The barium ion is highly toxic, causing intense stimulation on injection into any part

of the brain. Potassium chloride has a stimulant effect which may be suppressed by calcium chloride. Hypertonic solutions (3—4%) of sodium chloride cause slight stimulation which may not be a specific effect of the sodium ion. A. COHEN.

Deposition of gold and lead in the organism. V. HENRIQUES and H. OKKELS (Pflüger's Archiv, 1930, **225**, 364—371; Chem. Zentr., 1930, ii, 1876).—The colloidal metals are selectively deposited in the reticuloendothelial apparatus and complex compounds in the parenchyma cells; differential deposition is observed in the latter case. A. A. ELDRIDGE.

Acute toxicity of glyceryl trinitrate and sodium nitrite in rabbits. T. V. OLTMAN and L. A. CRANDALL, jun. (J. Pharm. Exp. Ther., 1931, **41**, 121—126).—The minimum lethal doses of glyceryl trinitrate and of sodium nitrite administered intravenously to adult rabbits are 45 mg. and 80—90 mg. per kg., respectively. Asphyxia is probably one of the main causes of death from lethal doses of these compounds. W. O. KERMACK.

Relative toxicities of some organic salts of triethyl lead hydroxide. H. GILMAN and O. M GRUHZIT (J. Pharm. Exp. Ther., 1931, **41**, 1—4).—The minimum toxic and lethal doses of the triethyl lead hydroxide salts of salicylic, *p*-toluenesulphonic, phenylacetic, furoic, *p*-aminobenzoic, furylacrylic, and phosphoric acids (cf. Gilman and Robinson, A., 1930, 1277) have been determined on rats and rabbits. They are all highly toxic with marked action on the mucous membranes and the nervous system. W. O. KERMACK.

Mercurial chemotherapy. I. Mercurial toxicity, its evaluation, mechanism, and relation to chemical constitution. II. Quantitative evaluation of mercurial diuresis and its relation to chemical constitution. E. FOURNEAU and K. I. MELVILLE (J. Pharm. Exp. Ther., 1931, **41**, 21—45, 47—64).—I. The toxic action on rabbits of four groups of mercury compounds injected intravenously has been investigated: (1) inorganic salts of mercury, (2) compounds of the formula Ar·Hg·OH, (3) compounds of the formula $R\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot Hg\cdot OH$, (4) compounds of the formula $Hg(S\cdot CS\cdot R)_2$. The water intake has a marked influence in decreasing the toxicity of mercury compounds only when administered by the mouth, and not when injected subcutaneously. The "minimum toxic dose" is defined as that weight of substance in g. per kg. of rabbit which, when injected intravenously into animals kept on a "basal water-free diet," leads to progressive emaciation and death in 7—14 days. The toxic action is diminished if the diuresis is controlled by the administration of a posterior pituitary extract. Of the compounds studied those belonging to the first group are the most toxic, the minimal toxic dose varying from 1·5 to 2·1 mg. of mercury. The compounds belonging to group (4) are almost equally toxic, although the mercury in these compounds is not precipitated by hydrogen sulphide. Compounds of group (2) are less toxic, the M.T.D. varying from 6·78 to 9·60 mg. of mercury, whilst compounds of group (3) have a M.T.D. from 3·1 to 4·68 mg. of mercury.

II. A method has been elaborated for evaluating the diuretic activity of mercury compounds injected intravenously into rabbits, based on the chemotherapeutic coefficient (*i.e.*, the ratio of minimum dose active diuretically to the minimum toxic dose) and the maximum increase of diuresis produced in rabbits kept under certain specific conditions of water elimination. Solubility appears to play an important role in determining the activity. W. O. KERMACK.

Influence of diuretics on calcium excretion. M. RACHMILEWITZ and E. STRANSKY (Arch. exp. Path. Pharm., 1930, **158**, 129—153).—The low calcium excretion of normal rabbits fed on oats is not affected by sodium sulphate, sodium acetate, or "salyrgan" given orally, and is slightly diminished by potassium acetate. Drinking water causes a small indefinite increase, and the rise caused by caffeine or sodium chloride (*per os*) is slow and protracted. Simultaneous administration of the last two exerts greater diuretic effect without increasing calcium excretion. Calcium gluconate is without effect on the normal diuresis and on the action of repeated administration of caffeine. A. COHEN.

Appearance of protein in bile. T. MATSUDA (Japan. J. Gastroenterol., 1930, **2**, 130—147).—Injury of the liver mechanically, or by carbon tetrachloride, chloroform, tolylenediamine, phosphorus, arsenic, alcohols, or certain organic dyes, causes excretion of protein in the bile. CHEMICAL ABSTRACTS.

Glucose threshold in kidney. S. IMAGAWA (Proc. Imp. Acad. Tokyo, 1930, **6**, 383—384).—Introduction of drugs (phloridzin, mercuric chloride, and potassium cyanide) into the glomerular circulation of the toad results in a glycosuria at low concentrations, whilst that into the capillaries around the tubules has the same effect only at much higher concentrations. This indicates the glomerulus as the seat of the renal sugar-threshold. F. O. HOWITT.

Hyperglycæmia in poisoning. H. JACOBY (Z. ges. exp. Med., 1930, **70**, 100—109; Chem. Zentr., 1930, ii, 2008).—High blood-sugar values are frequently observed in acute hypnotic poisoning. The values fall when oxygen is respired; a similar transient effect is observed in diabetes. Radium emanation causes a similar effect. In a case of oral hydrochloric acid poisoning an abnormally low blood-sugar value (30 mg. per 100 c.c.) was observed. A. A. ELDRIDGE.

Larocain," a new local anæsthetic. K. FROMHERZ (Arch. exp. Path. Pharm., 1930, **158**, 368—380).—An account of the pharmacological properties of "larocain," the monohydrochloride of the base $NEt_2\cdot CH_2\cdot CMe_2\cdot CH_2\cdot O\cdot CO\cdot C_6H_4\cdot NH_2(p)$. A. COHEN.

Local anæsthetic action of 23 isomeric octyl alcohols. H. SCHROEDER and D. I. MACHT (Arch. exp. Path. Pharm., 1930, **158**, 53—64).—The local anæsthetic actions of 23 isomeric octyl alcohols show the same relationships as their general pharmacological properties (cf. A., 1930, 954). The bearing of the phenomenon of synergism on the interpretation of pharmacological data is discussed. A. COHEN.

Significance of reaction of medium in the action of poisons. I. Influence of hydrogen-ion concentration on the action of chloral hydrate and camphor on isolated frog's heart. K. A. Schmelev. **II. Influence of hydrogen-ion concentration on the action of potassium and calcium ions on frog's heart.** N. V. Goljachovski (Arch. exp. Path. Pharm., 1930, **158**, 65—75, 76—89).—The depression of the pulse-rate of the isolated frog's heart by chloral hydrate (1 : 1000) and camphor (1 : 5000) in Ringer solutions of varying p_H is greater and the return to normal more difficult in acid than in alkaline medium. Chloral hydrate exerts greater effect on the contraction amplitude in acid solution, whilst the effects of camphor are most marked in alkaline and acid media, and only slight at p_H values of 6·60 and 7·31.

II. The systolic effects of calcium and potassium on the frog's heart are increased and the diastolic effects decreased by hydrogen ions. Hydroxyl ion has the opposite influence on these effects. Potassium–calcium antagonism is more marked in acid than in alkaline medium. A. Cohen.

Biological assay of analgesics and their mixtures. I. E. Hesse. **II.** E. Hesse, G. Roesler, and F. Buhler (Arch. exp. Path. Pharm., 1930, **158**, 233—246, 247—253).—I. A method is described for assaying analgesics by observing their influence on the reactions of healthy mice to mechanically induced pain. Several drugs have been examined and analgesia is observed with opiates, of which morphine is best, pyrazolones, and derivatives of *p*-aminophenol. Aniline derivatives show little action, and quinoline compounds and salicylates are inactive in contradistinction to clinical experience.

II. A second method of assay, based on the reactions of guinea-pigs to pain caused in an inflamed area of skin, shows that opiates, pyrazolones, salicylates, and the quinoline derivative, "atophan," are active, whilst "hexophan" and *p*-aminophenol derivatives are inactive. It is suggested that, excepting the opiates, the analgesia is due to direct action of the drug on the inflammatory focus. Data are also given for the action of a number of commercial preparations of mixtures of analgesics. A. Cohen.

[Antipyretic action of] sulphur-containing piperazine derivatives. E. Hesse and W. Loch (Arch. exp. Path. Pharm., 1930, **158**, 327—333).—The substances obtained by the condensation of methyl-, ethyl-, *n*-propyl-, *n*-butyl-, allyl-, phenyl-, and *p*-ethoxyphenyl-thiocarbimides with the additive compound of theophylline and piperazine have been examined for antipyretic properties. These are only possessed by the methyl and ethyl derivatives, which are active in a subcutaneous dose of 0·1 g. per kg. rabbit. Since the unsubstituted theophylline–piperazine compound is inactive, it is concluded that antipyretic properties are conferred by the thiocarbamyl group. The diuretic effect of the purine component of these substances is not influenced by the group containing sulphur. A. Cohen.

Thebaine and its derivatives. I. Influence of injection of thebaine and its derivatives on the carbohydrate metabolism. Y. Takeuchi (Sei-i-kwai Med. J., 1930, **49**, No. 6, 74—86).—Subcutaneous injection of thebaine hydrochloride into rabbits increased the blood-sugar and inorganic phosphorus. Dihydrothebaine and oxycodeinone cause similar effects, differences in degree being recorded. Chemical Abstracts.

Influence of p_H on the adsorptive fixation of cocaine hydrochloride by nerve fibres. J. Regnier and G. Valette (Compt. rend., 1931, **192**, 114—116).—Agitation of 0·25 g. of almost ash-free charcoal with 50 c.c. of a 0·005N solution of cocaine hydrochloride causes the fixation of 0·083 g. at p_H 3 and 0·127 g. at p_H 7·5 per g. of charcoal. When the charcoal is replaced by 10·0 g. of ox vagus the fixation rises from 0·08 mg. at p_H 3 to 0·45 mg. at p_H 7·6 per g. of nerve fibre. P. G. Marshall.

Effect of lipins and urine on the diazo-reaction of alkaloids. A. Schakir (Z. Immunität., 1930, **65**, 120—124; Chem. Zentr., 1930, ii, 1740).—In certain pathological urines the diazo-reaction of added morphine or heroin is inhibited. The active principle of such urine may be isolated by precipitation with lead acetate. A. A. Eldridge.

[Pharmacological] potential effects. H. Paffrath (Arch. exp. Path. Pharm., 1930, **158**, 304—313).—The intensity of the stimulant action of choline, acetylcholine, pilocarpine, trimethylamine, and histamine on the mucous membrane of the small intestines of several mammals is inversely proportional to their diffusibility through the membrane. The results support the theory that poisons act in accordance with a potential gradient between the interior of cells and the external medium, since slow permeation of tissues would tend to maintain the necessary *P.D.* A. Cohen.

Motor reactions of the small intestine to histamine. M. E. MacKay (Trans. Roy. Soc. Canada, 1930, [iii], **24**, V, 197—198).—The administration of histamine to dogs and cats anæsthetised by a mixture of chloralose and urethane markedly increases the motility of the intestine when injected in doses of 0·25—0·5 mg. intravenously, but not when injected subcutaneously or intra-intestinally. Characteristic effects are produced on the duodenum, jejunum, and ileum, respectively. Paralysis of the parasympathetic nervous system by atropine greatly diminishes but does not abolish the action. W. O. Kermack.

Importance of exact method of preparation of tincture of digitalis and the number of pigeons in the pigeon-emesis method. P. J. Hanzlik, A. B. Stockton, and S. S. Davis (J. Pharm. Exp. Ther., 1931, **41**, 5—10).—Tinctures of digitalis prepared from the same leaves with different percolation times may be of different strengths as determined by the pigeon-emesis method. W. O. Kermack.

Use of therapeutic effects as end-points in the biological titration of the digitalis substances. H. Gold, B. Gelfand, and W. Hitzig (J. Pharm. Exp. Ther., 1931, **41**, 89—102).—In the assay of digitalis with the cat as test animal more precise results are obtained when ventricular fibrillation is used as the end-point than when effects within the

therapeutic range of the drug are employed. The pigeon-emesis method of standardisation is criticised.

W. O. KERMACK.

Cell fats. R. DEGKWITZ (Klin. Woch., 1929, **8**, 2224—2229; Chem. Zentr., 1930, ii, 69).—Highly dispersed sodium oleate, lecithin, triolein, cholesterol, and cholesteryl ester are powerful cellular poisons at concentrations far below physiological. In experiments with *Paramecia* the toxicity is a physical effect, altering the relationship between the hydrophilic and hydrophobic colloids and producing a protoplasmic form incompatible with life.

A. A. ELDRIDGE.

Effects of pimento pepper on poultry. W. L. BROWN (Georgia Agric. Exp. Sta. Bull., 1930, No. 160, 11 pp.).—Addition of pimento to poultry rations increases the pigmentation of the shanks, comb, and wattles, the effect being more pronounced in cockerels than in pullets. Pimento pigment appears in chicks 5—6 days after hatching. A. G. POLLARD.

Titanium-alloy electrodes as a therapeutic agent. W. B. TROUP (Brit. J. Actinother., 1931, **5**, 235).—The titanium-alloy electrodes (98% W, 1·5% Ti, 0·5% Cr) generate a greater proportion of infra-red rays than other electrodes used in artificial light therapy and the radiation in certain regions of the spectrum is more penetrating than that from a pure tungsten arc. C. C. N. VASS.

Nature of the active radiations in the phenomena of photosensitisation. J. CUZIN (Bull. Soc. Chim. biol. 1930, **12**, 1401—1409; cf. A., 1930, 1215). —The action of radiations of various wave-lengths in sensitising eosin, methylene-blue, and hæmatoporphyrin in their action on the isolated intestine of the rabbit is studied. Ultra-violet light increases the amplitude and tone of the intestine; with eosin, the toxic action of light rays of all wave-lengths with the exception of blue light suppresses the depressive action of the dye on the intestine. The action of ultra-violet light on a dilute solution of methylene-blue increases its toxic effect, whilst with a concentrated solution it increases its depressive effect. Light of other wave-lengths has no action. Hæmatoporphyrin exhibits the strongest response. Without irradiation, it has little or no effect. Irradiation with total light and yellow light causes a marked depressive action, whilst, in order of decreasing strength, green, blue, and ultra-violet light have a similar effect.

B. LEVIN.

Metabolic effects of mitogenetic irradiation. A. GURVITSCH (Biochem. Z., 1930, **229**, 109—114; cf. Gesenius, A., 1930, 1620).—Results obtained under the experimental conditions used by Gesenius are not to be explained as contradicting those of the author. The possible effects of over-irradiation and the phenomenon of secondary irradiation must be taken into consideration. W. MCCARTNEY.

Action of X-rays on tissue cultures *in vitro*. L. DOLJANSKI, J. J. TRILLAT, P. L. DU NOUY, and A. ROGOZINSKI (Compt. rend., 1931, **192**, 304—306).—By means of an ionisation chamber the lethal dose of X-rays necessary completely to arrest the growth of a culture of fibroblasts is found to be of the order of 120,000 r (international units), a value of the same magnitude as that observed with other micro-organisms. J. W. BAKER.

Biological significance of the physical state of lyophilic colloids. F. F. NORD (Trans. Faraday Soc., 1930, **26**, 760—767).—A summary of the work of the author and his collaborators on the activation and protection of enzyme solutions by ethylene and acetylene and on the action of these hydrocarbons on the viscosity and surface tension of lyophilic colloids, *e.g.*, soap solutions and egg-albumin (cf. B., 1929, 994; A., 1930, 1367). The unsaturated hydrocarbons produce an increase in surface tension and a decrease in the viscosity of the lyophilic colloids and of the enzyme solutions, although they have no effect on pure water. It is concluded that they bring about an increase in the dispersion of the colloidal particles correlated with the observed increase in enzyme activity. W. O. KERMACK.

Apparatus for measuring catalase activity in plant and animal tissues. H. H. BUNZELL (Science, 1930, **72**, 505—506).—Descriptive. A unit of catalase activity is defined as that which produces in 5 min. the liberation of 1 γ of oxygen per g. of tissue.

L. S. THEOBALD.

Mechanism of oxidation processes. XXVI. Dehydrogenating enzymes of milk. H. WIELAND and T. F. MACRAE (Annalen. 1930, **483**, 217—250; cf. Wieland and Rosenfeld, A., 1930, 248).—In different samples of milk the power of promoting the oxidation of xanthine by methylene-blue is not in constant proportion to the power of promoting the oxidation of aldehydes by methylene-blue. In a sample of fresh milk the xanthine-dehydrogenase activity is relatively low, but slowly increases on keeping. This increase is brought about more rapidly by agitation. Similar although less marked alterations in activity occur in respect of the aldehyde-dehydrogenase. It appears that the union of the fat droplets into larger ones with the resultant decrease in surface at which the enzyme is probably adsorbed and partly inactivated is responsible for this phenomenon. This conclusion is supported by observations on the separated cream. The results obtained confirm the view (cf. Wieland and Rosenfeld, *loc. cit.*) that the xanthine- and aldehyde-dehydrogenases are separate enzymes. The xanthine-dehydrogenase is removed from whey by adsorption on calcium carbonate, leaving the aldehyde-dehydrogenase in solution, but the former is largely inactivated in the process. When the oxidation of aldehydes (acetaldehyde, formaldehyde, benzaldehyde, salicylaldehyde, or anisaldehyde) by oxygen takes place in presence of the dehydrogenase and ceric hydroxide, the hydrogen peroxide formed reacts to form cerium peroxide (cf. *loc. cit.*). The low values (about 60% of the theoretical) previously obtained when the hydrogen peroxide formed was determined are due to an error in the determination. By an improved method results are obtained more nearly approaching the theoretical. The effect of hydrogen cyanide on the oxidation of acetaldehyde, formaldehyde, and benzaldehyde has also been determined. The oxidation of the aldehyde in presence of methylene-blue is inhibited by small quantities of hydrogen peroxide, especially if this reacts with the enzyme in presence

of substrate. Observations have been made on the decolorisation of methylene-blue in presence of the enzyme when more than one substrate is present, *e.g.*, xanthine plus an aldehyde, or two different aldehydes. The enzyme solutions are also able to effect the dismutation of aldehyde (aliphatic or aromatic) into acid and alcohol, the optimum p_H being about 8·3. Evidence is adduced that the same enzyme is responsible for the aerobic and anaerobic oxidation in presence of methylene-blue and for dismutation. The effect of hydrogen cyanide on all three reactions is of the same order of activity.

W. O. KERMACK.

Mechanism of oxidative processes. XXVII. Dehydrogenases of muscle tissue. H. WIELAND and A. LAWSON (Annalen, 1931, **485**, 193—210).—The retarding influence of hydrogen cyanide on succinic acid dehydrogenase (A., 1930, 168) and catalase is of similar magnitude and hence this anti-catalyst cannot be used to retard the catalase activity preferentially and so detect the formation of hydrogen peroxide. In the presence of ceric hydroxide the activity of catalase is reduced to 10% of its original value and added hydrogen peroxide escapes the attack of this enzyme and is retained quantitatively as cerium peroxide. Hydrogen cyanide (0·002N) in the presence of ceric hydroxide has a greater retarding effect on succinate dehydrogenation than has hydrogen cyanide alone, although ceric hydroxide alone has almost no retarding effect. In the presence of ceric hydroxide increasing the concentration of hydrogen cyanide from 0·002—0·01N is without effect. At the latter concentration of hydrogen cyanide the reaction velocity is greater in the presence of ceric hydroxide. The enzyme from muscle fibre has also a dehydrogenating action on quinol (p_H 6·8), the velocity decreasing with decreasing concentration of quinol, and in this reaction an initial latent period is observed. Benzoquinone has a strong retarding influence which, however, depends on the quinol concentration. The retarding action of hydrogen cyanide is similar to that in succinate dehydrogenation. In the presence of 0·004—0·001N-quinol (p_H 6·8) and succinate the absorption of oxygen is somewhat more rapid than with 0·02N-succinate alone, suggesting the simultaneous action of two different enzymes, but with higher concentrations of quinol (0·04—0·02N) the reaction is strongly retarded. The ratio of the amounts of oxygen absorbed in 2 hrs. at p_H 6·8 by 0·02N-succinate and 0·02N-quinol, respectively, varies from 2·2 with a dehydrogenase preparation 4 days old to 0·21 with the same preparation after 17 days. Dehydrogenation of pyrocatechol, *p*-cresol, and tyrosine is also effected by the enzyme, but its activity is only 20, 10, and 2%, respectively, of that with quinol. Dihydroxyphenylalanine is unattacked. The ratio of the activities of the expressed muscle juice and of the tissue (from left ventricle of a horse's heart) is 3 : 2 for succinate dehydrogenation and 4 : 1 for dehydrogenation of quinol. Desiccation of the expressed juice over concentrated sulphuric acid in a vacuum destroys its quinol activity, but 50% of its succinate activity is still preserved. The partial separation of the two dehydrogenases which the above results suggest to be present is effected by precipitation of the centrifuged expressed juice with saturated ammonium sulphate. An aqueous suspension of the centrifuged precipitate retains most of the succinate dehydrogenase, but most of the quinol dehydrogenase remains in solution. Conversely, precipitation with acetone affords a preparation free from succinate dehydrogenase which, however, retains considerable activity towards quinol.

J. W. BAKER.

Peroxidase reagents producing quinoneimide dyes. II. A. CASOLARI (Biochim. Terap. sperim., 1929, **16**, 254—266; Chem. Zentr., 1930, ii, 2551).—The use of aromatic bases, or mixtures thereof, which are oxidised by hydrogen peroxide in presence of peroxidase to dyes of the quinonedi-imide series is recommended for the detection of blood and the distinction between fresh and boiled milk. A similar oxidation is effected by other peroxides, *e.g.*, ether containing peroxide or aged oils. The reactions are retarded by mineral acids, and inhibited even by acetic acid in high concentration, but must be carried out in dilute acetic acid solution. The reactions taking place by the use of various reagents are described.

A. A. ELDRIDGE.

Determination of peroxidase activity. J. D. GUTHRIE (J. Amer. Chem. Soc., 1931, **53**, 242—244).—The method utilises the formation of indophenol from *p*-phenylenediamine and α-naphthol in presence of a citrate buffer, by treatment with the extract (containing the enzyme) and dilute hydrogen peroxide. The amount of indophenol produced is determined colorimetrically.

H. BURTON.

Autoxidation of leucomethylene-blue. T. F. MACRAE (Ber., 1931, **64**, [*B*], 133—137).—Dissolved methylene-blue is hydrogenated in the presence of milk enzyme and the approximately calculated amount of hypoxanthine in an atmosphere of nitrogen, catalase being added to exclude the production of hydrogen peroxide. After destruction of the enzyme, the absorption of oxygen is measured in the solution with or without addition of ceric hydroxide or catalase. It is shown that the hydrogen peroxide formed has little part in the dehydrogenation of leucomethylene-blue. In the presence of ceric hydroxide, the hydrogen peroxide is almost completely retained and, in the absence of this acceptor, two thirds of the peroxide formed can be identified at p_H 8·0; the remainder is probably consumed by the uric acid arising from the hypoxanthine. Leucomethylene-blue at 8·0 is oxidised about ten times as rapidly by molecular oxygen as by hydrogen peroxide; the autoxidation is not restricted by hydrocyanic acid or carbon monoxide. Addition of iron under the experimental conditions causes a fivefold increase in the rate of oxidation, which is reduced to half by hydrocyanic acid in 125M concentration. The rate of oxidation exhibits normal dependence on the temperature.

H. WREN.

Carbohydrate-redoxase. H. VON EULER and R. NILSSON (Z. physiol. Chem., 1931, **194**, 260—268).—Aqueous extracts of the seeds of *Corchorus capsularis* contain co-zymase. The co-zymase-free extract does not decolorise methylene-blue in presence of sodium hexosediphosphate (cf. Deuticke, this vol., 122);

decolorisation proceeds rapidly when co-zymase is added. The decolorisation of methylene-blue by fresh rat-muscle is slightly accelerated by creatine; a dry muscle preparation is not affected. The muscle-juice, diluted with phosphate containing co-zymase, is without action on methylene-blue. Decolorisation is markedly accelerated by creatine or, better, by sodium creatinephosphate or hexosediphosphate. A dry ox-muscle preparation shows a similar behaviour with the phosphates, but not with creatine. Washed muscle does not cause reduction of methylene-blue either in absence or presence of creatine.

H. BURTON.

Enzymes and light. XVII. Effect of visible and ultra-violet light on the succinodehydrogenase of horse-muscle. L. PINCUSSEN and W. ROMAN (Biochem. Z., 1930, **229**, 281—290).—On curves showing the relation between the activity of succinodehydrogenase, in the system succinic acid–fumaric acid in the presence of malic acid, and the reaction of the medium in which it acts, two peaks appear. The peak representing highest activity is at p_H 6·9; the other is at p_H 7·7. In general, the enzyme is more active in the acid zone of hydrogen-ion concentration than in the alkaline. The activity of the enzyme is greatly reduced by exposure for 15 min. to ultra-violet light at p_H 6·0—8·0, but in the acid zone is not completely destroyed. Irradiation for 1 hr. with visible light also causes reduction of the activity, such reduction being greatest at the points corresponding with the peaks on the curves, but when this irradiation lasts for only 0·5 hr. the activity is so increased at weakly acid and weakly alkaline reactions that it surpasses that of the un-irradiated enzyme at the same reactions. When the reaction of the medium is neutral the activity of the enzyme is reduced by irradiation of short duration.

W. MCCARTNEY.

Substances protecting amylase. I. Introduction. II. Protective action of proteases. III. Protective action of proteins and digestion products. H. NAKAMURA (J. Soc. Chem. Ind. Japan, 1930, **33**, 521—522B, 523—524B, 524—526B). —I. The activity of takadiastase, measured by the formation of reducing sugar from starch under standard conditions, varies little between p_H 4·9 and 5·8. The decrease in activity after preliminary heating at 50° at various values of p_H and different concentrations is determined.

II. The addition of pepsin or papain solution, even after having been heated at 100° for 20 min., prevents heat-inactivation.

III. Peptone prevents heat-inactivation, and gelatin, egg-albumin, and caseinogen exert protective action, decreasing in strength in the order given. The solutions obtained by digestion with pepsin or papain also exert protective action, enhanced in the case of egg-albumin and pepsin. No activation phenomena are observed in any case.

R. K. CALLOW.

Glycogenolysis. H. K. BARRENSCHEEN, J. PANY, and R. BERGER (Biochem. Z., 1930, **229**, 196—215).—In the livers of guinea-pigs, rabbits, and dogs post-mortal decomposition of glycogen and the production of inorganic phosphate proceed in such a way that the curves representing these changes follow parallel courses which take the form of a series of steps. The inorganic phosphate is derived chiefly from that portion of the acid-soluble organic phosphate which is difficultly hydrolysed. Neither the decomposition of the glycogen nor the production of inorganic phosphate is affected *in vitro* by addition of insulin or by temporary poisoning with insulin. As a result of the decomposition of glycogen a *hexosemonophosphoric acid*, $[\alpha]_D^{8}$ −6·34° (*osazone*, m. p. 177°; *barium* salt, $[\alpha]_D^{18}$ —8·4°), not identical with the other known natural or synthetic substances can be isolated by Neuberg and Leibowitz's modification (A., 1927, 700) of Robison's method (A., 1923, i, 86) from both rabbit and dog livers.

W. MCCARTNEY.

Post-mortal production of lactic acid in the liver. E. FENZ and H. POPPER (Biochem. Z., 1930, **229**, 397—426).—The post-mortal lactic acid content of the human liver (and also of that of the guinea-pig) reaches a maximum about 7 hrs. after death. Pathological conditions have no great effect on the maximum amount of lactic acid produced nor does this amount depend on the total carbohydrate content. In human livers kept at 37° in sodium hydrogen carbonate solution or in disodium hydrogen phosphate solution for a period of 10—33 hrs. no further increase in the lactic acid content occurs even if dextrose be added. In guinea-pig livers placed immediately after death in a buffer solution and kept at 37° the power to produce lactic acid decreases in such a way that after about 7 hrs. no more can be detected and additions of dextrose, lævulose, glycogen, or hexosediphosphate usually have no effect on this decrease. The same holds, at least partly, of human livers, and their pathological condition is also without effect on this loss of power to produce lactic acid. As regards post-mortal lactic acid production human kidneys resemble human livers. The lactic acid content of practically all the organs from two human corpses and from two guinea-pigs has been determined.

W. MCCARTNEY.

Production of methylglyoxal and pyruvic acid by yeast under the influence of plasmolytic substances. C. NEUBERG and M. KOBEL (Biochem. Z., 1930, **229**, 255—262).—The process in which methylglyoxal and, later, pyruvic acid are produced from magnesium hexosemonophosphate by the action of yeast can be checked and the two compounds allowed to accumulate by the addition of one of many plasmolytic substances, of which toluene and bromobenzene are especially suitable. The substrate itself, if present in sufficient concentration, has the same effect. The dinitrophenylhydrazones of the two compounds can be distinguished from each other by the difference in the colours which they give (methylglyoxal, deep bluish-violet; pyruvic acid, brown then red) with alcoholic potassium hydroxide solution and can be separated by the use of sodium carbonate solution, in which the methylglyoxal compound is insoluble.

W. MCCARTNEY.

Carbohydrate metabolism of higher plants. Production of methylglyoxal by the enzymes of germinated seeds. C. NEUBERG and M. KOBEL (Biochem. Z., 1930, **229**, 433—442; cf. A., 1929,

722).—The enzyme which acts on magnesium hexosediphosphate in such a way as to lead to the production of methylglyoxal is present in germinated peas (*Pisum saccharatum*) and in germinated beans (*Vicia faba*). W. McCartney.

Glyoxalase. F. Sakuma (J. Biochem., Japan, 1930, **12**, 247—279).—The liver is richest in glyoxalase; values for cold-blooded animals are only half as great as those for warm-blooded animals. When the tissues are deprived of sugar the glyoxalase content also diminishes, that of the liver decreasing least rapidly. In germinating soya beans the glyoxalase content at first increases and then decreases after 7—8 days. The extraction of the enzyme is described. Dextrose or polysaccharides containing glucose accelerated the activity of glyoxalase, whereas phosphate inhibited it. Guanine and its derivatives and amino-acids cause a rapid disappearance of methylglyoxal with production of ammonia and carbon dioxide. Chemical Abstracts.

Kinetics of ester hydrolysis by enzymes. III. Influence of the indicator on the activity of esterases. IV. Behaviour of esterases towards lactones. E. Bamann and M. Schmeller (Z. physiol. Chem., 1931, **194**, 1—13, 14—20; cf. A., 1930, 956).—III. The retardation of ester hydrolysis caused by small amounts of indicator leads to inaccuracies in the method of Knaffl-Lenz (A., 1923, i, 621) for the titrimetric determination of liver-esterase. Data are presented for the hydrolysis of methyl butyrate by liver enzymes from man, horse, sheep, and rabbit, with varying concentrations of indicator and ester, using phenolphthalein, bromothymol-blue, and bromocresol-purple. The indicator effect decreases as p_H increases, and, in alkaline medium, gives way to an acceleration of the hydrolysis, which may be associated with a change of structure of the phthalein type of indicator. Thus, a 31% inactivation observed with 1 mg. of bromothymol-blue per 100 c.c. of reaction mixture at p_H 7·0 is replaced by an activation of 44% at 8·9.

Bromocresol-purple (0·04 mg. per 100 c.c.) and neutral-red (0·3 mg. per 100 c.c.) have no measurable effect on hydrolysis at p_H 6·8 and 7·3, respectively, and, under these conditions, are regarded as the most suitable indicators.

IV. γ-Butyrolactone, γ-valerolactone, coumarin, and santonin are not appreciably hydrolysed by liver-esterases in solutions buffered at p_H 8·9. It is probable that the intermediate lactone–enzyme complex decomposes slowly, since these lactones inhibit the hydrolysis of methyl butyrate by esterase to a degree which varies inversely with the concentration of ester. A. Cohen.

Substance suitable for use as a model for illustrating the mode of action of the pectases. C. Neuberg and C. Ostendorf (Biochem. Z., 1930, **229**, 464—466).—The properties of the calcium salt of methyl hydrogen *d*-tartrate (A., 1909, i, 361) make this substance suitable for use as a model in the study of the mode of action of the pectases. These decompose the compound liberating methyl alcohol and causing the precipitation of gelatinous calcium tartrate which eventually crystallises. W. McCartney.

Liberation of tyrosine and tryptophan from caseinogen by papain activated with hydrocyanic acid. T. Leipert and I. Hafner (Biochem. Z., 1930, **229**, 427—432).—Amino-nitrogen equivalent to 47% of its total nitrogen content was liberated from caseinogen as a result of digestion for 12 days with papain which had been activated by treatment with hydrogen cyanide. During this period all of the tyrosine in the caseinogen was set free, but the tryptophan was liberated only partly and at the same rate as were the remaining amino-acids. Activated papain in conjunction with trypsin liberated, in one week, 71% of the total nitrogen of caseinogen as amino-nitrogen, but the liberation of tyrosine and tryptophan was not otherwise affected by this combined action. W. McCartney.

Multiple nature of the enzyme carrier in the hydrolysis of polypeptides by yeast macerates. Production of a protein-free eluate which acts on higher polypeptides only. A. Fodor and L. Frankenthal (Biochem. Z., 1930, **229**, 16—27).—When the material precipitated by acid from diluted yeast macerates is adsorbed on kaolin and this is then kept for 2 hrs. at 37° in contact with a 2% solution of glycine the liquid which is obtained when the glycine solution is filtered is free from protein but retains the activity of the original macerate. Since this liquid exhibits specificity with regard to its effects on peptides, some of which it hydrolyses more rapidly than others, the authors' views concerning the anchoring and disconnecting of enzymes and their transference from one carrier to another are confirmed (cf. this vol., 262). W. McCartney.

Hydrolysis of proline-polypeptides by yeast and pancreas extracts and by pancreatin preparations. A. Fodor, M. Frankel, and S. Kuk (Biochem. Z., 1930, **229**, 28—40; cf. preceding abstract).—*dl*-Prolylalanine is readily hydrolysed by the water-insoluble part of dried pancreatin, but only slowly and partly by the water-soluble portion. Hydrolysis is also caused by macerates of fresh pancreatic glands (especially if such macerates are first purified by dialysis) and by the two active constituents of yeast macerates. *dl*-Alanylproline is hydrolysed by yeast macerates, but not by pancreatin. It follows from these results that the enzymic hydrolysis of polypeptides is not directly dependent on the presence in the latter of certain groups such as the free amino- or carboxyl groups. W. McCartney.

Specificity of animal proteases. XX. Mechanism of the enzymic fission of dipeptides. A. K. Balls and F. Kohler. **XXI. Causes of steric selection by enzymes.** E. Waldschmidt-Leitz and A. K. Balls (Ber., 1931, **64**, [*B*], 34—45, 45—48; cf. Waldschmidt-Leitz and others, A., 1929, 723; 1930, 957).—XX. The presence of a free amino-group but not of a free carboxyl group appears essential to the enzymic activity of that component of intestinal erepsin which hydrolyses dipeptides. The apparent minor importance of the second component of the dipeptide is not in harmony with the observed hydrolysis of glycyl-*d*-alanine and non-hydrolysis of glycyl-*l*-alanine by dipeptidase. The apparent contradiction is explained by the hypo-

thesis that the enzyme unites with the substrate by two haptophoric groups, the second of which is regarded as the imino-group of the peptide. Since *p*-nitroaminoacetanilide, *p*-aminoacetamidobenzoic acid, and nitroaminoacetamidobenzoic acid are hydrolysed by dipeptidase, whereas aminoacetanilide, aminoacet-*p*-toluidide, and *o*-aminoacetamidobenzoic acid are unaffected, the influence of the substituent (nitro-group or carboxyl) is ascribed to change in the acidic nature of the imino-group. The restriction of dipeptidase action by substances such as chloroacetyltyrosine and aceturic acid confirms the view that the imino-group is the second point of attachment of the enzyme. The following new compounds are described: *aminoacetanilide hydrochloride*, m. p. 170°; *aminoacet*-o-*toluidide*, m. p. 256°; o-*aminoacetamidobenzoic acid*, m. p. 236°; m-*aminoacetamidobenzoic acid*, m. p. 245°; *nitro*-o-*aminoacetamidobenzoic acid*, m. p. 245—260° according to the rate of heating (from *o*-aminoacetamidobenzoic acid, sulphuric acid monohydrate, and potassium nitrate at —5° to —10°); *chloroacet*-p-*toluidide*, m. p. 168—169°, from chloroacetyl chloride and *p*-toluidine in benzene; *aminoacet*-p-*toluidide*, m. p. 137° after softening at 95°; *chloroacet*-p-*chloroanilide*, m. p. 173°; *aminoacet*-p-*chloroanilide*, m. p. 85°; *chloroacet*-p-*nitroanilide*, m. p. 185°; *aminoacet*-p-*nitroanilide*, m. p. 165°.

XXI. The preparation of o-*chloroacetamido*-, m. p. 190°, m-*chloroacetamido*-, m. p. 232°, and *p*-chloroacetamido-benzoic acid, m. p. 257° (cf. Tropp, A., 1928, 1025), is described. Of these, only the *meta*-derivative is hydrolysed by carboxypolypeptidase from pancreas. The underlying causes are discussed.

H. Wren.

Nature of proteases. VII. Pepsin in cold- and warm-blooded animals. N. P. Pjatnitzkij (Z. physiol. Chem., 1931, **194**, 43—52; cf. Adova and Smorodincev, A., 1930, 1620).—Frog's gastric juice, obtained by the method of Smirnow, has p_H varying between 1·52 and 3·9. Its hydrolytic activity, referred to egg-albumin, for which the optimum p_H is 1·0—1·4, is 25% greater than that of dog's gastric juice, but only half of that for the dog when estimated on caseinogen. The stomach extract of a frog has smaller hydrolytic activity on egg-albumin than an extract of the mucous membrane of the dog's stomach. Pepsin preparations from cold- and warm-blooded animals appear to be identical. A. Cohen.

Plant proteases. XVI. Activation of animal and plant proteases by glutathione. W. Grassmann, O. von Schoenebeck, and H. Eibeler (Z. physiol. Chem., 1931, **194**, 124—136).—Reduced glutathione activates papain, yeast proteinase, and cathepsin, thus resembling cysteine (A., 1930, 500). The oxidised form has no activating power, and neither form has any action on pepsin. Yeast phytokinase (cf. Ambros and Harteneck, A., 1929, 606) is identical with glutathione. H. Burton.

Action of proteases on urease preparations. J. Zakowski (Biochem. Z., 1930, **229**, 41—84).—The activity of urease is reduced by as much as 80% by the action, at 30—40° and in media having certain hydrogen-ion concentrations, of papain or trypsin. Results obtained with activated and inactivated papain and trypsin indicate that it is not impossible, although not probable, that the diminution of activity (which is not caused by the presence of inhibitory substances) may be due to enzymes which attack the urease itself or the material which carries it. Erepsin has no effect on the activity of urease.

W. McCartney.

Action of arginase. VI. S. Edlbacher and H. Burchard (Z. physiol. Chem., 1931, **194**, 69—75; cf. A., 1928, 88).—Arginylarginine prepared from clupeine by the method of Kossel and Staudt (A., 1928, 81) is completely hydrolysed by a peptidase–arginase mixture from calf-liver extract. Purified arginase, obtained free from peptidase by adsorption of the latter on aluminium hydroxide, hydrolyses only one guanidyl group in arginylarginine.

A. Cohen.

Respiration and fermentation of top and bottom beer yeasts. K. Trautwein and J. Wassermann (Biochem. Z., 1930, **229**, 128—153).—Examination of the behaviour of biologically pure strains of yeast showed that the rates of respiration of top yeasts are on the average 77% greater than are those of bottom yeasts. The difference is related to the racial characteristics of the strains and is traced to adaptation to environment. In both types of yeast increase in rate of respiration is accompanied by increase in the degree of fermenting power, a constant ratio persisting between these two factors. The metabolic energy expended in respiration and fermentation by top yeast is 42% greater than that expended by bottom yeast. The proportion of energy involved in respiration is, for the top yeasts, 40% and for the bottom yeasts 32%. Of the sugar decomposed by the yeasts 2—3% is required for respiration and 98—97% is fermented.

W. McCartney.

Fourth form of cell-free fermentation by yeast. M. Kobel and M. Scheuer (Biochem. Z., 1930, **229**, 238—247).—The fermentation of yeast maceration juice may proceed in such a way that the fourth type of fermentation only occurs. When the juice is diluted six times and the initial concentration of magnesium hexosediphosphate in the fermenting liquid is 0·9749% 79% of the hexose is liberated and converted entirely into pyruvic acid and glycerol.

W. McCartney.

Hydrolysis of non-phosphorylated sugars by yeast with production of glycerol and pyruvic acid. C. Neuberg and M. Kobel (Biochem. Z., 1930, **229**, 446—454).—By the action of yeast on dextrose in the presence of magnesium phosphate, magnesium oxide, or disodium hydrogen phosphate glycerol and pyruvic acid can be produced, although the yields obtained are not so high as when salts of hexosephosphoric esters are used.

W. McCartney.

Iodo- and bromo-acetic acid poisoning in carbohydrate degradation. R. Nilsson, K. Zeile, and H. von Euler (Z. physiol. Chem., 1931, **194**, 53—68; cf. Lundsgaard, A., 1930, 954, 958).—When alcoholic fermentation is inhibited by iodo- or bromo-acetic acid, formation of hexosediphosphate is not observed, and hexosemonophosphate is not detected under conditions which do not prevent its formation in the case of sodium fluoride poisoning. Iodoacetic acid

also prevents acetaldehyde reduction, which is not affected by fluoride. In agreement with Lundsgaard, it is found that over a small range of concentrations of iodoacetic acid (0·001—0·0001M) oxygen consumption continues, whilst fermentation is completely inhibited. It is suggested that iodoacetic acid poisoning involves the later stages of the chain of fermentation reactions. A. COHEN.

Order of death of organisms larger than bacteria. O. RAHN (J. Gen. Physiol., 1931, **14**, 315—337).—The death of bacteria is brought about by the destruction of only one definite gene-like molecule in the cell. A discussion and criticism of previous work are given, from which it is shown that, of the larger organisms, only *Chlamydomonas* has a similar order of death. The mould, *Botrytis cinerea*, has more than one reacting molecule, and the flagellate *Colpidium*, together with erythrocytes, has two reacting molecules. P. G. MARSHALL.

Variations in the response to light of *Amœba proteus* with special reference to the effects of salts and of hydrogen-ion concentration. S. O. MAST and H. R. HULPIEU (Protoplasma, 1930, **11**, 412—431).—The effect of changing light intensity on the protoplasmic streaming in *A. proteus* is influenced by the presence of dissolved substances in the culture liquid. The reaction time (period between light change and response) is increased by the presence of hydrochloric acid and the chlorides of magnesium, calcium, and potassium and decreased by carbon dioxide. The effect of sodium chloride was irregular. A. G. POLLARD.

Hæmotoxin in *Sarcosporidia*. S. SATO (Kitasato Arch. Exp. Med., 1930, **7**, 201—212).—The thermostable hæmolytic principle of sarcosporidiotoxin is negative to protein tests, but the hæmagglutinative principle (destroyed at 85° in 30 min.) is positive. Inhibition or acceleration by serum fractions is recorded. CHEMICAL ABSTRACTS.

Effect of initial reaction of Raulin's medium on the culture of *Aspergillus niger*. C. LOPARDO, J. B. MARGARA, and J. DEL VECCHIO (Ann. farm. bioquim., 1930, **1**, 111—118).—*Aspergillus niger* cultivated at 37° in Raulin's medium of p_H 1·9—6·7 produces an increasing acidity which is maximal (p_H 1·8) on the third day. CHEMICAL ABSTRACTS.

Effect of ammonium salt on the growth of *Penicillium roqueforti* in cheese. N. S. GOLDING (Trans. Roy. Soc. Canada, 1930, [iii], **24**, V, 133—140).—Fresh Wensleydale cheese contains very little ammonia. The addition of ammonium chloride to the curd at salting does not favourably affect the rate or extent of growth of *P. roqueforti* on the cheese, but appears to exert a slight detrimental effect. W. O. KERMACK.

Biochemical transformations of acetic acid by the action of moulds. Chemistry of citric acid production. T. CHRZASZCZ and D. TIUKOV (Biochem. Z., 1930, **229**, 343—357; cf. A., 1930, 1218).—By the action of a certain species of *Penicillium* (a typical accumulator of citric acid) on alkaline solutions of the calcium, sodium, or potassium salt of acetic acid, succinic, fumaric, oxalic, l-malic, and citric acids and at least one other unidentified acid are produced. The number and amount of acids produced vary according to the salt used. Production of citric acid and possibly also of oxalic acid is favoured by the use of the alkali salts. The mechanism of the process of conversion is discussed and it is suggested that the production of citric acid from sugars by the action of moulds proceeds by way of the following substances in the order given: pyruvic acid and acetaldehyde, ethyl alcohol, acetic acid, succinic acid, fumaric acid, l-malic acid. W. MCCARTNEY.

Significance of aldehyde dismutation in acetic fermentation. A. BERTHO and K. P. BASU (Annalen, 1931, **485**, 26—42).—Further work is described in support of the view that aldehyde dismutation plays little part in acetic fermentation (Wieland and Bertho, A., 1929, 219; Bertho, *ibid.*, 1492) contrary to Neuberg and Windisch (A., 1926, 324) and Simon (A., 1930, 1477). It is found that with *B. pastorianum* under fully aerobic conditions the formation of alcohol from acetaldehyde takes place at less than the velocity of anaerobic dismutation. No significant variation in velocity with p_H is observed, contrary to Simon (*loc. cit.*). The alcohol formed is 2—10% of theory on the assumption of exclusive dismutation. Parallel measurements of the consumption of oxygen and of the formation of acetic acid are concordant with the predominance of dehydrogenation of acetaldehyde over dismutation. R. K. CALLOW.

Acids produced by various strains of propionic bacteria. P. W. WILSON, E. B. FRED, and W. H. PETERSON (Biochem. Z., 1930, **229**, 271—280).—Experiments with 11 strains of propionic bacteria and pure sugars or mixtures containing sugars show that dextrose, lactose, maltose, and sucrose are partly fermented by pure cultures of the bacteria and practically completely fermented by mixtures of the cultures with those of *Lactobacillus casei*, up to 75% of the sugar consumed being converted into volatile acids. The quantity of volatile acids produced during the fermentation varies with the strain of the bacteria used and those strains which are most effective with pure sugars are also most effective with mixtures. Of the latter molasses and hydrolysed starch are most rapidly fermented. The volatile acids produced consist chiefly of acetic and propionic acids in the molecular proportion 1 : 2·46. W. MCCARTNEY.

Formation of hydrogen peroxide by lactic acid bacteria. A. BERTHO and H. GLÜCK (Naturwiss., 1931, **19**, 88).—Certain facultative anaerobic, catalase-free lactic acid bacteria (*B. Delbrücki*, *B. iugurt*, and *B. acidophilus*) produce hydrogen peroxide in oxidative metabolism. The reaction is not influenced by a 0·0005M solution of hydrocyanic acid. The peroxide can be detected by titanium sulphate, and determined either as cerium peroxide or by direct titration. *Streptococcus casei* did not, under similar conditions, produce hydrogen peroxide. W. R. ANGUS.

The *Coccaceæ*. XVI. The genus *Leuconostoc*. G. J. HUCKER and C. S. PEDERSON (N.Y. State Agric. Exp. Sta. Tech. Bull., 1930, No. 167).—The fermentation of sugars by numerous strains of gas-producing, chain-forming cocci isolated from milk

products, fermenting vegetables, etc. indicates their classification as a separate genus, viz., *Leuconostoc*, Van Tieghem. These produce *l*-lactic and acetic acids, carbon dioxide, and ethyl alcohol during the fermentation of carbohydrates. Mannitol and, in most cases, dextran or lævulosan are produced from lævulose. Most species require growth accessory factors, *e.g.*, yeast or tomato juice. A. G. POLLARD.

Glycuronic acid, a constituent of the gum of root nodule bacteria. E. W. HOPKINS, W. H. PETERSON, and E. B. FRED (J. Amer. Chem. Soc., 1931, **53**, 306—309).—Glycuronic acid has been identified as a constituent of the gum produced by the root nodule bacteria of pea and red clover (A., 1930, 1478). H. BURTON.

Effect of Bordet's bacillus on rabbit's blood. S. TAKAHASHI (Sei-i-kwai Med. J., 1930, **49**, No. 1, 116—130).—*B. pertussis* increases the sedimentation velocity of the blood and the colloidal instability of the serum, normal values being reached after 10 days. CHEMICAL ABSTRACTS.

Gersbach's indole determination [of *B. coli*]. E. L. KRUGERS DAGNEAUX (Chem. Weekblad, 1931, **28**, 66—67).—The various methods for rapid identification of *B. coli* are discussed, and it is pointed out that the Gersbach indole method, whilst not a positive test in all cases, is important as a means of detecting recent infection, especially in milk. S. I. LEVY.

Oxybiotic metabolism of bacteria. I. Dependence of respiration of *Bacillus coli* on some physico-chemical and biological factors. T. WOHLFEIL (Zentr. Bakt. Par., 1930, **115**, 413—426; Chem. Zentr., 1930, ii, 77).—The respiration of *B. coli* is but little sensitive to p_H between 6·5 and 8·0. Young cultures washed with sodium chloride solution show an increased respiration over older cultures, the young, short bacilli having a relatively larger adsorption surface for oxygen. The temperature coefficient decreases with a rise in temperature and with the age of the culture. The initial process of protein digestion by bacteria is assumed to be a case of adsorption with which enzymic activity is connected. L. S. THEOBALD.

Peroxidase in relation to bacterial growth with special reference to the influenza bacillus. L. R. ANDERSON (J. Bact., 1930, **20**, 371—379).—The production of peroxidase serves to differentiate certain bacteria. The identity of peroxidase with the *X* factor of Thjotta and Avery is confirmed. A. G. POLLARD.

Nature of the growth-promoting principle in the potato. Culture of tubercle bacilli. N. UYEI (Amer. Rev. Tuberculosis, 1930, **22**, 203—217).—Of the various substances present in the potato, inositol, maltose, and dextrose are metabolic stimulants, stimulating the growth of tubercle bacilli only when these are present in large numbers, whilst soluble starch and dextrin, but not glycogen, are reproductive stimulants, effective when tubercle bacilli are present in any numbers. CHEMICAL ABSTRACTS.

Preparation of antigenic specific substance from streptococci and pneumococci (type 1). H. B. DAY (Brit. J. Exp. Path., 1930, **11**, 164—173).—Methods of extraction are described; heat is usually desirable, but extraction at 100° is destructive. The antigenic specific substance contains two groups: (1) a stable portion which reacts with immune serum, (2) an unstable antigenic portion which provokes the formation of antibody. The antigenic group resembles an enzyme in some properties. It is possible to obtain an antigenic type-specific substance apart from ordinary bacterial protein. CHEMICAL ABSTRACTS.

Increase of toxic properties of bacilli and of their toxins through weak fermentation. A. KOMIS (Zentr. Bakt. Par., 1930, **115**, 454—457; Chem. Zentr., 1930, ii, 77).—The toxicity of various bacilli is increased by weak fermentation with yeast at 37°. Strong and resistant forms of bacilli can be obtained by this means. L. S. THEOBALD.

Toxin of the gas-gangrene bacillus. II. A. EBEL (Biochem. Z., 1930, **229**, 265—268; A., 1930, 1623).—From solutions obtained from cultures by repeated precipitation with alcohol, electrodialysis, and precipitation with lead acetate, the toxin of the gas-gangrene bacillus can be purified and concentrated in ethereal alcohol solution. W. MCCARTNEY.

Relationship between diphtheria toxin and blood-sugar. T. USUI (Sei-i-kwai Med. J., 1930, **49**, No. 4, 38—50).—Only in serious cases were markedly high values of blood-sugar observed. Hyperglycæmia in guinea-pigs and rabbits is observed only when the toxin or organism is injected subcutaneously. It is considered that diphtheria antitoxin diminishes the hyperglycæmia to some extent. CHEMICAL ABSTRACTS.

Diphtheria toxin-antitoxin precipitate. F. MODERN and R. WERNICKE (Anal. Asoc. Quim. Argentina, 1930, **18**, 47—56).—Diphtheria toxin-antitoxin precipitate requires a minimum acidity of p_H 3·6 for complete solution. When kept in acid solution the antitoxin is liberated and the toxin is destroyed (cf. Ramon, A., 1924, i, 463, 1149; 1925, i, 339). The recovery of antitoxin is maximal at p_H 3·2—3·6 and 10—15°, and increases with time up to several weeks. The yield increases with increasing dilution, and the ratio of units of activity to protein may be raised to 18 times that of the original serum. R. K. CALLOW.

Purification of anti-diphtheria serum by adsorption with aluminium hydroxide. R. WERNICKE and F. MODERN (Anal. Asoc. Quím. Argentina, 1930, **18**, 98—111).—Dry, powdered aluminium hydroxide has little or no adsorptive power for the proteins or antitoxins. When aluminium hydroxide is precipitated in the serum, however, marked adsorption occurs, particularly at the neutral point. In acid or alkaline solution slight preferential adsorption of inactive proteins is observed. By elutriation of the precipitate at p_H >8·4 the proteins and antitoxins are recovered quantitatively. No useful concentration of the antitoxins is attained by these methods. R. K. CALLOW.

Effect of certain oxidation–reduction potential indicators on diphtheria toxin. P. J. MOLONEY and E. M. TAYLOR (Trans. Roy. Soc. Canada, 1930, [iii], **24**, V, 127—132).—Certain oxidation-reduction

indicators, especially those which are easily reduced, *e.g.*, chloroindophenol and phenolindophenol, accelerate the detoxification of diphtheria toxin at 36—39°. The indicators are more active in the oxidised than in the reduced form and the action increases with increased concentration of indicator and with increase of p_H between 6·5 and 7·5. The detoxified material retains its antigenic power. W. O. KERMACK.

Action of formaldehyde on the aggressive substance of blackleg filtrate, bacterin, and aggressin. J. P. SCOTT (J. Infect. Dis., 1930, **46**, 460—468).—Formaldehyde (0·5%) increases the antiserum neutralising potency of *C. chauvei* bacterins and filtrates. It inhibits the agglutininogen, but increases the activity of the protective antigenic complex. CHEMICAL ABSTRACTS.

Mechanism of bacterial action. J. H. QUASTEL (Trans. Faraday Soc., 1930, **26**, 853—861).—A summary of the author's theory of the activity and specificity of cellular enzymes (cf., A., 1927, 1113; 1928, 797). W. O. KERMACK.

Theories of the bacteriophage. J. BORDET (Proc. Roy. Soc., 1931, **B**, **107**, 398—417).—A review of the work of the author on bacteriophage, the view being expressed that the active principle is probably not a virus but possesses the characters of an enzyme capable of autolysing the bacteria, and itself being reproduced during the process of autolysis. W. O. KERMACK.

Balanced salt action as manifested in bacteriophage phenomena. F. M. BURNET and M. MCKIE (Austral. J. Exp. Biol., 1930, **7**, 183—198).—In presence of an excess of sodium, potassium, or ammonium ions, bacteriophage exhibits an increased susceptibility to the adverse effects of high temperature, but this may be partly or wholly counteracted by a sufficient concentration of calcium, barium, or magnesium ions. Bacteriophage is inactivated by certain dyes, but in presence of calcium salts inactivation does not occur. In the case of one phage, the rate of migration towards the anode in presence of calcium ions is greater than in presence of sodium ions, a result probably due to a shrinkage in the size of the particles in presence of the bivalent ions. In the case of other phages similar changes in cataphoretic velocity were not detected, possibly because of insufficiently accurate experimental methods. W. O. KERMACK.

Electrical behaviour of bacteriophages. F. M. BURNET and M. MCKIE (Austral. J. Exp. Biol., 1930, **7**, 199—209).—Various bacteriophages normally possess a negative charge as shown by experiments on their cataphoretic migration. W. O. KERMACK.

Immunisation with aluminium hydroxide mixtures of poliomyelitis virus. C. P. RHOADS (Science, 1930, **72**, 608).—The virus of poliomyelitis when adsorbed on aluminium hydroxide is incapable of producing the disease, but can induce active immunity in monkeys. Inactivation of the virus is promoted by p_H 5·5 and prevented by p_H 8·8. L. S. THEOBALD.

Influence of substitution on the colloid-chemical action of derivatives of acetic acid and phenol, and relationship to disinfective properties. R. LABES and E. JANSEN (Arch. exp. Path. Pharm., 1930, **158**, 1—28).—By observing the shift to the acid region of the optimum p_H for flocculation of denatured serum-albumin caused by substituted acetic acids (cf. Michaelis and Rona, A., 1919, i, 358), the influence of the substituents in increasing the affinity of the anions for protein has been arranged in the following series: $Ph > I > Br > Cl > NO_2 > Me > OH$. In the phenols this colloid-chemical action runs parallel with disinfective activity. A. COHEN.

Effect of substituted benzoic acids and aromatic sulphonic acids on the flocculation optimum of denatured serum-albumin. R. LABES and T. SCHUSTER (Arch. exp. Path. Pharm., 1930, **158**, 29—41).—The greater significance of orientation of substituents in determining the colloid-chemical action of the benzoic acids as compared with the phenols is attributed to the polar character of the former. Both the antiseptic activity and the influence on serum-albumin of iodobenzoic acids increase with the number of substituent iodine atoms, and the colloid-chemical action of sulphonic acids increases with the number of aromatic nuclei. A. COHEN.

Bacteriostatic action of certain components of commercial peptones as affected by conditions of oxidation and reduction. R. DUBOS (J. Exp. Med., 1930, **52**, 331—345).—The substances are bacteriostatic only in the oxidised form; their effect is overcome by the addition of reduced thiol compounds to the media. Commercial peptones differ greatly in their content of bacteriostatic substance, which may be removed by precipitation with acid and acetone. CHEMICAL ABSTRACTS.

Susceptibility of various bacteria to hydrogen sulphide. R. DOURIS and J. BECK (Ann. Inst. Pasteur, 1931, **46**, 73—77).—The bactericidal action of hydrogen sulphide is greater on cocci than on bacilli and is most marked on Gram-positive types. Motile bacteria are usually more resistant than non-motile. W. O. KERMACK.

Bactericidal action of thiocyanates. I. Hydrothiocyanic acid and sodium thiocyanate in neutral or acid solution. G. LOCKEMANN and W. ULRICH (Z. Hyg., 1930, **111**, 387—419; Chem. Zentr., 1930, ii, 1880—1881).—The disinfective action of sodium thiocyanate is much greater than that of the sodium halides; the activity is greatly increased with increase in hydrogen-ion concentration. Free hydrothiocyanic acid is a more efficient bactericide than trichloroacetic acid. A. A. ELDRIDGE.

Oligodynamic dilutions. J. MEYER (Chem.-Ztg., 1931, **55**, 85—86).—It has been claimed that dilutions of lead and silver nitrate down to 1 part in 10^{29} parts of water have an appreciable effect on organisms. This appears impossible, as it would require a very large container to secure the presence of one salt molecule at such dilution. At even rather less dilution the interaction between the salt and the glass would be a preponderating one. It appears likely that the true limit of any real effect is 1 part in 10^{10} in 10^{12}. C. IRWIN.

Reaction of blood-pressure to adrenaline in parathyroidectomised animals. R. S. Abramson and E. N. Speranska-Stepanova (Arkh. Biol. Nauk, 1929, **29**, 481—491).—In dogs and cats in which the blood-calcium was lowered by means of injection of oxalate, with or without parathyroidectomy, the adrenaline effect was pronounced regardless of the calcium level. Chemical Abstracts.

Biological detection of adrenaline in drugs, especially in presence of local anæsthetics. A. Stasiak and L. Rigó (Magyar Gyo. Taro. Ert., 1930, 6, 389—394; Chem. Zentr., 1930, ii, 2552).—Adrenaline inhibits the spontaneous contractions of the surviving mouse-uterus, whence it can be detected in presence of local anæsthetics and posterior pituitary extract. The sensitivity of the uterus towards adrenaline is increased by novocaine and diminished by β-eucaine and stovaine. A. A. Eldridge.

Influence of adrenaline and insulin on the excretion of sugar from the liver through the bile during continued ingestion of sucrose. N. M. Ivanov (Z. ges. exp. Med., 1930, **71**, 263—273; Chem. Zentr., 1930, ii, 2540).—Addition of sucrose (200 g.) to the ordinary diet does not markedly increase the bile-sugar of the dog unless adrenaline is administered simultaneously by subcutaneous injection. After injection of insulin the bile-sugar falls in spite of ingestion of sucrose; insulin causes an increase which appears only when large doses (400 g.) of sugar are administered for a long time. A. A. Eldridge.

Evaluation of insulin. A. Stasiak and B. Zboray (Magyar Gyo. Taro. Ert., 1930, **6**, 268—274; Chem. Zentr., 1930, ii, 1897—1898).—Marks' cross test has been simplified. Each animal ($2\pm0{\cdot}3$ kg.) receives 1 international unit administered in the same way; three samples of blood are drawn after 1·5, 3, and 5 hrs., respectively. The original and simplified methods are liable to an average error of 10%. Of 16 commercial preparations 14 gave values within 10% of those declared. A. A. Eldridge.

Insulin. S. Niitsu (Sei-i-kwai Med. J., 1930, **49**, No. 2, 1—20).—Subcutaneous injection of insulin in large amount causes a rapid decrease in blood-sugar, the minimum value being reached in 3 hrs. Inorganic phosphorus follows approximately the same course, but becomes normal at the seventh hour. Subarachnoid injection causes more gradual changes. Pituitrin introduced hypodermically produces hyperglycæmia, but a decrease in organic phosphorus; subarachnoid injection of pituitrin causes more marked changes. Chemical Abstracts.

Effect of insulin. V. M. Ogawa (Folia Pharmacol. Japon., 1929, **9**, No. 3, 137—149).—Insulin is destroyed in the rabbit's intestine, but a certain amount is resorbed in the intestinal mucosa. Insulin is destroyed more readily in the duodenum and jejunum on account of the alkalinity and the presence of proteolytic enzymes. Chemical Abstracts.

Effect of insulin, synthalin, and glukhorment on cellular fixation of dextrose. E. B. Salén and T. Nyrén (Acta Med. Scand., 1928, **69**, 69—98; Chem. Zentr., 1930, ii, 2201).—The increase in fixation of dextrose was, respectively, 180, 149, and 140%. A. A. Eldridge.

Action of proteolytic enzymes on crystalline insulin. A. F. Charles and D. A. Scott (Trans. Roy. Soc. Canada, 1930, [iii], **24**, V, 95—99).—When crystalline insulin is acted on by pepsin or trypsin its physiological activity disappears much more rapidly than does the protein present as indicated by precipitation with 3·3% trichloroacetic acid. It does not appear possible by means of these enzymes to hydrolyse insulin into a physiologically active protein of smaller molecular weight. W. O. Kermack.

Spectroscopic properties of insulin. H. des B. Sims and D. A. Scott (Trans. Roy. Soc. Canada, 1930, [iii], **24**, V, 117—119).—Amorphous and crystalline insulin of activities 13 and 25 units per mg., respectively, placed in the copper arc gave no evidence of inorganic material. The ultra-violet absorption spectrum of crystalline insulin dissolved in 0·001*N*-hydrochloric acid showed absorption bands centred at 2855 and 2740 Å., and another beyond 2340 Å. Satisfactory *X*-ray spectra were not obtained from insulin crystals. W. O. Kermack.

Detection of an insular hormone in the duodenum. N. B. Laughton and A. B. Macallum (Canad. Med. Assoc. J., 1930, **23**, 348).—Extracts of duodenal mucosa, when injected into normal rabbits or dogs prior to administration of dextrose, diminish the hyperglycæmia; they do not contain insulin, since they do not affect the hyperglycæmia of depancreatised dogs. The extracts do not give protein or peptone reactions, and the active principle is not adsorbed on bone charcoal or fuller's earth; they appear to contain a substance which stimulates the islets of Langerhans. The mechanism of insular failure is discussed. Chemical Abstracts.

Circulatory hormone. V. An internal secretory function of the pancreas. E. K. Frey, H. Kraut, and F. Schultz (Arch. exp. Path. Pharm., 1930, **158**, 334—347; cf. A., 1930, 1624).—The circulatory hormone (callicrein), identical with that from urine, is found in considerable quantity in normal pancreas and in fluid from pancreatic cysts. The hormone content of the urine of the dog is diminished in a few hours to 15% of its original value by extirpation of the pancreas, but is maintained if extirpation is not quite complete. Although callicrein is chemically different from insulin, some functional similarity between them is observed. Splenectomy causes a temporary and non-characteristic loss of the hormone from the urine, but extirpation of other glands has little effect. A. Cohen.

Action of pituitrin, pitressin, and pitocin on the blood-phosphatides. W. Raab (Endocrinol., 1930, **14**, 150—156).—The effects of pitressin and pitocin are irregular but in general are similar to that of pituitrin in depressing the blood-phosphatides. Injection of egg-yolk did not produce lecithinæmia. Chemical Abstracts.

Physiological properties of the growth-promoting extracts of the anterior pituitary lobe. H. M. Teel and H. Cushing (Endocrinol., 1930, **14**, 157—163).—Injection into dogs causes a fall in the

urea-, amino-acid-, and "undetermined" nitrogen, approximately in proportion to the respective concentration. Retention of nitrogen and phosphorus, and increased urinary excretion of calcium, were observed. CHEMICAL ABSTRACTS.

Ovary-stimulating hormone of the placenta. J. B. COLLIP (Canad. Med. Assoc. J., 1930, **22**, 761—764).—Methods for obtaining concentrated placental extracts are described. The yield of product is about 1 mg. per kg. Its potency is unaffected by boiling for 5 min. with dilute acetic acid or by treatment with pepsin or trypsin. In addition to "emmenin," the active fraction contains another hormone or hormones, apparently of protein-like nature.

CHEMICAL ABSTRACTS.

Isolation of the male sexual hormone in a water-soluble crystalline state. B. FRATTINI and M. MAINO (Arch. Ist. Biochim. Ital., 1930, **2**, 639—668).—Testes are extracted with boiling 1% acetic acid and the filtrate is treated with magnesium sulphate. The precipitate is extracted with 95% alcohol and the oil obtained by evaporation is emulsified in boiling water (p_H 5) and the mixture filtered. The turbid filtrate is treated with 4% of sodium hydroxide and filtered. The solution, which contains the hormone as a sodium salt, is treated with 1% of copper sulphate and the resultant precipitate, suspended in water, is decomposed with hydrogen sulphide. The ethereal extract of the solution when evaporated deposits the hormone in feathery aggregates of needles, soluble in organic solvents and in water containing a little alkali. The substance contains no nitrogen.

The crystalline substance promotes the growth of the comb and wattles of capons, and causes development of the seminal vesicles in immature or castrated rats. It also causes œstrus in ovariectomised rats and development of the uterus in immature rats. Parallel tests of the crystalline follicular hormone (A., 1930, 505) show that this promotes development of the genital tract in the male. The two hormones thus have in common the power of influencing the genital tract of both sexes, but differ in their effect on secondary sexual characteristics, for the promotion of comb-growth is specific to the male hormone. The œstrogenic action of the testes and urine of males is due to the male hormone, and the presence of the female hormone need not be assumed.

R. K. CALLOW.

Androkinin (male sexual hormone) in male blood. S. LOEWE, F. ROTHSCHILD, W. RAUTENBUSCH, and H. E. VOSS (Klin. Woch., 1930, **9**, 1407; Chem. Zentr., 1930, ii, 1868).—Bull's blood contains 1—2 mouse-units of androkinin per litre; with improved methods higher values would probably be obtained. A. A. ELDRIDGE.

Diazo-reaction of thyroxine and its inhibition by blood-constituents. W. KOMANT (Arch. exp. Path. Pharm., 1930, **158**, 116—128).—Thyroxine (and its methyl or ethyl ester), when treated with diazotised sulphanilic acid at p_H 9—10, gives a dark red colour which behaves as an indicator towards acid and alkali. A rose colour is developed at a dilution of 1 in 10^5. The reaction is not given by the bromine analogue of thyroxine, nor by 3 : 5-dichloro- and 3 : 5-dibromo-tyrosine; 3 : 5-di-iodotyrosine gives a slight positive reaction. The reaction is inhibited by serum-protein, uric acid, and, to a smaller extent, by some amino-acids. Urine destroys the colour after it has appeared. Additive compound formation between inhibitor and thyroxine is suggested as the cause of inhibition. Simultaneous intravenous injection of thyroxine and serum or glycine into rabbits does not influence the increased oxygen consumption observed with thyroxine alone.

Thyroxine gives green and blue colour reactions with methylene-blue and methyl-violet, respectively.

A. COHEN.

Action of thyroxine. E. ABDERHALDEN and E. WERTHEIMER (Z. ges. exp. Med., 1930, **72**, 472—489; Chem. Zentr., 1930, ii, 1567).—Protracted administration of thyroxine to rabbits, guinea-pigs, or rats leads to a diminution almost to zero of the heart muscle-glycogen, large quantities remaining in the liver and skeletal muscle. Differences have been observed between rats and guinea-pigs in the effect on the storage of glycogen of simultaneous administration of dextrose. A. A. ELDRIDGE.

Effect of substitution in the thyroxine molecule on its action. E. ABDERHALDEN and E. WERTHEIMER (Z. ges. exp. Med., 1928, **63**, 557—577; Chem. Zentr., 1930, ii, 1716).—Deiodothyroxine does not affect the metamorphosis of tadpoles or axolotls. Other substances related to thyroxine were active, but the necessary dose was higher than for thyroxine. Iodophenols have no action. Thyreoglobulin, iodoalbumin, and serum-iodoalbumin were active for axolotls, doubtless owing to their content of 3 : 5-di-iodotyrosine. A. A. ELDRIDGE.

Hormone of heart motion. XVII. Gastro-intestinal musculature of cold- and warm-blooded animals. L. HABERLANDT (Pflüger's Archiv, 1930, **225**, 384—388; Chem. Zentr., 1930, ii, 2147—2148).—The heart hormone (1 in 50—1000) promotes movement of the frog's stomach or of the intestine of warm-blooded animals, and hence differs from adrenaline; the effect is also observed after treatment with atropine. A. A. ELDRIDGE.

Vitamins of milk and their behaviour towards chemical, physical, and thermal attack. W. WEITZEL (Z. Fleisch- Milchhyg., 1930, **40**, 389—393; Chem. Zentr., 1930, ii, 1791).—The vitamin-*A*, -*B*, and -*C* content of milk is increased when green fodder is substituted for dry fodder. Vitamin-*C* is most sensitive to chemical, physical, and thermal conditions. Lack of vitamin-*D* can be remedied by ultra-violet irradiation; the vitamin-*E* content is insufficient. A. A. ELDRIDGE.

Carotene and vitamin-*A*. L. K. WOLFF, J. OVERHOFF, and M. VAN ECKELEN (Deut. med. Woch., 1930, **56**, 1428—1429; Chem. Zentr., 1930, ii, 2149).—The minimal rat-dose of carotene is 2—3 γ per day. Vitamin-*A* is not considered to be identical with carotene; both occur in animal products, but the former seldom in plants. Carotene may be converted by the organism into vitamin-*A*. The determination of vitamin-*A* in presence of carotene is described.

A. A. ELDRIDGE.

Vitamin-*A* in serum and liver. B. von Euler (Svensk Kem. Tidskr., 1930, **42**, 302—304).—Vitamin-*A* has been identified and determined by the antimony trichloride method in ethereal extracts of the serum and liver of rabbits and of the serum of sheep (wethers). The presence of more than traces of carotene to account for the reaction is ruled out. No differences with sex were found in rabbits. The subcutaneous fat gave no reaction. R. K. Callow.

Unsaponifiable material. III. Relation to avitaminosis-*A*. E. Igarashi (Sci-i-kwai Med. J., 1930, **49**, No. 3, 15—31).—The substance was prepared from various organs by the method previously described (A., 1929, 952, 1328); it is an oil, f. p. 20°, having an acid reaction. In experiments on rats the substance was successfully used as a substitute for vitamin-*A*. Chemical Abstracts.

Vitamin-*C* in sauerkraut. B. A. Lavrov and N. Jarussova (Biochem. Z., 1930, **229**, 115—127).—As regards its prophylactic antiscorbutic activity, the juice obtained from sauerkraut has about 5—10% of the potency of orange juice and is approximately as potent as unboiled cow's milk.

W. McCartney.

Effect of vitamin-*D* supplements on laying hens. J. H. Martin, S. E. Erikson, and W. M. Insko, jun. (Kentucky Agric. Exp. Sta. Bull., 1930, No. 304).—Egg production from yearling hens was increased by irradiation, exposure to sunlight, and the addition of 2% of cod-liver oil to the ration. Cod-liver oil used alone had no beneficial effect on pullets. Vitamin-*D* supplements improved the hardness and thickness of eggshells and improved hatchability. Analyses of bone ash contents and the inorganic phosphorus contents of the blood of chicken are recorded. A. G. Pollard.

Assay of irradiated ergosterol. H. Naser (Arch. exp. Path. Pharm., 1930, **158**, 201—210).—The method of assay proposed depends on the determination of the increase in inorganic serum-calcium and phosphorus caused by oral administration of irradiated ergosterol to rabbits (cf. Demole and Fromherz, A., 1930, 257). The effect of a dose of about 2 mg. per kg. body wt. can be detected. The calcium content is generally increased by 20—30%, but phosphorus increases more markedly, reaching a value three times as great as the normal on a super-toxic dose (above 10 mg. per kg. body-wt. daily). It is claimed that these effects are observed in 12 hrs., which is much earlier than the appearance of morphological changes.

No calcification is observed when cavities of teeth are filled with irradiated ergosterol. A. Cohen.

Irradiated ergosterol. A. Windaus.—See this vol., 320.

Conversion and action of ergosterol. W. Hirsch.—See this vol., 320.

Hypervitaminosis in hens. E. J. King and G. E. Hall (Biochem. Z., 1930, **229**, 315—322).—Administration of large harmful overdoses of irradiated ergosterol to hens has only a slight effect on the calcium and phosphorus contents of the blood-serum and causes no deposition of calcium in the organs. The phosphatase content of the bones and of the kidneys (but not of the intestines) is reduced, as a result of the treatment, to less than half of the normal value. W. McCartney.

Feeding power of plants. W. Thomas (Plant Physiol., 1930, **5**, 443—489).—The literature concerning the effects of root exudations, of the reaction of cell-sap, of the permeability of the root-cell membranes, and other factors on the rate and extent of the intake of minerals by plants is critically discussed. An extensive bibliography is appended.

A. G. Pollard.

Conception of balance with respect to the absorption of nitrogen, phosphorus, and potassium by plants and the influence of the level of nutrition. W. Thomas (Science, 1930, **72**, 425—427).—A discussion. L. S. Theobald.

Salt permeability of protoplasts. H. Weixl-Hofmann (Protoplasma, 1930, **11**, 210—277).—The course of the plasmolysis of the red epidermal cells of *Lamium purpureum* by hypertonic solutions of potassium chloride (0·2—0·5*M*) is examined, together with the effect of more concentrated solutions of potassium chloride alone and mixed with calcium chloride on the permeability of the cells and the nature of the plasmolytic effects.

A. G. Pollard.

The plasmolysis of algal cells. B. von Cholnoky (Protoplasma, 1930, **11**, 278—297).—Addition of cocaine to plasmolytic solutions increased the permeability of the cells. Characteristic differences occur in the effect of cocaine on mother and daughter cells. A. G. Pollard.

Relationship between the concentration of the soil solution and the physico-chemical properties of the leaf tissue fluids of cotton. J. A. Harris and T. A. Pascoe (J. Agric. Res., 1930, **41**, 767—788; cf. B., 1926, 842).—A positive correlation is established between the f.-p. depression, specific conductivity, the chloride and sulphate contents of the leaves of cotton, and the conductivity and chloride and sulphate contents of the soil in which they are grown. A. G. Pollard.

Hydrogen-ion concentration and buffer action of the expressed sap of maize. J. D. Sayre (Ohio Agric. Exp. Sta. Bull., 1930, No. 446, 38—39).—The sap of the sheath tissues of maize was more acid than that from any other part of the plant. The buffer effect of leaf-blade and sheath sap averaged 5—6 times that of stems. The phosphate, nitrate, total nitrogen, amino-acid, and colloidal contents and the conductivity of leaf-blade sap were higher than those of stems, but the sugar content was lower. There is no relationship between the p_H or total acidity of the sap and infestation by the European maize borer. A. G. Pollard.

Cambium and its derivative tissues. VI. Effect of hydrogen-ion concentration in vital staining. I. W. Bailey and C. Zirkle (J. Gen. Physiol., 1931, **14**, 363—383).—Two types of vacuole (A, B) occur, each with distinct staining properties. Auramine and many thiazine dyes stain both types, although type B rarely stains on the acid

side of p_H 5·4—5·8. Many azo-dyes and dyes of the acridine and triphenylmethane series accumulate only in type A vacuoles, whilst the effect of the external p_H is variable. A third group of dyes has no staining effect on either type A or B at any external p_H unless injury has previously taken place. The p_H of the contents of the vacuoles is an important factor in vital staining. P. G. MARSHALL.

Necessity and function of manganese in the growth of *Chlorella* sp. E. F. HOPKINS (Science, 1930, **72**, 609—610).—Manganese, as well as iron, is essential for growth of *Chlorella* sp.; at p_H 7·0, the increase in growth due to manganese is about 17-fold, and at p_H 8·0 about 170-fold. The optimum concentration of manganese is approximately 1 in 5×10^6 and at higher concentrations (1 in 5×10^4) a toxic effect becomes pronounced. The manganese appears to function by controlling the ratio of ferrous to ferric iron. L. S. THEOBALD.

Changes in the phosphorus content of growing mung beans. J. E. WEBSTER and C. DALBOM (J. Agric. Res., 1930, **41**, 819—824).—The inorganic phosphorus content of any particular organ of the mung bean remains practically constant after the early stages of growth. Phosphorus is stored in the tissues in an organic form. The amount of lipoid phosphorus in green tissue is very small and varies but little during growth. Variations of 2—3 weeks in the time of harvesting do not involve appreciable alterations in the total phosphorus content of the crop. There is no indication of the translocation of phosphorus from leaves to stems. Localisation of phosphorus probably follows the normal ash intake and is not the outcome of metabolic changes. A. G. POLLARD.

Natural chemical equilibrium regulative of growth by increase in cell number. F. S. HAMMETT (Protoplasma, 1930, **11**, 382—411).—The growth of plant and animal tissue involving increased cell numbers is considered as a manifestation of chemical reactions and governed by the laws of chemical equilibrium. The thiol group in chemical compounds is a specific stimulant of cell division and its partly oxidised reaction products specifically retard cell increase. The oxidation process is induced by living protoplasm, of which both types of sulphur compounds are natural constituents. A. G. POLLARD.

Diastatic and peroxidative activity of plants as influenced by external factors. H. KERN (Z. Bot., 1928, **21**, 193—252; Chem. Zentr., 1930, ii, 412—414).—The maximum diastatic activity of maize seedlings is observed 5—12 days after germination; maintenance at 60° considerably decreased the activity. Removal of water in a desiccator increased the saccharifiability in the whole seedling as well as in the root tips. Differences in the diastatic properties of the whole seedling and the root tips under different conditions of treatment are recorded. Ether narcosis diminishes the starch-forming power of the leaves and promotes the degradation of starch. The peroxidase activity was maximal after 8—9 days' germination. Moist heating at 50° diminished the peroxidase activity of the whole seedling and that of the root tips; dehydration in a desiccator also diminished the peroxidase activity. A. A. ELDRIDGE.

Distribution of dry matter and carbohydrates in the maturing maize stem. V. H. MORRIS and E. A. WELTON (Ohio Agric. Exp. Sta. Bull., 1930, No. 446, 39—40).—Examination of sections of growing maize stems from the lowest joint upwards shows an increasing dry matter and sucrose content and a decreasing proportion of reducing sugars. Periodical analyses of the whole stem from the period of tasselling to maturity show a progressive increase in dry matter and sucrose contents and a decline in the amount of reducing sugars with age. More than half of the total amounts of these constituents of the stem are situated in the lower four joints. This may be associated with the tendency of the maize borers to work in the lower portions of the stems. A. G. POLLARD.

Effects of defloration on fruit-spur composition and fruit-bud formation in the Oldenburg apple. G. F. POTTER, H. R. KRAYBILL, S. W. WENTWORTH, J. T. SULLIVAN, and P. T. BLOOD (New Hamps. Agric. Exp. Sta. Tech. Bull., 1930, No. 41, 25 pp.).—Comparison is made of the chemical composition of fruiting and non-fruiting spurs and of deflorated spurs of apples. The nitrogen content is highest and the starch content lowest in fruiting spurs, the proportions in deflorated spurs being affected by the presence of adjacent fruiting spurs. Among the three types of spurs, no consistent differences were observed in the contents of reducing substances, sucrose, or phloridzin. Variations in the phosphorus contents were similar to those of nitrogen. Ash constituents were lower in fruiting spurs than in others. During ripening of the fruit there is a steady increase in the proportions of sucrose and reducing sugars (which predominate) which considerably exceeds the corresponding change in the spur. The starch content of the spur always exceeds that of the fruit. Phloridzin is persistent in spurs but gradually disappears from maturing fruit. The percentage of nitrogen in the fruit, initially greater than in the spur, steadily declined with maturation to a very small figure. A. G. POLLARD.

Composition of, and fruit-bud formation in, non-bearing spurs of the Baldwin apple. G. F. POTTER and T. G. PHILLIPS (New. Hamps. Agric. Exp. Sta. Tech. Bull., 1930, No. 42, 43 pp.).—Relationships between fruit-bud formation and the chemical constituents of the spurs were examined. Conditions leading to the accumulation of insoluble nitrogen compounds in the spur were also those favouring fruit-bud formation. Accumulation of soluble carbohydrates in the spur is associated with decreased fruit-bud formation (cf. Kraybill *et al.*, *ibid.*, Bull. 29, 1925). A. G. POLLARD.

Distribution of saponin in plants during different stages of maturity. L. KROEBER (Heil-Gewürz-Pflanzen, 1930, **12**, 131—137; Chem. Zentr., 1930, ii, 76).—In *Saponaria*, the saponin content increases in the order leaves, roots, and flowers, and it also increases with the development of the plant. In August, the root contains twice as much saponin

as in November. Quick drying at 55° yields a stronger drug than is obtained by drying at the ordinary temperature. *Solidago serotina* is a saponin plant of unusually high hæmolytic titre and the highest saponin content appears in the leaves.

L. S. THEOBALD

Stimulatory effects of ultra-violet radiation on higher plants. H. J. FULLER (Science, 1930, **72**, 535—536).—When irradiated for 5 weeks by a quartz mercury vapour arc at a distance of 100 in. tomatoes and cucumbers show increased growth. The former show an increase of 33% over controls and the latter about 34%. The dry weight percentages of wet and ash weight percentages of dry weight are also greater by 19 and 13%, respectively, in the case of tomatoes. Filters transmitting wave-lengths of 313 mμ and 289 mμ were employed. L. S. THEOBALD.

Active constituents of Korean *Ledum palustre*. H. SUZUKI (Folia Pharmacol. Japon., 1930, **9**, 297—309).—The oil (yield 0·43%) has *d* 0·9987, b. p. 130—195°/80 mm. Its physiological effects are described.

CHEMICAL ABSTRACTS.

Jegosaponin, an active constituent of *Styrax Japonica*. Saponin cholesterol combination. T. KONDO (Folia Pharmacol. Japon., 1930, **9**, No. 4, 256—261).—The preparation of a jegosaponin-cholesterol, comparable with Windaus' digitonin-cholesterol, is described. The compound has m. p. 297° and appears to be a chemical individual; it has no hæmolytic effect on red blood-cells.

CHEMICAL ABSTRACTS.

Constituent of the rhizome of *Cimicifuga fœtida*, L., var. *intermedia regel*. K. OGIU (Folia Pharmacol. Japon., 1930, **10**, 11—12).—*Cimitin*, $C_{20}H_{34}O_7$, precipitated on dilution of the methyl-alcoholic extract (after preliminary extraction with ether and benzene), and recrystallised from hot 70% acetone, has m. p. 169°, decomp. 175°.

CHEMICAL ABSTRACTS.

Japanese persimmon grown in Florida. I. Analysis. J. TILT and R. B. HUBBELL. **II. Vitamin-*B* complex.** J. TILT, R. B. HUBBELL, and L. INMAN (J. Home Econ., 1930, **22**, 757—762, 762—765).—Analysis gave: water 76·27—81·71, reducing sugar 11·53—17·39, protein 0·43—0·87, ash 0·30—0·58, fibre 0·11—0·49%; the ash contained calcium, phosphorus, magnesium, sulphur, iron, copper, and manganese. The Tane Nashe variety is a poor source of vitamin-*B*. CHEMICAL ABSTRACTS.

Constituents of the root of *Lindera strychnifolia*, Vill. II. H. SUZUKI (J. Pharm. Soc. Japan, 1930, **50**, 714—720).—The unsaponifiable oil (Kondo and Sanada, *ibid.*, 1925, No. 526, 1047), $C_{15}H_{18}O_2$, b. p. 158°/5 mm., $[\alpha]_D^{15}$ −83° 1′ (in acetone), contains a double linking; it does not contain a hydroxyl group or form an oxime or semicarbazone. On catalytic reduction it forms a compound, b. p. 129—132°/5 mm., $[\alpha]_D^{15}$ −16° 36′. Catalytic reduction of linderan affords a compound, m. p. 211°. CHEMICAL ABSTRACTS.

Æsculetin dimethyl ether, a constituent of the fruit of *Artemisia capillaris*. I. S. SERA and C. SHIBUYE (J. Agric. Chem. Soc. Japan, 1930, **6**, 600—609). CHEMICAL ABSTRACTS.

Constituents of *Patrisia acuminata*. K. W. MERZ (Arch. Pharm., 1930, **268**, 592—593).—The root contained nothing volatile in steam, even in presence of alkali. Aqueous tartaric acid extracts a syrup containing an acidic substance, m. p. 268—270° (decomp.), physiologically inactive, but no alkaloid. A 10% alcohol extract yields, after purification with lead acetate, a hygroscopic material which is four times as toxic as the original drug.

H. E. F. NOTTON.

Vegetable proteins. I. Proteins of *Dolichos lab lab*. D. NARAYANAMURTI and C. V. RAMASWAMI (Biochem. J., 1930, **24**, 1650—1654).—The nitrogen of the globulin dolichosin forms about 80% of the nitrogen of the meal of *D. lab lab*. The best yield is obtained when the meal is extracted with four parts of water. The nitrogen distribution and the nutritionally essential amino-acids have been determined. The nutritional value of dolichosin as deduced from its composition is higher than that of other globulins. A method in which the extract is subjected to electrodialysis in order to avoid tyrosinase action is described. S. S. ZILVA.

Hydrogen cyanide. XXVI. New occurrences [in plants]. L. ROSENTHALER (Pharm. Acta Helv., 1929, **4**, 196—199; Chem. Zentr., 1930, ii, 932).—Additional occurrences of hydrogen cyanide in plants (12) are recorded. A. A. ELDRIDGE.

Hydrogen cyanide. Detection of substances which combine with hydrogen cyanide in distillates containing hydrocyanic acid. L. ROSENTHALER (Pharm. Acta Helv., 1929, **4**, 62—63; Chem. Zentr., 1930, i, 3086).—A method for determining whether distillates contain combined as well as free hydrogen cyanide is described. No combined hydrogen cyanide is present in the distillate obtained from *Schleichera trijuga*. L. S. THEOBALD.

Soya-bean lecithins. I. Separation of α- and β-series. B. SUZUKI and Y. YOKOYAMA (Proc. Imp. Acad. Tokyo, 1930, **6**, 341—344).—Experimental details are given for the isolation of lecithins from an alcoholic extract of soya beans as cadmium chloride double salts, from which fatty acids (saturated 44%, unsaturated 56%), α- and β-glycerophosphoric acids, and choline are obtained. The saturated acid is palmitic acid, and the unsaturated fraction contains oleic acid (47% of total acids), and smaller quantities of two acids which, on bromination, yield hexa- and tetra-bromostearic acids, m. p. 177—178° and 112—113°, respectively. Separation of the cadmium chloride salts of the α- and β-lecithins is effected by acetone, in which the α-complex is far less soluble. From the α-lecithins palmitic, di-, tetra-, and hexa-bromostearic acids have been obtained in the proportions 24·3, 32·4, 44·2, and 1·1%, whilst in the β-series the proportions are 20·1, 53·8, 24·8, and 1·4%.

A. COHEN.

Anthocyanins. L. W. KUILMAN (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 876—888).—The relations between anthocyanins and the assimilation process in plants are discussed. It is not possible to establish a lower assimilation value for cells containing anthocyanins, except when those cells have also a lower content of chlorophyll. E. S. HEDGES.

Colouring matters of red grapes and wines. L. CASALE (Annali Chim. Appl., 1930, 20, 559—566).—Variations in the colour of the colouring matter of the red grape as a result of salification are related to the amphoteric character of the colouring matter. The isoelectric point of oenin chloride (cf. Willstatter and Zollinger, A., 1915, i, 286) lies between p_H 5·4 and 5·8, and the two dissociation constants corresponding with the acid and basic forms are about $10^{-7\cdot66}$ and $10^{-10\cdot88}$, respectively. T. H. POPE.

Blossom xanthophylls. Pigment of the sunflower. L. ZECHMEISTER and P. TUZSON (Ber., 1930, 63, [B], 3203—3207).—The isolation is described from the blossoms of *Helianthus annuus* of a colourless, crystalline, sterol-like compound and of a pigment, $C_{40}H_{56}O_2$, m. p. 195°, $[\alpha]_C^{18}$ +75° in chloroform, identical with the lutein from egg-yolk. It is established that in the normal green leaf more than one type of xanthophyll, in addition to carotene and chlorophyll, exists, whereas the blossom pigments are either a mixture of xanthophylls comparable with that in the leaf or an individual xanthophyll. The use of the polarimeter for distinguishing between the different varieties of xanthophyll is advocated. H. WREN.

Degradation of nicotine in tobacco. A. FODOR and A. REIFENBERG (Biochem. Z., 1930, 228, 327—328).—The results of Faitelowitz (A., 1930, 1484) cannot be confirmed and his explanations are rejected. The process is not bacterial. W. MCCARTNEY.

Alterations occurring in the nitrogenous constituents of tobacco during air-drying. A. J. SMIRNOV and V. P. IZVOSCHIKOV (Biochem. Z., 1930, 228, 329—353).—During air-drying the amounts of proteins, polypeptides, nicotine, ammonia, and other bases and of other nitrogenous compounds in tobacco leaves undergo considerable variations. The mechanism of these changes and their connexion with the physiological processes which occur during drying are discussed. W. MCCARTNEY.

Influence of mosaic disease on nicotine content of the tobacco plant. K. SILBERSCHMIDT (Ber. deut. bot. Ges., 1930, 48, 122—129).—The nicotine content of tobacco leaf is increased by 40—100% in mosaic disease. A rise is also observed in leaves growing after inoculation of the plant with virus sap, and in cut leaves in the absence of sunlight. This is discussed in relation to a possible plant synthesis of nicotine from nitrous acid and formaldehyde. A. COHEN.

Fluorescence analysis of plants. G. KLEIN and H. LINSER (Oesterr. Bot. Z., 1930, 79, 125—163; Chem. Zentr., 1930, ii, 1257).—The fluorescence in ultra-violet light of various plant organs has been observed and compared with that of organic substances. The distribution of æsculin and fraxin in *Aesculis hippocastanum* can thereby be determined. A. A. ELDRIDGE.

Analysis of metachromatic colorations of plant tissues by organic dyes. A. T. CZAJA (Ber. deut. bot. Ges., 1930, 48, 100—104).—A substantive dye in colloidal solution is fractionally filtered by the cell-walls of plant-tissue. Different types of tissue, under the action of a single dye, may pass and retain fractions of different degrees of dispersion, resulting in different colourings. Basic dyes behave as indicators, and the colour of the tissue depends on the p_H of the cell-wall. A. COHEN.

Hydroxyquinoline sulphate as a preservative for plant tissues. C. F. SWINGLE (Bot. Gaz., 1930, 90, 333—334).—Botanical specimens are covered with water and hydroxyquinoline sulphate is added to make a solution of 0·1—1%. The preservative inhibits bacterial action, does not penetrate the tissues, and its action is not affected by exposure to the atmosphere. Precipitates are formed with iron salts. A. G. POLLARD.

Use of uricase-free seed of *Soya hispida*. Determination of allantoin. R. FOSSE, A. BRUNEL, P. DE GRAEVE, P. E. THOMAS, and J. SARAZIN (Compt. rend., 1930, 191, 1388—1390).—For recognition of allantoin in a dilution of 1 : 100,000 the solution is warmed with soya extract, containing no uricase, at 40° for 30 min. in the presence of chloroform. 1·0*N*-Hydrochloric acid is added to the filtrate to bring the normality to 0·1*N* and the liquid heated for 1 min. at 100°. To the warm solution 1% phenylhydrazine hydrochloride (4 drops per c.c.), 5% potassium ferricyanide (2 drops per c.c.), and concentrated hydrochloric acid (2·5 c.c. per c.c.) are added, when a red colour develops. For characterisation of allantoin in blood the proteins are removed by means of trichloroacetic acid and the above procedure is applied to the filtrate. A larger amount of potassium cyanide is required to inhibit the production of allantoic acid from uric acid by uricase when allantoin is present than in its absence. P. G. MARSHALL.

Micro-determination of iodine in organic substances. L. SCHEFFER (Biochem. Z., 1930, 228, 426—436).—Organic matter in the dried finely-powdered material is destroyed by heating at 250—300° in a nickel crucible on a sand-bath for several hours with potassium hydroxide, potassium nitrate being added if desired. The iodine in the residue is extracted with alcohol after all potassium hydroxide has been converted into carbonate by treatment with saturated ammonium carbonate solution and subsequent evaporation of all ammonia, and the alcoholic solution is evaporated to dryness without being allowed to boil. The residue is again heated for 10—30 min. in a porcelain crucible with potassium hydroxide solution, the product is extracted with water, and the extract acidified with nitric acid. Nitrite solution is then added and the mixture extracted with carbon tetrachloride. When the solution in this solvent is shaken with dilute phosphoric acid and saturated bleaching-powder solution the iodine is converted into iodate, which is determined, after concentration of the solution, by addition of potassium iodide and titration with sodium thiosulphate solution. Complete destruction of organic matter is not essential provided that the residue is moistened with warm water before being extracted with alcohol. W. MCCARTNEY.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

APRIL, 1931.

General, Physical, and Inorganic Chemistry.

Excitation function of atomic hydrogen. L. S. ORNSTEIN and H. LINDEMAN (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 1097—1100).—A preliminary account is given of a method of exciting atomic hydrogen by electrons of definite velocities. Intensity–exciting potential curves for the H_α and lines between 15 and 60 volts are given.

O. J. WALKER.

Relationships between the continuous and the many-lined spectrum of hydrogen. Y. HUKUMOTO (Sci. Rep. Tohoku, 1930, **19**, 773—792).—A detailed account of work previously noted (A., 1930, 969).

W. E. DOWNEY.

New band system of hydrogen and the conditions of its production. Z. BAY, W. FINKELNBURG, and W. STEINER (Z. physikal. Chem., 1931, **B. 11**, 351—362; cf. A., 1929, 111).—When a condensed discharge having a mean current strength of 50—200 amp. is passed through hydrogen at pressures between 0·5 and 5 mm., a group of fine lines of great intensity appears between λ 5836 and 5761 A., accompanied by other lines distributed over the whole spectrum, whilst the remaining complex line spectrum almost disappears.

F. L. USHER.

High-frequency and direct-current discharges in helium. F. L. JONES (Phil. Mag., 1931, [vii], **11**, 163—173).—Measurements of high-frequency and direct-current discharges in helium over the pressure range 1—35 mm. indicate that the mean force in the high-frequency discharges is the same as in the uniform positive column of direct-current discharges. The effect of minute traces of impurities on the luminosity and force of the discharges is discussed.

F. G. TRYHORN.

Excitation probabilities of singlet and triplet states. H. S. W. MASSEY and C. B. O. MOHR (Nature, 1931, **127**, 234—235).—The probability of excitation of the 2^3P and 2^1P states of helium as a function of the velocity of the exciting electrons has been calculated.

L. S. THEOBALD.

Beryllium isotope of mass 8, and fine structure measurements in the beryllium hydride bands. W. W. WATSON and A. E. PARKER (Physical Rev., 1931, [ii], **37**, 167—175; cf. A., 1928, 1305).—With the object of investigating the possible presence of the theoretically predicted Be^8 isotope in beryllium minerals an intense spectrogram of the λ 4991 BeH band was obtained. Every P and R line of the (0,0) band was accompanied by a very weak line in the position calculated for Be^8H, except where a strong line of another branch prevented measurement. The relative intensities of the Be^8H and Be^9H lines were about 1 : 2000, favouring the presence of the Be^8 isotope.

N. M. BLIGH.

Bands in the spectrum of boron hydride. W. LOCHTE-HOLTGREVEN and E. S. VAN DER VLEUGEL (Nature, 1931, **127**, 235—236).—The radiation emitted by a condensed discharge in boron trichloride shows widely-spaced bands near 4000 Å. which are ascribed to the molecule BH. The P and R lines of the strongest band are accompanied in certain cases by weak satellites due to the isotopic molecule $B^{10}H$. The moments of inertia found are I' $2{\cdot}32\times10^{-40}$ g.-cm.^{2} and I'' $2{\cdot}35\times10^{-40}$ g.-cm.^{2}, and the internuclear distances $r_0'=r_0''=1{\cdot}23\times10^{-8}$ cm.

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Rotation temperatures of band spectra in discharge tubes. II. W. LOCHTE-HOLTGREVEN (Z. Physik, 1931, **67**. 590—600; cf. A., 1930, 1331).—From quantitative intensity determinations of the rotation structure of the C_2 and CH bands for the electric discharge through different hydrocarbons, very high rotation temperatures are deduced. New results for acetylene and ethylene and rotation temperatures are discussed in connexion with the process of disintegration of hydrocarbons.

A. J. MEE.

Dispersion of internal energy in the quadruple and triple terms, $3sP$, $3pP$, $3pD$, in the spectra of carbon, nitrogen, oxygen, and fluorine at various degrees of ionisation. J. GILLES (Compt. rend., 1931, **192**, 350—352).—Relations are shown to exist between the intervals of certain terms of the same and different multiplicities in the spectra of B I, C I and II, N I—III, O I—IV, and F I and III.

C. A. SILBERRAD.

High-frequency discharge in nitrogen in presence of mercury. R. ZOUCKERMANN (Compt. rend., 1931, **192**, 409—411).—The spectra obtained on passing discharges of frequencies 3×10^7 and $10^7\times1/19$ through nitrogen at a pressure of 0·4 mm. in presence of mercury in an electrodeless tube show between 2400 and 4800 Å., the bands of N_2, N_2^+, and CN, several mercury lines. Previous results are discussed, and it is suggested that the bands of N_2^+ are due to collisions of the second kind.

C. A. SILBERRAD.

Discharge in gases. III. Changes in sparking potential of nitrogen. E. BADAREU (Bul. Fac. Stiinte Cernauti, 1930, **4**, 32—49; Chem. Zentr., 1930,

ii, 2613).—A study of the changes in the sparking potential of nitrogen between 0·05 and 2·85 mm. pressure as a function of the interval between two successive discharges, and of the previous discharge.

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Photo-electric effect with lead and mercury at low temperatures. J. C. McLENNAN, R. G. HUNTER, and J. H. McLEOD (Trans. Roy. Soc. Canada, 1930, [iii], **24**, III, 3—23).—Photo-electric currents from lead and mercury have been measured at temperatures down to that of liquid helium. No abrupt change in the photo-electric emission of electrons from lead as the latter was cooled through the temperature range of superconductivity was found. W. GOOD.

Photo-emission from potassium sensitised by sulphur, selenium, and tellurium. W. KLUGE (Z. Physik, 1931, **67**, 497—506).—Experiments are described showing that there exists an optimum layer thickness for sensitising photo-emission from potassium by sulphur, selenium, and tellurium; increased emission is due to a shift of the long wave-length limit, and to selective maxima at 410, 425, and 430 mμ, respectively. A. B. D. CASSIE.

Photo-electric electron emission from thin potassium and cæsium layers. R. FLEISCHER (Physikal. Z., 1931, **32**, 217—218).—For potassium there was a maximum sharing at 436 mμ of $37·9\times10^{-2}$ coul./g.-cal., quantum equivalent 1·48 coul./g.-cal., efficiency 25·7%. For cæsium at 492 mμ, the sharing is $17·1\times10^{-2}$ coul./g.-cal., quantum equivalent 1·66 coul./g.-cal., and efficiency 10·3%. A. J. MEE.

Electronic interference at organic liquids, especially oils. A. BÜHL and E. RUPP (Z. Physik, 1931, **67**, 572—581).—Definite interference can be obtained at oil surfaces by reflexion of electrons of 100—400 volts. Orientation of molecules can be determined. The position of the interference spots can be used to give the plane distances by Bragg's method. For triolein, d=12·3 Å., oleic acid, d=12 Å. (approx.), paraffin oil, d—4—5 Å. The method is suitable for surface analysis, inasmuch as vapour pressure has no effect on electronic reflexion. A. J. MEE.

Dependence of intensity of emission on the velocity of exciting electrons, and the relative intensities of electronically excited Cd and Zn lines. K. LARCHÉ (Z. Physik, 1931, **67**, 440—477).—The excitation functions for 42 cadmium and 72 zinc lines were determined between 3·8 and 500 volts. All lines showed one maximum, except those originating in $^1S_0$ levels, which have two (cf. A., 1930, 830). Relative intensities of cadmium and zinc lines between 6500 and 2300 Å. showed 7 triplets and 2 spark doublets which fit the Ornstein–Burger intensity relation. A. B. D. CASSIE.

Wave mechanics and the specific charge of the electron. F. SAUTER (Naturwiss., 1931, **19**, 165—166).

Effective cross-section of argon and hydrogen towards electrons of 0·2—6 volts. H. GAERTNER (Ann. Physik, 1931, [v], **8**, 135—161).—The method of Rusch (A., 1926, 989) for determining the effective cross-section towards slow electrons in a longitudinal field was so modified that it was possible to measure this value for electrons of 0·1 volt. The minimum value found for argon by Rusch at 0·4 volt was corrected and shows good agreement with the work of Townsend and Bailey and of Ramsauer and Kollath (A., 1929, 1123). A. J. MEE.

Ideal gas equation and the properties of the electron and proton. R. D. KLEEMAN (Z. Elektrochem., 1931, **37**, 77—80).—Mathematical. The ideal gas equation is expressed in a form such that the kinetic energy of the molecules is approximately independent of the volume within certain limits and becomes zero at infinite volume. Interaction of radiation and gas molecules is considered. It is shown that the potential energy of a proton or an electron resulting from its electric field can be converted into internal energy and *vice versa*; as a result of motion radiant energy can be absorbed and converted into internal energy, and can be re-emitted wholly or in part as radiation. H. F. GILLBE.

Discharge by electron impact in hydrogen. S. VENCOV (Ann. Physique, 1931, [x], **15**, 131—266).—The electronic discharge in hydrogen was investigated electrically and spectroscopically with the object of correlating critical potentials and the appearance of different spectra. Using a double-grid tube and three methods of potential determination serving as a check on each other, critical potentials were found at 11·5, 16·5, 29·7, and 13·5 volts. The form of the current–potential curves showed that the influence of secondary processes was negligible. The atomic spectrum of hydrogen under electronic bombardment was very weak below 18 volts and increased in intensity to a maximum at 30 volts. The Richardson triplet series of bands decreased in intensity with rise of potential, whilst the singlet system intensity reached a marked maximum and then decreased. The appearance of the continuous resembled, in general, that of the atomic spectrum. N. M. BLIGH.

Motion of electrons in argon. H. B. WAHLIN (Physical Rev., 1931, [ii], **37**, 260—262; cf. A., 1930, 1082).—The motion of electrons in argon was investigated by the alternating-potential method and results are shown to be in agreement with calculations based on Compton's theory. For low fields the mobility is a constant, but rises rapidly with the field. N. M. BLIGH.

Effect of water vapour on the mobilities of negative ions in air. J. J. NOLAN (Proc. Roy. Irish Acad., 1930, **39**, A, 82—99; cf. A., 1930, 658).—An apparatus for the measurement of mobilities of ions by the Rutherford–Franck alternating-field method is described. Negative ions in moist air favour certain sizes, with corresponding mobilities ranging from 1·5 to 2·4 cm./sec., and increasing with decrease of water vapour pressure. The maximum negative-ion mobility in air dried by contact with sulphuric acid was 2·4 cm./sec. Ions of mobility about 12 cm./sec. have about 0·1% concentration in air containing 0·87 mm. pressure of water vapour. N. M. BLIGH.

Production of an intense beam of hydrogen positive ions. L. R. MAXWELL (Rev. Sci. Instr., 1931, [ii], 2, 129—140).—An intense beam of hydrogen positive ions is obtained by placing a discharge chamber in a strong magnetic field parallel to the direction of motion of the ions. Beams corresponding with currents up to 3 milliamp. can be produced.

C. W. GIBBY.

Charging effect by passage of protons through helium. R. DOPEL (Naturwiss., 1931, **19**, 179—180).—An effect analogous to the Ramsauer effect but due to protons has been observed on passing *H*-canal rays through helium. W. E. DOWNEY.

Capture of electrons by positive ions. J. L. DESTOUCHES (Compt. rend., 1931, **192**, 345—348).—The author shows that his theory of the Davis–Barnes effect is in agreement with the results obtained by other workers (cf. Barnes etc., A., 1929, 971; 1930, 393; Henderson, A., 1925, ii, 922; Rutherford, A., 1924, ii, 225; Stetter, A., 1927, 494).

C. A. SILBERRAD.

Trapping of atoms in a magneto-cathodic or cathodic beam. E. HENRIOT, O. GOCHE, and (MLLE.) F. DONY-HENAULT (J. Phys. Radium, 1931, [vii], 2, 1—11).—An apparatus is described by which it is shown that atoms of tungsten, carbon, platinum, sodium, and sulphur vaporised from a small electrically heated furnace can be trapped in a cathodic or magneto-cathodic beam. N. M. BLIGH.

Theory and construction of the spherical mass spectrograph. H. MURAWKIN (Ann. Physik, 1931, [v], 8, 203—260).—It is shown that the principal radius is not in general the mean radius, and a correction is therefore necessary in the at. wt. formula. The effect of horizontal and vertical scattering on the resolving power is discussed and a new formula for the resolving power is given. The intensity is directly proportional to the slit width and inversely proportional to the cube of the mean radius. The resolving power of the instrument is almost independent of the apparatus constant, and can be increased with better indicating instruments. A. J. MEE.

Frequency of occurrence of elements. M. F. SOONAWALA (Indian J. Physics. 1930, **5**, 681—684; cf. A., 1929, 973).—From considerations previously discussed the value of the energy liberated in the nuclear synthesis of isotopes from rare gas nuclei is calculated for ten typical elements and groups, and considered in connexion with the atomic percentage of elements composing the earth. N. M. BLIGH.

At. wt. of nitrogen and silver. I. Ratio of ammonia to silver. G. P. BAXTER and C. H. GREENE (J. Amer. Chem. Soc., 1931. **53**, 604—613; cf. Honigschmid, Zintl, and Thilo, A., 1927, 806).—The ratio Ag : NH_3 is 6·33420, determined by way of the chlorides and bromides; hence the ratio NO_3 : NH_3 is 3·64083, and the at. wts. of nitrogen and silver are 14·0078 and 107·879, respectively.

J. G. A. GRIFFITHS.

Anomalous scattering of α-particles by light atoms. T. SEXL (Z. Physik, 1931, **67**, 766—779).—A detailed account of work already noted (A., 1930, 516).

Ionisation by α-rays passing through the thin walls of a small sphere. W. MUND (Bull. Soc. chim. Belg., 1930, **39**, 518—528; cf. A., 1925, ii, 732; Glockler, A., 1927, 1003).—The equation expressing the ionisation produced in a spherical vessel by the α-ray emission of radon and of its disintegration products contained in a small sphere enclosed therein is deduced in a modified form. J. W. SMITH.

Scattering of hard γ-rays. II. L. H. GRAY (Proc. Roy. Soc., 1931, **A**, **130**, 524—541; cf. A., 1930, 372).—The validity of the Klein–Nishina formulæ for heavy elements has been tested by comparing the intensity of the radiation scattered in the forward direction by heavy and light elements, using an ionisation chamber containing oxygen at 85 atm. pressure. The elements compared were magnesium, aluminium, copper, zinc, cadmium, tin, and lead, using radium-*C* γ-rays filtered through 4 cm. of lead, and thorium-*C''* γ-rays filtered through 3 cm. of lead. No variations in the scattering power of different elements have been found beyond such as might be attributed to experimental error (of the order of 1%), and it is concluded that the binding forces are without sensible influence on the scattering power of the extranuclear electrons. Not more than one third of the difference between the absorption coefficients of the thorium-*C''* γ-rays in heavy and light elements can be due to nuclear absorption resulting in the re-emission of approximately isotropic radiation.

L. L. BIRCUMSHAW.

Rate of decay of polonium in various places. L. BOGOIAVLENSKI (J. Phys. Radium, 1931, [vii], 2, 12—19; cf. A., 1929, 737, 1358).—The period of polonium kept from 4 to 5 months at 63 places in Russia varied from 135·5 to 141·1 days. N. M. BLIGH.

Groupings of radioactive atoms. E. L. HARRINGTON (Compt. rend., 1931, **192**, 414—415; cf. Jedrzejovski, also Chamie, A., 1929, 620).—Previous results are confirmed, but impurities are not necessary for the formation of the groupings. These are found predominantly at such points as scratches, leaflets, or edges of a mica plate. C. A. SILBERRAD.

Radiometer effect. E. BRÜCHE and W. LITTWIN (Z. Physik, 1931, **67**, 333—361).—The radiometer consisted of a platinum leaf 0·01 mm. thick hung between two platinum plates 0·01 mm. thick, one of which could be heated electrically. The radiometer effect was proportional to the excess temperature of the heated surface. At low pressures variation with pressure agreed with Knudsen's theoretical results (cf. A., 1930, 1246) for all gases except hydrogen and helium; at high pressures (0·01 mm.) the effect was inversely proportional to the pressure. At high pressures the effect is proportional to the square of the mean free path of the gas. A. B. D. CASSIE.

Dynamics of the atomic nucleus. P. FADDA (Nuovo Cim., 1930, **7**, clxiii—clxxxv; Chem. Zentr., 1930, ii, 2993).—A summary and discussion.

A. A. ELDRIDGE.

Quantum mechanics of electrons in crystal lattices. R. DE L. KRONIG and W. G. PENNEY (Proc. Roy. Soc., 1931, **A**, **130**, 499—513).—An investigation has been made of the mechanics of

electrons in periodic fields of potential such that the energy values and eigenfunctions of the wave-equation can be computed. The spectrum of permissible energy values is found to consist of continuous regions separated by finite intervals.

L. L. BIRCUMSHAW.

Modification of quanta by photo-ionisation. S. BHARGAVA and J. B. MUKERJIE (Nature, 1931, **127**, 273, 305).—Experiments are described indicating that the quantum can impart energy varying from $h\nu$ to $h\nu_k$ to the bound electron and can be modified to any frequency less than $\nu-\nu_k$.

L. S. THEOBALD.

Spectrum of cosmic rays. E. REGENER (Nature, 1931, **127**, 233—234).—Details of absorption of cosmic rays in Lake Constance to a depth of 236·5 m. are given. Four components of different penetrating powers are distinguished.

L. S. THEOBALD.

Cosmic-ray ionisation–depth curve, and the present evidence for atom building. R. A. MILLIKAN and G. H. CAMERON (Physical Rev., 1931, [ii], **37**, 235—252).—Measurements previously reported (cf. A., 1928, 1303) on the relation between cosmic-ray ionisation and depth have been corrected and extended in both directions. Evidence indicates that the strongest and most absorbable band arises from the formation of helium from hydrogen, and the next three bands from the formation of oxygen, silicon, and iron. Proofs are given that the cosmic rays enter the earth's atmosphere as photons, indicating that they must originate in interstellar space rather than in the atmosphere of the stars.

N. M. BLIGH.

Transmitted structural blue in microscopic objects. C. W. MASON (J. Physical Chem., 1931, **35**, 73—81).—Particle size or size of structure is correlated with the colours exhibited. Transmitted blue is apparent to the unaided eye with particles or structures coarser than 0·4 μ, and is due to greater deviation of red than blue either by diffraction or scattering. L. S. THEOBALD.

Absorption spectra of rare-earth double nitrates. D. W. PEARCE and J. A. HARRIS (Trans. Roy. Soc. Canada, 1930, [iii], **24**, III, 145—151).—Double nitrates of bivalent metals with cerium group rare earths were crystallised under identical conditions. From a comparative study of the relative intensity of the most characteristic absorption band of each element the relative efficiencies of the double nitrates as means of separation of the rare elements of this group were determined. W. GOOD.

Absorption of the carbonyl chromophore in the ultra-violet of short wave-length. H. LEY and B. ARENDS (Z. physikal. Chem., 1931, **B**, **12**, 132—138).—In hexane solution the maximum of the absorption band of acetone in the ultra-violet is at 187 mμ, and in aqueous solution at a shorter wave-length. Since the maximum of the band in the ultra-violet of long wave-length is displaced in the same direction, Scheibe's theory that the band in the ultra-violet of short wave-length originates in the electrons of the carbon atom of the carbonyl group (A., 1926, 774) is untenable. R. CUTHILL.

Application of the resonance radiometer to the reflexion spectrum of quartz. J. D. HARDY and S. SILVERMAN (Physical Rev., 1931, [ii], **37**, 176—181).—The reflexion spectrum of quartz was examined in the region 8—9·5 μ, using light from a Nernst glower and magnesium oxide filtration (cf. Pfund, A., 1930, 1235); high dispersion was obtained by an echelette grating spectrometer. N. M. BLIGH.

Behaviour of water with change of temperature and with addition of electrolytes as studied by the Raman effect. I. R. RAO (Proc. Roy. Soc., 1931, **A**, **130**, 489—499; cf. A., 1930, 662; Ganesan and Venkateswaran, A., 1929, 1215).—Accurate wave-length measurements of the bands in the visible and ultra-violet regions of the spectrum have been made. The maximum of the water band lies at about 2·92 μ, with the two extremes at 2·75 and 3·24 μ. In solutions of electrolytes (nitric acid, sodium nitrate and chlorate) the band becomes sharper with increase in concentration and the maximum shifts towards 2·70 μ, a second maximum appearing at 2·79 μ with 76% of nitric acid. A similar effect is found on rise of temperature. It is suggested that these results are due to changes in the proportions of single, double, and triple water molecules. L. L. BIRCUMSHAW.

Raman effect in salt solutions. II. H. BRAUNE and G. ENGELBRECHT (Z. physikal. Chem., 1931, **B**, **11**, 409—419; cf. A., 1930, 1344).—Mercuric iodide in alcohol shows a strong line, 150 cm.$^{-1}$ The values of $\Delta\nu$ for the bromide and iodide calculated from that in the chloride from heats of dissociation agree with the observed values, supporting the view that the observed frequency is due to symmetrical linear oscillation of the halogen atoms with respect to the mercury atom. The complex halides K_2HgCl_4, K_2HgBr_4, K_2HgI_4 give a Raman spectrum similar to that of the simple halides. Potassium cadmium chloride, like cadmium chloride, shows no Raman effect, but the complex iodide gives a strong line, 118 cm.$^{-1}$ A very weak line of the same frequency can be observed in concentrated solutions of cadmium iodide, and the effect is therefore attributed to the complex anion. Of complex cyanides, potassium argenticyanide alone has a Raman line corresponding with an oscillation of the CN radical with respect to the central atom. F. L. USHER.

Polarisation experiments with the Raman effect with liquids. G. PLACZEK and W. R. VAN WIJK (Z. Physik, 1931, **67**, 582—589).—The application of Wood's arrangement for polarisation experiments is possible, and is of advantage because of the short time of exposure necessary. The method was used for the investigation of the polarisation at the critical point of the continuum. A. J. MEE.

Raman effect in certain substances with a new apparatus. B. VENKATESACHAR and L. SIBAIYA (Indian J. Physics, 1930, **5**, 747—754).—An apparatus for the study of the Raman effect for substances in the inner of two coaxial tubes, surrounded by the exciting arc, is described. Results are tabulated for calcite, aragonite, and acetylene; halite, fluorite, and chalk gave negative results. Acetylene gave lines corresponding with the infra-red absorption

bands at 2·45 and 7·5 μ; the strong absorption band at 13·7 μ gave no corresponding Raman line. The temperature effect on the continuous wings accompanying unmodified lines in the scattered spectrum was studied, and their origin suggested (cf. Raman and Krishnan, A., 1929, 240). N. M. BLIGH.

Raman spectra of organic sulphides. V. N. THATTE and A. S. GANESAN (Nature, 1931, 127, 306).—Details of the Raman spectra of ethyl and allyl sulphides are recorded and discussed. The former is simple, whilst the latter is rich in lines.
L. S. THEOBALD.

Raman effects with liquid and gaseous nitrous oxide. J. C. MCLENNAN, H. D. SMITH, and J. O. WILHELM (Trans. Roy. Soc. Canada, 1930, [iii], 24, III, 197—205).—Two frequency shifts, 1282 and 2223 $cm.^{-1}$, were observed in a study of the Raman effect in liquid nitrous oxide. They are shown to correspond respectively with the inactive fundamental vibration of the nitrous oxide molecule and with the fundamental vibration of the central oxygen atom of the molecule along the line of centres of the two nitrogen atoms. W. GOOD.

Raman effect with acetylene. E. SEGRE (Atti R. Accad. Lincei, 1930, [vi], 12, 226—228).—Details are given of a method of measuring the Raman effect in gases in the visible region. For acetylene, five fine lines of frequencies 25,417, 25,377, 25,318, 22,725, and 20,950 were observed. A diffuse line at a frequency of approximately 21,930 was also noted, of which the interpretation is uncertain. F. G. TRYHORN.

Raman effect. X. Raman spectra of organic substances. A. DADIEU and K. W. F. KOHLRAUSCH (Monatsh., 1931, 57, 225—240; cf. this vol., 21).—Raman spectra of the following substances have been examined: propylamine, ethylenediamine, aniline, formamide, dicyanodiamide, diethylamine, diphenylamine, trimethylamine, triethylamine, methylnitroamine, chloral, ethyl chloroformate, chloroacetyl chloride, dimethyl ether, and diphenyl ether. The results are discussed. The third frequency characteristic of the oscillating point system $^{-}NH_2$ has not yet been discovered. F. L. USHER.

Ultra-violet absorption spectrum of acetylene. G. B. KISTIAKOWSKY (Physical Rev., 1931, [ii], 37, 276—278).—Photographs of the ultra-violet bands of carefully purified acetylene in absorption tubes illuminated by a hydrogen discharge tube showed no trace of bands between 3157 and 2236 Å. reported by Henri and Landau (A., 1913, ii, 267), which are attributed to impurities. Bands are observed only below 2400 Å., and are tabulated. The bands are arranged in three progressions and interpreted from infra-red absorption data (cf. Mecke, A., 1930, 1236).
N. M. BLIGH.

Rational classification of light-scattering media. M. GUREVIC (Physikal. Z., 1930, 31, 753—763).—A general theory of the reflexion and transmission of light at a surface consisting of light-scattering particles is developed which involves two constants characteristic of the medium of which the surface is composed. Experiments are described in which the predictions of the theory are fulfilled.
R. W. LUNT.

Fluorescence dissociation of silver iodide vapour. A. TERENIN (Physica, 1930, 10, 209—212; Chem. Zentr., 1930, ii, 2872).—The lines 3383 and 3281 Å. are emitted on photo-dissociation of silver iodide with different intensities dependent on the excitant wave-length. The absorption spectrum of the silver iodide molecule must possess maxima at 2100 and 2060 Å. The dissociation energy of silver iodide is 2·20 volts or 51 kg.-cal. per mol.
A. A. ELDRIDGE.

Photo-electric behaviour of salts, particularly of the action of longer wave-lengths on salts previously irradiated with shorter wave-lengths. J. KLAPHECKE (Z. Physik, 1931, 67, 478—496; cf. A., 1929, 1217).—The photo-electric effect was studied for sublimed, recrystallised, and dehydrated lead chloride and cadmium iodide. Photo-emission due to long wave-lengths increases rapidly with the number of water molecules present. The results indicate that photo-emission, inner electrical conductivity, phosphorescence, and colouring of the first kind are closely related. A. B. D. CASSIE.

Effect of space charge in a gas at low pressures. E. W. B. GILL (Phil. Mag., 1931, [vii], 11, 95—98).—It is found that, as with a three-electrode valve, so with a two-electrode valve under certain conditions when definite potentials are applied to the electrodes the current passing from the filament to the anode may have two or three different values.
F. G. TRYHORN.

Influence of thermal treatment on the characteristics of copper oxide rectifiers. L. DUBAR (Compt. rend., 1931, 192, 484—485).—By comparing the current passing from the oxide to copper with a *P.D.* of 4 volts the best method of treating the copper plate has been ascertained.
C. A. SILBERRAD.

Copper oxide rectifiers. L. DUBAR (Compt. rend., 1931, 192, 341—343).—The explanation of the action of the copper oxide rectifier as stated by Pelabon (cf. B., 1930, 565) is supported by the separate preparation of the semi-conducting layer of mixed cuprous and cupric oxides, and of the semi-insulating layer of pure cuprous oxide. C. A. SILBERRAD.

Uni-directional conductors (detectors). G. SIEMENS and W. DEMBERG (Z. Physik, 1931, 67, 375—387).—Experiments are described relating to the mechanism of the detector action of lead sulphide in dry and moist gases. R. W. LUNT.

Properties of cuprous oxide. O. VON AUWERS (Naturwiss., 1931, 19, 133—134).—The specific resistance of cuprous oxide artificially prepared varies between wide limits. To discover the cause of this, experiments were carried out with outgassed cuprous oxide. In the case of air and hydrogen, with decreasing pressure, the specific resistance decreases; with oxygen, decrease of pressure involves increase of specific resistance, but with nitrogen and neon there was no effect. The resistance increases with the amount of outgassing. Cuprous oxide has a transition point at 56°, above which the transparent oxide becomes opaque. Freshly prepared cuprous oxide has practically no coefficient of expansion up to 56°; above this, there is a measurable coefficient. For the

oxide which has been outgassed in a high vacuum there is a measurable coefficient which becomes smaller above 56°. The cuprous oxide lattice depends to a great extent on dissolved substances, and on those adsorbed at its surface. This appears to be general for metallic oxides, *e.g.*, the oxides of nickel, tin, and zinc. A. J. MEE.

Significance of electro- and magneto-photophoresis. F. EHRENHAFT, M. REISS, and E. WASSER (Z. Physik, 1931, **67**, 519—522). Electro- and magneto-photophoresis can be explained by assuming the accommodation coefficient dependent on the electric and magnetic fields. A. B. D. CASSIE.

Super-conductivity. W. MEISSNER (Z. ges. Kälteind., 1930, **37**, 174—177 : Chem. Zentr., 1930, ii, 2876).—A summary and discussion.

A. A. ELDRIDGE.

Conductivity of insulating oils. K. F. HERZFELD (Physical Rev., 1931, [ii], **37**, 287—291).—Theoretical. Methods developed in the study of conduction of electricity through gases (cf. *ibid.*, 1929, [ii], **34**, 791) are applied to the measurements of the space charge set up in insulating oils by a steady electric field, in order to determine the nature of the ions present. N. M. BLIGH.

Passage of continuous current through acetone. G. REBOUL and J. SAMBUSSY (Compt. rend., 1931, **192**, 490—491).—The variations in the current observed by Garrigue (cf. A., 1930, 1126) are traced to the presence of light. They disappear in darkness, the current then diminishing regularly and exponentially with time, as found by Lafond.

C. A. SILBERRAD.

Theory of dielectrics. G. GUÉBEN (Phil. Mag., 1931, [vii], **11**, 405—410).—A general expression for the current in a solid dielectric has been deduced, assuming that both ions and dipoles take part in the conduction of the current. R. CUTHILL.

Dielectric constant and conductivity of ionised gases. T. V. IONESCU and C. MIHUL (Compt. rend., 1931, **192**, 343—345).—A curve showing the variations with wave-length of the oscillator (cf. this vol., 285) is given, the results being some 30 times those calculated, which is attributed to resonance. This is supported by the fact that by modifying the method of experiment results have been obtained indicating that in certain circumstances the electrons are associated with molecules of the gas, in which case they possess a definite period of vibration.

C. A. SILBERRAD.

Dielectric constants of liquefied gases. J. C. MCLENNAN, R. C. JACOBSEN, and J. O. WILHELM (Trans. Roy. Soc. Canada, 1930, [iii], **24**, III, 37—46).—The method and results of measurements of the dielectric constants of liquid nitrogen, argon, methane, and nitrous oxide are given. W. GOOD.

Electric moment and molecular structure. I. Ethyl esters of mono- and di-carboxylic acids. C. P. SMYTH and W. S. WALLS. **II. *tert.*-Butyl and triphenylmethyl chlorides and alcohols.** C. P. SMYTH and R. W. DORNTE (J. Amer. Chem. Soc., 1931, **53**, 527—539, 545—555).—I. Dielectric constants and densities of benzene solutions of the esters at 25° and 50° are tabulated. The electric moments at 25° and 50°, respectively, are: ethyl formate, 1·94, 1·93; acetate, 1·86, 1·82; propionate, 1·81, 1·78; maleate, 2·54, 2·56; fumarate, 2·38, 2·40; oxalate, 2·49, 2·52; malonate, 2·54, 2·57; succinate, 2·14, 2·21; glutarate, 2·41, 2·42; adipate, 2·40, 2·42; sebacate, 2·49, 2·50, and hexadecamethylenedicarboxylate, 2·49, $2{\cdot}48 \pm 0{\cdot}02 \times 10^{-18}$ e.s.u. (cf. A., 1925, ii, 846). It is concluded that long-chain molecules have extended structures which do not bend appreciably in small external electric fields. Owing to free rotation, the relative positions of the carbethoxyl groups in the molecule have only small effects in the electric moment.

II. The dielectric constants and densities of heptane or benzene solutions of the substances have been determined at temperatures between −70° and 70°, and the following electric moments are recorded: *tert.*-butyl chloride, $2{\cdot}14 \times 10^{-18}$ e.s.u.; *tert.*-butyl alcohol, 1·65; triphenylchloromethane, 1·95; triphenylcarbinol, 2·11. The polarisation–concentration curves for *tert.*-butyl alcohol in heptane each exhibit a maximum and a minimum. The solutions in benzene conform approximately to the Debye equation. The polarisations indicate that the triphenylmethyl group, unlike the *tert.*-butyl, has a greater screening effect on the field of the dipole than has the *n*-butyl group. The moments of the butyl compounds (A., 1930, 135, 1093; Parts, *ibid.*, 667) are in harmony with the view that the inductive influence of the principal dipole is exerted along a carbon chain to a distance not greater than the second carbon atom.

J. G. A. GRIFFITHS.

Electric moments of organic molecules. VI. "*Ortho* effect" in derivatives of *p*-dichlorobenzene and of *s*-trichloro- and tribromo-benzene. O. HASSEL and E. NÆSHAGEN (Z. physikal. Chem., 1931, B, **12**, 79—88; cf. A., 1930, 1348).—Measurement of the dipole moments of the above compounds has yielded further examples of the "*ortho* effect." It seems possible that the *ortho* effect may be of value in determining the configuration of benzene derivatives with three or four substituents.

R. CUTHILL.

Intramolecular field and the dielectric constant. F. G. KEYES and J. G. KIRKWOOD (Physical Rev., 1931, [ii], **37**, 202—215).—Mathematical. A statistical calculation of the average internal field in a dielectric is made, and a relation is obtained between the dielectric constant, the molecular polarisability, the molal volume, and the density; the expression becomes identical with the Clausius–Mosotti relation at zero density, and is applied to dielectric constant measurements on air, nitrogen, hydrogen, carbon dioxide, and ammonia. N. M. BLIGH.

Pleochroic "giant" haloes in cordierite. M. S. KRISHNAN and C. MAHADEVAN (Indian J. Physics, 1930, **5**, 669—680; cf. A., 1927, 956).—More than 200 haloes in 20 thin sections of cordierite gneiss from South India were found to include a few "giant" haloes, having dimensions larger than for normal ranges of α-particles in the uranium and thorium series. They are shown to correspond with the ranges 9·3 cm. for radium-*C′* (cf. Philipp, A.,

1929, 371) and 11·5 cm. for thorium-C' (cf. Nimmo, *ibid.*). N. M. BLIGH.

Birefringence of safrole. PAUTHENIER and BART (Compt. rend., 1931, **192**, 352—353).—In contradiction to Leiser's statement (cf. A., 1911, ii, 563), safrole shows no residual birefringence. Its Kerr constant is $0·82\times10^{-7}$ for λ 5460 Å. No hysteresis occurs when the electrostatic field is varied.

C. A. SILBERRAD.

Magneto-optical dispersion of organic liquids in the ultra-violet region of the spectrum. II. Magneto-optical dispersion of methyl propionate, ethyl propionate, and ethyl formate. I. JENKINS and E. J. EVANS (Phil. Mag., 1931, [vii], **11**, 377—396; cf. this vol., 24).—The magneto-optical dispersion of the above liquids over the spectral range 0·30—0·45 μ can be represented by equations of the type $n\delta=K_1\lambda^2/(\lambda^2-\lambda_1^2)^2$, where δ and n are the values of Verdet's constant and the refractive index for a wave-length λ, K_1 is a constant which varies from liquid to liquid, and λ_1 is the wave-length of the absorption band. The natural dispersion over the range 0·2700—0·6678 is given by the equation $n^2-1=b_0+b_1/(\lambda^2-\lambda_1^2)$, where b_0 and b_1 are constants which increase with the mol. wt. of the liquid. For methyl propionate, ethyl propionate, and ethyl formate the values of λ_1 are 0·1066, 0·1075, and 0·1061 μ, respectively, and the values of e/m calculated from the rotatory power are $0·96\times10^7$, $0·99\times10^7$, and $0·99\times10^7$ e.m.u., respectively. R. CUTHILL.

Change in specific magnetic rotation in passing from the liquid to the gaseous state. R. DE MALLEMAN and P. GABIANO (Compt. rend., 1931, **192**, 487—489).—The specific magnetic rotations for the gaseous (Λ_g) and liquid (Λ_l) states of eleven paraffins or halogen derivatives thereof, benzene, and carbon disulphide are tabulated, and the values of Λ_g/Λ_l and of $9n\Lambda_l/(n^2+2)^2$ shown to agree respectively with those of $9n/(n^2+2)^2$ (as required by Lorentz' law), and Λ_g, with differences rarely as much as 5%.

C. A. SILBERRAD.

Diamagnetism of free electrons. E. TELLER (Z. Physik, 1931, **67**, 311—319).—Theoretical (cf. Landau, A., 1930, 1355).—Boundary conditions are taken into account, but the expression for diamagnetism of free electrons remains unchanged.

A. B. D. CASSIE.

Paramagnetism of polychromates. F. W. GRAY and J. DAKERS (Phil. Mag., 1931, [vii], **11**, 297—314).—The magnetic susceptibilities of chromium trioxide and potassium chromate, dichromate, trichromate, and tetrachromate have been measured. The best interpretation of the results is obtained by supposing that the structures of these molecules are similar to those previously postulated for halogenates and perhalogenates (A., 1930, 1101). In the addition of solid chromium trioxide to potassium chromate and the polychromates it appears that the first step is the depolymerisation of the trioxide, which has a deparamagnetising effect, then the single molecules of trioxide combine with single molecules of chromate, the rise in complexity having a paramagnetising effect.

R. CUTHILL.

Dependence of the susceptibility of diamagnetic metals on the field. W. J. DE HAAS and P. M. VAN ALPHEN (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 1106—1118; cf. this vol., 28).—As in the case of long single crystals of bismuth previously investigated, the susceptibility of a small single crystal ($5\times5\times5$ mm.) of bismuth is a periodic function of the field at 20·4° and 14·2° Abs. O. J. WALKER.

Magnetic susceptibilities and ionic moments in the palladium and platinum groups. A. N. GUTHRIE and L. T. BOURLAND (Physical Rev., 1931, [ii], **37**, 303—308; cf. Bose, A., 1928, 823; Cabrera, A., 1927, 926).—Predictions by Hund's method from spectroscopic theory were investigated by means of an improved Curie balance. Palladium and platinum followed approximately a Curie–Weiss law; ruthenium, rhodium, osmium, and iridium had paramagnetic susceptibilities which increased with rise of temperature. The compounds $RuCl_3$ and IrO_2 followed a Curie–Weiss law which gave for the ions Ru^{III} and Ir^{IV} moments of 9·8 and 13·8 Weiss magnetons per mol. respectively. The paramagnetic susceptibility of Rh_2O_3 was independent of, and that of RuO_2 increased rapidly with, temperature; $IrCl_3$ and $PtCl_2$ are diamagnetic with susceptibilities independent of temperature.

N. M. BLIGH.

Susceptibility of cupric sulphate pentahydrate at low temperatures; magneton numbers in the iron group. W. J. DE HAAS and C. J. GORTER (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 1101—1105).—The susceptibility of cupric sulphate pentahydrate between 290° and 14·29° Abs. has been measured. This substance obeys the Curie–Weiss law, with $\theta=-0·70°$ and $p=9·51$ Weiss magnetons. A comparison of the experimental magneton numbers in the iron group with those calculated from various theories shows that the best agreement is found in the case of the Bose–Stoner theory (cf. A., 1929, 1371). O. J. WALKER.

Magnetic susceptibilities of the polyoxymethylenes and formaldehyde solutions. W. GOOD (J. Roy. Tech. Coll. Glasgow, 1931, **2**, 401—409).—The magnetic susceptibilities (κ) of the four polyoxymethylenes were measured in a Curie balance (error ±1·5%). The values found (α $-0·503\times10^{-6}$, β $-0·501\times10^{-6}$, γ $-0·467\times10^{-6}$, δ $-0·417\times10^{-6}$, ordinary trioxymethylene, which is probably a mixture of the β- and γ-compounds, $-0·447\times10^{-6}$) are not in agreement with the theoretical values calculated by the law of additivity from the formulæ previously proposed. The results suggest that the polyoxymethylenes are mixtures of substances having the formula $CH_3·[O·CH_2]_n·O·CHO$. J. GRANT.

Diamagnetism of polyhalides. F. W. GRAY and J. DAKERS (Phil. Mag., 1931, [vii], **11**, 81—95).—Measurements have been made of the diamagnetism of numerous halides, and of simple and mixed polyhalides, chiefly derived from tetramethyl-, tetraethyl-, and phenyltrimethyl-ammonium hydroxide. The diamagnetism of these compounds is discussed from the the point of view previously stated (A., 1930, 1101).

F. G. TRYHORN.

Stereochemistry of crystalline compounds. IV. Atomic distances in crystals. P. NIGGLI (Z.

Krist., 1930, **76**, 235—251).—The distances between atoms in crystalline binary compounds and in the pure elements are tabulated, and the results discussed with reference to the positions of the elements in the periodic system. Certain regularities are deduced.

C. A. Silberrad.

Change of the magnetic moment of nitric oxide with temperature. E. C. Wiersma, W. J. de Haas, and W. H. Capel (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 1119—1124).—The magnetic moment of the nitric oxide molecule has been determined for the range 292·1—112·77° Abs. The values are in good agreement with those predicted by van Vleck (A., 1928, 572).

O. J. Walker.

Thermo-magnetic investigation of certain anhydrous compounds of cobalt and nickel. B. Cabrera and A. Duperier (Anal. Fís. Quím., 1931, **29**, 5—14).—The variation with temperature of the magnetic susceptibility of nickel and cobalt halides and sulphates has been determined at temperatures up to 500—700° Abs. The Curie–Weiss law is valid for cobalt fluoride and sulphate. Nickel fluoride and bromide apparently conform also to the law, but the chloride and sulphate exhibit deviations at the higher temperatures which indicate a transformation of the nickel structure at about 550° Abs.

H. F. Gillbe.

Theory of magnetism. K. Honda (Sci. Rep. Tohoku, 1930, **19**, 745—759).—A modification of the author's earlier theory (cf. A., 1928, 454) enables the gyromagnetic effect as well as the magnetic deflexion of atomic rays in a strong field to be explained.

W. E. Downey.

Hydrates of the alkaline-earth oxides. C. Nogareda (Anal. Fís. Quím., 1931, **29**, 33—64).—The dehydration isotherms of two specimens of calcium hydroxide of the approximate compositions $CaO,3\cdot55H_2O$ and $CaO,4\cdot6H_2O$, prepared by different methods, afford no evidence for the existence of hydrates of the hydroxide. Specimens having the composition of a monohydrate had mol. vol. 47·5—48·6, and appear to be a definite, labile compound. By the vacuum evaporation of a solution of calcium hydroxide at 30° hard transparent crystals of the hydroxide have been obtained without the intermediate formation of a hydrate; the mol. vol. of the crystalline hydroxide is the same as that of the amorphous form. Dehydration isotherms of strontium and barium hydroxides indicate that only the very stable monohydrates and the feebly stable octohydrates exist. The densities are: $Sr(OH)_2,8H_2O$ 1·860 (lit. 1·396—1·90), $Sr(OH)_2,H_2O$ 2·862, $Sr(OH)_2$ 3·305 (lit. 3·625), $Ba(OH)_2,8H_2O$ 2·164 (lit. 1·656) $Ba(OH)_2,H_2O$ 3·743, and $Ba(OH)_2$ 4·463.

H. F. Gillbe.

Hydrates of the alkaline-earth peroxides. II. Constitution. C. Nogareda (Anal. Fís. Quím., 1931, **29**, 131—145).—Octohydrated calcium, strontium, and barium peroxides have *d* 1·700, 1·951, and 2·291, respectively, and the calculated mol. vol. of the anhydrous peroxides are 21·2, 28·3, and 30·0. The volume of the second oxygen atom is thus about 25% of the normal value, viz., 2·9—3·0. All the alkaline-earth peroxides react as true peroxides, *e.g.*, they liberate iodine from neutral iodide solutions and do not yield free hydrogen peroxide when extracted with ether. Isothermal dehydration of the octohydrates proceeds continuously, without any indication of the formation of lower hydrates, until 7·5 mols. of water have been evolved, when decomposition of the peroxides commences. Hydrated strontium peroxide is considerably more stable than the barium and calcium compounds. The dehydrated substances are deficient in oxygen, and the residual water is eliminated only at temperatures above 200°. It appears that the product of dehydration of the octohydrates at the ordinary temperature consists of anhydrous peroxide with about 20% of hydroxide resulting from partial hydrolysis.

H. F. Gillbe.

Structure and properties of hydrated oxalic acid. M. A. Rakuzin (Chem.-Ztg., 1931, **55**, 128).—It is shown by discussion of previous work that the water present in crystallised oxalic acid must be regarded as water of crystallisation, and not of constitution. A specimen of the acid when exposed to the air for 29 days at 20° did not lose a trace of water.

H. F. Gillbe.

Stability relationships of complexes formed between metallic salts and organic molecules. Compounds of zinc halides with amines, and their heats of formation. W. Hieber and H. Appel (Z. anorg. Chem., 1931, **196**, 193—212).—The heats of formation of a number of complexes of (solid) zinc chloride, bromide, and iodide with (gaseous) pyridine, aniline, hydrazine, ethylenediamine, and *o*-phenylenediamine have been determined from measurements of the heats of dissolution of the complexes and their components and of the latent heats of evaporation of the organic constituents. The results, expressed as valency–affinity diagrams by plotting the heat of formation against the co-ordination valency, are similar to those obtained with cobalt complexes (A., 1930, 421); thus hydrazine and ethylenediamine behave co-ordinatively as bivalent compounds, and the complexes are of cyclic structure. The heats of formation of the amino-complexes exceed the values for the corresponding ammonia derivatives, and in general diminish in the order ethylenediamine, pyridine, aniline, ammonia, hydrazine. The anion has a specific influence on the stability of the complexes. Whereas the stability of the cobalt compounds diminishes in the order chloride, bromide, iodide, such an effect scarcely exists with the zinc compounds, and in certain series the bromides possess a maximum stability. In complexes of zinc chloride and bromide with from 1 to 3 mols. of *o*-phenylenediamine the latter functions co-ordinatively as a bivalent compound and the complex is therefore cyclic.

The latent heats of evaporation of pyridine, ethylenediamine, and hydrazine at 0° are 10·21±0·05, 16·14±0·08, and 11·50±0·06 kg.-cal. per mol., respectively.

H. F. Gillbe.

Formation of molecular aggregates in radon-gas mixtures containing polar molecules. E. L. Harrington and O. A. Gratias (Phil. Mag., 1931, [vii], **11**, 285—296).—A continuation of the investigation previously described (A., 1928, 1301) has shown that the presence of polar molecules favours, and is

perhaps necessary for, the formation of molecular aggregates in gas mixtures containing radon and its disintegration products. In no case was the formation of aggregates observed when only non-polar molecules were present. R. CUTHILL.

Scattering of X-rays by water and aqueous salt solutions. W. GOOD (Helv. phys. Acta, 1930, 3, 205—248; Chem. Zentr., 1930, ii, 2485—2486).—The application of a correction factor leads to results different from those of other investigators. With concentrated solutions of salts the two water maxima are weakened or absent; hence the formation of such "ice crystallites" is prevented by the marked hydration of the ions. A. A. ELDRIDGE.

Methods in crystal analysis. I. Fourier series and the interpretation of X-ray data. II. The enhancement principle and the Fourier series of certain types of functions. A. L. PATTERSON (Z. Krist., 1930, 76, 177—186, 187—200).—The direct application of Fourier analysis to crystal structure problems without the aid of parameter determination is attempted. C. A. SILBERRAD.

X-Ray examination of microscopic crystals. I, II. O. KRATKY (Z. Krist., 1930, 73, 567—571; 76, 261—276).—A description of a suitable apparatus. C. A. SILBERRAD.

Interferometric determination of molecular form. I. H. MARK (Z. angew. Chem., 1931, 44, 125—130).—A survey of recent work on the application of the X-ray interferometer to the investigation of the molecular form of simple aliphatic compounds and vapours. H. F. GILLBE.

X-Ray interference at di- and tri-atomic molecules of light gases. H. GAJEWSKI (Physikal. Z., 1931, 32, 219—221).—Scattering experiments were carried out with nitrogen, oxygen, carbon dioxide, ammonia, and the vapours of carbon disulphide and water. The results are used for the determination of the internal dimensions of molecules. A. J. MEE.

Raman lines in X-ray spectra. G. A. LINDSAY (Nature, 1931, 127, 305).—Modified lines of a copper radiation scattered by carbon, similar to those described by Ray (A., 1930, 1334), could not be observed. L. S. THEOBALD.

Determination of the thickness of thin transparent crystal layers. G. BAUER (Ann. Physik, 1931, [v], 8, 7—47).—Wiener's correction term (*ibid.*, 1887, 31, 632) determining the thickness of a thin parallel layer lying between two parallel plates is determined for any angle of incidence, and for multiple reflexions. Approximation formulæ are given for layers thin compared with the air thickness, and for layers of thickness comparable with this air space. These formulæ are applied to experimental observations on layers from 1 mμ to several μ in thickness. Experimental conditions necessary to obtain good interference fringes with white light are given in detail; the method is extended to the determination of the thickness of wedge-shaped layers, both thick and thin. The dispersion of lead chloride is between 270 and 650 mμ. This method is applicable to the determination of absolute absorption coefficients for layers such as those used by Hilsch and Pohl (A., 1928, 812). A. B. D. CASSIE.

Nature of a crystallisation centre. A. GLAZUNOV (Coll. Czech. Chem. Comm., 1931, 3, 76—80).—The process of crystallisation is discussed with reference to the structure of the nuclei. Crystallisation in absence of extraneous matter will commence when the temperature at any point falls below a certain level; the volume thus affected will be large compared with the dimension of the crystal lattice. All crystals which grow from one centre form a single grain (crystallite), usually of heterogeneous structure. H. F. GILLBE.

Artificial etched figures on α-sulphur. J. NOVÁK (Z. Krist., 1930, 76, 169—173).—Natural crystals of α-sulphur (from Girgenti) were etched very slowly by a mixture of 92% of ethyl ether and 8% of carbon disulphide. The resulting figures clearly indicate enantiomorphic hemihedry, confirming assignment of α-sulphur to the bisphenoidal class of the orthorhombic system. C. A. SILBERRAD.

Internal and surface structure of organic liquids. J. J. TRILLAT (J. Chim. phys., 1930, 27, 525—542).—Probable causes of error in the X-ray investigation of the internal structure of liquids are discussed and an improved photographic technique, whereby disturbances due to the continuous background and to the walls of the containing vessel are in part eliminated, is described; results are given for a series of fatty acids, alcohols, and triglycerides (cf. A., 1930, 672). H. F. GILLBE.

X-Ray examination of hydrides of titanium, zirconium, vanadium, and tantalum. G. HÄGG (Z. physikal. Chem., 1931, B, 11, 433—454; cf. A., 1930, 147).—The products formed by heating some metals in hydrogen have been examined. Vanadium gave diagrams from which no definite information could be obtained. Titanium gives a product, homogeneous between 50 and 60 at.-% H, having face-centred cubic lattice, a 4·40 Å. Zirconium, 20—33 at.-% H, face-centred cubic, a 4·66 Å.; 33 at.-%, hexagonal close-packed, a 3·335, c 5·453 Å.; 50 at.-%, face-centred cubic, a 4·765 Å.; 67 at.-%, face-centred tetragonal, a 4·964, c 4·440 Å. Tantalum, 33 at.-% H, hexagonal close-packed, a 3·094, c 4·923 Å.; 50 at.-%, space-centred rhombic, a 4·811, b 4·781, c 3·434 Å. In the hydride phases with 50 at.-% H the effective radius of the hydrogen atom is 0·46 Å. F. L. USHER.

Crystal structure of lanthanum. J. C. McLENNAN and R. W. McKAY (Trans. Roy. Soc. Canada, 1930, [iii], 24, III, 33—35).—The crystal structure of metallic lanthanum was investigated by the X-ray powder method. Hexagonal close-packing was found, the side of the unit cell being equal to 3·72 Å. W. GOOD.

Crystal structure of uranium. J. C. McLENNAN and R. W. McKAY (Trans. Roy Soc. Canada, 1930, [iii], 24, III, 1—2).—The crystal structure of metallic uranium has been investigated by the X-ray powder method. The spacings were those of a body-centred cubic arrangement with the side of the unit cell equal to 3·43 Å. W. GOOD.

Atomic grouping and its properties. Experiments on the alloy $AuCu_3$. G. SACHS and J. WEERTS (Z. Physik, 1931, **67**, 507—515).—*X*-ray photographs showed that the alloy $AuCu_3$ solidified to a single crystal at 800° retains its face-centred cubic structure after annealing for 10 days at 350°. Variations in elastic and electrical properties which occurred during this annealing must therefore be due to subatomic changes. A. B. D. CASSIE.

Lattice constants of copper-nickel mixed crystals. W. G. BURGERS and J. C. M. BASART (Z. Krist., 1930, **75**, 155—157; Chem. Zentr., 1930, ii, 2739).—The values deviate from those required by Vegard's additivity law. A. A. ELDRIDGE.

***X*-Ray investigations of the crystal structure of the ε-phase in the Cu-Sn system.** J. O. LINDE (Ann. Physik, 1931, [v], **8**, 124—128).—*X*-Ray photographs of the alloy Cu_3Sn in the powdered state showed the two atoms regularly arranged in a grating structure, which could not be correlated with the simple hexagonal packing of spheres. A. B. D. CASSIE.

***X*-Ray examination of the system sulphur–selenium. II. Space lattice of monoclinic selenium I.** F. HALLA, F. X. BOSCH, and E. MEHL (Z. physikal. Chem., 1931, **B**, **11**, 455—463; cf. A., 1930, 1503).—The simplest unit cell has *a* 11·50, *b'* 8·98, *c'* 8·98 Å., β 90° 57', and contains 32 atoms. Space-group C_{2h}^5. The crystal molecule is probably Se_8. F. L. USHER.

Regularities in the crystal structure of hydrides, borides, carbides, and nitrides of the transition elements. G. HAGG (Z. physikal. Chem., 1931, **B**, **12**, 33—56; cf. A., 1930, 147).—In binary systems consisting of a transition element and hydrogen, boron, carbon, or nitrogen, the phases consist of simple metallic lattices with the metalloid atoms in the interstices, provided that the ratio of the radius of the metalloid atom to that of the metal atom does not exceed 0·59. Phases of this interstitial type are mostly homogeneous for compositions in the neighbourhood of those corresponding with the formulæ M_4X, M_2X, MX, and MX_2, where M is the metal. The metal lattice has usually the cubical closest spherical packing or the hexagonal closest spherical packing, the co-ordination number in both cases being 12. In a few instances, however, the lattice is the body-centred cubic or simple hexagonal with the axial ratio 1; in either case the co-ordination number is 8. R. CUTHILL.

Crystal structure and polymorphism of hydrogen halides. G. NATTA (Nature, 1931, **127**, 235).—The cubic modification of hydrogen chloride has *a* 5·44±0·01 Å. at the transition temperature [98° ?]; the volume of the elementary cell is 161×10^{-24} c.c.; $d_{calc.}$ for a cell containing 4 mols. is 1·49. At 85° Abs. the second form of hydrogen chloride shows numerous lines of which only a certain number correspond with the tetragonal system for *c/a* 1·10 with *a* 5·27 Å. Hydrogen bromide is also dimorphous, the high-temperature modification showing at 100° Abs. a face-centred cubic structure, *a* 5·77 Å., $d_{calc.}$ for a cell of 4 mols. 2·78, and the volume of the elementary cell 192×10^{-24} c.c. The low-temperature modification shows tetragonal symmetry (or possibly pseudotetragonal) with *a* 5·55 Å., *c/a* 1·10, and the volume of the cell 188×10^{-24} c.c. at 90° Abs. Conclusions concerning the structure of hydrogen iodide (A., 1930, 1099) are revised. The structure is face-centred tetragonal and not face-centred cubic, with *c/a* 1·08, and *a* 6·10 Å. at 100° Abs., $d_{calc.}$ 3·45, and the volume of the cell is 245×10^{-24} c.c. The calculated ionic radii are Cl' 1·92, Br' 2·04, and I' 2·21. L. S. THEOBALD.

[Crystal] structure of strontium bromide hexahydrate. Z. HERRMANN (Z. anorg. Chem., 1931, **196**, 79—84).—The orthohexagonal unit cell contains two molecules and has *a* 8·212, *c* 4·146, and *b* 14·23 Å. The space-group is C_{6}^{1}. H. F. GILLBE.

Crystal structure of cadmium chloride. L. PAULING and J. L. HOARD (Z. Krist., 1930, **74**, 546—551; Chem. Zentr., 1930, ii, 2103).—Cadmium chloride has *a* 6·23 Å., α 36° 2'; space-group C_{3v}^5, D_3^7, or D_{3d}^5. A. A. ELDRIDGE.

Crystal structure of barium tungstate. II. J. PALACIOS and I. NAVARRO (Anal. Fís. Quím., 1931, **29**, 21—32; cf. A., 1930, 279).—The positions of the oxygen atoms in the elementary prism have been determined and the results are in fair agreement with those derived theoretically from the positions of the barium and tungsten atoms. A microphotometric method for the determination of the relative reflexion intensities is described. H. F. GILLBE.

Habit-variation in crystals of barium and lead nitrates. H. E. BUCKLEY (Z. Krist., 1930, **76**, 147—168; cf. this vol., 151).—Crystallisation was effected in three ways. With barium nitrate the octahedral faces ordinarily predominate, but with very slow evaporation the cubic; a trace of carbonate has the same effect. Lead nitrate behaves similarly, but changes its habit more readily. The effect of minute additions of many substances on the habit is described. C. A. SILBERRAD.

Crystal structure of calcium chromate. J. H. CLOUSE (Z. Krist., 1930, **76**, 285—286).—Calcium chromate, *d* 3·22, is tetragonal; the unit cell has *a* 7·10, *c* 6·19, and contains four molecules. The lattice is body-centred, space-group D_{4h}^{19}. It is isomorphous with zircon and yttrium phosphate and vanadate. Strontium chromate is monoclinic, and like lead chromate isomorphous with monazite. C. A. SILBERRAD.

Structure of silver permanganate. W. BÜSSEM and K. HERRMANN (Z. Krist., 1930, **74**, 458—468; Chem. Zentr., 1930, ii, 2102).—Silver permanganate has *a* 5·66, *b* 8·27, *c* 7·12 Å., with 4 mols. of $AgMnO_4$ in the unit cell; space-group C_{2h}^5. A. A. ELDRIDGE.

Structure of cubic modification of perchlorates. K. HERRMANN and W. ILGE (Z. Krist., 1930, **75**, 41—66; Chem. Zentr., 1930, ii, 2739).—The following values of *a* (Å.), *n* (number of mols. in the unit cube), and *d* are recorded for perchlorates: potassium (340°) 7·47, 4, 2·181; ammonium (270°) 7·63, 4, 1·732; thallous (280°) 7·61, —, 4·58; cæsium (250°) 7·96, —, 3·025; rubidium (320°) 7·65, —, 2·71; sodium (380°) 7·25, —, 2·11; silver (200°) 6·92, —,

4·10. The space-group is T^2 or T_h^3. The lattice is ionic of the rock-salt type. A. A. ELDRIDGE.

Fine structure of Tutton's salts. I. Space-group. W. HOFMANN (Z. Krist., 1930, 75, 158—159; Chem. Zentr., 1930, ii, 2868—2869).—The following values for a (±0·02 Å.), b (±0·02 Å), c (±0·01 Å.), and β are recorded: $(NH_4)_2Mg(SO_4)_2,6H_2O$ 9·28, 12·57, 6·20, 107° 6′; $(NH_4)_2Fe(SO_4)_2,6H_2O$ 9·28, 12·58, 6·22, 106° 50′; $(NH_4)_2Zn(SO_4)_2,6H_2O$ 9·20, 12·47, 6·23, 106° 52′. The unit monoclinic-prismatic cell contains 2 mols.; space-group C_{2h}^5.

A. A. ELDRIDGE.

Crystal structure of cementite. S. B. HENDRICKS (Z. Krist., 1930, 74, 534—545; Chem. Zentr., 1930, ii, 2103).—Cementite has a 4·518, b 5·069, c 6·736 Å., with 4 mols. of Fe_3C in the unit cell.

A. A. ELDRIDGE.

Crystal structure of Fe_2P, Fe_2N, Fe_3N, and FeB. S. B. HENDRICKS and P. B. KOSTING (Z. Krist., 1930, 74, 511—533; Chem. Zentr., 1930, ii, 2103).—The compound Fe_3N has a 2·695√3; c 4·362 Å., closest packed hexagonal; space-group D_6^6. Fe_2N forms with Fe_3N a continuous series of mixed crystals; it has a 4·79, c 4·42 Å., space-group D_{3a}^1. FeB has a 4·053, b 5·495, c 2·946 Å., with 3·75 mols. in the unit cell; space-group V_h^{16}. Fe_2P has a 5·852, c 3·453 Å., with 3 mols. in the unit cell; space-group D_{3h}^3.

A. A. ELDRIDGE.

Crystal structure of martensite. E. ÖHMAN (Nature, 1931, 127, 270—272).—X-Ray photograms of quenched steel have been obtained in which the line (101) of the tetragonal phase is separated from the (111) line of γ-iron. The curves showing axial dimensions (a and c) as a function of carbon content converge to a point corresponding with the edge of the elementary cube of pure α-iron (cf. Kurdjumov and Kaminsky, A., 1928, 1178), confirming the view that the tetragonal martensite is a supersaturated solution of carbon in α-iron. L. S. THEOBALD.

Crystal structure of columbite. J. H. STURDIVANT (Z. Krist., 1930, 75, 88—108; Chem. Zentr., 1930, ii, 2757).—A specimen of columbotantalite, $(Fe,Mn)(Nb,Ta)_2O_6$, consisting chiefly of columbite, had a 5·082, b 14·238, c 5·730 Å., with 4 mols. in the unit cell: space-group V_h^{14}. A. A. ELDRIDGE.

Structure of enstatite, $MgSiO_3$. B. E. WARREN and D. I. MODELL (Z. Krist., 1930, 75, 1—14; Chem. Zentr., 1930, ii, 2757—2758).—Hypersthene crystals were used: a 18·20, b 8·86, c 5·20 Å., the unit cell containing 16 mols. of $(Mg,Fe)SiO_3$; space-group V_h^{15}.

A. A. ELDRIDGE.

Structure of danburite. C. DUNBAR and F. MACHATSCHKI (Z. Krist., 1930, 76, 133—146).—Danburite, $CaB_2Si_2O_8$, is orthorhombic, the unit cell has a 8·75, b 8·01, c 7·72 Å., and contains 4 molecules; space-group V_h^{16}. C. A. SILBERRAD.

Structure of chrysotile. B. E. WARREN and W. L. BRAGG (Z. Krist., 1930, 76, 201—210).—Chrysotile, $H_4Mg_3Si_2O_9$, is monoclinic, the unit cell has a 14·66, b 18·5, c 5·33 Å., β 93° 16′; space-group probably C_{2h}^3. The structure indicates $(OH)_6Mg_6Si_4O_{11},H_2O$, four to the unit cell. C. A. SILBERRAD.

Crystal structure of muscovite. W. W. JACKSON and J. WEST (Z. Krist., 1930, 76, 211—227).—Muscovite (from Hundholmen), $KH_2Al_3(SiO_4)_3$, is monoclinic; the unit cell has a 5·18, b 9·02, c 20·04 Å., β 95° 30′, and contains 4 molecules. The space-group is C_{2h}^6. C. A. SILBERRAD.

Crystal structure of bixbyite and the C-modification of the sesquioxides. L. PAULING and M. D. SHAPPELL (Z. Krist., 1930, 75, 128—142; Chem. Zentr., 1930, ii, 2739).—Bixbyite has a 9·365 Å., with 16 mols. of $(Mn,Fe)_2O_3$ in the unit cube; space-group T_h^7. The C-modifications of the sesquioxides probably have the same structure as bixbyite.

A. A. ELDRIDGE.

[Crystal form of sodium cyanoplatinite.] O. MÜGGE (Z. Krist., 1930, 75, 32—40; Chem. Zentr., 1930, ii, 2992—2993).—Sodium cyanoplatinite trihydrate, triclinic, has $a:b:c$=1·7108 : 1 : 0·8139, α 94° 57′, β 92° 17′, γ 89° 13·5′. A. A. ELDRIDGE.

Crystallographic relationships between epidote and zoisite. B. GOSSNER and F. MUSSGNUG (Zentr. Min. Geol., 1930, A, 369—371; Chem. Zentr., 1930, ii, 3125).—Epidote has a 8·96, b 5·63, c 10·20 Å., β 115° 24′; zoisite has a 16·21 (=2×8·10), b 5·63, c 10·08, β 90°. The unit cell of zoisite contains 4 mols. of $Al_2Ca_2(SiO_4)_3(AlOH)$; epidote has only 2 mols. in the unit cell. A. A. ELDRIDGE.

Comparison of the crystal structures of an additive and a substitution compound. E. HERTEL and K. SCHNEIDER (Z. physikal. Chem., 1931, B, 12, 109—114).—The crystals of aniline picrate and 2 : 4 : 6-trinitrodiphenylamine both have the space-group C_{2h} and two of the principal periods of identity have nearly the same value for each. The difference in the values of the third period of identity is ascribed to the space occupied by the additional molecule of water in the picrate and to a peculiar molecular arrangement in the substitution compound.

R. CUTHILL.

Crystallographic constants. II. G. GILTA (Bull. Soc. chim. Belg., 1930, 39, 581—589).—The crystallography of a number of organic compounds has been examined. 1 : 4-Dihydroxy-1 : 4-dimethyl*cyclo*hexane, m. p. 193°, is monoclinic, whilst the form m. p. 166° is orthorhombic pseudoquadratic. 2-Acetoxy-*m*-toluic acid, αααββγγ-heptachloropropane, αββ-trichloroacrylamide, and calcium di-*s*-dichloro*iso*propyl phosphate all crystallise in monoclinic forms. The angles of orientation and the parameters are tabulated.

J. W. SMITH.

Silk fibroin. III. O. KRATKY and S. KURIYAMA (Z. physikal. Chem., 1931, B, 11, 363—380; cf. A., 1929, 1222).—Considerable differences are apparent between the lattice structure of fibroin from *Bombyx mori* and from *Satonia*. In *Satonia* the lattice constants are: a 6·46, b 15·43, c 7·2 Å., α 90°, β 90°, γ 61° 10′. In *Bombyx* six possible lattice types are conformable with the measurements.

F. L. USHER.

X-Ray determination of the mol. wt. of methylbixin. J. HENGSTENBURG and R. KUHN (Z. Krist., 1930, 76, 174—175).—Methylbixin is pseudorhombic monoclinic, d 1·10; the unit cell has a 10·48, b 17·59, c 13·40 Å. The calculated mol. wt., 412±2·5%, agrees

better with $C_{26}H_{32}O_4$ (Kuhn, A., 1929, 1456) than with $C_{..}H_{30}O$, (Karrer, *ibid.*, 1075).

C. A. SILBERRAD.

Structure of cellulose nitrate. DESMAROUX and MATHIEU (Compt. rend., 1931, **192**, 354—355; cf. this vol., 290).—The *X*-ray diagrams previously described indicate the anisotropy of the structure. They are compared with the Debye–Scherrer diagrams of nitrated ramie obtained by Naray-Szabo and others (cf. A., 1928, 48, 818). C. A. SILBERRAD.

Changes in electrical resistance due to magnetism and hardness. S. R. WILLIAMS and R. A. SANDERSON (Physical Rev., 1931, [ii], **37**, 309—314; cf. B., 1927, 604).—The increase of resistance of nickel rods due to the magnetic field varied largely with, but the specific resistance was independent of, the degree of hardness (cf. McKeehan, A., 1930, 1504).

N. M. BLIGH.

Magnetostriction of overstrained [metallic] materials. J. S. RANKIN (J. Roy. Tech. Coll. Glasgow, 1931, **2**, 385—395).—The author's experiments (B., 1930, 376) are extended to the effect produced by permanent stretch and by wire-drawing on the change in length observed when iron, steel, and nickel are magnetised. Recovery from overstrain was not observed with nickel. J. GRANT.

Recrystallisation of single aluminium crystals. III. Connexion between deformation phenomena and recrystallisation texture for aluminium. W. G. BURGERS and P. C. LOUWERSE (Z. Physik, 1931, **67**, 605—678).—In order to discover the connexion between a definite deformation and the recrystallisation texture in subsequent recrystallisation, the deformation and recrystallisation of externally, homogeneously strained single aluminium crystals were investigated. A. J. MEE.

Hardening of metals by rotating magnetic fields. E. G. HERBERT (Proc. Roy. Soc., 1931, **A, 130**, 514—523; cf. B., 1929, 818).—Metals super-hardened by the "cloud-burst" method become still harder by a process of ageing, probably due to atomic re-arrangement. It was proved that in a magnetic material this re-arrangement might be assisted by effecting an artificial atomic disturbance, such as might be caused by a magnetic polarity of changing direction.

L. L. BIRCUMSHAW.

Production of single metal crystals. L. GRAF (Z. Physik, 1931, **67**, 388—416).—A new method of making single crystals in an oven, using induction heating, is described. Single crystals were produced from copper, silver, gold, nickel, and gold–silver, gold–copper, and palladium–copper alloys. A simple procedure is given for determining the crystal axes by the *X*-ray rotating-crystal method.

A. B. D. CASSIE.

Polishing of surfaces. J. M. MACAULAY (J. Roy. Tech. Coll. Glasgow, 1931, **2**, 378—385).—The theory (A., 1926, 998) that the process of surface-polishing by friction involves raising the surface material to its m. p. is supported by the fact that red lead and lead dioxide are changed to litharge, and precipitated chalk to lime, when used as polishing agents on flint glass or cork under a pressure of 1 lb. per in.^{2} for 1—17 hrs. J. GRANT.

Allotropic transformation of calcium. E. RINCK (Compt. rend., 1931, **192**, 421—423).—Cooling and resistance curves for metallic calcium show discontinuities near 450°, indicating two forms of calcium: Caα stable below, and Caβ stable above 450°. Attempts to obtain Caβ at the ordinary temperature by sudden cooling failed. C. A. SILBERRAD.

Degree of orientation in hard-drawn copper wires. W. A. WOOD (Phil. Mag., 1931, [vii], **11**, 610—617).—A method is described whereby the degree of orientation may be determined with the aid of a photometer. A core effect is found to exist. A non-oriented layer encloses an oriented core, the line of demarcation being quite sharp. The results are discussed in connexion with the mechanical action of dies. E. S. HEDGES.

Allotropy in liquids. I. A. SMITS (Z. physikal. Chem., 1931, **153**, 287—298).—The theory of allotropy is re-stated and developed, especially in its application to liquid helium and ethyl ether.

H. F. GILLBE.

Determination of mol. wt. from dialysis coefficients. H. BRINTZINGER and W. BRINTZINGER (Z. anorg. Chem., 1931, **196**, 33—43).—Measurements with a large number of sugars and alcohols demonstrate the validity of the linear relationship between the dialysis coefficient and (mol. wt.)$^{\frac{1}{2}}$ (cf., A., 1930, 153), especially for cellophane diaphragms. The constants for different substances vary among themselves less than do those derived from diffusion coefficient measurements, and diminish only slowly with increase of concentration. The presence of other substances within reasonable concentration limits does not interfere with the determination of dialysis coefficients. A convenient form of apparatus is described. Measurements with purified tannin indicate that this substance is a mixture of compounds having different mol. wt., but after dialysis for 2 hrs. the mol. wt. assumes a steady value of 1790.

H. F. GILLBE.

Velocity of sound in substances in the solid and liquid states. M. REICH and O. STIERSTADT (Physikal. Z., 1931, **32**, 124—130).—The directional effect in hearing was utilised for the determination of the velocity of sound and the compressibility. The change of velocity at the m. p. was determined for ice-water, mercury, lead, cadmium, tin, and bismuth. Except in the case of bismuth, the velocity of sound is almost twice as great in the solid as in the liquid state. A. J. MEE.

Dispersion and refractive index of nitrogen measured as functions of pressure by displacement interferometry. C. E. BENNETT (Physical Rev., 1931, [ii], **37**, 263—275).—An apparatus for the simultaneous measurement of the dispersion and refractive index of nitrogen over a pressure range 1—7 atm. at 0° and 30° is described. The Lorentz–Lorenz relation is followed, and the dispersion is a linear function of the pressure. Values of n at *N.T.P.* for λ 4811, 5893, and 6362 Å. are 1·0002991, 1·0002969, and 1·0002967, respectively. Reduction to infinite wave-length leads to the value 1·000585 for the dielectric constant. N. M. BLIGH.

Thermal conductivity of gases. E. BRUCHE and W. LITTWIN (Z. Physik, 1931, 67, 362—374).—The resistance and temperature of a platinum foil with a constant current passing across it were determined with the foil surrounded by thirteen different gases at pressures between 10^{-5} and 1 mm. Krypton has an extremely low conductivity ($1 \cdot 9 \times 10^{-5}$) and xenon indicates a still lower one. A. B. D. CASSIE.

Estimation of specific heats of gases from vapour-pressure curves. M. TRAUTZ and W. BADSTUBNER (Ann. Physik, 1931, [v], 8, 185—202).—By applying the Clausius equation to experimental vapour-pressure curves, the (negative) temperature coefficient of the mol. heat of evaporation was obtained. The approximate relationship $C_v = c_p - 12$ is given, where C_v refers to the vapour, and c_p to the condensed phase. From this relationship, and a knowledge of the vapour-pressure curve and the determined mol. heat of the condensed phase, it is possible to obtain values of the gas-mol. heat.

A. J. MEE.

Methods and apparatus in use at the Bureau of Physico-Chemical Standards. III. F. B. MARTI (Bull. Soc. chim. Belg., 1930, 39, 590—626).—Methods for the purification of several solid organic compounds are described. The technique employed for the accurate measurement of m. p., b. p., and of density, viscosity, and surface tension of the compounds in the fused state is detailed. Precision measurements of the rotatory power of mannitol have also been made. J. W. SMITH.

Organic compounds proposed as temperature standards. F. BURRIEL (Anal. Fís. Quím., 1931, 29, 89—125).—The following redetermined m. p. and b. p. are recommended as standards of temperature: salol 41·68°, —, benzophenone 47·85°, 305·9°, naphthalene 80·06°, 217·96°, benzoic acid 122·45°, $250 \cdot 0_5$°, phthalic anhydride 131·60°, 285·1°, mannitol 166·00°, —, anthracene $216 \cdot 0_5$°, 339·9°, carbazole $240 \cdot 3_5$°, —, anthraquinone $284 \cdot 8_4$°, $376 \cdot 8_5$°. The values of $d_{liq.}$, viscosity, surface tension, rotatory power, and heat of combustion have also been accurately determined.

H. F. GILLBE.

Vapour pressures of some hydrocarbons. E. G. LINDER (J. Physical Chem., 1931, 35, 531—535).—Vapour-pressure data, obtained near 0° by a modification of the Ramsay–Young method, are recorded for 39 hydrocarbons. Disagreements with previous values, notably in the case of mesitylene, *o*- and *p*-xylene, ethylbenzene, *n*- and *iso*-propylbenzene are noted. L. S. THEOBALD.

Properties of saturated vapours including steam. A. PRESS (Phil. Mag., 1931, [vii], 11, 111—118).—Two functional equations are derived from the first law of thermodynamics, of which the first represents the universal characteristic and includes Callendar's fundamental equation as a special case applying to the mixture region, and the second gives a theoretical basis to all equations of state of the van der Waals type. F. G. TRYHORN.

Thermodynamics of supercooled phases. N. VON RASCHEVSKY (Z. Physik, 1931, 67, 531—532).—Entropy remains valid for supercooled phases.

A. B. D. CASSIE.

Calculation of entropy and enthalpy of moist gases. G. VAN LERBERGHE and P. GLANSDORFF (Bull. Acad. roy. Belg., 1931, [v], 17, 60—72).—Mathematical. The conception of affinity due to Donder is applied to the biphasic system formed by a volatile liquid in the presence of a permanent gas. The entropy values are derived as functions of experimental variables, thus rendering it possible to construct entropy diagrams. J. R. I. HEPBURN.

Change of density of ethyl ether with temperature. J. MAZUR (Nature, 1931, 127, 270).—The density of ethyl ether increases from 0·6964 at 35° to 0·8595 at −105·4°; at lower temperatures, the density still increases but at a much slower rate (cf. A., 1930, 1501, 1554; this vol., 148). At the f. p., −117·2°, the density is 0·8654. L. S. THEOBALD.

Compressibility isotherms of methane at pressures to 1000 atm. and at temperatures from −70° to 200°. H. M. KVALNES and V. L. GADDY (J. Amer. Chem. Soc., 1931, 53, 394—399).—In an extension of previous work, the results of Keyes and Burks (A., 1927, 719) are confirmed. The isotherms have considerable curvature except in the pressure range 500—1000 atm. at 100°. At about 533 atm., methane exhibits a constant deviation from the ideal gas law within the range 100° to 200° (cf. nitrogen and carbon monoxide, Bartlett and others, A., 1930, 678, 679). J. G. A. GRIFFITHS.

Vapour pressure of pyridine. P. A. VAN DER MEULEN and R. F. MANN (J. Amer. Chem. Soc., 1931, 53, 451—453).—At temperatures between −20° and 120°, the vapour pressure of pyridine is given by the relation $\log p(\text{mm.}) = 6 \cdot 8827 - 1281 \cdot 3/(t^\circ + 205)$.

J. G. A. GRIFFITHS.

Relation between orthobaric volumes and temperature. J. HORIUTI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, 15, 89—104).—The equation already deduced (A., 1926, 1198) has been tested for sixteen substances. E is an additive quantity. The orthobaric densities of krypton are calculated.

C. W. GIBBY.

Effect of temperature on the viscosity of air. A. O. RANKINE (Phil. Mag., 1931, [vii], 11, 225—227).—A critical examination of the facts does not sustain the contention of Shilling and Laxton that there is a small but steady deviation from Sutherland's law in the case of air. F. G. TRYHORN.

Viscosity and inner friction in solids. B. GUTENBERG and H. SCHLECHTWEG (Physikal. Z., 1930, 31, 745—753).

Physical constants of the system methane–hydrogen. F. A. FREETH and T. T. H. VERSCHOYLE (Proc. Roy. Soc., 1931, A, 130, 453—463).—Determinations of the isotherm of methane at 0° (Keyes and Burks, A., 1927, 719) have been extended to 215 atm. The isotherm at 20° has also been determined by the method previously described (Verschoyle, A., 1926, 894). The accuracy did not exceed 1 in 500, but it is evident that a pv_A minimum exists at 160—165 atm. for the isotherms at 0° and 20°. The results are in good agreement with those of Keyes and Burks (*loc. cit.*), but the isotherm for 0° derived from their equation of state begins to fail rapidly at pressures

above 125 atm. (corresponding with a specific volume of about 8·5 cm.^{3} per g.). Determinations of the triple point (temperature $-182·46°$, pressure 8·737 cm.) were made with samples of methane prepared by two different methods, the vapour pressures of the solid were measured down to $-208°$, and the m.-p. curve was followed to a pressure of 46 atm. In the system methane–hydrogen the upper portion of the three-phase curve is found to have the same form as in the binary systems carbon monoxide–hydrogen and nitrogen–hydrogen. From a $p-x$ isotherm measured at $-182·5°$, the critical point of contact appears to lie at about 60 atm., the corresponding proportion of methane in the vapour phase being about 1%.

L. L. Bircumshaw.

Viscosity, heat conductivity, and diffusion in gas mixtures. XIII. Diffusion constants of dilute gas mixtures. M. Trautz and W. Ries (Ann. Physik, 1931, [v], **8**, 163—184).—The apparatus of Wuppermann was used to determine the diffusion constant of one gas in another, using benzene–hydrogen and carbon tetrachloride–hydrogen mixtures. The values obained were 0·363 and 0·342 c.c. per sec., respectively. The former value agrees with that obtained by the use of another apparatus. The square-root rule does not appear to apply to these two mixtures, whereas it holds very well for benzene–oxygen.

A. J. Mee.

Mixing contraction of liquids. N. Gerasimov (Physikal. Z., 1931, **32**, 226—229).—Mathematical. The analogy of the mixture of two kinds of lead shot varying in diameter is examined, and applied to the case of the mixture of two liquids. The results derived correspond closely with experiment.

A. J. Mee.

Hydrodynamics of systems of variable viscosity. IV. M. Reiner (Kolloid-Z., 1931, **54**, 175—181; cf. A., 1930, 145).—Theoretical. Mathematical formulæ are derived for the fluidity of non-Newtonian liquids.

E. S. Hedges.

X-Ray investigations on copper–arsenic alloys. N. Katoh (Z. Krist., 1930, **76**, 228—234).—The α-phase alloys, *i.e.*, solid solutions of arsenic in copper containing up to 4%Cu, have the face-centred lattice of copper. The edge of the unit cube increases from 3·608 Å. for pure copper to 3·640 A. for the saturated solution; $d_{calc.}$ 8·75. The β-phase, homogeneous from 28·6 to 29·6% As, and consisting of Cu_3As with small amounts of copper or arsenic in solid solution, has a hexagonal unit cell containing six molecules (cf. Machatschki, A., 1930, 1352). For maximum copper and arsenic content, respectively, a is 7·121 and 7·095; c 7·293 and 7·0267. A quenched alloy containing 38·7% As shows no β-phase.

C. A. Silberrad.

System Fe–C–Si. II. Section through the tridimensional diagram at 8% Si. A. Kriz and F. Poboril (Coll. Czech. Chem. Comm., 1931, **3**, 61—72).—Previous work (B., 1930, 1031) has been extended to alloys containing Si 8% and C 0·14—2·7%. Increase of the silicon content from 6 to 8% causes the disappearance of the homogeneous γ phase, of the three-phase γ+carbon+liquid region, and of the γ+carbon and γ+liquid regions. The pearlitic transformation of alloys containing more than 0·48% C ceases when melting commences. An invariant point occurs at 1160°. The γ edge of the four-phase plane which touches the single-phase (γ) region lies between 6 and 8% Si, and the α′ edge, which touches the homogeneous α region, lies above 8% Si. The A2 transformation in alloys containing 8% Si occurs at 655° in the α+carbon region.

H. F. Gillbe.

Thermal analysis of the system lithium–silver. S. Pastorello (Gazzetta, 1931, **61**, 47—51; cf. A., 1930, 1359).—Two compounds, AgLi (m. p. 955°) and $AgLi_3$ (m. p. 450°), are indicated as well as three eutectic points at 610°, 410°, and 180° corresponding with 30, 70, and 100 at.-% Li, respectively. No solid solutions are formed. X-Ray analysis shows the existence of AlLi, similar to AgLi, with a body-centred lattice, a 3·23 Å.

O. J. Walker.

Molecular constitution of the α solid solutions of tin in copper and of the corresponding liquid solutions examined thermodynamically. F. H. Jeffery (Trans. Faraday Soc., 1931, **27**, 136—137).—Application of the equation previously derived (A., 1930, 406) to the data for the system copper–tin shows that the α-phase and also the liquid phase between 1083° and 800° consist of solutions of the compound Cu_4Sn in solid and liquid copper, respectively, the molecules of copper being monatomic in both cases.

O. J. Walker.

Molecular constitution of the β solid solutions of tin in copper examined thermodynamically. F. H. Jeffery (Trans. Faraday Soc., 1931, **27**, 137—139; cf. preceding abstract).—The β-phase of the copper–tin system consists of solid solutions of monatomic tin in monatomic copper.

O. J. Walker.

Structural analogies of binary alloys of the transition elements with zinc, cadmium, and aluminium. W. Ekman (Z. physikal. Chem., 1931, B, **12**, 57—78).—The X-ray diagrams of binary alloys of zinc with iron, cobalt, nickel, rhodium, palladium, and platinum and of alloys of nickel with cadmium show that in all these systems a phase with the structure of γ-brass is capable of existence. In each case the region of homogeneity extends on either side of a composition corresponding with an at. ratio of the transition element to the other component of 5 : 21. If the transition elements are assumed to possess zero valency, this composition represents a ratio of valency electrons to atoms of 21 : 13 (cf. Westgren and Phragmen, A., 1929, 987). The iron–zinc phase is homogeneous between 19 and 23 at.-% Fe, the cobalt–zinc phase between 15 and 22 at.-% Co, and the nickel–zinc phase between 15 and 19 at.-% Ni. In the system cobalt–zinc a phase having the structure of β-manganese may be present, and in the system cobalt–aluminium a phase similar to β-brass, the region of homogeneity of the latter phase including a mixture for which the ratio of valency electrons to atoms is 3 : 2. The formation of all the above phases from their constituent elements is accompanied by a considerable diminution in volume.

R. Cuthill.

Solubilities in the system water–iodine to 200°. F. C. Kracek (J. Physical Chem., 1931, **35**, 417—

422).—Above 112·3°, the system water–iodine forms two liquid layers, the mutual solubility increasing with a rise in temperature. The solubility curves have been determined up to 200°. Below 112·3°, the solutions are saturated with solid iodine. The aqueous and iodine layers at the invariant temperature, 112·3°, contain 0·0517 and 98·3 mol.-% I, respectively. The m. p. of iodine is 113·7° and the critical solution temperature is estimated to be at approximately 300°. L. S. THEOBALD.

Determination of the solubilities of some fluosilicates. (MISS) K. K. WORTHINGTON and M. M. HARING (Ind. Eng. Chem. [Anal.], 1931, **3**, 7—9).—The solubilities and densities of saturated solutions of sodium, magnesium, zinc, lead, and copper fluosilicates at 20° are 0·733%, 1·0054; 37·94%, 1·2395; 49·94%, 1·4336; 81·90%, 2·4314; and 59·08%, 1·6175, respectively. Methods for the analysis of these compounds are critically examined; volumetric methods are untrustworthy if the compound is readily hydrolysed or if it is derived from an amphoteric base. The most trustworthy process for the heavy metal fluosilicates consists in converting into sulphate by heating to vigorous fuming with sulphuric acid containing a little nitric acid. The heavy metal salts are efflorescent and decompose slowly; lead fluosilicate is particularly unstable, and both the solid and its solutions are therefore highly corrosive. H. F. GILLBE.

Solubilities of alkali chlorides and sulphates in anhydrous alcohols. E. R. KIRN and H. L. DUNLAP (J. Amer. Chem. Soc., 1931, **53**, 391—394).—The data refer to anhydrous sodium and potassium salts in methyl, ethyl, *n*-propyl, *iso*propyl, *n*-butyl, and *iso*butyl alcohols between 20° and 50°. Potassium sulphate is insoluble in these liquids. The solubility of sodium sulphate in methyl alcohol decreases with rise of temperature, whilst in ethyl and *iso*propyl alcohol it passes through a maximum. This salt is insoluble in the other alcohols. The solubilities of the chlorides in methyl alcohol decrease and in the butyl alcohols increase with rise of temperature. The solubilities in the other solvents pass through maxima. J. G. A. GRIFFITHS.

Solubility of thallous iodate in ethyl alcohol–water mixtures. V. K. LAMER and F. H. GOLDMAN (J. Amer. Chem. Soc., 1931, **53**, 473—476; cf. A., 1929, 1387).—Solvents containing 0—47 wt.-% of ethyl alcohol have been used at 25°. The average ionic radii calculated from Born's equation for the electrostatic work of transfer are 0·78 and 0·9 Å., which compares with values of *a* ranging from 1·05 to 1·6 given by the data for the solubility in salt solutions. J. G. A. GRIFFITHS.

Dissolution of carbon dioxide in fused tellurium. A. ŠIMEK and J. ŠMÍDA (Coll. Czech. Chem. Comm., 1931, **3**, 93—95).—A preliminary determination gave for the solubility of carbon dioxide in tellurium at 485° the value 0·16 c.c. per c.c. This is about one third of the value calculated from the observed lowering of the m. p. of tellurium in an atmosphere of carbon dioxide. H. F. GILLBE.

Concentration currents and the cause of stratification of solutions. A. K. BOLDYREV (Z. Krist., 1930, **74**, 552—553; Chem. Zentr., 1930, ii, 2101).—The direction of concentration currents produced when a crystal is suspended in a solution differentiates between supersaturated (upwards) and unsaturated (downwards) solutions. "Stratification" of supersaturated solutions (observed by Semjatschenski) containing three crystals suspended at different heights, wherein the weight of the lowest crystal and the density of the lower portion of the solution increase at the expense of the upper, is discussed; stratification takes place only when the crystals are present. A. A. ELDRIDGE.

Absorption of gas from a current of air. II. M. M. DUBININ, S. I. PARSCHIN, and A. A. PUPIREV. **III.** M. M. DUBININ, L. A. SOLOVIEV, and G. K. SCHILIN (J. Russ. Phys. Chem. Soc., 1930, **62**, 1947—1951, 1953—1956; cf. A., 1930, 989).—II. The protective action of adsorbent charcoal, measured by the time, θ, during which it is able to remove completely small quantities of chlorine from a current of air, is incomplete below a certain critical thickness of layer; above this thickness θ is proportional to the thickness of layer. The value of the critical thickness as determined experimentally differs from that calculated from Mecklenburg and Kubelka's formula (Z. Elektrochem., 1925, **31**, 488).

III. Traces of chlorine in air may be detected by passing the gas over a filter-paper moistened in a starch–potassium iodide solution. The sensitivity of this reaction depends on adsorption of chlorine on the filter-paper. R. TRUSZKOWSKI.

Adsorption. H. SCHLÜTER (Z. physikal. Chem., 1931, **153**, 68—82).—Measurements of the adsorption of pentane and carbon disulphide vapours on powdered glass and silver have given results which are contradictory to the unimolecular layer theory. The adsorption was followed up to the production of adsorption layers having a thickness of 50 mols., and the fact that silver powder behaves similarly to glass disposes of the view that the apparently high degree of adsorption on glass is due to dissolution of the vapour by swelling of the outer film of glass. The results can be expressed in the form $N=ab^P$, where N is the number of molecular layers, P the pressure, and a and b are constants. E. S. HEDGES.

Adsorption of ethylene by wood charcoal, silicic acid gel, and aluminium oxide. A. MAGNUS and H. WINDECK (Z. physikal. Chem., 1931, **153**, 113—126).—The adsorption isotherms of ethylene, using wood charcoal, silica gel, and aluminium oxide as adsorbents, have been determined over the pressure range 0·02—600 mm. A marked difference was observed between the behaviour of charcoal on the one hand and the oxide adsorbents on the other. The initial portion of the curve for charcoal rises relatively steeply. The heats of adsorption are less for silica gel and aluminium oxide than for wood charcoal. E. S. HEDGES.

Vapour-adsorption capacity of silica gels as affected by the extent of drying before wet-heat treatment and by the temperature of acid treatment and activation. H. N. HOLMES and A. L. ELDER (J. Physical Chem., 1931, **35**, 82—92; cf. B., 1926, 438).—Eleven silica gels showed a decreased

(2—34%) adsorption capacity for benzene after ageing for 3—6 years. With four of the gels, activation temperatures up to 800° do not greatly affect the adsorption capacity for benzene, but a large decrease results if the activation temperature rises to 1000°. A rise in the temperature in the acid treatment of a gel from 30° to 100° increases its porosity, and a gel capable of adsorbing 156% of its own weight of benzene from an air stream saturated with benzene at 30° has been prepared. The most porous gels which still possess a firm structure have been made from gels dried to 50—60% moisture content before acid treatment. Such gels have large capacities for adsorbing benzene under high partial pressures, but are not efficient at lower partial pressures. Vitreous gels and Patrick's glassy gel are equally efficient under low partial pressures of benzene and the most efficient removal of vapour is obtained by a combination of the two types of gel. L. S. THEOBALD.

Adsorption of gas mixtures by silica. E. C. MARKHAM and A. F. BENTON (J. Amer. Chem. Soc., 1931, **53**, 497—507).—The adsorption on silica (silicic acid dried at 250°) of oxygen, carbon monoxide, and carbon dioxide, and of each gas in the binary mixtures at 1 atm. has been determined at 100°, and for the first two gases at 0°. By an extension of Langmuir's theory it is shown the adsorption of a gas from a mixture should be less than that from the pure gas at the same partial pressure. The equation is supported by data for mixtures of oxygen and carbon monoxide, but the anomalous results with mixtures containing carbon dioxide may be caused by mutual interaction of the adsorbed molecules.

J. G. A. GRIFFITHS.

Specific adsorptive properties of active charcoals. II. Sugar charcoal. M. M. DUBININ (J. Russ. Phys. Chem. Soc., 1930, **62**, 1829—1846).—Ordinary sugar charcoal possesses feeble adsorptive power; inorganic acids are adsorbed in the order of diminishing basicity and organic acids in the order of diminishing mol. wt., whilst alkalis are not adsorbed. The order of adsorption of these acids is reversed when the charcoal is activated by heating in air or carbon dioxide at 600—1000°; the product adsorbs alkali when activated in the presence of oxygen, but not in its absence. These effects are ascribed to the formation of different suboxides of carbon, according to the temperature of activation, and to the inversion of the charge present on the surface of the grains of charcoal on immersion in aqueous solutions.

R. TRUSZKOWSKI.

Adsorption of organic acids by platinum-black. II. M. S. PLATONOV, J. A. BORGMAN, and G. J. SALMAN (J. Russ. Phys. Chem. Soc., 1930, **62**, 1975—1989; cf. A., 1930, 28).—The adsorption of organic acids on platinum-black depends chiefly on their structure, and only to a smaller extent on their mol. wt. and solubility. Traube's rule is followed by saturated monobasic but not by dibasic acids. Acids possessing a normal chain are more strongly adsorbed than are *iso*-acids. *cis*-Isomerides and unsaturated acids are more strongly adsorbed than *trans*-isomerides and saturated acids, respectively. *o*-Nitrobenzoic acid is adsorbed to a smaller extent than is the *m*-isomeride, whilst the contrary is the case with hydroxybenzoic acids. In general, the introduction of substituents into the benzene ring increases adsorption. The velocity of hydrogenation of citraconic, itaconic, mesaconic, and the isomeric crotonic acids is proportional to their adsorption by platinum-black. This rule applies to all substances yielding the same product of hydrogenation; in other cases no parallelism is found. The adsorptive qualities of platinum-black may be considerably modified without markedly affecting its catalytic properties, and the reverse is also the case. R. TRUSZKOWSKI.

Oxide hydrates. XXXV. Crystalline oxides and oxide hydrates of aluminium as adsorbents for organic dyes. G. F. HUTTIG and A. PETER (Kolloid-Z., 1931, **54**, 140—147).—The adsorption of methyl-violet, methylene-blue, Congo-red, eosin, and Bordeaux-red R by various crystalline forms of aluminium oxide and hydrated oxide has been measured. The results can be expressed by the Freundlich adsorption isotherm. The general adsorption capacity of the substances examined decreases in the order böhmite>γ-aluminium oxide>diaspore>hydrargillite>corundum, but the selectivity of the adsorbents varies in the reverse direction. The adsorptive power of a given crystalline form is altered by the presence of impurities. With increasing hydrogen-ion concentration greater amounts of the acid dyes eosin and Bordeaux-red R and smaller amounts of the basic dyes methyl-violet and methylene-blue are adsorbed. E. S. HEDGES.

Adsorption of chromate ions by colloidal aluminium hydroxide. B. H. PETERSON and K. H. STORKS (J. Physical Chem., 1931, **35**, 649—652).—The adsorption of potassium chromate by colloidal aluminium hydroxide has been determined at concentrations above and below that required for coagulation. Three distinct types of adsorption occur; these are represented by (i) neutralisation of the charge on the sol particle, (iii) surface adsorption, not electrical in type, and (ii) a combination of (i) and (iii).

L. S. THEOBALD.

Acid adsorption and stability of cellulose nitrate. D. R. WIGGAM (J. Physical Chem., 1931, **35**, 536—539).—Nitric and sulphuric acids (0·01*N*) are adsorbed to the same extent by cellulose nitrate; adsorption of hydrochloric acid is slightly less. Adsorption of bases apparently does not take place. Acid retained by the fibre lowers the resistance to heat of a given sample of cellulose nitrate and equal amounts of the three above-mentioned acids lower the heat-resistance to approximately the same extent. Acid adsorption plotted against stability (methyl-violet test) gives a smooth curve. For cellulose nitrate of high nitrogen content the effect on stability of the acid adsorbed is not serious when this is of the order of 3×10^{-6} g.-mol. per g. or less.

L. S. THEOBALD.

Adsorption. J. TERWELLEN (Z. physikal. Chem., 1931, **153**, 52—67).—Ageing phenomena do not take place in sols of methyl-violet and methylene-blue so long as the substances are pure and oxygen and light are excluded. The adsorption of these two dyes by silver and nickel wire has been measured by a spectrophotometric method, the surface of the adsorbent being

determined by direct measurement. The results are not in accordance with Langmuir's unimolecular film theory. The amount adsorbed increases with the concentration of the solution beyond the value required for a saturated unimolecular layer and at the highest concentrations the molecular thickness of the adsorbed film of methyl-violet on silver is 4, and on nickel 5, methylene-blue on silver 11, and on nickel 5. Van der Waals forces are probably involved in the formation of these multimolecular layers. The results given above show that the amount adsorbed at saturation depends on both the adsorbent and the dye, and it is not therefore permissible to compare the surface areas of two different materials by measuring the ratio of their adsorbent capacities for a dye. The adsorbing power of the metal wire is reduced by previous heating, suggesting that adsorption takes place at certain active spots on the wire, probably indicating a distortion of the crystal space lattice.

E. S. HEDGES.

Activation energy of adsorption processes. H. S. TAYLOR (J. Amer. Chem. Soc., 1931, **53**, 578—597).—The adsorption process *per se* is not necessarily rapid, and may be immeasurably slow; for each process there is a characteristic velocity which is determined by the same factors which affect the velocity of chemical reactions, viz., temperature, pressure, concentration, and nature of adsorbing surface. The effect of these has been examined on the assumption that there are two types of adsorption for the same gas. One of these is characterised by a low or negligible energy of activation and, in general, a low heat of adsorption ("secondary" or "reversible" adsorption) and the other by a large energy of activation and frequently with a high heat of adsorption ("primary" or "irreversible" adsorption). The theory receives support from the data for the adsorption of hydrogen, oxygen, carbon monoxide, nitrogen, water vapour, and sulphur dioxide on various substances. Certain abnormalities are explained.

J. G. A. GRIFFITHS.

Velocity of adsorption processes and promoter action. H. S. TAYLOR and A. T. WILLIAMSON (J. Amer. Chem. Soc., 1931, **53**, 813—814; cf. preceding abstract).—Hydrogen is adsorbed immeasurably slowly by an active manganous oxide catalyst at 0° and 100°, but at 305° the velocity of adsorption rises to a value 10-fold that at 184°, corresponding with an energy of activation of about 10,000 g.-cal. Manganous oxide promoted with chromium oxide adsorbs hydrogen very slowly at 0°, but at 184° the adsorption is about 700 times as fast as with the unpromoted catalyst. The adsorptive capacity per g. is also much greater. In all of these cases, the adsorption is reversible.

J. G. A. GRIFFITHS.

Kinetics of surface processes at crystal lattices. I. Adsorption system barium sulphate–electrolyte solution. L. IMRE (Z. physikal. Chem., 1931, —286).—The time course of tho adsorption of actinium and lead on barium sulphate surfaces under a variety of conditions has been investigated quantitatively. The time–adsorption curves for any given system are characteristic of the adsorbed ion, ut are influenced by the quantity and nature of the adsorbent, the composition of the solution, and the temperature. The results are capable of interpretation if it is assumed that the process takes place in a series of stages, of which the earlier, relatively rapid, stages are determined by the valency of the adsorbed ion, and the later by the specific affinity of the ion for the lattice ions of the adsorbent. By taking into consideration the valency of the ions, the solubility of the adsorption complex, and the recrystallisation processes in the adsorbent, a mathematical expression has been derived for the kinetics of the adsorption. In conformity with this, the adsorption of actinium is shown to be the resultant of two effects, each of which obeys an exponential law; in the case of lead the later stages at least are more complex.

H. F. GILLBE.

Adsorption of ions on a surface film. R. S. BRADLEY (Phil. Mag., 1931, [vii], **11**, 449—453).—An expression has been deduced for the potential due to a uniform plane array of dipoles oriented perpendicularly to the surface and this is used to calculate the magnitude of the layer of ions adsorbed in the film on the surface of a liquid (cf. Lyons and Rideal, A., 1929, 875).

R. CUTHILL.

Inner adsorption in crystalline salts. I. N. STRANSKI (Kolloidchem. Beih., 1931, **32**, 197—204).—Objections are raised against the theory of adsorption and crystal growth developed by Balarev (A., 1930, 684) on the ground that the considerations involved are based largely on a misunderstanding of the Gibbs relation.

E. S. HEDGES.

Nature of the specific property of molecular surface fields. Structure of active carbon and inversion effect of adsorption and heat of wetting. B. ILJIN and J. SIMANOV (Z. Physik, 1930, **66**, 613—618).—Debye photographs of hydrophobic and quasi-hydrophilic carbon revealed no difference in their structure, although there is an inversion of adsorption from aqueous solutions of fatty acids, and heats of wetting of the homologous alcohol series. Inversion of adsorption effects cannot therefore be ascribed to a difference in the molecular surface fields.

A. B. D. CASSIE.

Adsorptive binding. H. CASSEL and F. SALDITT (Naturwiss., 1931, **19**, 110—111).—The surface tension σ of pure mercury has been measured by the method of maximum drop pressure, in the absence of air, in contact with its own vapour and the vapours of various substances at different temperatures and pressures. According to the method of Gibbs, the σ–p isotherms permit the calculation of the amount of adsorption. In agreement with the conclusions of London and Pólanyi (this vol., 161), the magnitude of the dipole moment plays only a secondary role in adsorption. Within the experimental accuracy (0·1%) water vapour causes no change in the surface tension of mercury over the temperature range 0—50° and at pressures up to 62 mm. Below the saturation pressure water is generally not adsorbed on mercury. On the other hand, ethyl ether, with a much smaller dipole moment, shows large adsorption, and this is greater still with hexane, *cyclo*hexane, and benzene, which possess no dipole moments. In the series methyl, ethyl, and propyl alcohols the adsorption increases with increasing length of the hydrocarbon chain, independently of the magnitudes of their dipole

moments. From the S form of their $\sigma-p$ curves it is deduced that these compounds exist only as associated molecules in the adsorbed state. The same behaviour is shown by nitromethane, which has almost double the dipole moment of water. J. W. SMITH.

Surface tension of crystals. D. BALAREV (Kolloidchem. Beih., 1931, **32**, 205—211).—It is shown theoretically that the relation found by Ostwald and Freundlich between solubility, particle size, and surface tension cannot hold for homogeneous surfaces, but is valid when the surface tension is greater at the edges and solid angles of the crystal. The increase of surface tension with decreasing particle size begins to be apparent when colloidal dimensions are reached. E. S. HEDGES.

Matter in the film state. A. V. BLOM (Kolloid-Z., 1931, **54**, 210—220).—The conception of a film as a particular state of matter intermediate in properties between dispersoids and compact solid matter is developed. Films are considered as (1) unimolecular films, (2) Hardy films, having a thickness of not more than 10^{-4} cm., and (3) zone films, where the thickness is greater than 10^{-4} cm. and the forces acting between the molecules are not entirely of a surface character. Films may be formed by either physical or chemical processes. For film formation by evaporation two relations are derived: (1) the amount of evaporation per unit time is constant; (2) the velocity of film formation at any given time is proportional to the amount of the volatile portion remaining. The adhesion of films can be measured by determining the weight required to remove a surface brought into contact with the film, and some experimental results on these lines are briefly described. With continuous drying of films of resin in amyl alcohol the stickiness at first increases, passes through a maximum, and later decreases. The adhesive properties are not entirely connected with the rate of evaporation of the solvent, however, for the stickiness of oil varnish alters very considerably on exposure to ultra-violet light, whilst the rate of evaporation is unchanged thereby. E. S. HEDGES.

Thermoelastic effect in cellulose ester films. J. G. MCNALLY and S. E. SHEPPARD (J. Physical Chem., 1931, **35**, 100—114).—The heat changes associated with the stretching of films of cellulose nitrate and acetate have been investigated, and the coefficients of thermal expansion at different temperatures and stresses have been measured. The nitrate film cools on stretching up to the yield point, after which it warms until it breaks. The amount of heat evolved is greater than that absorbed. The acetate film behaves in a similar manner. The inversion of the thermal effect is not due to the increased rate of extension after the yield point is reached. When the structure of the film is altered by drying under a large stress, the region of strain corresponding with the exothermic reaction disappears. The thermoelastic properties of coagulated films are independent of their content of volatile solvent. The thermal coefficient of expansion of cellulose nitrate is a poorly-defined quantity which depends on stress, previous mechanical and thermal history, and temperature. At low temperatures and moderate stresses, a negative thermal expansion, analogous to the Joule effect in caoutchouc, has been observed. L. S. THEOBALD.

Cohesion. I. H. TERTSCH (Z. Krist., 1930, **74**, 476—500; Chem. Zentr., 1930, ii, 2101).—Cleavage by drawing, pressure, and shock are differentiated and means for determination are described. Experiments were performed on the cleavage by tension of rock salt. A. A. ELDRIDGE.

Surface processes in coagulating precipitates. II. Mechanism of adsorption in electrolyte solutions. L. IMRE (Z. physikal. Chem., 1931, **153**, 127—142; cf. A., 1930, 287).—The time-course of the adsorption of ions at the surface of ageing suspensions of the silver halides has been followed by a radioactive-indicator method. The effect varies with the nature of the adsorption compound formed between the ion and the oppositely charged ionic component of the adsorbing particle. In cases where a sparingly soluble compound is produced the adsorption increases very slowly or remains constant, but where the compound is readily soluble more or less strong desorption occurs. During the ageing the structure of the particles is supposed to open up in consequence of the crystallisation tendency, thus enabling an exchange reaction to take place with the ions adsorbed in the vicinity of the space lattice. The adsorptive capacity of the silver halides for readily soluble electrolytes increases in the order chloride < bromide < iodide. E. S. HEDGES.

System electrolyte–water. Partition of the ions of a salt pair during diffusion through a membrane. H. BRINTZINGER and W. BRINTZINGER (Z. anorg. Chem., 1931, **196**, 61—64).—Measurement of the dialysis coefficient of the ions present in solutions containing lithium chloride and potassium iodide or lithium chloride and potassium sulphate indicate that the more rapidly moving cation tends to diffuse in company with the more rapid anion. Thus the potassium ion, which has the smaller surface electric field, diffuses principally with the iodide ion in the first solution and with the chloride ion in the second. H. F. GILLBE.

Membrane and osmosis. I. F. A. H. SCHREINEMAKERS (Rec. trav. chim., 1931, **50**, 221—229).—The osmotic system consisting of an "inactive" membrane permeable only to water and placed between two liquids is treated theoretically. O. J. WALKER.

Measurements with the aid of the dialysis method. Enzymic decomposition of starch and thermal decomposition of dextrin in presence of acid. H. BRINTZINGER and W. BRINTZINGER (Z. anorg. Chem., 1931, **196**, 50—54).—Measurements of the dialysis coefficients of starch solutions to which diastase has been added show that the first stage of the hydrolysis is very rapid, but that after the mol. wt. has fallen to about 800 the reaction proceeds very slowly to completion. The process appears to take place in four stages, with the production of intermediate compounds of mol. wt. 22,800, 3700, and 600, in accordance with Biltz' results from viscosity measurements. Hydrolysis of a dextrin of mol. wt. 10,460 by acid proceeds continuously, with no evidence

of the formation of intermediate compounds of definite composition. H. F. GILLBE.

Disturbance of neutrality of solutions in electrodialysis. S. OKA (J. Soc. Chem. Ind. Japan, 1931, **34**, 4—9B).—The electrolysis of 0·005*N*-potassium chloride solutions has been carried out using a constant voltage in a cell divided into three compartments by diaphragms of the same material. In different experiments parchment-paper, filter-paper impregnated with collodion and also with chromated gelatin were used as diaphragms. During the electrolysis the of the solution fell to a low, nearly constant value, which, however, showed a tendency to rise slightly as electrolysis was further continued. It appears that the development of acidity or basicity is conditioned by the relative amounts of hydrogen and hydroxyl ions which enter the middle chamber. The mobilities of the ions as they pass through the pores of the diaphragms seem to be different from those in the bulk of the solution and the difference is probably occasioned by the electrokinetic potential of the diaphragms. This theory provides qualitative explanations of other observations made in the experiments.
H. INGLESON.

Blocking effect of membranes. G. H. BISHOP, F. URBAN, and H. L. WHITE (J. Physical Chem., 1931, **35**, 137—143).—The flow of dilute solutions of potassium chloride through glass capillaries has been investigated and the results are discussed in relation to the blocking effect of membranes. The streaming potential of a given capillary varies from time to time and capillaries from the same piece of glass when treated in the same way and used under identical conditions show significant differences in streaming potential. With cellophane membranes, the gradual decrease in the rate of filtration and the absence of a measurable streaming potential may be associated with the electrical phenomena taking place in the various pores of the membrane. L. S. THEOBALD.

Viscosity and density of rubidium nitrate solutions. H. G. SMITH, J. H. WOLFENDEN, and (SIR) H. HARTLEY (J.C.S., 1931, 403—409).—The relative viscosity and the relative density of aqueous solutions of rubidium nitrate have been measured at 18° and 25° over the concentration range 0·092—1·786*N*. The relative viscosity of rubidium nitrate solutions can be represented by the Jones–Dole equation (A., 1929, 1385) at concentrations below 0·2*N* and the coefficient *A* of those authors is shown to have the negative value and negative temperature coefficient which they postulate. The molecular solution volume of rubidium nitrate at various concentrations has been calculated and is shown to fall in the normal periodic sequence of the alkali nitrates. E. S. HEDGES.

Specific heat of solutions of sodium sulphate. M. AUMÉRAS (Compt. rend., 1931, **192**, 359—361).—The specific heat at 20° of solutions containing 80 to 550 mols. of water per mol. of decahydrate has been determined. The results generally are slightly higher than those previously obtained. C. A. SILBERRAD.

Absorption of aqueous solutions of tartaric acid. G. BRUHAT (Compt. rend., 1931, **192**, 489—490).—The results of Lucas and Schwob (this vol., 302) are more directly opposed to the existence of two forms of tartaric acid in solution than those of the author (cf. A., 1930, 1341). C. A. SILBERRAD.

Variation of extinction coefficient of solutions with temperature. II. A. K. BHATTACHARYA and N. R. DHAR (J. Physical Chem., 1931, **35**, 653—655; cf. A., 1930, 120).—The extinction coefficients of solutions of neocyanine, ferric thiocyanate, sodium cobaltinitrite, and mixtures of solutions of sodium malonate and iodine, sodium tartrate and iodine, citric and chromic acids, lactic and chromic acids, citric acid and potassium permanganate, tartaric acid and potassium permanganate increase with a rise in temperature. This increase is attributed to a diminution in hydration of the solutes which partly explains the increase in quantum yield with rise in temperature. L. S. THEOBALD.

Hydrotropy. C. NEUBERG and F. WEINMANN (Biochem. Z., 1930, **229**, 467—479).—When solutions of salts of optically active acids are mixed with optically active non-conducting liquids which also exhibit surface activity and the optical rotation of the mixtures is measured an alteration of the rotation additional to that caused by the simple superposition of the rotations of the constituents is always observed. This alteration is not due to physical causes. Hydrotropy is probably a chemical phenomenon involving the formation of loose additive compounds of some kind. W. MCCARTNEY.

Porous disc method of measuring osmotic pressure. F. T. MARTIN and L. H. SCHULTZ (J. Physical Chem., 1931, **35**, 638—648).—Measurements of the osmotic pressure of dilute solutions of potassium chloride by the method of Townend (A., 1929, 134), considerably modified, show that the porous disc method offers promising possibilities. Slight inequalities of temperature within the apparatus are a source of error. L. S. THEOBALD.

Use of acetamide as solvent for cryoscopy. E. CHERBULIEZ and G. DE MANDROT (Helv. Chim. Acta, 1931, **14**, 183—186).—Acetamide is a suitable solvent for the determination of the mol. wts. of the decomposition products of caseinogen, although the cryoscopic constant, *K*, varies with the concentration. Values of *K* are given for solutions of acetanilide, hippuric acid, and diketopiperazine in acetamide.
O. J. WALKER.

Ebullioscopic studies of the cadmium alkali halides. (MLLE.) C. HUN (Compt. rend., 1931, **192**, 355—356).—From b. p. observations (cf. Bourion, Rouyer, etc., A., 1927, 841; 1930, 853, 1120) the existence of the complexes $(NH_4)_2[CdCl_4]$, $(NH_4)_2[CdBr_4]$, and $(NH_4)_2[CdI_4]$ is inferred. Equilibrium constants for the potassium, ammonium, and sodium complexes corresponding with $2MX+CdX_2 \rightleftharpoons M_2[CdX_4]$ are, respectively, for the chlorides 0·605, 0·796, 1·12; for the bromides 0·0832, 0·208, 0·156; and for the iodides 0·006, 0·0576, 0·585.
C. A. SILBERRAD.

Preparation of colloidal silver sols using alkaloids. M. O. CHARMANDARIAN and A. V. SAMOILOVA (J. Russ. Phys. Chem. Soc., 1930, **62**,

1915—1918).—Yellow to orange silver sols are obtained by the action of brucine, nicotine, opium, or atropine on solutions of silver nitrate. In the case of nicotine, small concentrations of alkaloid yield a yellow sol, which is flocculated by higher concentrations, whilst at still higher concentrations stable orange-coloured sols are obtained.

R. TRUSZKOWSKI.

Mechanism of formation of colloidal silver. H. Q. WOODARD (J. Physical Chem., 1931, **35**, 425—431).—The formation of silver sols by the method previously used (A., 1930, 289) has been investigated in solutions of different electrolytes. Attention has been directed to the composition of the liquid remaining after precipitation of the sol by prolonged arcing, whilst the fate of the cation of the original solution has been followed by titration or by determinations of p_H. Sol formation is favoured by a rise in temperature. The results support the view that the formation of colloidal silver by the Bredig method involves a reaction between the silver and the electrolyte simultaneously with the formation of a metal–anion complex. L. S. THEOBALD.

Preparation of colloidal metallic lead and lead phosphate. V. COFMAN (Rev. gén. Colloid., 1930, **8**, 337—357).—Colloidal lead may be prepared conveniently by placing granulated lead under water and agitating the granules with two lead electrodes which are connected to a supply of 110 volts. Up to a certain point the concentration of the sol increases with the duration of sparking, but a considerable amount of lead sponge forms also and the containing vessel should be kept in ice. The sol is stabilised by small quantities of gelatin, sodium thiosulphate, and potassium and calcium chlorides, whether added before or immediately after the preparation. Determinations of particle size by the centrifugal method gave values between 0·5 and 0·1 μ. Colloidal lead phosphate is prepared in a form suitable for the treatment of cancer by adding a 1·028% solution of trisodium phosphate drop by drop to an equal volume of solution containing 1·46% of lead acetate, both solutions being kept at 60°. The sol is stabilised by gelatin and by gum arabic. The effects of temperature of mixing, hydrogen-ion concentration, and excess of reagent have been studied. Experiments with the ultracentrifuge indicate a particle radius of 16·2 for colloidal lead phosphate prepared in the presence of gelatin. E. S. HEDGES.

Colloidal nature of cuprammonium solution. A. J. STAMM (J. Physical Chem., 1931, **35**, 659—660).—Ultracentrifuging shows that cuprammonium solutions contain a colloidally dispersed material. This is regarded as a copper hydroxide sol.

L. S. THEOBALD.

Dispersoidal investigations on selenium. I. K. JUNA (Bull. Chem. Soc. Japan, 1931, **6**, 23—24).—The formation of colloidal solutions of selenium when solutions of the element in hydrazine hydrate are poured into water, alcohol, or glycerol is due to atmospheric carbon dioxide and oxygen and does not occur in an atmosphere of nitrogen. O. J. WALKER.

Photometric measurement of concentration and dispersity in colloidal solutions. III. T. TEORELL (Kolloid-Z., 1931, **54**, 150—156; cf. this vol., 164).—Measurements carried out in the Zeiss nephelometer show that the weakening in the intensity of light passing through a mastic sol is due mainly to scattering. The results also indicate that only in sols of low concentration is the intensity of scattered light proportional to the concentration; at higher concentrations the relative scattering becomes less and the amount of scattered light passes through a maximum, after which it falls. The use of red light is recommended for nephelometric observations with colourless sols. E. S. HEDGES.

Application of a photo-element to the determination of the relation between the dispersion of light and the number and dimensions of particles in disperse systems. N. N. ANDREEV, N. A. KUDRJAVZEV, and T. A. SCHTESSEL (J. Russ. Phys. Chem. Soc., 1930, **62**, 2091—2099).—The expression $K=I/ns$ is derived, in which K is a constant ($5{\cdot}32\times10^{-18}$), and I is the dispersion of light given by a suspension containing n particles each of surface s. This expression is verified for suspensions of *Staphylococcus albus*, and of spores of *Trichophyton asteroides* and *Penicillium glaucum*. R. TRUSZKOWSKI.

Dielectric behaviour of disperse systems. R. FRICKE and L. HAVESTADT (Z. anorg. Chem., 1931, **196**, 120—128).—The effect on the dielectric constant of the addition of acid or alkali to thorium hydroxide and aluminium hydroxide suspensions is described. When dilute hydrochloric acid is added to a stannic acid sol the viscosity of the latter increases until the sol becomes strongly thixotropic, and the dielectric constant simultaneously diminishes; immediately prior to flocculation the sol becomes mobile and no longer thixotropic, whilst after flocculation the dielectric constant falls very rapidly. The appearance of thixotropy appears to counteract the fall of dielectric constant due to diminution of the surface charge, whilst coagulation causes a fall of the dielectric constant as a result of the disappearance of the polarisable surface. This view is apparently contradicted by the fall of the dielectric constant of gelatin sols on ageing. Possibly the dielectric constant is influenced by the occurrence of thixotropy only when the sol particles are of an elongated form.

H. F. GILLBE.

Effect of radiations on colloids. III. Effect of ultra-violet light on emulsions. P. C. SINHA and P. B. GANGULI (Kolloid-Z., 1931, **54**, 147—150).—Further evidence is adduced to show that the coagulating effect of radiations on colloids is due to a photochemical influence of the radiation on the stabilising electrolyte. Various oil-in-water emulsions were prepared, using sodium oleate as the emulsifier, and magnesium oleate was used to emulsify water in benzene. When irradiated by ultra-violet light, the emulsions of benzene, light petroleum, coconut oil, and olive oil were coagulated, whilst emulsions of sperm oil, poppy-seed oil, and carbon disulphide remained unchanged. Aqueous solutions of sodium oleate alone gave a precipitate of acid soap with simultaneous increase in alkalinity and electrical conductivity when irradiated under similar conditions.

E. S. HEDGES.

Ion interchanges in aluminium oxychloride hydrosols. A. W. THOMAS and T. H. WHITEHEAD (J. Physical Chem., 1931, **35**, 27—47).—The ageing of aluminium oxychloride sols at 20° is accompanied by an increase in the p_H of the sol, whilst heating at 80° for 4 days lowers the p_H, which does not return to the original value at 25°. Heating for only 3 hrs. has no measurable effect. Hydrolysis does not account for these changes. The addition of neutral salts produces an increase in the p_H of the positively-charged sols, the effect increasing in the order nitrate, halide, sulphate, acetate, and oxalate. The results and the constitution of sols are explained in accordance with the extension of the Werner theory by Bjerrum and by Stiasny. L. S. THEOBALD.

Mechanism of the coagulation of sols by electrolytes. I. Ferric oxide sol. H. B. WIESER (J. Physical Chem., 1931, **35**, 1—26).—The change in chloride concentration accompanying the stepwise addition of various electrolytes to three different ferric oxide sols containing a slight excess of hydrochloric acid or ferric chloride as stabilising electrolyte has been determined by a potentiometric method. Only a part of the chloride which is found in the supernatant liquid after coagulation can be detected potentiometrically in the original sol before the electrolyte is added, and the chloride determined after stepwise addition of the electrolyte consists of that originally present in the sol together with an additional amount which is displaced when the added anion is taken up. Curves showing the increase in chloride ion on adding potassium sulphate, nitrate, chromate, ferricyanide, oxalate, and citrate to three different ferric oxide sols are given and discussed. At concentrations up to and including that of precipitation, the multivalent anions are practically completely taken up by the sol, and the chloride displaced is less than half the amount equivalent to the multivalent anion taken up. At the precipitation concentration, the chloride in the supernatant solution is equivalent to or slightly greater than the amount of multivalent ion added. The curves showing the chloride displaced are practically linear at the commencement of the stepwise addition of multivalent anions, but as the precipitating concentration is approached the amount of chloride displaced for a given increment of precipitating ion becomes greater. Above the precipitation concentration, the curves have the form of an adsorption isotherm. The chloride displacement curves and the precipitating power of the bivalent anions are similar, but the ferricyanide ion coagulates the sol at a lower concentration with less displacement of chloride at the precipitation value. The curve for the nitrate follows a lower course than those for the multivalent anions. The micelle of the ferric oxide sols, exclusive of the outer layer, can be represented by the formula $x\mathrm{Fe_2O_3},y\mathrm{HCl},z\mathrm{H_2O}$, which corresponds with the observed facts that the micelle contains some chloride which is not displaced by electrolyte, and that the composition varies with the conditions of preparation and subsequent history. The outer layer, which largely determines colloidal properties, consists of an ionic double layer, the inner portion consisting of adsorbed hydrogen or ferric ions and the outer portion a diffuse layer of chloride ions. An adsorption mechanism which accounts for the change in composition, the nature of the double layer, and the decreased charge on the micelle when electrolytes are added to the sol is outlined and discussed in relation to Pauli's solubility theory. L. S. THEOBALD.

Coagulation of ferric oxide hydrosols. C. H. SORUM (J. Amer. Chem. Soc., 1931, **53**, 812).—A reply to Dhar (A., 1930, 1517). J. G. A. GRIFFITHS.

Polyhydroxy-compounds in the synthesis of electro-negative sols. VI. Hydrophilic properties of ferric hydroxide sols obtained in the presence of mannitol. A. DUMANSKI and T. A. GRANSKAYA (J. Russ. Phys. Chem. Soc., 1930, **62**, 1879—1884).—Coagulation in the system ferric hydroxide sol–ether–alcohol is represented graphically using triangular co-ordinates. The hydrophilic properties of this sol, prepared by the addition of sodium hydroxide to ferric chloride in the presence of mannitol, are most pronounced at the isoelectric point. R. TRUSZKOWSKI.

Influence of light on the flocculation of colloidal solutions in a fluorescent medium. Action of antioxygenic substances. A. BOUTARIC and J. BOUCHARD (Compt. rend., 1931, **192**, 357—358; cf. this vol., 305).—The reduction of the time required for coagulation when a colloidal sol (*e.g.*, of arsenious sulphide) to which fluorescein has been added is illuminated by ultra-violet light, as compared with the time required for this in darkness, diminishes more or less logarithmically with the fluorescing power. If the latter is diminished by the addition of an antioxygenic substance (*e.g.*, a phenol, *p*-phenylenediamine, or tannin) the photosensitising power of the fluorescent material is also diminished. The possible value of the presence of fluorescent substances and of the absence of antioxygenic material in the agglutination of microbes is pointed out. C. A. SILBERRAD.

Kinetics of the coagulation of suspensoids. I. K. JABLCZYŃSKI (Kolloid-Z., 1931, **54**, 164—169).—Von Smoluchovski's equation has been applied to systems in which coagulation tends to an equilibrium and where all the particles are charged. The following equation is given: $k=1/t \cdot \log [n(n_0-z)/n_0(n-z)]$, where n is the total number of particles after time t, n_0 the original total number, and z the number of charged particles. The equation is in agreement with experimental data. The measurement of coagulation velocity by the spectrophotometric method is also examined mathematically and the equations developed are supported by experiments. E. S. HEDGES.

Hæmoglobin coagulation. II. S. L. PUPKO (Kolloid-Z., 1931, **54**, 170—175).—The coagulation of hæmoglobin by potassium, calcium, and ferric chlorides in the presence of methyl and ethyl alcohols has been studied by making viscosity measurements, varying the concentration of alcohol and electrolyte and keeping a constant concentration of hæmoglobin. In the presence of methyl alcohol the viscosity either remains constant or decreases during coagulation, whilst in the presence of ethyl alcohol the viscosity either remains constant or increases. The valency of the cation has scarcely any effect on the viscosity

change. The system is stabilised by high concentrations of calcium chloride and ethyl alcohol. Ferric chloride at concentrations between 0·1 and $2N$ stabilises hæmoglobin when ethyl alcohol is also present, but coagulation occurs at higher concentrations.

E. S. HEDGES.

Formation of Liesegang rings. (MISS) S. ROY (Kolloid-Z., 1931, **54**, 190—193).—Directions are given for obtaining periodic structures by precipitation in the following systems: mercuric iodide in gels of vanadium pentoxide, ceric hydroxide, zinc and manganese arsenates; thallous iodide in gels of starch, agar, zinc and manganese arsenates; cuprous iodide in agar; silver iodide in starch; silver chromate in ceric hydroxide; barium and thallous chromates and silver iodide in silicic acid. The influence of light in a number of cases of periodic precipitation has also been examined and the conclusion has been reached that the periodicity is in general more marked when diffusion takes place in the light than in the dark. The most notable difference was found with mercuric iodide; in the dark, alternating layers of yellow colloidal mercuric iodide and red crystals were formed, whilst in the light red crystals of mercuric iodide alternated with clear spaces devoid of precipitate. It is maintained that the influence of light is an acceleration of the process of coagulation. The peptising influence of agar, starch, gelatin, and silicic acid on the precipitates has been studied.

E. S. HEDGES.

Influence of electrolytes on the syneresis and clotting of [goat's] blood. S. PRAKASH and N. R. DHAR (J. Physical Chem., 1931, **35**, 629—637).—Syneresis decreases with an increase in concentration of added electrolyte; it may even be inhibited and in a few cases clotting of blood may be prevented by electrolytes. The results obtained are explained by the tendency of the blood to adsorb ions of a similar charge and thus to increase its stability. The stabilising effect is in the order sodium citrate > potassium oxalate > sodium hydroxide > potassium fluoride > calcium chloride > potassium chloride > ammonium sulphate. The stabilising effect of fluorides, citrates, or oxalates is not due to removal of calcium ions from the blood but to the adsorbed anions.

L. S. THEOBALD.

Reversibility of protein coagulation. M. L. ANSON and A. E. MIRSKY (J. Physical Chem., 1931, **35**, 185—193).—A discussion. With hæmoglobin, globin, or serum-albumin, coagulation appears to be reversible.

L. S. THEOBALD.

Ageing of aqueous ferric chloride solutions. A. LOTTERMOSER and E. LESCHE (Kolloidchem. Beih., 1931, **32**, 157—168).—The ageing of very dilute solutions (10^{-3}—$10^{-6}M$) and of ferric hydroxide sols has been followed by determinations of electrical conductivity and by colorimetric measurements. The more concentrated solutions of ferric chloride increase continuously in conductivity, whilst the more dilute solutions undergo an initial increase, which is followed by a continuous decrease. In no case is a constant end-value obtained. Both ferric chloride solutions and ferric hydroxide sols are temperature-irreversible systems.

E. S. HEDGES.

Dye sols. II. Dissolution of Congo acid by neutral salts. R. TANAKA (Kolloid-Z., 1931, **54**, 156—164; cf. this vol., 37).—The addition of neutral salts to Congo acid sol produces a colour change to red. Small amounts of potassium chloride dissolve the substance, but coagulation occurs when higher concentrations are used. Medium concentrations give the maximum red coloration and such sols have a stronger acid reaction than the original sol. Potassium iodide produces a more intense red coloration. With calcium chloride the amount of dye dissolved is greatest for medium concentrations of the electrolyte, and the position of this maximum is independent of the hydrogen-ion concentration of the solution, the effect clearly depending on the concentration of salt. Increasing hydrogen-ion concentration has the effect of diminishing the intensity of the red coloration and alters the concentration range of the change. Measurements of hydrogen-ion concentration show that the colour change cannot be traced to the initial presence of some free alkali, but is a true peptising effect of the neutral salt. The possibility of the formation of an additive compound between the neutral salt and the acid dye is discussed.

E. S. HEDGES.

Molecular dispersion of dissolved silicic and titanic acids. H. BRINTZINGER and W. BRINTZINGER (Z. anorg. Chem., 1931, **196**, 44—49).—The process of ageing of silicic acid solutions, prepared by hydrolysis of the tetraethyl ester, has been studied by means of dialysis coefficient measurements. In presence of $0{\cdot}002N$-hydrochloric acid a disilicic acid, $2SiO_2,2H_2O$, is first formed and polymerises completely within 1 day to $4SiO_2,3H_2O$; after 2 days an octosilicic acid, $8SiO_2,4H_2O$, is formed, and after 4 days an acid of mol. wt. 862. Further aggregation results in the production of a mixture of acids until an acid of mol. wt. 8260 is formed (45 days). After 110 days the dialysis coefficient falls to zero. In $0{\cdot}001N$-hydrochloric acid solution even the first product is a mixture of complexes, and aggregation proceeds more rapidly than in the more strongly acid solutions; a definite complex of mol. wt. 8260 is again produced, and there is evidence of the formation of an acid of mol. wt. 32,870. True solutions of titanic acid are extremely unstable; within a few hours the solute is completely converted into colloidally dispersed hydrated titanium dioxide. The results obtained demonstrate the value of the dialysis method for studying the gradual conversion from the molecular into the colloidal state.

H. F. GILLBE.

Sorption phenomena and chemical processes. VI. Composition of alkali-cellulose and imbibition by cellulose. S. M. LIEPATOV [with N. M. SOKOLOVA] (J. Russ. Phys. Chem. Soc., 1930, **62**, 1785—1793).—Cellulose forms a compound, $(C_6H_{10}O_5,3NaOH)_n$, when treated with aqueous alkali. The imbibition of cellulose films in water is due to entry of water within the pores of the membrane, whilst in alkaline solutions the cellulose molecules are covered by a unimolecular layer of water.

R. TRUSZKOWSKI.

Depolarisation and light absorption by alkaline protein solutions. G. ETTISCH, H. SACHSSE, and B. LANGE (Biochem. Z., 1931, **230**, 93—114).—The

variation in the ratio of the horizontal to the vertical component of the polarised light from illuminated serum-albumin and -globulin solutions in presence of different concentrations of alkali has been investigated. Addition of alkali to the protein solution results in a temporary change of the ratio dependent on the amount added and the state of hydration of the particles. This effect is not apparent at low alkali concentrations where neutralisation of the acid valencies present only occurs. At high alkali concentrations a disintegration of the particles occurs, a phenomenon more apparent with globulin than with albumin. This disintegration is clearly shown by the depolarisation, but not so definitely by the absorption spectra. F. O. HOWITT.

Viscosity of alkaline protein solutions. G. ETTISCH and H. SACHSSE (Biochem. Z., 1931, **230**, 115—128).—The viscosities of ovalbumin and globulin in presence of acid and alkali have been examined. The effect of alkalis on the proteins is essentially a time reaction. Low concentrations of alkali (0·2—0·3%) do not increase the viscosity to any appreciable extent, but with a concentration of 0·5% the viscosity increases, reaching a maximum in 4 hrs. and then decreasing in the case of globulin. With albumin, a maximum is reached in about 8 hrs. and thereafter a steady value is maintained. The effect of addition of copper sulphate on the viscosity of an alkaline protein solution is small at low protein concentrations, but is very marked at high concentrations. The mechanism of these changes with reference to the splitting up of the protein particles is discussed. F. O. HOWITT.

Calcium acetate gels. II. C. G. SMITH (Kolloid-Z., 1931, **54**, 181—190; cf. A., 1929, 879).—A further study of the formation of calcium acetate gels by adding a concentrated solution of the salt to alcohol indicates that the process is primarily one of dehydration. If dehydration takes place slowly, a gel having a definite structure is formed, but when the dehydration is too rapid, a structureless gelatinous precipitate is obtained. Rapid dehydration can be effected by the addition of acetone or pyridine, particularly the former; on the other hand, slow dehydration may be brought about by increasing the amount of water in the alcohol, with the production of more stable gels. Organic liquids which have no dehydrating effect have no influence on the gel formation. The gel is also formed by the addition of sodium or magnesium acetate, presumably through repression of dissociation, causing an association of the calcium acetate molecules. Electrolytes which react chemically with calcium acetate are inimical to the formation of the gel. The electrolytic dissociation of the calcium acetate is in any case never strong in the presence of the alcohol, and this factor is believed to be important in determining the conditions of gel formation. Photomicrographs of the gels show that these have in most cases a honeycomb type of structure, the calcium acetate being the disperse phase. Benzene, carbon disulphide, and acetone cause a phase reversal, droplets of the liquid being found in a network of calcium acetate. When the gel is kept, the particles of calcium acetate increase in size eventually to visible dimensions, the smaller particles disappearing; simultaneously an increase in opalescence is observed and syneresis occurs. When the calcium acetate forms the continuous medium the crystallites gradually accumulate at the knots of the network, forming clumps, so that the structure opens and the liquid is syneretically expressed. The force producing this change is probably molecular attraction due to the high residual valency of the calcium acetate and is also due to the affinity of the alcohol for the water of hydration. Both fine, hairlike crystals of the anhydrous salt and needles of the monohydrate can be observed in the gels. E. S. HEDGES.

Refractive index of gelatin solutions and the supposed hydration of the dispersed particles. G. ROSSI and A. MARESCOTTI (Gazzetta, 1931, **61**, 14—26).—The refractive index of solutions of gelatin is not exactly a linear function of the concentration. The deviations are ascribed to the hydration of the gelatin, and measurements at various temperatures indicate that the degree of hydration may vary with the temperature. Solutions of gelatin containing certain sodium salts, viz. iodide, bromide, citrate, and sulphate, behave differently, according as the salts increase or decrease the viscosity, but the actual changes in the refractive index are difficult to explain. O. J. WALKER.

Diffusion in gelatin gels. W. STILES and G. S. ADAIR (J. Amer. Chem. Soc., 1931, **53**, 619—620).—The results of the authors (A., 1922, ii, 125) are said to be in essential agreement with those of Friedman and Kraemer (A., 1930, 693). J. G. A. GRIFFITHS.

Structure of gelatin gels. Gelatinisation temperature and strength as function of p_H. Y. GARREAU, P. GIRARD, and N. MARINESCO (Compt. rend. Soc. Biol., 1930, **103**, 551—554; Chem. Zentr., 1930, ii, 2238).—Consideration of the equilibrium between free and coupled dipoles in gelatin solution suggests that the p_H has a considerable influence on the degree of dissociation of the dipole and the physical properties dependent thereon. The gelatinisation temperature and strength are minimal at p_H 4·7 and change with the p_H similarly to change in dielectric constant. A. A. ELDRIDGE.

Swelling and hydration of gelatin. J. H. NORTHROP and M. KUNITZ (J. Physical Chem., 1931, **35**, 162—184).—A summary of previous work (J. Gen. Physiol., 1926—1930). The swelling, osmotic pressure, viscosity, and syneresis of gelatin sols or gels can be quantitatively explained by assuming that they are two-phase, three-component systems. The solid phase consists of micelles of an insoluble ingredient of gelatin, whilst the liquid phase is a solution of the "insoluble" fraction and of a "soluble" fraction in water. L. S. THEOBALD.

Silver migration in partly swollen gelatin layers. E. WAGNER and K. SCHAUM (Z. wiss. Phot., 1931, **28**, 325—328).—A test has been made to ascertain whether, when a drop of water on a silver in gelatin film dries, and a raised ring of gelatin with a central depression is formed, the silver is also displaced in a similar manner. A section of such a layer of gelatin was examined with the microscope

when immersed in glycerol solution of the same refractive index as the gelatin. The gelatin surface was then invisible and the silver was seen to be heaped up in the same form as the gelatin surface. The effect is permanent, as a fourteen-year-old film showed a similar appearance. J. LEWKOWITSCH.

Hydrolysis during washing of the system gelatin plus silver nitrate. H. H. SCHMIDT and F. PRETSCHNER (Z. wiss. Phot., 1931, **28**, 328—332).—If a mixture of silver nitrate and gelatin solution is gelled, shredded, washed, and then analysed, more silver is found than that equivalent to the nitrogen present (as nitrate). If washing is continued till the gel is free from nitrate, some silver still remains and the gel is light-sensitive and can be physically developed. The gel on melting and regelling turns turbid, and thereafter is transparent when melted and turbid when solid; the opacity is due to silver oxide. The silver cannot be entirely removed by washing or by sodium sulphite. When this gel is treated with potassium chloride, bromide, or iodide, washed, and analysed, free silver is still found, the amounts decreasing from chloride to iodide. These facts support the authors' theory of the occurrence of free silver in an emulsion (cf. B., 1930, 586, 587, 929; 1931, 223). J. LEWKOWITSCH.

Morphology of chemical reactions in gels. IV. F. M. SCHEMJAKIN (J. Russ. Phys. Chem. Soc., 1930, **62**, 1885—1894; cf. this vol., 38).—The same variation in the appearance of the figure produced by placing a drop of one reagent on gelatin impregnated with another is produced by diminishing the concentration of the first or augmenting that of the second reagent. The structure of different periodic precipitation figures is described, and theories relating to the mechanism of these reactions are advanced. R. TRUSZKOWSKI.

Equilibrium between egg-albumin and calcium and potassium salts. M. GIUFFRÈ (Biochem. Z., 1930, **229**, 296—310; cf. A., 1928, 1388).—When solutions of egg-albumin (purified by electro-ultrafiltration) are mixed with solutions of calcium salts (chloride, sulphate, thiocyanate) or of potassium chloride, adsorption of the salts by the albumin or loose combination between them takes place. The amount of salt adsorbed (or combined) increases as its concentration is increased and for ratios less than 500 millimols. of salt to 100 g. of albumin no saturation point is reached. With low or moderate concentrations of salt the extent to which the adsorption (or combination) takes place is greater with calcium than with potassium, but with the higher concentrations there is no difference in this respect between the two metals. When both calcium and potassium chlorides are present together each behaves towards the albumin as if the other were absent. With calcium sulphate the extent of adsorption (or combination) is 10% greater, with calcium thiocyanate 25% less, than with calcium chloride. W. MCCARTNEY.

Changes in the X-ray spectrum of inulin during swelling in water. J. R. KATZ and J. C. DERKSEN (Rec. trav. chim., 1931, **50**, 248—251).—The changes taking place during the swelling of inulin have been studied by measuring the X-ray spectra of samples containing various amounts of water up to the fully saturated state. From this state down to about 8% of water there is no change in the spectrum, but below this amount changes in the intensities of interference rings are observed. At this degree of hydration, also, the water vapour-pressure curve of inulin begins to rise steeply. It is probable that the swelling of inulin is accompanied not only by the formation of aqueous shells round the micelles, but also by some other process the nature of which is not clear. O. J. WALKER.

Theory of thixotropy. E. A. HAUSER (J. Rheology, 1931, **2**, 5—9).—A review of the literature leads to the conclusion that thixotropy depends on the presence of a disperse phase of anisotropic character, the particles being capable of forming solvated sheaths of a non-spherical shape. The gel condition is reached when these sheaths come into contact with their maximum possible surfaces. Agitation causes a mechanical disruption of the sheath structure, thereby transforming the gel into a sol. E. S. HEDGES.

Glue and gelatin. G. C. HERINGA and H. R. KRUYT (Chem. Weekblad, 1931, **28**, 142—150).—A discussion of the relations between probable structures, and particularly of the results of X-ray examination. The reduction of Congo-red by formaldehyde proceeds more slowly when the indicator is adsorbed on the surface of the glue micelle. The dye is not only adsorbed on the surface of the micelle, but slowly diffuses into it. Abnormalities in swelling are described. The influence of colloids on one another is put forward as a basis for explanation of cell aggregation in living matter. S. I. LEVY.

Chylomicron emulsion. S. DE W. LUDLUM, A. E. TAFT, and R. L. NUGENT (J. Physical Chem., 1931, **35**, 269—288).—The nature of the surface films surrounding chylomicrons has been investigated. The p_H of the isoelectric point of chylomicrons in human serum has been determined by a flocculation and by a cataphoretic method. In all cases the values lie between p_H 4·6 and 5·4, and between the accepted values for the isoelectric points of serum-albumin and serum-globulin. The more exact cataphoretic method indicates an isoelectric point between 4·8 and 5·0. This affords strong evidence that the chylomicrons are surrounded by protein films, which may be composed of mixed serum-albumin and serum-globulin. Experiments with strong acid, alkali, 95% alcohol, and ammonium sulphate confirm the view that protein precipitants should cause aggregation of chylomicrons. The application of the Mudd interface technique indicates that the chylomicrons are lipoid droplets surrounded by protein films. L. S. THEOBALD.

Sol and coacervate of ichthyocoll. H. G. B. DE JONG and N. F. DE VRIES (Rec. trav. chim., 1931, **50**, 238—247).—Ichthyocoll was prepared by making a hot aqueous extract of the drug ichthyocolla, centrifuging, filtering, adding sodium hydroxide, precipitating and washing with alcohol, and drying the product in air. The product had an ash content of 0·38% and dissolved readily in warm water. Experi-

ments with the sol were conducted at 37°. A 0·73% sol behaved in accordance with Poiseuille's law. The curve connecting the viscosity with p_H closely resembles that of gelatin over the range p_H 1—4, but above p_H 4 marked differences occur. The curve is nearly flat between p_H 5 and 10, and there is a maximum at about p_H 8—9. When cooled, the sol is turbid between p_H 6·7 and 9·3, the maximum turbidity being at about p_H 9. The isoelectric point of ichthyocoll is also in the neighbourhood of p_H 8—9. The viscosity rises again above p_H 9 and passes through another maximum at p_H 12. The influence of electrolytes on the postively-charged ichthyocoll sol has been studied at different hydrogen-ion concentrations; potassium, calcium, and luteocobaltic chlorides have practically the same effect, but notable differences are shown by the effects of potassium chloride, sulphate, and ferricyanide, where the valency of the oppositely-charged ion is altered. Simple coacervation of the sol is brought about by the addition of alcohol, resorcinol, etc. to the isoelectric sol. Complex coacervation occurs when the positive ichthyocoll sol is added to the negative sols of gum arabic, thymus and yeast nucleates, egg and soya-bean lecithins, and when the negative ichthyocoll sol (above p_H 9) is added to the negative clupein sol. No coacervation results from mixing positive ichthyocoll with negative gelatin over the region p_H 5—9 and this is connected with the peculiar course of the viscosity curve over this region, the electrical attraction being insufficient to overcome the solvation tendency. E. S. HEDGES.

Swelling pressure of rubber. P. STAMBERGER (Nature, 1931, **127**, 274).—The swelling pressure, P, can be represented by the formula $P=KV^{-2}$, where V is the volume of solvent bound to unit weight of gel and K is a constant characteristic for all solvents and gels. L. S. THEOBALD.

Influence of size, shape, and conductivity on cataphoretic mobility, and its biological significance. A review. H. A. ABRAMSON (J. Physical Chem., 1931, **35**, 289—308).—Particles which have cataphoretic mobilities independent of size and shape are tabulated. The cataphoretic mobility of oil droplets and the data relating to the factor of proportionality in the general equation for cataphoretic and electroendosmotic mobilities are discussed. Size and shape do not primarily cause changes in the mobility of red blood cells. L. S. THEOBALD.

Effect of alkali salts on cataphoresis and precipitation of colloidal gold. Hofmeister series. A. LAGEMANN (Kolloidchem. Beih., 1931, **32**, 212—48).—The effect of alkali halides in reducing the charge of the particles of a gold sol has been measured by a cataphoretic method and has been compared with the coagulating effect. The positive alkali ions reduce the negative charge of the gold particles in the following order of increasing effectiveness: Li<Na<K<Rb. The halogen ions exert an antagonistic effect in the order Br<Cl<F. The univalent positive ions do not discharge the colloid particles completely; with increasing concentration of the electro charge is reduced at first rapidly and then slowly, tending asymptotically towards a limiting value, the maximum discharge increasing with the at. wt. of the ion. The variation of the charge on the colloid with concentration of the added electrolyte can be represented by an adsorption curve. The coagulation of colloidal gold by the same electrolytes follows the same ionic series as that observed in the discharging effect, but there is no proportionality between the coagulating and discharging effects. E. S. HEDGES.

Influence of surface-active substances and electrolytes representing both kinds of ions on the electrophoretic migration velocity of lyophobic sols. S. H. WHANG (Kolloidchem. Beih., 1931, **32**, 169—196).—Measurements of the electrical migration velocity of the particles of quartz suspensions and of sols of arsenious sulphide and ferric hydroxide have been made in the presence of surface-active compounds (alcohols, fatty acids, and amines) and also in the presence of a large number of inorganic electrolytes. The influence of the surface-active substances cannot be expressed by any simple and general rule. The addition of the lower alcohols causes a lowering of the cataphoretic migration velocity of a quartz suspension, whilst the velocity is increased by amyl and hexyl alcohols. The fatty acids lower the velocity of cataphoresis, but all bases, whether active or inactive in capillary properties, increase the velocity very considerably. The results obtained in the study of the influence of inorganic electrolytes are consistent in showing that the oppositely-charged ion reduces the migration velocity of the particle in proportion to the mobility of the ion. At the same time, the ion of similar charge to the particle has an antagonistic effect, increasing the velocity of the particle in proportion to the mobility of the ion. These results are discussed in relation to those of other investigators. E. S. HEDGES.

Electrophoresis and the diffuse ionic layer. M. MOONEY (J. Physical Chem., 1931, **35**, 331—344).—The theory of the diffuse ionic layer and its influence on the electrophoresis of a sphere is outlined. A formula for the limiting slope of the mobility–curvature curve is developed. The electrophoretic mobilities of oil drops in electrolytes, determined by the microscopic method, are in approximate agreement with the theory as applied to dilute aqueous solutions. Formulæ for surface charge and surface conductivity are given, and various anomalous effects in cataphoresis are discussed. The Debye–Hückel formula for cataphoresis is limited to conditions in which the colloidal particle is much smaller than its diffuse ionic layer. L. S. THEOBALD.

Equation for a perfect gas according to thermodynamics and the properties of electrons and protons. R. D. KLEEMAN (Z. anorg. Chem., 1931, **196**, 284—288).—Theoretical. E. S. HEDGES.

Diffusion as a pulsation process. W. JAZYNA (JACYNO) (Z. Physik, 1931, **67**, 278—288).—Theoretical. The various points of view regarding the process of diffusion are considered, and the pulsation theory is treated on the basis of formal thermodynamics. A. J. MEE.

Nuclear spin and the third law of thermodynamics. Entropy of iodine. W. F. GIAUQUE

(J. Amer. Chem. Soc., 1931, **53**, 507—514; cf. this vol., 294).—According to heat capacity, vapour pressure, and spectroscopic data for iodine, the heat of sublimation is 15,640 g.-cal. per mol. at 0° Abs. and 14,877 at 298° Abs.; the vapour pressure of the solid is given by $\log_{10}p(\text{atm.})=-3512\cdot3/T-2\cdot013\log_{10}T+13\cdot374$, whilst the entropy, S_{298}, of the gas is 62·29 and that of the solid 27·9 g.-cal. per 1° per mol. These values afford correct entropy changes in reactions, but are less than the absolute entropies by the (unknown) entropy due to nuclear spin, the effect of which persists to below 10° Abs. Molecular rotation of the type existing in solid hydrogen does not occur in solid iodine, but both para- and ortho-iodine retain their respective spin multiplicities in the solid state. J. G. A. Griffiths.

Le Chatelier–Braun principle. I. Thermodynamic proof. H. S. Frank (Lingnan Sci. J., 1930, **9**, 81—90).—A discussion of the principle and its application to salt solutions. Chemical Abstracts.

Van 't Hoff's stability rule. B. Bruzs (Rec. trav. chim., 1931, **50**, 230—237).—A simple thermodynamic derivation is given of van 't Hoff's stability rule that of two modifications of a system the one with the higher specific heat becomes stable at higher temperatures. The rule is shown to be supported by the experimental data at present available, although in the case of gas–solid systems and of the two forms of hydrogen low temperatures must be considered to obtain the correct result. O. J. Walker.

Quantitative relation between the slopes *dP/dT* of the lines representing univariant equilibria at an invariant point. (Mlle.) A. E. Korvezee, (Mlle.) N. H. J. M. Voogd, and F. E. C. Scheffer (Rec. trav. chim., 1931, **50**, 252—255).—A relation between the slopes of the pressure–temperature curves and the compositions of the various phases at an invariant point is derived for binary and ternary systems. O. J. Walker.

Graphical treatment of the thermodynamics of the rectifying column. W. H. Keesom (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 901—908).—Using certain simplifying suppositions, the energy changes in a rectifying column used for separating the constituents of a binary mixture are deduced thermodynamically and the results set out in graphical form. J. W. Smith.

Superheating and intensive drying of liquids. A. Smits (Z. physikal. Chem., 1931, **153**, 253—254).—Polemical against Cohen and Cohen-de Meester (this vol., 294). H. F. Gillbe.

Influence of intensive drying on the establishment of internal equilibrium. I. A. Smits, E. L. Swart, P. Bruin, and W. M. Mazee (Z. physikal. Chem., 1931, **153**, 255—261).—The observed elevation of the b. p. of liquids after intensive drying is ascribed to superheating, caused possibly by the removal of dust by the prolonged contact with the drying agent. It is suggested that the presence of dust may act catalytically on the establishment of the internal equilibrium of the liquid, but no evidence could be obtained of the abnormally low vapour pressure of a dust-free liquid, resulting from surface evaporation, which would be anticipated on this view; removal of all traces of dust has, however, been shown to conduce to superheating. Sources of error in vapour-pressure measurements with dry liquids are noted, of which the principal is due to the presence of gas in the liquid. No effect of intensive drying for 8 months has been observed with liquids completely free from gases. H. F. Gillbe.

Equilibrium of the simplest *cis–trans*-isomerides (dichloroethylenes) in the vapour [phase]. L. Ebert and R. Büll (Z. physikal. Chem., 1931, **152**, 451—452).—Preliminary communication. The vapour of dichloroethylene at 300° contains about 63% of the *cis*-component, the same equilibrium being reached from either side. The b. p. of the pure liquids are: *cis*- 60·14±0·04°, *trans*- 47·48±0·04°. F. L. Usher.

Cryoscopic study of paraldehyde in solutions of calcium and strontium chloride. F. Bourion and E. Rouyer (Compt. rend., 1931, **192**, 557—559).—The values of the cryoscopic constant are said to indicate that the triple molecule $(C_2H_4O)_3$ is stable in the salt solutions (cf. this vol., 35). C. A. Silberrad.

Electrolytic dissociation. Fundamental hypotheses and assumptions of the electrostatic theory of electrolytic dissociation and an attempt to explain it without assuming dielectric action. K. Fredenhagen (Z. physikal. Chem., 1931, **152**, 321—379; cf. A., 1929, 648; 1930, 421, 537).—The author's views are amplified and summarised. It is not permissible, in view of the strict thermodynamic connexion between the effect of the dielectric constant on dissociation and its effect on solvent power, to consider either of these properties separately. The relative solvent powers of water, ammonia, hydrogen cyanide, and hydrogen fluoride for a number of salts are often in a sense opposite to that required by the electrostatic theory. The limited applicability of the Nernst–Thomson rule depends on the fact that the same factor, *i.e.*, internal pressure, is influential in determining both the value of the dielectric constant of a solvent and the extent of dissociation of a solute in it, but complete parallelism is found only among chemically similar solvents. The underlying cause of ionisation is the preferential (chemical) attraction of the solute for one or the other constituent of the polar solvent. The theory accounts for the large difference between the electrical conductivity of fused salts and that of pure ionising solvents, and serves to explain qualitatively a number of phenomena not accounted for by the electrostatic theory. F. L. Usher.

Dissociation of strong electrolytes. III. Complete dissociation and optical properties. M. B. Jacobs and C. V. King (J. Physical Chem., 1931, **35**, 480—487; cf. A., 1930, 995).—A discussion of the views of previous workers on optical data. The view of the additivity of optical properties is no longer tenable, and percentage dissociation cannot be calculated with certainty from colour or absorption data. Evidence for the existence of a small number of undis-

sociated molecules or ion groups even in the highly dissociated electrolytes continues to grow.

L. S. THEOBALD.

Raman effect and electrolytic dissociation. L. A. WOODWARD (Physikal. Z., 1931, **32**, 212—214).—Each molecular species of a scattering system gives its own characteristic Raman effect, with an intensity proportional to the corresponding concentration. For solutions of electrolytes, therefore, this can be used to find the degree of ionisation. For solutions of ordinary salts the Raman effect of the ions only is obtained; hence salts appear to be completely dissociated in solution. For nitric acid, results similar to those obtained by Rao were found. For sulphuric acid, anomalous intensity changes were found. A series of solutions was investigated so that the exposure times were inversely proportional to the concentrations. If there were no anomalies there should be the same intensity in each case. There are, however, variations in the curves showing the formation of the HSO_4' ion and the SO_4'' ion at different dilutions. Iodic and trichloroacetic acids of different concentrations have also been investigated. Both gave an intensive Raman effect, but no anomalies connected with ionisation were apparent. For a saturated solution of hydrogen chloride at 25°, no Raman line could be found. From the vapour pressure, however, it is known that undissociated HCl molecules must exist in the solution, but the concentration of these is evidently so small that no Raman effect can be produced.

A. J. MEE.

Selenium cells as colorimeters. III. A. MICKWITZ (Z. anorg. Chem., 1931, **196**, 113—119).—Extrapolation of measurements with the selenium cell of the light absorption of colloidal nickel and cobalt sulphide solutions together with theoretical considerations relating to the composition of the disperse phase when formed by the action of sodium or hydrogen sulphide on a solution of a salt of the metal indicate that the solubility (expressed in terms of metal) is for Ni(SH)(OH) $0{\cdot}8\times10^{-5}$, for Co(SH)(OH) $0{\cdot}3\times10^{-5}$, and for $Co(SH)_2$ 1×10^{-5} parts per 100.

H. F. GILLBE.

Solubility of acids in salt solutions. IV. Solubility and activity coefficient of benzoic acid in aqueous benzoate solutions. E. LARSSON (Z. physikal. Chem., 1931, **153**, 299—308).—The solubility of benzoic acid at 18° in solutions of chlorides, bromides, iodides, nitrates, perchlorates, di- and tri-chloroacetates, benzenesulphonates, and β-naphthol-sulphonates containing sodium benzoate to repress the ionisation of the acid has been measured, and the activity coefficient of the benzoic acid molecule in each solution has been calculated. The influence of the alkali and alkaline-earth chlorides and nitrates decreases with increase of the at. wt. of the cation, and the analogous condition obtains for the potassium halides. The difference between the activity coefficient in a chloride and in a nitrate solution is independent of the nature of the cation, and it appears that the total effect is the resultant of two component effects, of which one is characteristic of the anion and the other of the cation. By assuming that the components are equal in the case of potassium chloride, the specific influences of the various ions have been calculated. The results are in general in accordance with the Debye–Hückel theory, but in certain cases, and notably those involving large organic anions which cannot be regarded as spherical and carrying a central point charge, the activity coefficient is less than unity, although benzoic acid lowers the dielectric constant of water.

H. F. GILLBE.

Dissociation of mercuric halides. H. BRAUNE and S. KNOKE (Z. physikal. Chem., 1931, **152**, 409—431; cf. A., 1928, 829).—The dissociation of mercuric chloride, bromide, and iodide has been determined at different temperatures up to 1200°, and the calculated heats of dissociation agree well with those furnished by calorimetric data. The calculated moments of inertia of the molecules are in the ratio 1 : 0·48 : 0·22 for the iodide, bromide, and chloride, respectively.

F. L. USHER.

Optical dissociation of mercury halides. V. KONDRATÉEV (Z. physikal. Chem., 1931, B, **11**, 470—474; cf. Sponer, this vol., 432).—On the assumption that the optical dissociation of the mercuric halides is represented by the equation $HgX_2+h\nu=HgX+X^*$, the heats of formation of the di- and tri-atomic molecules are calculated from spectrographic and thermochemical data. The values thus obtained, considered correct within a few kg.-cal., are: (Hg,Cl) 27, (Hg,Br) 20, (Hg,I) 12; (HgCl,Cl) 79, (HgBr,Br) 65, (HgI,I) 53 kg.-cal.

F. L. USHER.

Equilibrium between chlorine, bromine, and bromine monochloride. W. JOST (Z. physikal. Chem., 1931, **153**, 143—152).—The chemical equilibrium in mixtures of gaseous bromine and chlorine has been examined by a spectro-photometric method and the existence of bromine monochloride has been confirmed. The heat of formation of this compound has been calculated to be $0{\cdot}75\pm0{\cdot}5$ kg.-cal.

E. S. HEDGES.

Equilibrium between vapour and liquid phase in the system acetic acid–ethyl acetate. L. L. SCHMIDT (J. Russ. Phys. Chem. Soc., 1930, **62**, 1847—1858).—The total and partial vapour-pressure curves of the above system show that the proportion of associated acetic acid molecules in the gaseous phase rises with concentration of acetic acid in the mixture; in general, Gibbs' dissociation law is applicable to such systems.

R. TRUSZKOWSKI.

Melting diagram of the system zirconium dioxide–beryllium oxide. O. RUFF, F. EBERT, and H. VON WARTENBERG (Z. anorg. Chem., 1931, **196**, 335—336).—A reinvestigation of this system has failed to confirm the existence of the high-melting compound, $3BeO,2ZrO_2$, formerly reported (A., 1930, 847).

E. S. HEDGES.

Binary system potassium nitrate–calcium nitrate. A. P. ROSTKOVSKI (J. Russ. Phys. Chem. Soc., 1930, **62**, 2055—2059).—The fusion diagram indicates the formation of a compound, $4KNO_3,Ca(NO_3)_2$, with a transition point at 174° and 71·3% KNO_3. The eutectic point is at 145° and 65·8% KNO_3. The system is characterised by the formation of viscid melts, which readily exhibit supercooling with the formation of vitreous masses. The above double compound is not formed in aqueous solutions.

R. TRUSZKOWSKI.

Polymorphism of rubidium nitrate, and the system $RbNO_3$–RbCl. A. P. ROSTKOVSKI (J. Russ. Phys. Chem. Soc., 1930, **62**, 2067—2070).—A fourth polymorph of rubidium nitrate, transition point 290—292°, is described. The fusion diagram of the system $RbNO_3$–RbCl indicates the formation of two double compounds with transition points at 338° and 10·4 mol.-% $RbNO_3$ and 394° and 24 mol.-% $RbNO_3$.
R. TRUSZKOWSKI.

Crystallisation of copper from fused cuprous chloride. V. SIHVONEN (Z. Elektrochem., 1931, **37**, 80—82).—If a mixture of fused cuprous chloride and metallic copper be heated unevenly the metal separates in the cooler part of the system as dendritic crystals. The presence of thermoelectric currents reduces the yield of copper, as a result of the formation of cupric chloride by the chlorine ions which are discharged at the hotter electrode. The crystallisation effect is due to a displacement of the equilibrium $2Cu^{\cdot} \rightleftharpoons Cu+Cu^{\cdot\cdot}$, the direction of the displacement with temperature being the same as in aqueous solutions.
H. F. GILLBE.

Cupric-cuprous equilibrium in cupric sulphate and perchlorate solutions, and the anodic behaviour of copper. E. HEINERTH (Z. Elektrochem., 1931, **37**, 61—76).—The equilibria between cupric and cuprous ions in acid solutions of the sulphate and perchlorate have been investigated by shaking a solution of the cupric salt with powdered copper in an atmosphere of nitrogen and analysis of the resulting solution. Equilibrium is attained within a few hours. The ratio $[Cu^{\cdot\cdot}]^{\frac{1}{2}}/[Cu^{\cdot}]$ is independent of variations of concentration, acidity, and total ionic concentration within wide limits, and in the sulphate solutions falls from 1429 at 20° to 500 at 40° and 205 at 60°; in the perchlorate solutions the results are less readily reproducible. The heat tone of the reaction $Cu^{\cdot\cdot}+Cu \longrightarrow 2Cu^{\cdot}$ at 20—60° is 18·8 kg.-cal. The normal potential of the process $Cu \longrightarrow Cu^{\cdot}$ at 25° is 0·525 volt. It has been confirmed experimentally that on dilution of a solution which is in equilibrium with respect to cuprous and cupric ions supersaturation with respect to the former does not occur. The anodic dissolution of copper in acid solutions of the sulphate has been investigated by the determination of current density–voltage curves. The polarisation diminishes with rise of temperature and increases with increase of acidity, and the formation of an anode sludge follows a course parallel with that of the polarisation. H. F. GILLBE.

Water of hydration of crystalline compounds. III. Tensimetric analysis of the systems $CoSO_4$–H_2O, $Na_3[Fe(C_2O_4)_3]$–H_2O, and $K_3[Fe(C_2O_4)_3]$–H_2O. A. P. ROSTKOVSKI (J. Russ. Phys. Chem. Soc., 1930, **62**, 2061—2065).—The vapour-pressure isotherms of the above systems were determined at 25°. Cobalt sulphate forms hydrates with 1, 6, and 7 mols. of water, sodium ferrioxalate combines with 2 and 5, and potassium ferrioxalate with 3 mols. of water. In the first two systems there is no formation of solid solutions, but the last gives an uninterrupted series of solutions of trihydrate in anhydrous salt.
R. TRUSZKOWSKI.

Oxide hydrates. XXXVI. System ferrous oxide–water and its conversion into the system ferric oxide–water. G. F. HÜTTIG and H. MÖLDNER (Z. anorg. Chem., 1931, **196**, 177—187).—Observations on the dehydration of hydrated ferrous hydroxide indicate that the reaction $3FeO,H_2O \longrightarrow Fe_3O_4+2H_2O+H_2$ takes place to a small extent. Ferrous hydroxide exhibits a characteristic Debye diagram, and must be regarded as a definite compound. The primary decomposition is irreversible and occurs in two stages, viz., at 220—234° and at 261—277°; the remaining water (0·4 mol.) is evolved continuously on raising the temperature. The product of the oxidation of ferrous hydroxide, Fe_3O_4,nH_2O, has the same Debye diagram as magnetite, and loses water readily and continuously with rise of temperature. On ageing the water becomes still more loosely combined and the substance loses its ability to become oxidised completely in the air to the ferric state. The conversion of ferrous hydroxide into the ferric state is discussed. H. F. GILLBE.

Equilibrium constants for the decomposition of ammonium hydrogen carbonate. W. K. HUTCHINSON (J.C.S., 1931, 410—412).—By determining the partial pressure of ammonia, carbon dioxide, and water vapour in equilibrium with a saturated aqueous solution of ammonium hydrogen carbonate, the equilibrium constant, which is also the constant for the dissociation of the solid, has been calculated. The constant K is given by the equation $\log_{10} K=33{\cdot}88-40{,}600/2{\cdot}303RT$ and is satisfied over a wide range of concentrations of carbon dioxide and ammonia. The value 40,600 g.-cal. for the heat of formation of solid ammonium hydrogen carbonate is in good agreement with accepted values.
E. S. HEDGES.

Equilibria in salt lake waters. The ternary system: sodium hydrogen carbonate–sodium sulphate–water. S. Z. MAKAROV and N. M. WAKSBERG (J. Russ. Phys. Chem. Soc., 1930, **62**, 1863—1870).—The phase diagram of the above system shows neither compound nor solid solution formation. Determinations must be made in an atmosphere of carbon dioxide, in order to avoid formation of sodium carbonate. R. TRUSZKOWSKI.

Heats of formation of gaseous halides of mercury, cadmium, and zinc. H. SPONER (Z. physikal. Chem., 1931, **B**, **11**, 425—432).—Approximate values for the heats of formation of the diatomic molecules, and of the triatomic molecules from the former and a halogen atom, are calculated on the basis of Wieland's analysis (A., 1929, 1127) of the band spectra of the gaseous halides of mercury, cadmium, and zinc. The values in kg.-cal. are: (Hg,Cl) 32, (Hg,Br) 25, (Cd,Br) 60, (Cd,I) 32, (Zn,I) 46; (HgCl,Cl) 72, (HgBr,Br) 62, (CdI,I) 48. F. L. USHER.

Heats of formation of nitrides. I. Manganese and chromium nitrides. B. NEUMANN, C. KRÖGER, and H. HAEBLER (Z. anorg. Chem., 1931, **196**, 65—78).—A method and apparatus for the direct determination of the heat of formation of nitrides have been developed. The metal is heated electrically in a calorimeter bomb containing nitrogen under pressure to a temperature at which the reaction velocity is sufficiently high to ensure a reasonably high conversion into nitride. Measurements with manganese

indicate that the quantity of nitrogen taken up by the metal does not alter with variation of pressure between 10 and 25 atm., and corresponds with the compound Mn_5N_2; the heat of formation is $57,180\pm400$ g.-cal. Combustion of manganese containing nitride in oxygen yields a value of about 62 kg.-cal. The heat of formation of chromium nitride, CrN, is $29,500\pm500$ g.-cal., whilst the value calculated from the dissociation pressure curve is 23·7—24·5 kg.-cal. at 20°. H. F. GILLBE.

Heats of combustion of methane and carbon monoxide. F. D. ROSSINI (Bur. Stand. J. Res., 1931, **6**, 37—49).—The heat of combustion of methane to form carbon dioxide and liquid water has been found to be $889,700\pm300$ international joules per mol. at 30° under a constant pressure of 1 atm. The heat of combustion of carbon monoxide to form carbon dioxide is $282,925\pm120$ international joules per mol. at 30° and 1 atm. R. CUTHILL.

Vapour pressure and heat of dilution. VIII. Heat of dilution of sucrose in aqueous solution and of carbamide and calcium chloride in alcoholic solution. R. B. VALLENDER and E. P. PERMAN (Trans. Faraday Soc., 1931, **27**, 124—135).—Using the method previously described (cf. A., 1929, 1389), the heats of dilution have been determined over wide ranges of concentration and temperature. For sucrose all the heats of dilution are negative and never greater than 3 g.-cal. per g. of water. At high concentrations the heat of dilution–concentration curves intersect at very nearly the same point. In ethyl alcohol solution carbamide gives very small positive and calcium chloride negative heats of dilution. Using the Kirchhoff equation to calculate the heats of dilution from the vapour pressure good agreement is obtained in the case of carbamide and of calcium chloride in alcohol, but not for the sugar solutions. The osmotic pressures of sucrose solutions calculated from the heats of dilution by means of Porter's equation (A., 1918, ii, 64) agree well with the experimental values. O. J. WALKER.

Transport numbers of hydrogen chloride in ethyl alcohol. J. W. WOOLCOCK, (SIR) H. HARTLEY, and O. L. HUGHES (Phil. Mag., 1931, [vii], **11**, 222—225).—The most probable value for the transport number of the hydrogen ion at infinite dilution at 25° in hydrogen chloride solutions is given as $0·71\pm0·01$; this is derived from measurements of the *E.M.F.* of cells of the type Ag,AgCl|HCl in EtOH (C_1) : HCl in EtOH(C_2)|AgCl,Ag, with and without liquid junctions. F. G. TRYHORN.

Determination of transport numbers of metals in the electrolysis of their alloys. I. R. SPRINGER and R. FRENA (Monatsh., 1931, **57**, 112—164; cf. Kremann and others, A., 1930, 1253).—Amalgams of sodium, potassium, and tin, allowed to solidify in capillary tubes, have been electrolysed at various current densities and the resulting changes in composition along the length of the tube determined. From the results of these experiments and from data furnished by similar experiments by Kremann and his co-workers it is found that the nineteen alloys studied fall into three groups, viz., (1) potassium, lead, and tin amalgams, tin–lead, tin–antimony, bismuth–tin, bismuth–cadmium, and potassium–sodium, in which one component migrates to the cathode and the other to the anode; (2) amalgams of sodium and of bismuth, tin–zinc, tin–aluminium, silver–aluminium, silver–bismuth, and tin–cadmium, in which the components either behave as in (1) or both migrate to the anode, according to experimental conditions; and (3) silver–tin, silver–antimony, and lead–sodium, in which both metals migrate to the anode under all the conditions observed. It is considered that the normal behaviour is that shown by the first group, and that divergences are largely attributable to errors in analysis or to irregularities of composition not due to passage of the current. F. L. USHER.

Electrolytic transference of water in 0·1*N* solutions of hydrobromic and hydriodic acids and in *N*-potassium iodide solution. J. BABOROVSKÝ and A. WAGNER (Coll. Czech. Chem. Comm., 1931, **3**, 53—60).—Measurements of the electrolytic transference of water (ω) have been made by Baborovsky's method (A., 1927, 1140; cf. A., 1928, 954). In hydrobromic acid solutions the presence of a membrane increases the quantity of electrolyte transferred, and the values of ω are not the same at the anode and cathode. Hydriodic acid solutions, even at 0·1*N* concentration, yield uncertain results owing to oxidation and the formation of complexes, whilst difficulties arise with potassium iodide solutions as a result of the dissolution of silver iodide from the (silver) electrodes. After correction for this disturbance the anode values of ω are smaller than the cathode values. The transport number of the cation derived from the cathode measurements shows the better agreement with the accepted values. In *N* solution the iodide ion is associated with 2 mols. of water. H. F. GILLBE.

Conductivity of electrolytes. III. Design of cells. G. JONES and G. M. BOLLINGER (J. Amer. Chem. Soc., 1931, **53**, 411—451; cf. A., 1929, 1161).—The ratio of the resistances of two cells filled with portions of the same solution varies with the conductivity in a less complicated manner than that observed by Parker (A., 1923, ii, 530, 722). The variations, when high frequencies and resistances are used to eliminate polarisation errors, have been traced to the existence, between the parts of the cell of opposite polarity, of a capacitative shunt which, in the usual design of cell, is of sufficient magnitude to make the observed resistance of the electrolyte less than the true resistance. The error varies as the square of the capacitance and directly as the resistance in the shunt, but is independent of the platinisation of the electrodes. With horizontal cells in which the distance between the vertical filling and electrical contact tubes of opposite polarity is about 15 cm., the effect is eliminated, and provided polarisation is absent, the results are trustworthy to 0·01%. The suitability of a cell is demonstrated by the constancy of the apparent resistance when the frequency is varied between 1090 and 4000 cycles per sec. The ratio of the resistances of a pair of cells filled with a common solution is independent of the electrolyte (cf. Randall and Scott, A., 1927, 421) and thus there

is no longer any support for Parker's theory that adsorption is responsible for the effect previously observed (*loc. cit.*). J. G. A. GRIFFITHS.

Conductivity measurements in methyl ethyl ketone and acetone. P. WALDEN and E. J. BIRR (Z. physikal. Chem., 1931, **153**, 1—51).—Methyl ethyl ketone was purified until the product had a conductivity of 5×10^{-8} reciprocal ohm. Measurements of density and viscosity were made at different temperatures, and the variation of density with temperature can be represented by the formula $d^t=0{\cdot}82737(1-0{\cdot}0012635t)$. The conductivities of solutions of the following substances in methyl ethyl ketone have been determined at 25° up to dilutions of $10^{-5}M$: tetramethylammonium picrate, tetraethylammonium picrate, iodide, perchlorate, chloride, bromide, and nitrate, tetra-*n*-propylammonium picrate, iodide, and perchlorate, tetra-*n*-butylammonium picrate, tetra*iso*amylammonium picrate, iodide, and perchlorate, ethylammonium picrate, bromide, and iodide, *iso*butylammonium picrate and chloride, *iso*amylammonium picrate and chloride, *n*-cetylammonium picrate dimethylammonium picrate, diethylammonium picrate chloride, and iodide, di*iso*amylammonium picrate and chloride, triethylammonium picrate and chloride, tri*iso*amylammonium picrate, chloride, and iodide, lithium picrate, sodium picrate and iodide, potassium picrate and iodide, silver picrate, barium perchlorate, cadmium picrate and iodide, mercuric chloride and iodide. Conductivity values have also been determined for solutions of the picrates of lithium, tetra-*n*-propylammonium, tetra-*n*-butylammonium, and tetra*iso*amylammonium in acetone. The results establish the validity of Kohlrausch's square-root rule, the law of independent migration of ions, Stokes' law for ions, and Walden's rule for these non-aqueous solutions. Both strong and weak electrolytes exist. The ionic mobilities in methyl ethyl ketone and in acetone have been calculated from Walden's rule and calculation has been made of the degree of solvation of alkali and halogen ions in methyl ethyl ketone, methylamine, and ethylene dichloride. E. S. HEDGES.

Conductivity data of aqueous mixtures of hydrogen peroxide and organic acids. W. H. HATCHER and M. G. STURROCK (Canad. J. Res., 1931, 4, 35—38).—The conductivities of solutions of formic, acetic, propionic, and glycollic acids containing hydrogen peroxide have been determined. With formic acid the conductivity decreases to a constant value within 4 hrs., whereas with glycollic and acetic acids there is at first a rapid fall and then a slow rise to a constant value, which is attained within 30 hrs. The conductivity of the propionic acid solutions rises continuously to a maximum, and the change is completed within 3 hrs. It appears that the conductivity of the peracid formed in each case approximates to that of the complex ultimately formed.
H. F. GILLBE.

Interfacial electrical conductivity. K. ŠANDERA (Coll. Czech. Chem. Comm., 1931, **3**, 96—102).—The influence of solids of large surface area, such as sand and activated carbon, on the conductivity of potassium chloride solutions has been studied. The size and form of the grains have a pronounced influence. Thus finely-divided calcium carbonate causes an increase of conductivity, and the effect increases with the volume of the powder added, whereas with sand, as a result of the smaller surface and greater screening effect, the conductivity decreases; with activated carbon the influence of the surface is still more marked. A theoretical equation relating the change of conductivity with the volume of solid present is in fair agreement with most of the observed values.
H. F. GILLBE.

Electro-osmosis and electrolytic transference in aqueous solutions. J. VELÍŠEK and A. VASÍČEK (Coll. Czech. Chem. Comm., 1931, **3**, 111—115).—A discussion of the two principal methods for the study of electro-osmosis, viz., the chemical and the physical. The latter, although simpler and more rapid, is the less accurate, and does not serve to distinguish the fraction of the total transference due to the electrolyte and that due to the solvent. H. F. GILLBE.

Electro-endosmosis. IV. Electro-endosmosis of some organic liquids against a glass surface. F. FAIRBROTHER and M. BALKIN (J.C.S., 1931, 389—403).—The "bubble-tube" method has been used to measure the velocity of electro-endosmosis of formamide, furfuraldehyde, nitrobenzene, *o*-nitrotoluene, ethyl ether, chloroform, acetone, *n*-propyl alcohol, *n*-butyl alcohol, benzaldehyde, aniline, propionic acid, benzene, carbon tetrachloride, and water through a diaphragm of sintered Jena Geräte glass powder. Considerable attention was given to the purification and drying of the liquids, as it was observed that traces of impurities gave erroneous results even in solvents of low ionising power. The electrokinetic potential has been calculated in each case and the values are of the same order of magnitude. Benzene and carbon tetrachloride, having practically no dipole moment, give no electro-endosmosis even under a *P.D.* of 910 volts across a diaphragm only 5 mm. thick; ether is negatively charged towards the glass, and the rest of the organic liquids and water are positively charged. The product of the velocity of electro-endosmosis and the viscosity of the liquid increases with the dielectric constant, but the relation is not linear. The connexion between the velocity of electro-endosmosis and the dipole moment of the molecules is discussed, and the experimental results indicate a close relation between the electro-endosmosis and the product of the number of molecules in the interface and their dipole moment. E. S. HEDGES.

Effect of breadth of junction on *E.M.F.* of simple concentration cell. G. SCATCHARD and and T. F. BUEHRER (J. Amer. Chem. Soc., 1931, **53**, 574—578; cf. A., 1925, ii, 398).—The *E.M.F.* of a cell is independent of the thickness of a junction of the "mixture boundary" type (cf. Henderson, A., 1908, ii, 655). The *E.M.F.* of the cell Hg,HgCl|HCl(C_1)|HCl(C_2)|HgCl,Hg increases by 0·005—0·058 millivolt when the flowing liquid junction is made very thin. This effect is attributed to thermal changes at the boundary due to mixing of the solutions.
J. G. A. GRIFFITHS.

Change of *E.M.F.* of zinc with thermal working. A. SCHUKAREV and L. VERESCHTHAGIN (Physikal. Z.,

1931, **32**, 230).—A test piece of zinc was heated at 200° for a long period, and the changes in its *E.M.F.* were examined. There were marked variations with time, but the curve obtained does not correspond with any simple function. A. J. MEE.

Temperature measurements at working electrodes. IV. B. BRUZS (Z. physikal. Chem., 1931, **153**, 309—319; cf. A., 1930, 546).—A method is described for measuring the heat effect at a working electrode. Determinations at a $Hg|Hg_2^{++}$ interface in 0·1—1·0*M*-perchlorate and -nitrate solutions yield for the entropy of the mercurous ion in *M* solutions 29±1 g.-cal. per degree; the entropy increases slowly with decrease of concentration. H. F. GILLBE.

Electrochemistry of magnesium. S. BODFORSS (Z. physikal. Chem., 1931, **153**, 83—106).—The potential of magnesium has been measured in solutions of magnesium sulphate containing sulphuric acid, solutions of magnesium chloride containing hydrochloric acid, and in acetate, citrate, and tartrate buffer solutions. The results indicate that the magnesium potential is a function of the hydrogen-ion concentration of the solution. As the hydrogen-ion concentration is increased the potential becomes more negative, passes through a maximum, and then moves in the positive direction. The potential also depends on the nature of the anion, for at constant hydrogen-ion concentration the negative potential increases in the order acetate<tartrate<citrate. The addition of neutral substances which are known to promote the formation of complexes (*e.g.*, pyrocatechol) causes the potential to become more negative. A marked increase of the negative potential is brought about by the addition of ammonium salts, carbon dioxide, and carbon monoxide, even in small concentrations. The small quantities involved cannot exert any considerable influence on the reaction $Mg \longrightarrow Mg^{\cdot\cdot}+2\ominus$, and it is believed that this equation does not represent the process determining the electrode potential. The evidence adduced leads to a working hypothesis that the potential is determined by the reaction $Mg \longrightarrow Mg^{\cdot}+\ominus$ or $2Mg \longrightarrow Mg_2^{\cdot\cdot}+2\ominus$.
E. S. HEDGES.

Potential of lead–gold alloys. F. GRIENGL and R. BAUM (Monatsh., 1931, **57**, 165—176; cf. Laurie, J.C.S., 1894, **65**, 1031).—The curve obtained by plotting potential against composition is completely changed by tempering in air at 200—300° below the m. p., which causes a minimum to appear at 60% Au. This effect is attributed to a layer of oxide, since the potential of an alloy with 65% Au tempered in nitrogen is the same as that of the untempered metal. The results support Laurie's experiments and indicate that the potentials of the compounds AuPb and Au_2Pb are near to that of lead. F. L. USHER.

Reduction potential of quadrivalent to tervalent iridium in hydrochloric acid solution. S. C. WOO (J. Amer. Chem. Soc., 1931, **53**, 469—472).—The *E.M.F.* of the cell $Ir|IrCl_6'''(c)+IrCl_6''(c)+HCl(1N)|HCl(1N)|H_2(1\text{ atm.}),Pt$ at 20° and 25° is −1·0313 −1·0264 volts, respectively, when *c*=0·002—0·008*f*. The reduction potential of the reaction $IrCl_6'''(c)+1N\text{-}HCl=IrCl_6''(c)+1N\text{-}HCl+e$ is 1·021 at 25°, referred to the normal hydrogen electrode; the corresponding changes of free energy and heat content are −23,540 and −30,400 g.-cal., respectively.
J. G. A. GRIFFITHS.

Reduction potential of thymoquinhydrone. E. BILLMANN and J. MUUS (Ber., 1931, **64**, [*B*], 310—314).—Measurements of the *E.M.F.* of Pt^+|benzquinhydrone, 0·1*N*-HCl, thymoquinhydrone|Pt^- give 0·5923 and 0·5867 volt for the reduction potential of the thymoquinhydrone electrode at 18° and 25° respectively. Similarly the combination Pt^+|benzoquinhydrone, 0·01*N*-HCl, 0·09*N*-KCl, thymoquinhydrone|Pt^- gives 0·5927 and 0·5866 volt respectively. H. WREN.

Oxidation–reduction potentials of alkali chlorites. II. G. R. LEVI and D. GHIRON (Atti R. Accad. Lincei, 1930, [vi], **12**, 158—161).—At 20° the *E.M.F.* of the cell $Pt^-|0\cdot1N\text{-}KClO_2[\text{or }Ca(ClO_2)_2]:KMnO_4,0\cdot1N|Pt^+$ is 0·175 volt. In discharge, the chlorite is oxidised to chlorate and the permanganate reduced to manganese dioxide. For the cell $Pt^-|KClO_2, 0\cdot1N: NaClO, 0\cdot1N|Pt^+$ the initial *E.M.F.* at 20° is 0 084 volt, but rises in a few hours to 0·100 volt and then diminishes regularly with time. The reaction $NaClO_2+NaClO=NaCl+NaClO_3$ occurs. The cells $Pt^+|KClO_2, 0\cdot1N: H_2O_2, 0\cdot1M|Pt^-$, and $Pt^+|KClO_2, 0\cdot1N: FeSO_4, 0\cdot1M|Pt^-$ both have an *E.M.F.* of 0·25 volt. F. G. TRYHORN.

Electrokinetic potentials. VI. Electrical phenomena at interfaces. VII. Temperature coefficient of the ζ-potential. H. B. BULL and R. A. GORTNER (J. Physical Chem., 1931, **35**, 308—330, 456—465; cf. A., 1930, 1124).—VI. The ζ-potential and surface conductance at a cellulose interface have been measured for aqueous solutions (up to $1\cdot6\times10^{-3}N$) of sodium, potassium, calcium, magnesium, and thallic chlorides, and potassium carbonate, sulphate, and phosphate by the streaming potential method previously described (*loc. cit.*). In general, the ζ-potential decreases with an increase in concentration of the electrolyte in the aqueous phase, but this decrease may be accompanied by an increase in the charge on the particle. The decrease in ζ-potential is more nearly related to a decrease in the thickness of the double layer. In agreement with the results of McClendon (A., 1928, 22), the thickness of the double layer is found to decrease with an increase in concentration of the electrolyte. From Smoluchowski's equation expressions have been derived for the charge per unit area at the interface and for the thickness of the double layer. In connexion with the effect of electrolytes on the stability of a colloid, the results suggest that salts do not reduce the charge on the particle to zero or to a critical value, but decrease the thickness of the double layer, allowing the particles to approach closely enough to adhere to each other.

VII. The temperature coefficients of the ζ-potential for the interfaces water–cellulose, cellulose–sodium chloride ($10^{-4}N$), and ethyl alcohol–cellulose have been determined between 20° and 51°. A marked positive coefficient is shown at the last-named interface, but the relationship is not strictly linear. The temperature coefficient is higher than those for the other two systems. A maximum at approximately 40°

occurs at these two interfaces. The temperature coefficient of aqueous systems can generally be neglected in streaming potentials measured under ordinary laboratory conditions. L. S. THEOBALD.

Theory of dissolution of metals. II. M. STRAUMANIS (Z. physikal. Chem., 1931, **153**, 107—111).—A reply to the criticisms of Thiel (this vol., 46; cf. Straumanis, A., 1930, 1125). The "difference effect" cannot be treated as a pure resistance phenomenon. The displacement of potential in the positive direction through the electrolytic dissolution of metals is due partly to the vectorial properties of the metal space lattice. E. S. HEDGES.

[Theory of dissolution of metals.] A. THIEL (Z. physikal. Chem., 1931, **153**, 112).—Polemical (cf. preceding abstract). E. S. HEDGES.

Influence of foreign gases in gaseous decompositions. N. NAGASAKO (Z. physikal. Chem., 1931, B, **11**, 420—424).—The effect of the presence of a foreign gas on the course of a unimolecular gaseous decomposition can be expressed by introducing an empirical constant into the usual formula for the unimolecular reaction coefficient. This empirical constant is evaluated for several indifferent gases and applied to the decomposition of nitrous oxide and of methyl ether; good agreement is found between the observed and calculated velocity coefficients. F. L. USHER.

Debased ["entartete"] explosions and periods of induction. N. SEMENOV (Z. physikal. Chem., 1931, B, **11**, 464—469).—Theoretical. Explosive gas reactions, and the thermal decomposition of explosive solids or liquids, in which considerable initial retardation is observed, are considered as autocatalytic processes in which the catalyst is an intermediate rather than an end product. F. L. USHER.

Fifty years' experimental research on the influence of steam on the combustion of carbonic oxide. W. A. BONE (J.C.S., 1931, 338—361).—The third Liversidge lecture delivered on Dec. 11. R. CUTHILL.

Flame speeds in the "inflammation" and "detonation" of moist carbon monoxide–oxygen mixtures. W. A. BONE and R. P. FRASER (Proc. Roy. Soc., 1931, A, **130**, 542—551; cf. Bone, Fraser, and Witt, A., 1927, 424).—The results of measurements by the electrical and photographic methods (*loc. cit.*) of the initial speeds of inflammation of moist carbon monoxide–oxygen mixtures, when ignited at the ordinary temperature and atmospheric pressure at the open end of a glass tube 2·5 cm. internal diameter and 126 cm. long, the other end being closed, show that the "lower limit" mixture for inflammation is one containing 15—20% of carbon monoxide, the explosion range extending up to about 92·5% of the monoxide. The mixture giving the maximum speed contains about 80% of carbon monoxide. A photographic method for measuring the speed of detonation of moist carbon monoxide–oxygen mixtures is described, two photographs of the horizontally-advancing detonation flame being taken at distances 60 m. apart. The final establishment of detonation (as distinct from the "pre-detonation" phase) is proved by the pronounced banded appearance of the advancing flame and the constancy of the flame speed. The experimental results show that the "detonation range" lies between about 40 and 80% carbon monoxide content, the observed rates of detonation in a tube 1·3 cm. internal diameter all lying between 1700 and 1800 m. per sec., approximately. The rate is sensibly higher in a tube 2·5 cm. in diameter. A well-marked maximum rate of detonation (as also of inflammation) occurs at the $3CO+O_2$ mixture, instead of at the theoretical $2CO+O_2$ mixture, indicating that whereas an excess of carbon monoxide (up to $3CO+O_2$) increases the flame speed, a corresponding excess of oxygen always diminishes it. This circumstance is unaltered by diluting the medium with argon, helium, or nitrogen. L. L. BIRCUMSHAW.

Effect of anti-knock materials on the speed of flame in a closed tube. Y. NAGAI.—See B., 1931, 188.

Extinction of benzine–air explosions by carbon tetrachloride. A. H. BELINFANTE.—See B., 1931, 188.

Thermal decomposition of nitrogen pentoxide at low pressures. J. H. HODGES and E. F. LINHORST (Proc. Nat. Acad. Sci., 1931, **17**, 28—33).—The velocity of thermal decomposition of nitrogen pentoxide has been measured at 35° and pressures between 0·12 and 0·001 mm. The reaction is unimolecular at nitrogen pentoxide partial pressures greater than 0·06 mm., and the velocity coefficient is 0·00801; at lower partial pressures the unimolecular coefficient decreases, and at about 0·004 mm. the reaction becomes bimolecular and has then a velocity coefficient of about 1·2. H. F. GILLBE.

Action of water vapour on phosphorus. J. ZAWADZKI and T. BORUCKI (Przemysł Chem., 1931, **15**, 76—82).—The velocity of reaction between phosphorus and water vapours in a porcelain tube is very small, even at 1000°. The presence of ferric oxide greatly accelerates reaction, practically the whole of the phosphoric oxide produced combining with the catalyst. When ferric phosphate is used as the catalyst, it retains a large proportion of the phosphoric oxide produced at the commencement of the reaction; only after saturation of the catalyst are phosphoric oxide and hydrogen found in equivalent proportions in the reaction mixture. Under these conditions the reaction proceeds very rapidly at 650°. The amounts of phosphine produced diminish as the reaction temperature is raised. Cupric oxide absorbs phosphorus from the vapours with the formation of phosphides; it only very feebly catalyses the reaction of formation of phosphoric oxide. R. TRUSZKOWSKI.

Kinetics of polymerisation of ethylene at pressures above 1 atm. R. N. PEASE (J. Amer. Chem. Soc., 613—619; cf. A., 1930, 709; Wheeler and Wood, *ibid.*, 1399).—The polymerisation of ethylene at 2·5, 5, and 10 atm. to C_nH_{2n} hydrocarbons in a copper bomb at temperatures between 350° and 500° is approximately bimolecular; the proportion of liquid polymeride increases during the reaction, but little hydrogen and methane are produced. The

temperature coefficient is 2·3 per 25°. A mechanism is proposed which requires that the reaction at low pressures should be of the third order.

J. G. A. GRIFFITHS.

Decomposition of hypobromous acid. F. POLLAK and E. DOKTOR (Z. anorg. Chem., 1931, **196**, 89—112).—Dilute (up to $0·3M$) solutions of hypobromous acid may be prepared by treatment of concentrated silver nitrate solution with bromine and distillation of the filtered solution in a vacuum. If mercuric oxide be used, the mercuric bromide remaining in solution causes reversal of the reaction on heating, whilst silver carbonate reacts but slowly and silver oxide causes decomposition of the acid. The distillate contains also nitric acid, bromine, and hydrobromic acid. The rate of decomposition of hypobromous acid diminishes with time. Of the two probable modes of decomposition, viz., $5HBrO \longrightarrow HBrO_3+2H_2O+2Br_2$ and $4HBrO \longrightarrow O_2+2H_2O+2Br_2$, the former predominates in the dark at the ordinary temperature; this reaction is bimolecular and appears to be independent of the hydrogen-ion concentration of the solution. Bubbling nitrogen through the solution is without influence. Although bromous acid is a probable intermediate product of the decomposition, it does not appear to be formed in measurable quantity.

H. F. GILLBE.

Velocity of dissolution of oxygen in water. IV. S. MIYAMOTO and A. NAKATA (Bull. Chem. Soc. Japan, 1931, **6**, 9—22; cf. this vol., 175).—The velocity of dissolution of oxygen in water has been determined by measuring the velocity of oxidation of sodium sulphite solutions under conditions of zero concentration of oxygen in the surface solution/oxygen. The velocity of oxidation is independent of the concentration of sodium sulphite and is proportional to the boundary surface area. It is assumed that only those molecules of oxygen of which the component of velocity perpendicular to the boundary surface is greater than a threshold value u_0 can enter the liquid phase. The value of u_0 is found to be $1·65\times10^5$ cm. per sec. and is independent of the temperature. The dissolution velocities of oxygen in water determined by various workers are compared.

O. J. WALKER.

Kinetics of the transformation of the various forms and hydrates of calcium sulphate. W. FEITKNECHT (Helv. Chim. Acta, 1931, **14**, 85—90).—Measurements have been made of the velocity of dehydration of the various hydrated forms of calcium sulphate. The removal of water was allowed to proceed in a high vacuum over phosphorus pentoxide, and the resulting products were examined by means of the Debye–Scherrer diagrams. The dihydrate gives a characteristic S-shaped velocity–time curve, showing that the decomposition proceeds from single localised nuclei, which in the case of well-formed crystals require a certain time for their formation. The time increases rapidly with fall of temperature, so that at 20° the dihydrate can be kept for several hours in a vacuum without losing water. The crystalline hemihydrate shows no induction period, the dehydration velocity being greatest at the beginning. The resulting product, soluble anhydrite, has a lattice different from that of the hemihydrate. In this case the decomposition does not proceed from single nuclei, but takes place uniformly throughout the solid phase. In the transformation of the soluble anhydrite to native anhydrite there is a discontinuous change in the lattice structure.

O. J. WALKER.

Reaction velocity in the system Ag_2CO_3 Ag_2O+CO_2. W. D. SPENCER and B. TOPLEY (Trans. Faraday Soc., 1931, **27**, 94—102).—Reaction velocity measurements in the above system (cf. A., 1930, 39) have been extended to include the recombination of silver oxide with carbon dioxide and the decomposition of the "synthetic" carbonate so formed. The type of curve obtained for the recombination depends on the pressure of the gas and the state of dryness of the solid. At pressures several times greater than the equilibrium pressure the curves are in two distinct parts. The factors determining the amount of reaction in an assigned time interval are discussed, and the possibility of an optimum pressure is accounted for. In the region underlying the zone in which recombination has occurred the chemically unchanged silver oxide is made less reactive, but when this modified oxide is converted into carbonate the oxide which it yields on subsequent decomposition is as reactive as before. Water vapour appears to promote the reaction indirectly by facilitating penetration of carbon dioxide through the carbonate formed initially. The rapid reaction in the first part of the recombination is not much affected by a degree of dryness sufficient to inhibit almost completely the second part.

O. J. WALKER.

Kinetics of dissolution. A. S. FEDOROV (J. Russ. Phys. Chem. Soc., 1930, **62**, 1859—1861).—Benzoic acid is fused on to a glass rod, which is rotated successively in four 100-c.c. portions of water, for 10, 15, 20, and 30 min., and the acidity of each portion is determined. The rate of dissolution is given by $K=\{\log_e C_s-\log_e (C_s-C)\}/t$, where C_s is the saturation concentration, and C is the concentration found after time t.

R. TRUSZKOWSKI.

Rate of dissolution of metals in acids. Theory of local elements. W. GUERTLER and B. BLUMENTHAL (Z. physikal. Chem., 1931, **152**, 197—234).—The rate of dissolution of zinc in hydrochloric acid has been studied from the point of view of the theory of Ericson-Auren and Palmaer. The chemical and mechanical conditions under which observations are reproducible were determined by preliminary experiments with iron, nickel, and copper. In the main series of experiments zinc was used, the rates of dissolution in $0·1N$ and $0·2N$ acid of two specimens, containing, respectively, 0·08 and 1·01% of lead, being measured. Contrary to the statement of Ericson-Aurén and Palmaer, the rate is not proportional to the concentration of acid nor to the electrical conductivity of the liquid, but is determined chiefly by the overvoltage of hydrogen, which decreases during the course of the dissolution in consequence of the increasing surface area of the cathodic impurities and the resulting diminution of the cathode current density. When the variation of the hydrogen overvoltage with time is taken into account, the observed rate of dissolution is in agreement with the theory of

local elements and can be quantitatively expressed by the formula of Ericson-Aurén and Palmaer.

F. L. USHER.

Corrosion of copper. L. W. HAASE.—See B., 1931, 204.

Corrosion of lead. M. WERNER.—See B., 1931, 206.

Methods of corrosion testing. E. K. O. SCHMIDT.—See B., 1931, 204.

Effect of carbon tetrachloride, trichloroethylene, and tetrachloroethane on metals. J. FORMÁNEK.—See B., 1931, 206.

Corrosion of iron by carbon tetrachloride. J. MILBAUER (Coll. Czech. Chem. Comm., 1931, 3, 73—75).—The presence of ethyl alcohol increases the rate of corrosion of iron by boiling carbon tetrachloride. Data are given of the quantity of iron dissolved in 1 hr. by various mixtures of the tetrachloride, water, and alcohol; the maximum effect is produced with a mixture containing carbon tetrachloride 70%, water 2·7%, and alcohol 27·3%. Other chlorinated hydrocarbons behave similarly, although the attack is less rapid.

H. F. GILLBE.

Kinetics of reduction of cuprous oxide. I. Reduction at low pressures. Oxidation of copper at low pressures. F. J. WILKINS (J.C.S., 1931, 330—335).—The rate of reduction of cuprous oxide by hydrogen at a pressure of 0·03—0·15 mm. and at 144—250° under such conditions that the area of the interface copper–cuprous oxide remains constant and the water is removed as it is formed may be represented by the equation $\log_e p_0/p = kt$, where p_0 is the initial gas pressure, p the pressure after time t, and k is a constant. The heat of activation calculated from the temperature coefficient is 18,000 g.-cal. It is considered that the reduction consists of the following consecutive reactions: (a) condensation of hydrogen at the oxide–hydrogen interface, (b) evaporation of hydrogen from this interface into the body of the oxide, (c) diffusion of hydrogen through the cuprous oxide, (d) reaction between hydrogen and oxide at the oxide–metal interface, (e) diffusion of water from the reaction centre through the oxide layer, (f) desorption of the water. If it is assumed that the rate of the reaction as a whole is determined by the rate of stage (b), the experimental velocity equation is accounted for, and the heat of activation must be supposed to represent the heat of evaporation of adsorbed hydrogen into cuprous oxide.

Measurements of the rate of oxidation of copper at oxygen pressures of about 0·01 mm. at 144—218° are in agreement with the theory previously advanced (following abstract).

R. CUTHILL.

Kinetics of oxidation of copper: the establishment of sorption equilibria. F. J. WILKINS (Phil. Mag., 1931, [vii], 11, 422—432).—A general equation for the kinetics of the oxidation of copper is deduced on the assumption that the oxidation is the resultant of the following consecutive processes: condensation of oxygen at the oxide–oxygen interface, evaporation of the oxygen into the oxide, diffusion of oxygen through the oxide (cf. A., 1930, 1129). A simplified form of the equation, applicable when sorption equilibrium between the oxide and gas phase has been reached, *i.e.*, when the oxide has reached absorption and adsorption equilibrium, is in satisfactory agreement with the experimental data. The time necessary for the establishment of sorption equilibrium increases with increase in the degree of activation of the surface, which is considered to show that oxygen adsorbed on cuprous oxide is able to diffuse laterally.

R. CUTHILL.

Detonation of solid explosives. P. LAFFITTE and M. PATRY.—See B., 1931, 224.

Acid–base catalysis according to Bronsted. I. M. KOLTHOFF (Chem. Weekblad, 1931, 28, 110—121).—A survey.

H. F. GILLBE.

Inhibition of chemical reactions. IV. Site of anti-oxygenic action. Oxidation of sodium sulphite and benzaldehyde. K. C. BAILEY and (MISS) V. H. FFRENCH (J.C.S., 1931, 420—428; cf. A., 1930, 429).—By passing a stream of air bubbles through an aqueous solution of *iso*propyl or *sec.*-butyl alcohol and analysing the bubble films, it has been shown that a layer of alcohol molecules 1—2 mols. deep is formed on the surface of the solution when the solute concentration reaches about 1·5—2 g. per litre. When these alcohols are used to inhibit the oxidation of sodium sulphite in aqueous solution, the graph of oxidation velocity against alcohol concentration does not, however, show any discontinuity at the above concentration. It is therefore concluded that the mechanism of the autoxidation of benzaldehyde is not the same as that of the oxidation of sodium sulphite, and it seems possible that in the former reaction accumulation of the inhibitor at the gas–liquid interface may be the deciding factor in inhibition.

R. CUTHILL.

Properties of the chlorides of sulphur. V. Metastable states. T. M. LOWRY and G. JESSOP (J.C.S., 1931, 323—329; cf. A., 1930, 842).—The period of induction in the combination of sulphur monochloride with chlorine may be eliminated by adding iodine as catalyst and reduced by adding antimony pentachloride. The autocatalytic character of the reaction is ascribed to the presence in the reaction product of the chlorides SCl_4 and S_3Cl_4. Even at −80° sulphur dichloride and chlorine combine instantaneously to form the solid tetrachloride, and if an equilibrium mixture of chlorine, tetrachloride, and dichloride at −20° is frozen, then heated at −20° again, the original position of equilibrium is reached at once. The separation of tetrachloride on freezing a liquid mixture having the composition of the dichloride exhibits, however, a time-lag, and the same is true of the melting of solid tetrachloride in liquid dichloride. From observations on the density of such a liquid mixture it is deduced that the equilibrium concentration of dichloride is about 85% at 0° and about 75% at 100°.

R. CUTHILL.

Catalytic influences in three-carbon tautomerism. II. Action of acid catalysts on ketones. G. A. R. KON (J.C.S., 1931, 248—251; cf. A., 1929, 927).—In the isomeric change at 100° of *cyclo*hexylideneacetone into the βγ-form under the influence of aqueous-alcoholic sulphuric, hydrochloric,

or oxalic acid, equilibrium is reached when 23% remains unchanged. The presence of impurities was the reason for the somewhat different value obtained using alkaline catalysts, but acid catalysts, especially oxalic acid, act much less rapidly than alkaline catalysts. The equilibrium point in the isomerisation of *iso*pulegone in presence of alcoholic sulphuric acid at 100° or sodium ethoxide at 25° corresponds with pure pulegone. R. CUTHILL.

Active iron. VI. Characterisation by benzidine-peroxidase and catalase [reactions]. A. SIMON and T. REETZ (Annalen, 1931, 485, 73—112).—The peroxidase activity of ferrous hydrogen carbonate (I), ferric chloride (II), sodium pentacyanomonoaquoferroate (III), and hæmoglobin, measured by the benzidine–hydrogen peroxide method (this vol., 57) in aqueous-alcoholic solutions of varying p_H, is greatest at p_H 3·92 (acetic acid, slightly different results being obtained with hydrochloric acid); under identical conditions I and II are equally active, III is less active, and hæmoglobin has an activity of a totally higher order. Sodium pentacyanomonoaquoferriate (IV) has a maximum activity similar to that of II at p_H 7·2. In aqueous solution the relation of activity to p_H is approximately the same except that III and IV now have their maxima at p_H 5, but the activity itself is much higher in the cases of I and II than of III and IV.

The identical behaviour of ferrous and ferric salts is due to the equilibrium $Fe^{\cdot\cdot} \rightleftharpoons Fe^{\cdot\cdot\cdot}$ resulting from the simultaneous oxidising and reducing properties of the solution, and the maxima at p_H 3·92 to the suppression of ionisation in more alkaline solutions and irreversible oxidation of ferrous to ferric ions in strongly acid media. Qualitative experiments show that at p_H 4 ferric salts can oxidise benzidine to benzidine-blue, but that the power is lost at p_H 2. Potential measurements confirm this, and indicate that the oxidation potential of benzidine di-imide, which is stable at p_H 2, is greater than that of ferric salts; in agreement with this, ferrous salts are immediately oxidised by the di-imide to ferric salts. The different behaviour of aqueous and alcoholic solutions is shown to be due to the oxidation of alcohol to acetaldehyde by hydrogen peroxide in the presence of ferrous iron (ferrous salts or ferric salts and benzidine); this reaction is catalysed to a much smaller extent by the complex salts or by hæmoglobin.

The peroxidase and catalase activity of mineral water (Canstatt) is slightly inferior to that of I, but of the same order, and is undoubtedly due to ferrous ions. The difference in behaviour of natural waters and synthetic ferrous hydrogen carbonate solutions observed by Baudisch is confirmed, and is due to incomplete dissolution of the iron which is present as an extremely fine suspension rapidly converted into ferrous carbonate on keeping: $Fe+Fe(HCO_3)_2=2FeCO_3+H_2$. This reaction and the direct oxidation of the solution are catalysed by light, but a solution that maintains its activity indefinitely, even in the light, if oxygen is completely excluded is obtained by filtration of the solution prepared in the usual way under a high pressure of carbon dioxide.

The reduction of nitrates to ammonia by freshly-prepared ferrous hydroxide or carbonate in neutral solution in presence of oxygen (Baudisch, A., 1920, ii, 687) also occurs in absence of oxygen. Although reduced by small amounts of alkali, presumably on account of suppression of ionisation, the activity is regained in strongly alkaline solutions, possibly on account of dissolution of the iron as ferrite. In this case also preparations maintain their activity if preserved in complete absence of air.

The catalase activity of iron, measured by the velocity of decomposition of hydrogen peroxide in aqueous solution, is not influenced to the same extent by the hydrogen-ion concentration as is the peroxidase effect, although the ill-defined maxima are approximately the same. Ferrous salts (I and ferrous sulphate) show great activity, slightly dependent so far as magnitude is concerned on the anion, but this is rapidly lost on account of oxidation to the inactive ferric salt. The complex salts (III and IV) have an activity of a lower order, which, however, is almost unchanged with time. Hæmoglobin exerts its maximum activity at p_H 4·95, and only slightly less at p_H 7·2, and in general behaviour resembles the complex salts, except that its activity is of a considerably higher order. The activity of ox-blood is still greater, and reaches a maximum at p_H 7·2.

It is concluded that in the compounds I—IV the activity is a function of the ferrous ion, either present originally, or formed during the reaction. Hæmoglobin and blood possess in addition a specific activity. H. A. PIGGOTT.

Catalysis of hydrogenation. A. S. GINSBERG and A. P. IVANOV (J. Russ. Phys. Chem. Soc., 1930, 62, 1991—1999).—A very active catalyst can be prepared by the addition of palladium or platinum chloride to 10 to 20 times its weight of powdered metal, the best results being given by aluminium, nickel, magnesium, beryllium, iron, tungsten, and tin, whilst arsenic, tellurium, zinc, silver, and mercury are unsuitable for the purpose. This catalyst is particularly suitable for the hydrogenation of aliphatic compounds, aromatic compounds being reduced only very slowly in its presence. R. TRUSZKOWSKI.

Catalytic hydrogenation. III. Presence of hydrogen ions among thermions as ordinarily obtained. O. SCHMIDT (Z. physikal. Chem., 1931, 152, 269—283; cf. A., 1928, 582).—The suggestion that catalytic hydrogenation may be due to reaction in the gas phase with hydrogen ions emitted by the heated metallic catalyst is not in agreement with the theory of thermionic emission. The experiments of Hüttemann, who reported the presence of such ions, have been repeated with an improved form of mass spectrograph, using heated wires of platinum and of palladium–silver. No hydrogen ions (whether H_2^+ or H^+) could be detected. This result in no way precludes the possibility of reaction with protons in the metal phase. F. L. USHER.

Catalytic reduction and hydrogenation of phenols by hydrogen under pressure. H. TROPSCH.—See B., 1931, 194.

Catalytic reduction of carbon monoxide at ordinary pressure. VII. Influence of alkalis on an iron–copper catalyst. S. KODAMA and K.

FUJIMURA (J. Soc. Chem. Ind. Japan, 1931, **34**, 14—16B).—With a fine iron-copper catalyst (1 : 1) prepared from the nitrates 140 litres of water-gas gave at 270°, with a space velocity of 230—240, 3·0 c.c. of oil together with a small amount of solid resembling vaseline. The addition of sodium carbonate (0·005—0·05 mol.) to the catalyst increased its initial activity and favoured the production of higher hydrocarbons. This increase in activity was, however, not permanent, and the unactivated catalyst retained its activity for a longer time. The loss of activity of the alkaline catalyst seems to be due to the deposition of the higher hydrocarbons on its surface. The best result, 3·1 c.c. of oil from 143 litres of gas, was obtained with a catalyst of the composition Fe : Cu : Na_2CO_3= 1 : 1 : 0·005. H. INGLESON.

Catalytic decomposition of cetyl alcohol. C. SANDONNINI and S. BEZZI (Atti R. Accad. Lincei, 1930, [vi], **12**, 154—158).—Analyses have been made of the products obtained by passing cetyl alcohol vapour over the oxides of aluminium, zinc, chromium, and iron at temperatures of 340—350°. The behaviour of cetyl alcohol is analogous to that of alcohols lower in the series. A yield of approximately 60% of hexadecylene is obtained in the reaction employing alumina. F. G. TRYHORN.

"Triatomic hydrogen." E. HIEDEMANN (Z. physikal. Chem., 1931, **153**, 210—240).—By the action of an electric discharge in hydrogen contained in a glass vessel at about 0·06 mm. pressure a small yield is obtained of a gas which is condensed by liquid air; on admitting a further supply of hydrogen and repeating the discharge, no action takes place unless the vessel is heated and degassed beforehand. The condensate is shown by physical measurements to be neither hydrogen nor water vapour, and its reaction with sodium indicates that it consists of a mixture of compounds containing 4 and 6 atoms of hydrogen in the molecule. All the reactions of "hyzone" are exhibited by the mixture, together with others which show it to be composed principally of silicon hydrides, with disilane predominating. The gas yields a positive reaction with Nessler's reagent, even in total absence of nitrogen, and a brown coloration with lead acetate solution, and reduces tungstic oxide to the dioxide; these reactions are given also by silicon hydride mixtures prepared in the usual manner. The extensive literature relating to "hyzone" is reviewed, and in all cases the substance described appears to be silicon hydride or hydrogen sulphide; there is no evidence whatever for the existence of triatomic hydrogen. H. F. GILLBE.

Hyzone [triatomic hydrogen]. R. SCHWARZ and P. ROYEN (Z. anorg. Chem., 1931, **196**, 11—25).—Comparative dilatometric measurements with argon and hydrogen subjected to the silent electric discharge at 25°, −76°, and −185° and at pressures of 3—4 mm. show that at low temperatures hydrogen undergoes a considerable contraction over a period of 70—80 min.; at the ordinary temperature the effect is masked by thermal phenomena. The magnitude of the contraction is compatible with the formation of a unimolecular adsorption layer such that saturation of the surface corresponds with about 60% of the maximum density of packing, calculated from a maximum adsorption coefficient of 10^6 atoms per cm.[2] A contraction of the order reported by Wendt and Landauer (A., 1922, ii, 369), viz., 27%, could not be realised, and is ascribed to a "clean-up" effect. There is thus no evidence for the formation of triatomic hydrogen during the silent electric discharge. H. F. GILLBE.

Formation of ammonia from its elements in the electric discharge. M. ALSFELD and E. WILHELMY (Ann. Physik, 1931, [v], **8**, 89—123).—The influence of temperature on the ammonia synthesis in the ozoniser discharge becomes marked at 400°, and is correlated with adsorption phenomena. The Townshend, corona, glow, and arc discharges are compared. On development of the negative corona from the Townshend discharge, a pronounced diminution in yield is brought about by traces of electrically negative gases. In the glow discharge the cathode fall is important. The positive column is less sensitive to pressure changes than the negative corona. The cathode material does not appreciably influence the yield except for platinum, where the catalytic effect increases the yield by 30%. In the anomalous cathode fall the yield per unit current is greater than in the normal cathode fall; an oxide cathode decreases this yield, but, calculated with respect to energy, the yield is almost the same, due to diminished potential across the tube. The dependence of yield on the ratio of nitrogen to hydrogen is the same for the corona and glow discharges. The maximum yield takes place when the cathode fall is a minimum, and when the nitrogen content is approximately 60%. A. B. D. CASSIE.

Influence of electric discharges in the Siemens tube on sulphur vapour. R. SCHWARZ and P. ROYEN (Z. anorg. Chem., 1931, **196**, 1—10).—The influence of the silent electric discharge on sulphur vapour admixed with argon at 465° has been investigated by dilatometric measurements. The increased expansion of the mixture as compared with that observed with argon alone is ascribed solely to thermal dissociation and not to a breakdown of the sulphur molecules under the action of the discharge, but the nature of the subsequent contraction indicates that triatomic molecules of sulphur may be formed. Further knowledge of the physical constants of sulphur is necessary before the results can be fully interpreted. H. F. GILLBE.

Reduction of arsenic acid and arsenates to arsine at the mercury cathode. I. W. V. LLOYD (Trans. Faraday Soc., 1931, **27**, 89—94).—The potential changes which take place at mercury and other cathodes during the reduction of arsenic acid in sulphuric acid solutions containing up to 180 mg. of elementary arsenic (in 10 c.c.) have been measured. The arsenic acid solution was admitted to the cathode during periods varying from 20 to 60 min. When measured by a commutator method the overvoltage of the mercury cathode decreases by 0·5 volt during the addition of the arsenic acid to a value representing the overvoltage of arsenic, which suggests that some arsenic is deposited on the mercury. The amount deposited is, however, very small. With uninter-

rupted current the decrease in overvoltage is less and varies directly with increasing concentration of the arsenic acid. In view of this decrease, the reduction of the whole of the arsenic acid to arsine is difficult. By using a zinc amalgam cathode or by adding zinc sulphate the decrease in overvoltage is smaller and a greater yield of arsine is obtained. The efficiency of the cathodes for reducing arsenic acid is, however, not dependent on the overvoltage alone, since lead and tin, which have approximately the same overvoltages as mercury, are not so efficient at the same apparent current densities. The reduction is facilitated by increasing the current density, the concentration of the acid electrolyte, and the time of electrolysis. The efficiency of the process, calculated as the percentage of hydrogen produced at the cathode which is converted into arsine, varied from 1·71 to 14·1% under the best conditions. O. J. WALKER.

Simple deposition of reactive metals on noble metals. A. S. RUSSELL (Nature, 1931, **127**, 273—274).—Evidence of the deposition of uranium, titanium, tungsten, and molybdenum on mercury, copper, and tin is obtained when a liquid amalgam is shaken with an acid solution of a compound of the metal in question. After the addition of pure zinc, the minimum concentration of sulphuric acid at which hydrogen is evolved may reach 0·001 of that with the amalgam alone. When these metals are deposited electrolytically on a mercury cathode they behave towards the evolution of hydrogen in the same way as does the amalgam shaken with a solution.
L. S. THEOBALD.

Formation of ethylene and acetylene during electric discharges in methane. K. PETERS and O. H. WAGNER (Z. physikal. Chem., 1931, **153**, 161—186).—The formation of acetylene and ethylene from mixtures of hydrogen and methane under the influence of the electric discharge has been studied under a variety of conditions of pressure, gas velocity and composition, energy input, and form of the reaction vessel. The minimum energy consumption for the production of acetylene is 13 kw.-hrs. per m.^{3}, and the most satisfactory value for the production of ethylene is 53 kw.-hrs. per m.^{3} Under these conditions, and with a gas mixture containing 2 mols. of methane per mol. of hydrogen, the concentration of acetylene in the product is 4·2%, and of ethylene 0·8%. It is apparently impossible to repress the formation of acetylene and increase the yield of ethylene, except at very low pressures, when the energy consumption becomes much greater than at 10—40 mm. The concentration of acetylene in the product increases with increase of the quantity of energy dissipated, the maximum attainable concentration being about 20%, whilst with ethylene the maximum does not exceed 3%. Study of the spectrum of the gas mixture during the discharge indicates that two reaction zones are present; in one only the :CH bands are visible, whilst in the other the Swan spectrum, the Balmer series, and the carbon line spectrum also appear. The mechanism of the reactions is discussed. In the zone from which the Swan spectrum is emitted acetylene may be produced either by combination of two :CH radicals or by the action of active hydrogen on the ·C:C· radical. Ethylene is formed by the polymerisation of groups resulting from the decomposition of the methane molecule. H. F. GILLBE.

Photo-reaction of hydrogen and iodine monochloride. S. E. ASHLEY and W. WEST (Nature, 1931, **127**, 308).—In agreement with the observations of Mellor and Iredale (this vol., 180), hydrogen and iodine monochloride react under the influence of a mercury arc light, forming hydrogen chloride and iodine. No appreciable amount of hydrogen iodide has been observed. The photo-reaction between iodine chloride and methane, with a rate large compared with that of the hydrogen reaction, has also been established. L. S. THEOBALD.

Photochemical decomposition of hydrogen peroxide in aqueous solution in the presence of sodium nitroprusside. I. M. QURESHI (J. Physical Chem., 1931, **35**, 656—658).—An aqueous solution of hydrogen peroxide containing a small quantity of sodium nitroprusside decomposes on exposure to light and the decomposition continues after illumination ceases. Hydrogen peroxide solution also decomposes in the dark if the sodium nitroprusside solution is previously exposed to light.
L. S. THEOBALD.

Influence of the absorption of light on the velocity of photochemical reactions. A. K. BHATTACHARYA and N. R. DHAR (Z. anorg. Chem., 1931, **196**, 26—32).—The velocity of the reaction between potassium oxalate and iodine under the influence of radiation of wave-length 8500 Å. is approximately proportional to the quantity of energy absorbed. The reaction between ferrous sulphate and iodine has been studied under varied conditions; when the velocity of the thermal reaction is reduced by addition of suphuric acid and the mixture is exposed to sunlight, the exponent of the velocity–absorption or velocity–intensity relationship is about 0·2, but it increases with decrease of the ratio of the velocities of the photocatalysed and thermal reactions. Thus with radiation of wave-length 7304 Å., which is no longer absorbed by the reacting system, and in absence of sulphuric acid, the exponent is 1·5. A similar effect is observed with the reaction between citric and chromic acids; under the influence of continuous radiation from an electric lamp the exponent is 0·5, but at 5650 Å. the relationship becomes linear. The main factors governing the relationship between the velocity of a photochemical reaction and the quantity of light absorbed are the wave-length of the absorbed radiation and the relative acceleration caused by the absorption. H. F. GILLBE.

Direct photography of ionisation in insulating materials. A. GEMANT (Naturwiss., 1931, **19**, 109).—A photo-sensitive film in an electric field between plate electrodes is blackened when a critical voltage is exceeded. This is due to the ionisation of neighbouring dielectrics. The effect is observed when liquid or solid insulating materials as well as when gases are introduced between the electrodes. Whether the primary action is due to charge carriers of high velocity or to the secondary action of the accompanying photo-phenomena is not yet decided, but the evidence so far favours the latter. When semi-

conducting photographic paper is used as part of the electrode the structure of the insulator can be investigated by application of the breakdown potential. The ionisation process itself can also be investigated to some extent and, unlike other methods, by applying direct current. Some dielectrics glow with alternating current, but not with direct current.

J. W. Smith.

Photochemical polariser. F. Weigert and F. Stiebel (Naturwiss., 1931, 19, 108).—When clear transparent gaslight plates are insolated with polarised red light and then developed in the ordinary way, negative induced dichroism is produced. If, however, instead of being developed, the plate is treated with chromic acid, then insolated with non-polarised red light, and developed, a positive induced photodichroism is obtained. The initial insolation with polarised light, followed by the chromic acid treatment, converts the film into a photochemical polariser, and of the almost equal amounts of each component absorbed only that in a vibrational direction at right angles to the initial excitation is active. This effect is to be anticipated on the micellar theory of the latent image, and hence supports this view. On account of the close relationship between this new photo-dichroism and Albert's reversal, which is a general photographic phenomenon, the new property may also occur with highly sensitive, large-grained photographic emulsions. J. W. Smith.

Accumulation effect in photographic plates and its influence on the exactitude of photographic photometry. N. Barabaschev and B. Semejkin (Z. wiss. Phot., 1931, 28, 333—340).—The action of a given exposure on a plate increases with the time between exposure and development. The increase in density is greatest in the first two days. If the plate is slightly fogged before exposure, the effect is still apparent, but to a different degree. Old plates do not show the effect so strongly. The possible inaccuracies of characteristic curves in view of these results are discussed. J. Lewkowitsch.

Photochemical studies. XII. Photochemical reaction between nitric oxide and mercury vapour. W. A. Noyes, jun. (J. Amer. Chem. Soc., 1931, 53, 514—526).—The resonance radiation of mercury effects a decrease of pressure to approximately half the initial value in the system nitric oxide–mercury vapour at 25°; the residual gas is probably nitrogen. Mercury oxide is not deposited on the illuminated zones of the walls. The unimolecular velocity coefficient is independent of initial pressures of nitric oxide between 0·1 and 0·0035 mm. The reaction is sensitised by mercury and probably proceeds by $Hg(2^3P_1$ or $2^3P_0)+NO \longrightarrow NO(\text{excited})+Hg(1^1S_0)$. The quenching of the fluorescence of mercury vapour by nitric oxide at 600—700° is 10% less than at 25° and is ascribed, in part, to the production of mercury atoms in the 2^3P_0 state.

J. G. A. Griffiths.

Photochemical dissociation of triatomic molecules. II. Potassium cyanide. D. S. Villars (J. Amer. Chem. Soc., 1931, 53, 405—411).—Potassium cyanide vapour at 830° exhibits no absorption, but at 875° two regions are observed with longer wave-length boundaries at about 2175 Å. (5·7 volts) and 2900 Å. (4·3 volts). The former region is interpreted as the dissociation into a normal and an excited dissociation product, whilst the latter region indicates dissociation of the ionic molecule into a normal potassium atom and CN radical. This accords with the energy of dissociation, 3·8 volts, deduced from thermal data and an approximate evaluation of the heat of sublimation (48·75 kg.-cal.). The relation between the "ionic" and "atomic" forms of a molecule is discussed. J. G. A. Griffiths.

Photochemical interaction of ethylene and ammonia. H. S. Taylor and H. J. Emeléus (J. Amer. Chem. Soc., 1931, 53, 562—574; cf. A., 1930, 871).—It is now shown that the photo-decomposition of ammonia is unaffected by the presence of ethylene, but the yield of free hydrogen and nitrogen is diminished. Under the conditions employed, the polymerisation of ethylene alone is small, but in the presence of ammonia, an oily product is obtained which retards the reaction and contains, as almost non-volatile substances, most of the nitrogen from the decomposed ammonia. The velocity of reaction is independent of the pressure of ammonia when absorption of light is complete. The temperature coefficient is about 1·04 per 10°. The yield of saturated hydrocarbons is comparatively small, and the results afford evidence of the relative efficiency of the possible modes of formation of saturated hydrocarbons from ethylene and atomic hydrogen.

J. G. A. Griffiths.

Influence of light, carbon monoxide, and benzoquinone on the reduction of methylene-blue. H. Tamiya, T. Hida, and K. Tanaka (Acta Phytochim., 1930, 5, 119—155).—Pyruvic acid, kojic acid, ethyl acetoacetate, phloroglucinol, resorcinol, etc. in absence of oxygen and at suitable p_H and only under the influence of light are capable of decolorising methylene-blue. All these substances exhibit keto-enol tautomerism. The decolorisation of methylene-blue by the dehydrase of acetic bacteria or liver extract is also accelerated by light. Since screening with methylene-blue filters has the same effect as darkness, the effect is due to activation of the methylene-blue molecule. Carbon monoxide inhibits the bacterial reduction of methylene-blue but not the reduction by liver extract or the non-enzymic reduction. The degree of inhibition is determined mainly by the proportion of methylene-blue to carbon monoxide, and is not affected by light. It appears to be due to some effect of the gas in hindering the adsorption of the dye at the cell surface, and not to any effect on the enzyme itself. In the case of liver extract it is noted that in complete absence of oxygen decolorisation of methylene-blue takes place at the same rate whether hydrogen or carbon monoxide is present, whereas if a trace of oxygen is present, the rate with hydrogen is much slower, whilst that with carbon monoxide is unchanged. The explanation lies in the presence of a trace of hæmoglobin; in presence of hydrogen the trace of oxygen forms oxyhæmoglobin, the formation of which is prevented by carbon monoxide, and this is reduced before the methylene-blue, which is itself more readily reduced

than free oxygen. Here attempts to study the effect of light led to inconclusive results, since both the carbon monoxide-hæmoglobin and methylene-blue are affected by light. It is concluded that actions other than its combination with the iron-porphyrins must be taken into account when considering the action of carbon monoxide on cell processes. Both the chemical and enzymic decolorisation of methylene-blue are distinctly inhibited by $0.001M$-benzoquinone. The question whether this indicates the identity of the dehydrases which in the presence of suitable donators reduce methylene-blue and benzoquinone is discussed and left open. A modified Thunberg vessel for treating substrates containing volatile constituents is figured. F. E. DAY.

Decomposition of cholesterol by X-rays. A. H. ROFFO and L. M. CORREA (Strahlenther., 1930, **36**, 528—532; Chem. Zentr., 1930, ii, 3002—3003).—Decomposition of cholesterol by X-rays occurs in solution only when the solvent contains chlorine; the effect is due to liberation of chlorine. Carbon tetrachloride is more sensitive than chloroform. A. A. ELDRIDGE.

Effect of X-irradiation on cholesterol and its fatty acid esters *in vitro* and *in vivo*. R. HUMMEL (Strahlenther., 1930, **36**, 533—538; Chem. Zentr., 1930, ii, 3003).—In chloroform solution both free cholesterol and its fatty acid esters are decomposed by X-radiation. Similar decomposition was not observed in fat or blood-serum solutions or with deposits of cholesterol in mouse liver. A. A. ELDRIDGE.

Action of short electromagnetic waves on photographic plates. M. LEVITSKY (Physikal Z., 1930, **31**, 769—771).—A number of experiments are described in confirmation of the author's earlier work on the action of radio-waves of short wave-length on a photographic plate after it has been given a short exposure to sunlight. The radiation from a spark was concentrated by means of a quartz lens and after passage through a 1 or 2 mm. grating was reflected on to the plate. Photographic reproductions of the diffraction patterns thus obtained are given. It is suggested that the radiation concerned produces resonance of the silver bromide lattice in the photographic film with the result that an increased blackening appears in those regions in which the radiation is concentrated by the diffraction grating. R. W. LUNT.

Polysulphides of the alkali metals. II. Lithium. T. G. PEARSON and P. L. ROBINSON (J.C.S., 1931, 413—420; cf. A., 1930, 1136).—The action of sulphur on aqueous and alcoholic solutions of lithium monosulphide yields solutions which contain polysulphides but give no definite crystalline products. From a solution of sulphur in a solution of lithium hydrogen sulphide in absolute alcohol, however, *lithium tetrasulphide dialcoholate*, $Li_2S_4,2EtOH$, separates, being formed by the reaction $2LiHS+3S=Li_2S_4+H_2S$. Molten lithium and sulphur react under naphthalene to give a mixture of the monosulphide with a little disulphide. Thermal analysis of the system lithium monosulphide–sulphur indicates that the only sulphides stable at atmospheric pressure are the monosulphide, stable at its m. p., 900—975°, and the disulphide, slightly decomposed at its m. p., 369·5°. R. CUTHILL.

Co-ordinated compounds of the alkali metals. III. F. M. BREWER (J.C.S., 1931, 361—368; cf. A., 1926, 71).—The following *compounds* have been prepared by interaction of salicylaldehyde with alkali hydroxides or carbonates: $C_7H_5O_2Li,C_7H_6O_2$, $C_7H_5O_2K,2C_7H_6O_2$, $C_7H_5O_2Rb$, $C_7H_5O_2Rb,C_7H_6O_2$, $C_7H_5O_2Rb,2C_7H_6O_2$, $C_7H_5O_2Cs,C_7H_6O_2$, and $C_7H_5O_2Cs,2C_7H_6O_2$. By the reaction of rubidium carbonate and benzoylacetone *rubidium benzoylacetone*, $C_{10}H_9O_2Rb$, m. p. 131°, is obtained. All these compounds are yellow. Taking into account the compounds previously described, the following covalency numbers are established: lithium, 4; sodium, 4; potassium, 4 and 6; rubidium, 4 and 6; cæsium, 4 and 6. The stability of the co-ordinated compounds of the alkali metals must depend on the atomic number and atomic volume of the metal. As the atomic number increases the increasing ease of ionisation opposes the tendency to co-ordination, but in the elements of higher atomic number the maximum co-ordination number increases, whereas with increasing atomic volume the nucleus holds additional electrons less and less readily. R. CUTHILL.

Action of iron and nickel on alkali metal salts. L. HACKSPILL and H. J. PINCK (Bull. Soc. chim., 1931, [iv], **49**, 54—70).—The reaction between iron and nickel and alkali metal salts has been studied in an apparatus evacuated to a pressure of 10^{-3} mm. Iron displaces the alkali metals with the exception of lithium from the sulphates and arsenates heated at the m. p.; from the thiocyanates, after a preliminary decomposition to the cyanide, at 650°; from the borates and phosphates at about 1400°; and from the aluminates at the m. p. of iron. Lithium is formed when the oxide or silicate is heated with iron at 1300°. The other salts of lithium either decompose or volatilise without reaction. Nickel is able to displace the alkali metals only from their hydroxides or sulphides. F. J. WILKINS.

Complex sodium silver thiosulphates. E. CARRIERE and RAULET (Compt. rend., 1931, **192**, 423—425).—The interaction of silver chloride and sodium thiosulphate occurs according to the equation, $AgCl+Na_2S_2O_3=NaCl+NaAgS_2O_3$. The value of $K(=[S_2O_3'']/[AgS_2O_3'][Cl'])$ at 20° for concentrations of sodium chloride and silver nitrate (to form the silver chloride) of $0.009N$ is 8·6, and varies from 23 to 4 when the temperature varies from 5° to 45°. The heat of formation of AgS_2O_3' from Ag^+ and S_2O_3'' is 7·7 kg.-cal. Conductivity determinations confirm these results. C. A. SILBERRAD.

Hypophosphites of cæsium and rubidium. L. HACKSPILL and J. WEISS (Compt. rend., 1931, **192**, 425—426).—Cæsium and rubidium hypophosphites are prepared either from the sulphates and barium hypophosphite, or from the free alkali and hypophosphorous acid. When dried over sulphuric acid they have compositions $CsH_2PO_2,0.5H_2O$ ($d^{18.5}$ 2·81), and RbH_2PO_2 (d^{17} 2·32). Both are very hygroscopic. On heating decomposition begins at 140°, is rapid at

200°, but is completed only at 500°. Below 300° it is represented by $5MH_2PO_2=MH_2PO_4+2M_2HPO_3+2PH_3$; above that temperature by $MH_2PO_4=MPO_3+H_2O$ and $2M_2HPO_3+H_2O=M_4P_2O_7+2H_2$, but the volume of hydrogen is always slightly in excess of that of phosphine, and a small quantity of a yellowish-brown insoluble solid, possibly a suboxide of phosphorus, is formed. C. A. SILBERRAD.

Stabilisation of blue cupric hydroxide. H. A. NEVILLE and C. T. OSWALD (J. Physical Chem., 1931, **35**, 60—72).—Precipitation in the presence of gelatin stabilises the blue compound formed by the action of sodium hydroxide (1·25*N*) on *N*-copper nitrate. The gelatin (0·025% by weight of mixed solutions) is completely removed from solution by adsorption on the precipitate. The blue compound can be prepared at 0° and under water remains stable at this temperature, but slowly turns black at the ordinary temperature. It is also stable at the ordinary temperature after being dried slowly in an electric refrigerator. An increase in alkalinity of the solution up to a certain concentration accelerates the blackening of the precipitate and then delays the change. *X*-Ray examination shows the blue preparations, both moist and dry, to have a definite crystal structure which differs from that of black copper oxide; from this and other evidence the blue substance is considered to be cupric hydroxide rather than hydrous cupric oxide. The ultimate particle size of the hydroxide is smaller than that of cupric oxide. A colloidal solution of copper hydroxide, peptised by the combined action of alkali and gelatin, has been obtained.

L. S. THEOBALD.

Modifications of silver iodide. R. BLOCH and H. MÖLLER (Z. physikal. Chem., 1931, **152**, 245—268).—*X*-Ray analysis confirms the existence of two modifications of silver iodide stable below 146°. The cubic variety (zinc blende type) can be prepared by grinding any coarsely crystalline preparation, whilst the hexagonal variety (wurtzite type) is obtained by crystallising the fused substance and protecting the resulting crystals from fracture or heating. The latter modification is also obtained by crystallising the iodide from its solution in a concentrated solution of potassium iodide, hydriodic acid, or mercuric nitrate. Ordinary precipitated silver iodide is a mixture of the two varieties. By heating above 146° a new cubic modification having a distinct *X*-ray diagram is formed. The conditions of stability of the three modifications are shown in a *p–t* diagram. When the "hot" cubic modification is formed by heating either of the other two, it reverts on cooling to the variety used to prepare it. This behaviour is attributed to the persistence of nuclei beyond the range of stability of the parent substance. The rate of formation of nuclei and the rate of growth of each of the modifications have been studied.

F. L. USHER.

Zinc and barium ferrites. J. GUILLISSEN and P. J. VAN RYSSELBERGE (Trans. Amer. Electrochem. Soc., **59**, Preprint, 11 pp.).—At temperatures below 580° the reaction between zinc and ferric oxides is very slow, but at higher temperatures zinc ferrite is formed. During the first two or three hours' heating the reaction is in accordance with Tammann's logarithmic law, but later an apparent equilibrium is attained. The ratio zinc as ferrite : total zinc rises from 78·8 at 600° to 98·8 at 890°. Thermal analysis yields no evidence of the formation of zinc ferrites more basic than $ZnFe_2O_4$ at temperatures up to 1070°. Zinc ferrite dissolves very slowly, and the more slowly the higher is its temperature of formation, in *N*- and 2*N*-sulphuric acid. Air containing 7·5% of sulphur dioxide when passed over the ferrite heated at 450° decomposes it slowly with the formation of zinc sulphate, but the reaction is too slow to be of technical importance. The reaction between barium carbonate and ferric oxide commences at temperatures below 700°; the formation of barium ferrite at 720° at first follows Tammann's law, but tends towards an equilibrium; on stirring, the reaction proceeds, although with reduced velocity. The results are discussed, and it appears that diffusion is the main factor in reactions between solids. H. F. GILLBE.

Reactions occurring in the solid state. (MME.) MATHIEU, MATHIEU, and PAIÓ (Compt. rend., 1931, **192**, 416—418).—The change in mol. volume occurring in the following reactions which take place in the dry state on pounding the ingredients together in a mortar has been determined: (1) $Hg+I_2=HgI_2$; (2) ZnS(wurtzite)=ZnS(blende); (3) $3K_2SO_4+Na_2SO_4=3K_2SO_4,Na_2SO_4$; (4) $HgSO_4+2HgO=SO_3,3HgO$; (5) $HgSO_4+HgI_2=HgSO_4,HgI_2$; (6) $(PbI)_2CO_3=PbI_2+PbCO_3$; (7) $[3HgO,2SO_3,2H_2O]=2[3HgO,SO_3]+2H_2O$. The occurrence of the reactions in all but (1) and (6), where colour changes occur, is proved by means of *X*-ray photographs. No connexion can be traced between the occurrence of such reactions and change in mol. volume, there being increases in (1), (4), and (6), decreases in (2) and (3), and practically no change in (5). C. A. SILBERRAD.

Principles of the genetic development of material. III. Chemical and structural forms of aluminium hydroxide. I. V. KOHLSCHÜTTER [with W. BEUTLER, L. SPRENGER, and M. BERLIN] (Helv. Chim. Acta, 1931, **14**, 3—49).—A detailed study has been made of the various transformations undergone by α-aluminium hydroxide during ageing. The hydroxide was prepared by the anodic dissolution of aluminium and precipitation by the hydroxyl ions formed at the cathode during the electrolysis of 0·25*N*-sodium chloride (and in some cases of 0·25*N*-potassium nitrate) solutions under standard conditions. Small amounts of a reproducible standard α-hydroxide can be freshly prepared for each experiment in this way, and the product is probably a purer form of the α-hydroxide described by Willstätter, Kraut, and Erbacher (A., 1926, 34). This hydroxide, which has the approximate composition $Al_2O_3,4H_2O$ and is formed as a flocculent transparent gel, is the most active form of aluminium hydroxide. It is readily soluble in dilute hydrochloric acid, sodium hydroxide, and even in ammonia solution. By rapid centrifuging and washing it forms a faintly opalescent sol, which is very sensitive towards anions, particularly the sulphate ion. The positive character of the α-hydroxide is shown also by cataphoresis experiments.

During the ageing of the α-hydroxide two transformations take place. At the ordinary temperature, and more rapidly at 70°, the α-form is transformed into the β-hydroxide, which, although still transparent, is no longer loose and flocculent, but dense and plastic. The decrease in reactivity of the β-form is shown most clearly by its diminished solubility in hydrochloric acid and in ammonia solution, and also by its diminished absorbing power. It has the approximate composition $Al_2O_3,1{\cdot}16H_2O$. The $\alpha \longrightarrow \beta$ transformation is accelerated by the addition of methyl or ethyl alcohol, formaldehyde, acetone, ethyl ether, toluene, or chloroform, and is retarded by carbon dioxide. Before the change $\alpha \longrightarrow \beta$ is complete a further transformation to the third γ-form commences. The transparent plastic β-form gradually becomes opaque during 8—10 days, after which no further changes are observed. After shaking the γ-gel settles quickly to a small volume and forms with dilute hydrochloric acid a milky sol containing clear ultramicroscopic particles in rapid motion, a characteristic property of the γ-sol. The γ-hydroxide has the approximate composition $Al_2O_3,2{\cdot}39H_2O$ before, and $Al_2O_3,3H_2O$ after, treatment with dilute hydrochloric acid, and probably consists of bayerite dispersed in colloidal β-hydroxide.

The ageing process of α-aluminium hydroxide consists, therefore, of the two changes: (1) $\alpha \longrightarrow \beta$ and (2) $\alpha \longrightarrow$ bayerite, the γ-hydroxide being a mixed product of both changes. If (1) is accelerated by dehydrating agents (2) is suppressed and no γ-formation occurs, whereas acceleration of (2) by hydroxyl ions results in a coarse γ-hydroxide rich in bayerite.

O. J. WALKER.

Preparation of anhydrous aluminium chloride from natural aluminous raw materials. V. I. SPITZIN and O. M. GVOSDEVA (Z. anorg. Chem., 1931, **196**, 289—311).—The conditions for the formation of anhydrous aluminium chloride from pure alumina, bauxite, and kaolin by mixing the substance with carbon in various forms and passing either chlorine or hydrogen chloride over the mixture have been investigated. The raw material can be freed from iron by a preliminary treatment with hydrogen chloride at 400—900°. The form of the carbon used is important; the best results are obtained with wood charcoal and the poorest with petroleum carbon. Pressing the mixture into briquette form has no deleterious effect. When hydrogen chloride is the reagent an excess of carbon is necessary and a rapid stream of gas is desirable, but when chlorine is used the velocity of the gas stream is unimportant and an excess of carbon is not essential. For small amounts of material chlorine and hydrogen chloride are almost equally effective, but chlorine is a more energetic reagent than hydrogen chloride where greater amounts are involved. When silica is present it is chlorinated simultaneously and the aluminium appears to act as a catalyst for this reaction. The most favourable temperature for reaction is 800°. Mixtures of chlorine and hydrogen chloride produce less attack on the silica; the lower is the percentage of chlorine the smaller is the relative amount of silicon tetrachloride formed, but the slower is the velocity of the whole reaction. A small addition of hydrogen chloride to chlorine gives a gas which is more reactive than pure chlorine. Addition of silicon tetrachloride vapour to the chlorine has the effect of reducing the attack on the silica without affecting the attack on the alumina.

E. S. HEDGES.

Kaolin. R. SCHWARZ and W. KLOS (Z. anorg. Chem., 1931, **196**, 213—219).—The behaviour of kaolin when heated from 20° to 1000° has been investigated by dilatometric measurements. After absorbed water has been evolved the kaolin expands continuously to a maximum at 582°, and thereafter the specific volume diminishes as the water of constitution is driven off. Discontinuities in the curve at 846° and 938° correspond with the decomposition of metakaolin and with the formation of mullite, respectively. The volume–temperature curve of the ignited material is approximately linear at temperatures up to 940°, the expansion coefficient being $3{\cdot}10$—$3{\cdot}93 \times 10^{-6}$ for material ignited at 1000° and $4{\cdot}37$—$5{\cdot}16 \times 10^{-6}$ for material ignited at 1500°. At temperatures above 940° the ignited kaolin contracts somewhat, an indication that the metakaolin is not wholly decomposed. The dilatometric behaviour of rehydrated kaolin and the influence of thermal treatment have been investigated, and results are given also for a number of mixtures of kaolin with felspar, quartz, and alumina.

H. F. GILLBE.

Concentration and isolation of the element of atomic number 61. L. ROLLA (Atti R. Accad. Lincei, 1930, [vi], **12**, 270—272; cf. A., 1928, 261).—Details are given of the technique at present being used in the fractional crystallisation of large quantities of commercial didymium nitrate in order to obtain illinium in a state sufficiently pure to be examined by means of *X*-rays.

O. J. WALKER.

Silicic acids. II. W. DILTHEY and W. NAGEL (J. pr. Chem., 1931, [ii], **129**, 178—188; cf. A., 1929, 280).—The principal factors affecting the degree of hydration of the silica obtained by interaction between silicon tetrachloride and triphenylcarbinol in a variety of solvents at various temperatures are the nature of the solvent and the temperature; the relative amount of triphenylcarbinol and the time of reaction are without marked effect. The water content of the preparations varies between 16·4% and 28·7%, and there is no evidence of the existence of a definite hydrate corresponding with metasilicic acid, $SiO(OH)_2$. The dehydrating action of solvents is in the order ether < chloroform < carbon tetrachloride. The various preparations have the same order of solubility in water (determined by dialysis), viz., about 6%, and in this respect resemble the silicic acid precipitated from aqueous silicates.

H. A. PIGGOTT.

Silicic acid and silicates. I. F. W. MEIER and L. SCHUSTER (Z. anorg. Chem., 1931, **196**, 220—224).—The fraction of a sample of quartz powder soluble in water was about 1·4%, and was not increased by addition of hydrochloric acid; on the contrary, increase of the acid concentration from 0·1% to 2·5% caused a reduction of the quantity dissolved. The action of 0·5—20% sodium carbonate solutions on

quartz and the subsequent action of hydrochloric acid have been investigated. The activation of part of the silica, whereby it becomes converted into a soluble form, is effected by the water as well as by the alkali, and the soluble material may be extracted, at least in part, by washing with 10% hydrochloric acid. If, however, the activated material is digested with acid for a longer period the activating action of the alkali becomes apparent, and the quantity which enters into solution is proportional to the concentration of the alkali. H. F. GILLBE.

Decomposition of carborundum. N. SLOMNESCO (Compt. rend., 1931, **192**, 361).—Carborundum in a very finely divided state is slowly dissolved with evolution of silicon tetrafluoride and carbon dioxide by concentrated hydrofluoric acid to which a little concentrated nitric acid has been added. C. A. SILBERRAD.

Complex pyrocatechol derivatives of quadrivalent elements. A. ROSENHEIM, B. RAIBMANN, and G. SCHENDEL (Z. anorg. Chem., 1931, **196**, 160—176).—A number of complex *compounds* of pyrocatechol with quadrivalent silicon have been prepared. By addition of freshly-precipitated silica to a solution of pyrocatechol containing the appropriate alkali, crystalline $(NH_4)_2[Si(C_6H_4O_2)_3],9H_2O$, $K_2[Si(C_6H_4O_2)_3],8H_2O$, and $Ba[Si(C_6H_4O_2)_3],C_6H_6O_2,17H_2O$ are obtained, whilst by double decomposition the guanidinium salt ($+7H_2O$) separates; yellow crystals of the acid salts $(C_5H_6N)H[Si(C_6H_4O_2)_3]$ and $(C_6H_6\cdot NMe_2)H[Si(C_6H_4O_2)_3]$, and the compound $(NH_4)_2[Si(C_6H_3O_2\cdot CHO)_3],8H_2O$ have also been prepared. The sodium and normal pyridinium salts have been obtained only as syrupy liquids. By analogous methods the compounds $K_2[Ti(C_6H_4O_2)_3],5H_2O$ and $Rb_2[Ti(C_6H_4O_2)_3,5H_2O$, which readily lose 4 mols. of water to form the monohydrates, have been prepared, and crystalline magnesium, zinc, manganese, cobalt, nickel, and barium salts ($8H_2O$), and the pyridinium ($4H_2O$), quinolinium ($1H_2O$), and xylidinium ($1H_2O$) salts have been obtained. The anilinium and toluidinium salts are anomalous, in that they crystallise with $1H_2O$ and 1 mol. of the base. By dissolution of the monohydrated potassium and rubidium salts in hot aniline compounds are obtained wherein the water is replaced by 4 mols. of aniline. An optically active cinchoninium salt has been prepared; for the anion $[M]_D$ is about $+3500$. The complexes containing zirconium, thorium, or uranium are of more complicated structure than the silicon and titanium compounds; the following have been prepared:

$2\{(NH_4)_2[Zr(C_6H_4O_2)_3]\},C_6H_4(OH)_2,5H_2O$;
$(NH_4)_2[Zr(C_6H_4O_2)_3],C_6H_4(OH)_2,1\cdot5H_2O$;
$K_2[Zr_2(C_6H_4O_2)_5],20H_2O$;
$(CH_6N_3)_2[Zr(C_6H_4O_2)_3],6H_2O$;
$(C_5H_6N)_2[Zr(C_6H_4O_2)_5],7H_2O$;
$(NH_4)_2[Th(C_6H_4O_2)_3],5H_2O$;
$(NH_4)_2[Th_3(C_6H_4O_2)_6(OH)_2],10H_2O$;
$K_2[Th_3(C_6H_4O_2)_7],20H_2O$;
$(CH_6N_3)_2[Th_2(C_6H_4O_2)_3(OH)_4],10H_2O$;
$(C_5H_6N)_2[Th_2(C_6H_4O_2)_3(OH)_4],10H_2O$; and
$2\{(NH_4)_2[U(C_6H_4O_2)_3]\}C_6H_6O_2,8H_2O$.

H. F. GILLBE.

Potassium fluotitanate. II. H. GINSBERG and G. HOLDER (Z. anorg. Chem., 1931, **196**, 188—192; cf. A., 1930, 1007).—Isothermal dehydration curves of moist hydrated potassium fluotitanate indicate that a monohydrate exists; it has been isolated by exposing the material to the air at 24° and 59% humidity. Under these conditions the monohydrate is stable, but at 32—35° the anhydrous salt is formed within 48 hrs. The anhydrous salt may be obtained also by crystallisation from solutions containing from 20% to 40% of hydrofluoric acid. It is apparently impossible to prepare the compound K_2TiF_6,HF in the pure state; mixtures of the normal and acid compounds are always obtained. The oxy-salt K_2TiOF_6 has been prepared by heating the anhydrous fluotitanate in dry air, fluorine being evolved. H. F. GILLBE.

Preparation of titanium white. P. ASKENASY and K. HEISE (Z. anorg. Chem., 1931, **196**, 257—283).—The presence of titanium interferes with the determination of iron by the thiocyanate colorimetric method, but the procedure is made applicable to ferriferous titanium compounds by shaking the coloured liquid with ethyl ether freed from traces of alcohol, in which case no colour is given by the titanium. The effects of variation of the concentration of acid, temperature, and reaction time on the decomposition of ilmenite by sulphuric acid have been examined in detail; the amount of the precipitated mixture of basic titanium sulphate and metatitanic acid depends on the concentration of acid. When iron is present, the product is coloured yellow by ferric oxide, even when care is taken to reduce the iron to the ferrous state. The iron can be removed by treatment with acid at the expense of a considerable loss of titanium, but the methods recommended for purification are to pass sulphur monochloride vapour over the yellow product at 800° or to pass chlorine after a preliminary reduction of the ferric oxide with hydrogen. When the metatitanic acid is precipitated from concentrated sulphuric acid under pressure the iron content is only 0·3%, and this is reduced to 0·1% by the addition of sodium, ammonium, or magnesium sulphate to the reaction mixture. A product free from iron is obtained by precipitating the titanium as potassium titanium oxalate and hydrolysing the product. Orthotitanic acid is precipitated quantitatively in the cold at p_H 4·0. Under these conditions ferrous sulphate remains in solution and by redissolving the orthotitanic acid in sulphuric acid and precipitating again by hydrolysis at 95° an iron-free metatitanic acid which has the requisite properties for a pigment is produced. A more opaque white pigment is produced by the simultaneous precipitation of metatitanic acid and barium sulphate than by mechanically mixing the two pigments. E. S. HEDGES.

Germanium. IV. R. SCHWARZ, P. W. SCHENK, and H. GIESE (Ber., 1931, **64**, [B], 362—368; cf. A., 1929, 1407).—Ethyl orthogermanate was hydrolysed by water at 0° and the product subjected to isothermal dehydration. Evidence of the existence of a hydrated germanium dioxide was not obtained. The Röntgen diagram showed that the material very

rapidly became crystalline and had the same lattice as the anhydrous dioxide.

Determinations of the m. p. of germanium dioxide by the method of Shepherd and Rankin (A., 1909, ii, 725) gave the value 1115°±3°.

If a mixture of germanium tetrachloride and oxygen is circulated over granular quartz or felspar at 950°, *germanium oxychloride*, Ge_2OCl_6, a colourless liquid, b. p. 70°/13 mm., m. p. about −60°, d^{20} 2·057, is produced. It decomposes when boiled at the atmospheric pressure with evolution of white clouds of the dioxide. An oxychloride, $GeOCl_2$, could not be prepared.

Germanium tetrachloride is converted by sulphur trioxide (1 : 6) at 160° into *germanium sulphate*, $Ge(SO_4)_2$, a colourless, odourless powder, d^{2-} 3·92, which is hydrolysed by water and yields sodium germanate and sulphate when treated with sodium hydroxide. It suffers incipient thermal decomposition at 200°. H. WREN.

Behaviour of nitroso-*R*-salt with certain mineral salts. A. BERNARDI and M. A. SCHWARZ (Annali Chim. Appl., 1931, **21**, 45—50).—The following compounds are obtained by treating inorganic salts with nitroso-*R*-salt (cf. van Klooster, A., 1921, ii, 415): $(C_{10}H_5O_8NS_2Na_2)_2Pb,PbNO_3$; $(C_{10}H_5O_8NS_2Na_2)Ag,AgNO_3$,3 and $8H_2O$; $(C_{10}H_5O_8NS_2Na_2)_2Ba,BaCl_2,6H_2O$; $(C_{10}H_5O_8NS_2Na_2)_2Ca,CaCl_2$. Aqueous solutions of barium chloride (1·5% or more) and calcium chloride (5% or more) but not those of strontium chloride are precipitated by the reagent, the calcium compound redissolving on heating. In aqueous solutions acidified with hydrochloric acid calcium is not precipitated, strontium is precipitated only from its concentrated solutions as a greyish-green crystalline mass, and barium gives an orange-yellow precipitate at a much lower concentration, this and the strontium precipitate being dissolved on heating. In aqueous solution rendered alkaline with ammonia all three metals are precipitated. All these precipitations are slow and are complete only after the lapse of at least 24 hrs. The presence of alcohol in the solutions favours the precipitation. The reaction furnishes a means of separating calcium from barium. T. H. POPE.

Reactions in the solid state at high temperatures. VII. Reactions of niobium and tantalum pentoxides with metal oxides and alkaline-earth carbonates. W. JANDER and H. FREY (Z. anorg. Chem., 1931, **196**, 321—334).—By means of heating curves reactions between barium, strontium, calcium, magnesium, zinc, and cupric oxides, and barium, strontium, and calcium carbonates with tantalum and niobium pentoxides in the solid state have been investigated. The curves for the alkaline-earth oxides showed evidence of chemical reaction, but no such evidence was obtained for magnesium, zinc, and cupric oxides. The reactions with the alkaline-earth carbonates begin about 400—500° and among the products the following new *compounds* have been found: $2BaO,Ta_2O_5$; $4BaO,Ta_2O_5$; $2SrO,Ta_2O_5$; $4SrO,Ta_2O_5$: $4CaO,Ta_2O_5$; BaO,Nb_2O_5; $4BaO,Nb_2O_5$; SrO,Nb_2O_5; $4SrO,Nb_2O_5$; $5CaO,Nb_2O_5$. These substances are readily decomposed by acids. E. S. HEDGES.

Production of oxygen from lime and chlorine. O. R. SWEENEY, J. W HUSSEY, and W. RALSTON.—See B., 1931, 199.

Complexity of sulphur trioxide. A. SMITS [with P. SCHOENMAKER] (Z. physikal. Chem., 1931, **152**, 432—450; cf. A., 1925, ii, 267; 1926, 669, 785).—A review of previous work and an account of the principal results of the author's investigations. F. L. USHER.

Chromatic reactions of the molybdenumoctacyanides. G. A. BARBIERI (Atti R. Accad. Lincei, 1930, [vi], **12**, 148—153).—The parallelism between the ions $[Mo^{IV}(CN)_8]''''$ and $[Mo^{V}(CN)_8]'''$ on the one hand, and $[Fe^{II}(CN)_6]''''$ and $[Fe^{III}(CN)_6]'''$ on the other, is shown by the strongly coloured products which they form in reaction with such substances as ferric and ferrous salts, uranyl salts, molybdic acid, and salts of silver and copper. F. G. TRYHORN.

Crystal formation in sintered tungsten rods. M. HÜNIGER (Tech.-Wiss Abh. Osram-Konzern, 1930, **1**, 124—132; Chem. Zentr., 1930, ii, 2992).—Tungsten powder with or without addition of thorium dioxide affords by relatively brief heating crystals of varying size up to single crystals. Crystal growth is conditioned not by the colour, density, etc. of the tungsten powder but by its mode of preparation and mechanical treatment and by the thoria content. The conditions of reduction are more important than the mode of preparation of the tungstic acid. A. A. ELDRIDGE.

Existence of violet tungsten oxide, W_4O_{11}. E. TARJÁN (Naturwiss., 1931, **19**, 166—167).—Blue tungsten oxide, W_2O_5, does not exist in presence of hydrogen–water vapour mixtures at 700—1000°, but the oxide W_4O_{11} has been isolated; it exists under conditions which are within the limits of stability of W_2O_5, as stated by Chaudron (A., 1920, ii, 379), *e.g.*, with 15—30% of hydrogen in the gaseous phase at 900°, and is formed also in presence of carbon monoxide–carbon dioxide mixtures under conditions within the limits calculated by van Liempt for the existence of W_2O_5, *e.g.*, with 25% of carbon monoxide in the gaseous phase at 900°. On reduction W_4O_{11} yields first the dioxide and then tungsten, without the formation of intermediate products. It possesses a well-defined crystalline structure and appears as reddish-violet needles with a metallic lustre; the *X*-ray diagram indicates a characteristic lattice of triclinic symmetry. The same oxide is produced when a compressed mixture of tungstic oxide and the dioxide is heated in an inert atmosphere; in many of its properties, such as its chemical inertness and metallic conductivity, it resembles the tungsten-bronzes obtained by heating tungstates with tungsten dioxide. Conflicting reports on the tungsten oxides are in part due to confusion between blue reduction products and the violet oxide. H. F. GILLBE.

Complex bromine derivatives of quinquevalent tungsten. H. PAULSSEN-VON BECK (Z. anorg. Chem., 1931, **196**, 85—88).—By the action of hydrobromic acid on potassium oxalatotungstate and treatment of the product with rubidium or cæsium sulphate the *compounds* $Rb_2(WOBr_5)$ and $Cs_2(WOBr_5)$ have been prepared, the former as olive-brown octahedral

crystals and the latter as a greenish-yellow crystalline powder; the *ammonium* salt is similar but unstable. The *compounds* $(C_5H_5NH)(WOBr_4)$ and $(Et_4N)(WOBr_4,H_2O)$ have also been prepared. All these compounds are less soluble in hydrobromic acid than are the corresponding chlorine derivatives in hydrochloric acid, and the solutions are green. The bromine compounds hydrolyse more readily than the chlorine compounds, but may be kept without decomposition in an atmosphere of carbon dioxide.

H. F. GILLBE.

Determination of the degree of aggregation of isopolyacid ions with the aid of dialysis coefficients. H. BRINTZINGER and W. BRINTZINGER (Z. anorg. Chem., 1931, **196**, 55—60).—The dialysis coefficients of tungstate solutions at various values of p_H show that monotungstate alone exists above p_H 6·6±0·1, and that in more strongly acid solutions (p_H 6·6—4·5) a hexatungstate ion, W_6O_{21}'''''', is present. Analogous measurements with molybdate solutions show that the simple molybdate is converted into a trimolybdate at p_H 6·2±0·1, that a hexamolybdate is produced at p_H 4·7+0·15, and that a dodecamolybdate is formed at p_H 1·8±0·2. The measurements are independent of the cation provided that the same cation is present in the external solution. The results accord closely with those of Jander derived from diffusion measurements and the method has the advantages of simplicity and rapidity.

H. F. GILLBE.

Purification of perchloric acid by vacuum distillation. G. F. SMITH and O. E. GOEHLER (Ind. Eng. Chem. [Anal.], 1931, **3**, 48—52).—Conditions governing the vacuum distillation of perchloric acid are described and dimensioned drawings are given of suitable types of still-head, including four designs of the cold-target type, which is particularly suitable since the mechanism of the distillation probably involves the projection of gaseous molecules through a surface layer of oxonium perchlorate. Any tendency to ebullition due to the evolution of dissolved gases may be checked by previously cooling the acid to −5° to −10°, which serves also to remove metallic perchlorates, or by heating to 200° and constant composition (72%). Data relating to the rate of distillation and the composition of the product at various temperatures and pressures are given; the rate is proportional to the degree of superheating employed, whilst the maximum difference of composition of acids distilled at 0·5 mm. and 7 mm. pressure is 0·30%. The composition corresponds with the dihydrate when the pressure is 5·7 mm. If not more than 4% of sulphuric acid is present in the crude acid the quantity in the distillate does not exceed 0·001% if the process is carried out at a low temperature and pressure; with up to 36% of phosphoric acid in the crude acid only a trace is found in the distillate.

H. F. GILLBE.

Dissociation of concentrated perchloric acid during vacuum distillation at moderately low pressures. Preparation of anhydrous perchloric acid. O. E. GOEHLER and G. F. SMITH (Ind. Eng. Chem. [Anal.], 1931, **3**, 55—58).—An apparatus is described whereby 7—10% yields of anhydrous perchloric acid may be prepared by direct distillation of the 73·3—73·6% acid, without the aid of a dehydrating agent, at a pressure of 12—15 mm. The process is non-dangerous if the detailed directions given are followed closely, and the product appears to be more stable than that prepared by other methods; it does not discolour if kept at the temperature of liquid air for two months, and does not explode at the ordinary temperature until it has been stored for about 4 weeks. The mechanism of the process involves the reactions $4HClO_4,2H_2O \longrightarrow 2HClO_4,3H_2O+2OH_3ClO_4$ and $2OH_3ClO_4 \longrightarrow HClO_4,2H_2O+HClO_4$. The first equation represents the formation of a surface film of oriented oxonium perchlorate molecules, which accounts for the superheating and absence of ebullition during the distillation. On account of the low distillation temperature (110—120°) the decomposition into dihydrate and anhydrous acid, which is known to take place at 110°, is not disturbed by the vapour of the lower hydrates.

H. F. GILLBE.

Oxonium structure of hydrated perchloric acid. G. F. SMITH and O. E. GOEHLER (Ind. Eng. Chem. [Anal.], 1931, **3**, 58—61).—On seeding a supercooled solution of perchloric acid having approximately the composition of the dihydrate (*i.e.*, 73·6%) the crystal at first formed undergoes a transformation at about −19° with absorption of heat. The product of this change is oxonium perchlorate monohydrate, OH_3ClO_4,H_2O. The α and β forms of perchloric acid trihydrate are regarded as the result of an analogous transition, viz., $HClO_4,3H_2O \longrightarrow OH_3ClO_4,2H_2O$. The m.-p. of oxonium perchlorate is 49·905°±0·005, and the m. p. curve shows no indication of a transition $OH_3ClO_4 \longrightarrow HClO_4,H_2O$. It appears therefore that the oxonium structure is common to all the hydrated perchloric acids.

H. F. GILLBE.

Working up iodine residues. F. T. VAN VOORST (Chem. Weekblad, 1931, **28**, 129—130).—The methods described in the literature are reviewed. If thiocyanates are absent, cuprous iodide may be precipitated by addition of copper sulphate and sodium hydrogen sulphite solutions; iodine is liberated from the precipitate by treatment with sulphuric acid and sodium dichromate, distilled from the resulting liquor, washed, and dried.

S. I. LEVY.

Physical and chemical properties of rhenium. C. AGTE, H. ALTERTHUM, K. BECKER, G. HEYNE, and K. MOERS (Z. anorg. Chem., 1931, **196**, 129—159).—New determinations of the principal physical properties of rhenium are given (see this vol., 288). Methods of isolation of the metal are compared; by reduction of potassium perrhenate with hydrogen at 1000° fairly pure rhenium is obtained in 95% yield as a light crystalline powder. The separation of the metal by passage of the vapour of the mixture of chlorides obtained by heating the metal at 500—1000° in a current of chlorine over a tungsten filament at 1800° and low pressure, and the growth of the crystals obtained, are described; tungsten, molybdenum, tantalum, or platinum filaments do not alloy with rhenium during the process. The yield of metal is only 10—20%. The vapour of the peroxide may

be reduced in the same manner. At high temperatures rhenium is more resistant to the action of oxidising gases than is tungsten; it oxidises in air, although more slowly than tungsten, at temperatures above 1000°, but in presence of only 10% of oxygen it is not attacked below 1600°. Rhenium is not attacked by moist hydrogen at any temperature, but in moist nitrogen corrosion commences at 1900°; the metal is rendered passive towards water vapour, but not towards oxygen, by heating at 2000° in moist hydrogen. Various reactions of rhenium are described, especially in relation to their analytical applications (cf. A., 1929, 1408). Mercurous and thallous perrhenates are precipitated from a 0·1% solution of the potassium salt, and characteristic precipitates are formed with brucine and veratrine. For the microchemical detection of rhenium the colourless crystalline precipitate of cæsium perrhenate, which is rendered violet by potassium permanganate, and the blue needles formed in presence of methylene-blue are characteristic. The metal is best determined as ammonium perrhenate. The spectral lines at 3000, 3425, 3452, and 3462 Å. are the most persistent (cf. A., 1928, 1344). Rhenium dissolves readily in nitric acid, with formation of perrhenic acid, with difficulty in sulphuric acid, and inappreciably in hydrochloric and hydrofluoric acids. No carbide, nitride, or carbonyl could be prepared, but a boride appears to exist. Attempts to prepare an amalgam by various methods were unsuccessful.

H. F. GILLBE.

Iron nitrosyls and their behaviour on autoxidation. H. REIHLEN, E. ELBEN, and J. EVERET (Annalen, 1931, **485**, 43—52).—The compound $Fe(NO)_2(S·CS·OEt)_2$ (cf. Manchot and Davidson, A., 1929, 526) is formed with theoretical absorption of nitric oxide and in quantitative yield when prepared in a mixture of chloroform and water, thus confirming the above constitution in which the iron is most probably bivalent. It is completely decomposed at 60° in a high vacuum, giving ethyl dithiocarbonate free from nitrosyl xanthate; during its formation there is no evidence of a labile additive product of ferrous xanthate and nitric oxide. In carefully dried benzene solution it absorbs one atom of oxygen with great rapidity, and appears to yield a mixture of $FeNO_2(NO)(S·CS·OEt)_2$ and $FeNO_2(S·CS·OEt)_2$. A totally different behaviour is shown by the compound $[Fe(SEt)(NO)_2]_2$, which in dry chloroform or benzene absorbs only about 0·03 atom of oxygen in 20 min.—1 hr., and then decomposes completely. The *compound* $Fe(S·CO_2Et)(NO)_2$, obtained as dark brown crystals by interaction of potassium ethyl thiocarbonate (Bender's salt), ferrous sulphate, and nitric oxide in aqueous chloroform, shows a similar behaviour, but the period of induction is shorter. This behaviour towards oxygen is used as an argument against the univalency of iron in compounds of the latter type, which are regarded as complexes of tervalent iron in which the nitrosyl radicals are present as acidic residues.

H. A. PIGGOTT.

Cobaltic sulphate as oxidising agent. S. SWANN, jun., and T. S. XANTHAKOS (J. Amer. Chem. Soc., 1931, **53**, 400—404).—Optimal yields of cobaltic sulphate are obtained electrolytically from solutions of cobaltous sulphate $10N$ with respect to sulphuric acid and maintained below 10°. Current densities of 0·01—0·2 amp. per cm.² at a platinum anode are employed. The resulting suspension of cobaltic sulphate is a strong oxidising agent towards many organic compounds; formic, tartaric, citric, and malic acids are converted almost quantitatively into carbon dioxide.

J. G. A. GRIFFITHS.

Quantitative chemical analysis by means of absorption of X-rays. N. H. MOXNES (Z. physikal. Chem., 1931, **152**, 380—408; cf. A., 1929, 1254).—The procedure used in measuring the absorption of X-ray spectral lines is described in detail. A photographic photometric method was used. The method applied to zinc and nickel has yielded results 75% too high and 30% too low, respectively.

F. L. USHER.

Radioactivity method for the examination of pulverised substances. W. ŠEBESTA (Z. Physik, 1930, **66**, 598—618).—Measurements of the range of α-particles emitted by a mixture of a pulverised substance and a normal radioactive preparation may be readily applied to the analysis of powdered mixtures. The powder is spread in a layer such that an increase in its thickness leaves the range of emitted α-particles unchanged; the ionisation current due to emission in all directions above the layer then gives a measure of the quantity of one substance in the mixture. The method is described in detail.

A. B. D. CASSIE.

Analysis of a mixture of volatile liquids. M. LEMARCHANDS (Bull. Soc. chim., 1931, [iv], **49**, 80—84).—A method of determining the relative proportions of the constituents of a liquid mixture depends on the measurement of the latent heat of vaporisation of the mixture.

F. J. WILKINS.

Hydrogen-ion determinations with low-resistance glass electrodes. G. R. ROBERTSON (Ind. Eng. Chem. [Anal.], 1931, **3**, 5—7).—By the use of glass electrodes of 2—3 megohms resistance in conjunction with a d'Arsonval type of galvanometer, p_H measurements may be carried out to within 0·02. Owing to the variability of the glass surface potentials it is necessary to obtain the p_H of the solution under investigation by interpolation, using two buffer solutions of higher and lower p_H respectively. By decreasing the resistance of the glass electrodes the resistance to polarisation appears to have been increased; recovery after polarisation by large currents is, however, slower than with the quinhydrone electrode.

H. F. GILLBE.

Application of hydrazine in electrometric titrations. G. HOLST (Svensk Kem. Tidskr., 1931, **43**, 2—17).—The potentials of gold, mercury, and platinum electrodes in dilute solutions of hydrazine have been measured against a normal calomel electrode. Solutions of p_H 2·2—8·0, containing 1% of 0·1M-hydrazine sulphate, were employed. In acid solutions the platinum electrode is more positive than the gold, whilst in neutral and alkaline solutions the reverse is the case. Both electrodes show increasing negative potentials with an increase of the p_H of the solution, but the results are somewhat irregular. Using a

platinised platinum electrode in a closed nitrogen-filled cell the results showed the potential to be a linear decreasing function of the hydrogen-ion concentration between the limits p_H 1—13. Experiments with a Michaelis hydrogen electrode in buffer solutions of p_H 4·16 and 8·30 showed that the addition of a hydrazine solution of similar p_H had no effect on the potential. A mercury electrode in dilute hydrazine solutions is uniformly more positive than either gold or platinum, but a long period, up to 15 hrs., is necessary before equilibrium is reached. Both potassium dichromate and vanadic acid can be sharply titrated electrometrically with hydrazine sulphate solution, using gold or platinum electrodes, but attempts to determine copper and mercury either in ammoniacal solution or in one containing sodium hydroxide and tartrates were not satisfactory; experiments to determine molybdates and ferric salts also failed. Hydrochloric acid can be titrated with sodium hydroxide after addition of 1 c.c. of 0·1*M*-hydrazine sulphate; the change in potential is sharp if a platinised platinum electrode is used, but less satisfactory with one of gold. H. F. Harwood.

Measurement of p_H by means of a glass electrode and a triode valve. S. O. Rawling and G. B. Harrison (Phot. J., 1931, **71**, 108—112).—The significance of p_H is indicated and a simple method for its measurement is described (cf. A., 1930, 1151). H. F. Gillbe.

Differential potentiometric titration. IV. (*a*) Adaptation to hydrogen electrodes. (*b*) Test of standards for precise acidimetry. D. A. MacInnes and I. A. Cowperthwaite (J. Amer. Chem. Soc., 1931, **53**, 555—562).—(*a*) The application to hydrogen electrodes of the method previously described (A., 1929, 666) requires hydrogen free from the smallest traces of oxygen. (*b*) The end-point of the titration of 0·2*N*-sodium hydroxide with diluted constant-boiling hydrochloric acid, potassium hydrogen phthalate, and benzoic acid is determined to within 0·01%. J. G. A. Griffiths.

Tables for the calculation of p_H from the *E.M.F.* determined with the quinhydrone electrode. V. Morani (Annali Chim. Appl., 1931, **21**, 83—104).—Introduction into Nernst's concentration cell formula of the most recent values for *R* and *F* gives for the thermodynamic factor the value 0·0577457 at 18°. In calculations of p_H from the results of potentiometric determinations of *E.M.F.*, this factor is rounded off to 0·577 which, although it comes within the errors of the determination with the quinhydrone electrode, may vitiate the most exact calculations. This difficulty may be obviated by considering the values obtained as valid at 17·77° instead of at 18°. Tables are given showing (1) correction factors for converting the *E.M.F.* at any temperature between 10° and 26° into the corresponding value at 17·77° and (2) values of p_H (0 to 8·5) calculated from values of the *E.M.F.* varying from —0·1176 to 0·3728 at 17·77° in accordance with the expression $p_H=2{\cdot}04+v^{17\cdot77}/0{\cdot}0577$. T. H. Pope.

Determination of hydrogen-ion concentration by means of indicators. E. Leikola and P. Noponen (Acta Soc. Med. Fenn. "Duodecim," 1929, **11**, 18 pp.; Chem. Zentr., 1930, ii, 2922).—Leikola and Kerppola's method of colour imitation (A., 1930, 446) is employed, solutions of cobalt nitrate (6%), potassium dichromate (0·1%), nickel sulphate (15%), and (ammoniacal) copper sulphate (0·5%) being used to prepare the standard solutions. A. A. Eldridge.

Perchloric acid as a new standard in acidimetry. G. F. Smith and W. W. Koch (Ind. Eng. Chem. [Anal.], 1931, **3**, 52—55).—By distillation of pure 72% perchloric acid in a special type of Claisen flask until 50% has been removed and collecting the remainder of the distillate separately an acid of 73·6%±0·03 concentration and d_4^{25} 1·7128±0·0004 is obtained. The rate of distillation is not of importance and varies according to the temperature, which may be between 60° and 95°; the most satisfactory pressure is 5—6 mm., but the composition is almost constant between the limits 2 and 7 mm. If the acid used contains 70 or 71% of perchloric acid, the first 65 or 60%, respectively, should be rejected. A normal solution is obtained by dissolving 136·4201 g. of the redistilled acid in 1 litre. The advantages of perchloric acid over constant-boiling hydrochloric acid for the preparation of standard solutions are the absence of the need for exact pressure control, the freedom from troubles due to entrainment and bumping, and the rapidity of the process. H. F. Gillbe.

Analysis of mixtures of hydrogen, methane, and ethane. O. J. Walker and S. N. Shukla (J.C.S., 1931, 368—370).—The ethane is determined from the contraction in volume which occurs when the gas mixture is cooled with liquid air to condense out the ethane, and the hydrogen from the contraction which occurs when the residue is treated with palladium; the amount of methane is obtained by difference. With 5—10 c.c. of mixture the average errors are: ethane ±0·8%, hydrogen ±1·1%, and methane ±2·6%. Increased precision is attained by exploding the residual methane. R. Cuthill.

Determination of small concentrations of chlorine. V. N. Kolitscheva and R. V. Teis (J. Russ. Phys. Chem. Soc., 1930, **62**, 1957—1973).—0·007 Mg.-% of chloride ion can be determined with an error not exceeding 1%, using Kleinman's nephelometer, whilst electrotitrimetrically trustworthy values may be obtained for solutions containing not less than 0·014 mg. Porter's colorimetric method (A., 1926, 927) is suitable for quantities of chlorine not less than 0·001 mg., whilst by means of Alfthan's method, depending on the coloration produced by the action of chlorine on hydrochloric acid solutions of dimethyl-*p*-phenylenediamine, 0·0007 mg. can be determined. Iodometric methods, depending on the absorption of chlorine from air by potassium iodide or arsenious acid solutions, give trustworthy results for solutions containing not less than 0·07—0·10 mg. of chloride ion. R. Truszkowski.

Mercurimetry. O. Tomíček and O. Procke (Coll. Czech. Chem. Comm., 1931, **3**, 116—125). The theory of the use of sodium nitroprusside as

indicator for the titration of chloride and bromide with a mercuric salt is discussed. The solubility of mercuric nitroprusside is less than 5×10^{-5} g.-mol. per litre. The potentiometric titration of halide, thiocyanate, and nitroprusside with mercuric nitrate is described. Cyanide may be determined by adding the greater part of the nitrate solution to the slightly acid solution, and then stirring and completing the titration in the usual manner. Reverse titration is not satisfactory, as reduction of the mercuric salt takes place. The use of nitroprusside as indicator yields practically the same end-point as the potentiometric method if allowance be made for the volume of nitrate solution required to produce turbidity, which is about 0·2—0·4 c.c. of 0·1*N*-solution in a total volume of 200 c.c. when 0·1 g. of the indicator is present. Mercurous nitrate cannot be used satisfactorily for the titration. H. F. GILLBE.

Detection of chlorate in the presence of perchlorate and nitrate. T. P. RAIKOVA-KOVATSCHEVA (Z. anal. Chem. 1930, **82**, 415—417).—Chlorate may be detected in perchlorates or nitrates by shaking the solid salt with **5** c.c. of saturated aqueous hydrogen sulphide; as little as 0·01 mg. of chlorate produces an opalescence, due to separation of sulphur, in 5 min. A. R. POWELL.

Oxonium perchlorate as a reference standard for the construction of a density-composition table for concentrated perchloric acid solutions. G. F. SMITH and O. E. GOEHLER (Ind. Eng. Chem. [Anal.], 1931, **3**, 61—63).—The lack of a satisfactory chemical method for the analysis of 65—75% perchloric acid solutions has led to the adoption of oxonium perchlorate, the purity of which may be checked by determination of the m. p. (49·905°), as a standard for the preparation of solutions of known composition. A density–composition table has been prepared for 63—75% perchloric acid solutions; for the 70—73% acid dd/dC, where C is the percentage concentration, is approximately linear and equal to 0·01343, whilst for more dilute solutions the value may be taken as 0·01351. The solution of composition corresponding with the dihydrate (73·6%) has d_4^{25} 1·71282±0·00005, and the 72·4% constant-boiling acid (203°/760 mm.) has d_4^{25} 1·6964 approximately. H. F. GILLBE.

Direct and reverse titration of sulphuric acid with barium hydroxide. I. M. KOLTHOFF and E. B. SANDELL (Ind. Eng. Chem. [Anal.], 1931, **3**, 115—117).—The best results in the titration of sulphuric acid with barium hydroxide are obtained by working at the ordinary temperature and adding more base after the first colour change of the indicator, boiling and adding more hydroxide until the colour persists for 15—30 sec., and then cooling and completing the titration. In the reverse method hydroxide is partly adsorbed and partly occluded by the precipitate, and after boiling with acid to remove adsorbed portion the error due to occlusion is still about 1%. The most satisfactory procedure is to add the barium hydroxide solution to an excess of potassium sulphate solution at the ordinary temperature, titrate, boil, and complete the titration in the cooled solution; the error is 0·0—0·2%. Addition of the potassium sulphate solution to the hydroxide causes large errors (1%). Precipitation of the acid by barium chloride is unsatisfactory. It is advisable to use potassium hydrogen phthalate for the standardisation of barium hydroxide solutions. H. F. GILLBE.

Determination of sulphur by means of the turbidimeter. S. W. PARR and W. D. STALEY (Ind. Eng. Chem. [Anal.], 1931, **3**, 66—67).—The turbidimeter described contains a centrally placed hollow plunger fitted with an optical glass plate at the lower end and an eyepiece at the upper end; the plunger can be raised or lowered by means of a rack and pinion. Beneath the optical glass bottom of the turbidimeter tube is placed a 2 c.-p. lamp supplied with constant current adjusted by a rheostat and voltmeter. In making a determination the plunger is moved until the filament just disappears, and a calibration curve is constructed showing the relationship between the height of the plunger and the sulphate content of the solution. The instrument is very compact and gives satisfactorily concordant and rapid results even in unskilled hands. H. F. GILLBE.

Volumetric determination of persulphate. A. KURTENACKER and H. KUBINA (Z. anal. Chem., 1931, **83**, 14—36).—Various methods which have been proposed by previous authors have been critically examined and modifications introduced in some cases to increase their accuracy. Reduction of persulphate with ferrous sulphate proceeds instantaneously at the ordinary temperature when the solution contains 10 c.c. of phosphoric acid (*d* 1·7) per 100 c.c. Reduction with methyl alcohol followed by titration with alkali gives high results, probably due to the formation of formic acid. The decomposition of persulphates on boiling their aqueous solutions is accelerated by the addition of 10 c.c. of 0·1*N*-silver nitrate per 100 c.c.; the resulting sulphuric acid may be titrated with alkali. Methods involving reduction of the persulphate with oxalic acid, alkali arsenite, or alkali iodide all yield erratic results due to catalytic action in the presence of air. A. R. POWELL.

Polarographic studies with the dropping mercury cathode. XVII. Reduction of nitric oxide and the determination of nitrites. J. HEYROVSKY and V. NEJEDLÝ (Coll. Czech. Chem. Comm., 1931, **3**, 126—133).—Neutral or alkaline solutions of nitrite are not reduced at the dropping mercury cathode, but with acidified solutions there is a wave in the polarograph curve at −0·77 volt (*N*-calomel electrode). The saturation current increases to a maximum on addition of acid up to a five-fold excess, and in more strongly acid solutions is proportional only to the nitrite concentration. The wave is due to the reduction of nitric oxide produced by decomposition of the liberated nitrous acid, as is shown by the appearance of a similar wave in an acidified solution of nitrogen peroxide. The actual reduction process is a secondary reaction caused by electrically deposited hydrogen atoms, and the product is ammonia. Since the polarographic method serves to detect 1 part of nitrite in 10^6, and the height of the wave is proportional to the nitrite con-

centration, the method may be employed to determine nitrite, *e.g.*, in explosives. H. F. GILLBE.

Volumetric determination of phosphoric acid. R. BIAZZO (Annali Chim. Appl., 1931, **21**, 75—81).—The phosphoric acid is precipitated by means of excess of standard ammonium molybdate, the excess of this being determined in the filtrate by titration with standard lead acetate. When this titration is nearing completion, a little of the clear filtered solution is tested with a drop of the lead acetate, this procedure being repeated until no further precipitation is produced in this way. The titres of the two standard solutions are determined by tests on known amounts of phosphoric acid. The titration occupies 10—15 min. and parallel determinations give concordant results. T. H. POPE.

Determination of arsenic in bismuth and barium salts. L. W. GREEN and R. E. SCHOETZOW. —See B., 1931, 199.

Determination of carbon monoxide. E. DITTRICH.—See B., 1931, 230.

Influence of hydrogen on determination of carbon monoxide with the Dräger apparatus. J. G. DE VOOGD and A. VAN DER LINDEN (Chem. Weekblad, 1931, **28**, 133—134).—Relatively large quantities of hydrogen introduce only slight errors. S. I. LEVY.

Determination of helium and neon. V. A. SOKOLOV (Neft. Choz., 1930, **19**, 292—297).—A method for the analysis of mixtures of helium and neon, depending on the difference in density, and an appropriate balance are described. CHEMICAL ABSTRACTS.

Determination of potassium by the sodium cobaltinitrite method. P. J. VAN RYSSELBERGE (Ind. Eng. Chem. [Anal.], 1931, **3**, 3—4).—The weight of a sodium potassium cobaltinitrite precipitate increases with the time of settling to a limit which varies with the concentration and volume of the solution and with the manner of addition of the reagent. For accurate results, *i.e.*, within 1·3%, several solutions, of known and unknown composition, must be treated with the cobaltinitrite reagent under identical conditions, and the precipitate, after being kept for 24 hrs. and being filtered and washed, must be dried at 120° for a constant time. The potassium content of the "unknown" precipitates may be deduced from the composition of the "known" precipitates. The ratio of sodium to potassium in the solution to be analysed should be not less than 25, and should be approximately the same for all the solutions. H. F. GILLBE.

Rapid colorimetric determination of potassium. E. R. CALEY (J. Amer. Chem. Soc., 1931, **53**, 539—545; cf. A., 1930, 562).—0·001—0·01 G. of potassium (as chloride) in 1 c.c. of water is precipitated as picrate by means of 7·5 c.c. of saturated picric acid in 95% alcohol. After 40 min. at 20°, the precipitate is collected in a medium-porosity sintered glass funnel and freed from picric acid by washing with ether. The precipitate is dissolved in 50 c.c. of water and compared colorimetrically with standards prepared in a similar manner. Rubidium and cæsium behave similarly. Alkaline-earth, aluminium, and ferric chlorides do not interfere; in presence of unknown quantities of sodium the sample should not weigh more than 20 mg. J. G. A. GRIFFITHS.

Oxalate method of determining the titre of potassium thiocyanate, using borax. N. A. TANANAEV and N. A. LAZARKIEWITSCH.—See B., 1931, 245.

Determination of sodium carbonate in sodium hydrogen carbonate. A. K. BABKO.—See B., 1931, 244.

Volumetric determination of small quantities of silver. J. GOLSE (Bull. Soc. Pharm. Bordeaux, 1930, **68**, 53—64; Chem. Zentr., 1930, ii, 2677).—A solution of 2·5 g. of potassium iodide and 3·5 g. of mercuric iodide per litre is used as precipitant. The precipitate, $2AgI,HgI_2$, always contains silver iodide; hence for less than 15 mg. the quantity of silver a must be increased by $0{\cdot}002a^2$, or for larger quantities by $0{\cdot}00125(10a+a^2)$. A micro-procedure is described (cf. A., 1930, 1264). A. A. ELDRIDGE.

Rapid determination of calcium in lead alloys of low calcium content. L. I. SHAW, C. F. WHITTEMORE, and T. H. WESTBY.—See B., 1931, 254.

Determination of beryllium in aluminium. H. V. CHURCHILL, R. W. BRIDGES, and M. F. LEE.—See B., 1931, 253.

Separation of beryllia and alumina. A. TRAVERS and SCHNOUTKA (Compt. rend., 1931, **192**, 285—287).—Berthier's sulphite method has been reinvestigated. A solution of beryllium hydrogen sulphite evaporated to dryness on the water-bath or heated under pressure (2 kg.) gives no precipitate. Aluminium hydrogen sulphite similarly treated is quantitatively precipitated as an ill-defined basic sulphite, which when prepared under pressure is partly oxidised to the soluble sulphate. On prolonged ebullition the solution of beryllium sulphite deposits the hydroxide, which, however, redissolves on cooling if ebullition has not been too prolonged; in presence of an alkali hydrogen sulphite a precipitate is formed only from a dilute solution, and this redissolves on cooling; from a concentrated solution one is formed only on prolonged ebullition, and redissolves on dilution and cooling. The product is a complex soluble basic beryllium sodium sulphite, stable in the cold, but partly decomposed on boiling. The behaviour of aluminium hydrogen sulphite is unchanged by addition of alkali hydrogen sulphite. Beryllium and aluminium may therefore be separated as follows: the freshly-precipitated gel of the mixed hydroxides is dissolved in excess of alkali, the solution is saturated with sulphur dioxide, boiled for about 10 min., allowed to cool, and kept for several hours. The aluminium is precipitated quantitatively, but carries down a little beryllium, which is completely separated on repeating the process. Precipitation of aluminium in a medium of p_H 4 prevents formation of beryllium aluminate. C. A. SILBERRAD.

Effect of ammonium chloride on the results obtained by Schmitz' method of determining magnesium. J. MAJDEL (Z. anal. Chem., 1930, **82**,

425—429).—The results for magnesium obtained by this method (A., 1906, ii, 705) are about 3% low when no ammonium chloride is present in the solution before addition of phosphate. The best results (0·22% low) are obtained with 2—3 g. of ammonium chloride; with large amounts lower figures are obtained until with 4—6 g. of chloride there is a constant error of −1·1% of the magnesia. Hence it is advisable to remove all ammonium salts from a magnesium solution before precipitation and then to add the optimum quantity of ammonium chloride (2—2·5 g.).

A. R. POWELL.

Luminescence analysis. III. Alkaline-earth group and numerical characterisation of luminescence. E. BEUTEL and A. KUTZELNIGG (Monatsh., 1931, 57, 15—19; cf. B., 1931, 403).—The nitrides of magnesium, calcium, and barium, and oxides, hydroxides, carbonates, and sulphates of calcium, strontium, and barium give luminescence effects which cannot always be distinguished visually. The use of a step photometer with three filters enables the effect given by each substance to be defined by four numbers. The electronegative constituent of the compound exercises a greater influence than does the metal.

F. L. USHER.

Distinction between magnesite and dolomite by means of X-rays. F. HALLA (Monatsh., 1931, 57, 1—8).—Photographs taken with a small Debye-Scherrer camera afford a means of discriminating rapidly between dolomite and a mixture of its components.

F. L. USHER.

Determination of calcium and magnesium in dolomitic limestones by means of sucrose. A. C. SHEAD and B. J. HEINRICH.—See B., 1931, 245.

Determination of small quantities of zinc in presence of lead. M. E. STAS (Pharm. Weekblad, 1931, 68, 93—97).—The influence of lead on the determination of small quantities of zinc by precipitation with 8-hydroxyquinoline and titration of the precipitate with bromate-bromide has been investigated. Lead at concentrations below 2 g. per litre does not interfere, but at higher concentrations the lead compound separates. The method is more accurate and is applicable to a wider concentration range than nephelometric methods.

H. F. GILLBE.

Rapid determination of various elements after precipitation by the classical methods. II. J. DICK (Z. anal. Chem., 1930, 82, 401—415; cf. A., 1930, 901).—The precipitates obtained by treating hot neutral solutions of zinc, manganese, cadmium, or cobalt salts with a large excess of ammonium dihydrogen phosphate may be weighed as $M^{II}NH_4PO_4,H_2O$ after washing with cold 0·1% ammonium phosphate solution, 65% alcohol, and 95% ether in succession and drying in a vacuum desiccator for 30 min. Washing with alcohol and ether followed by vacuum drying is also applicable to the preparation of bismuth, selenium, tellurium, and cuprous thiocyanate precipitates for weighing.

A. R. POWELL.

Gravimetric and direct volumetric determination of cadmium. R. C. WILEY (Ind. Eng. Chem. [Anal.], 1931, 3, 14—15).—Cadmium may be determined by precipitation at the b. p. from a neutral or slightly acid solution with ammonium molybdate solution rendered slightly acid to litmus by addition of acetic acid. The crystalline precipitate, which is readily collected if kept for 2 hrs. or more at the b. p., should be dried at 120°. If during the precipitation the stirrer strikes the sides of the vessel crystals of cadmium molybdate adhere tenaciously, and are difficult to remove. For the volumetric determination of cadmium the solution is rendered just acid by addition of ammonia and acetic acid and titrated with an ammonium molybdate solution containing 714 g. of molybdenum trioxide per litre. The end-point is recognised by employing as an external indicator a chloroform solution of pyrogallol, which assumes a deep brown colour in presence of molybdate ion. Ammonium salts increase the solubility of cadmium molybdate and influence the results of the volumetric method appreciably. The end-point is sharper with ammonium molybdate than with the sodium salt.

H. F. GILLBE.

Separation of lead, barium, and calcium sulphates by ammonium acetate. W. W. SCOTT and S. M. ALLDREDGE (Ind. Eng. Chem. [Anal.], 1931, 3, 32—33).—Whereas lead may be completely separated from barium by extraction of the sulphates with hot 50% ammonium acetate solution the separation from calcium is incomplete; up to 8·5% of the calcium present may enter the solution, but the quantity appears to be governed by physical factors such as the time required for filtration and the degree of cooling during filtration. With increase of the Ba : Pb ratio the difficulty of extracting all the lead increases, until with a ratio of 100 : 1 only 95% of the lead dissolves; the cause may be the formation of an insoluble lead–barium complex salt, or, more probably, occlusion. The presence of barium reduces the tendency of calcium sulphate to dissolve in ammonium acetate solution.

H. F. GILLBE.

Separation of lead from barium, strontium, and calcium with ammonium acetate. J. MAJDEL (Z. anal. Chem., 1931, 83, 36—45).—When a solution containing lead and barium is evaporated with sulphuric acid until copious fumes are evolved and, after cooling, water is added the precipitate invariably contains more or less of a double sulphate of lead and barium which is insoluble in ammonium acetate solution. With a lead : barium ratio of 1 : 0·1 the proportion of insoluble lead is 5·5%, with a 1 : 1 ratio 46·5%, and with a 1 : 2 ratio 80·5%. Strontium also forms a double sulphate with lead, but this compound is completely soluble in ammonium acetate solution, and hence high results are obtained in the gravimetric determination of lead in the presence of strontium. With small quantities of calcium there is no interference, but with larger quantities high results for lead are obtained gravimetrically. The only satisfactory procedure for separating lead from the alkaline earths is that involving precipitation of the lead with hydrogen sulphide in hydrochloric acid solution.

A. R. POWELL.

Determination of lead dioxide and red lead. G. BRUHNS.—See B., 1931, 246.

The Spacu reaction. Volumetric determination of copper. J. GOLSE (Bull. Soc. chim., 1931, [iv], **49**, 84—100).—The Spacu reaction gives rise to the formation of copper dipyridine thiocyanate, $[Cu(C_5H_5N)_2](SCN)_2$, when pyridine and an alkali metal thiocyanate are added to a solution of a cupric salt. In the presence of excess of the thiocyanate this reaction is complete. A method for the volumetric determination of copper depends on the determination of the excess of thiocyanate. The conditions under which satisfactory results are obtained when permanganate is used are described. It is, however, more satisfactory to use the Volhard or the hypobromite method for the determination of the thiocyanate. Detailed directions are given.

F. J. WILKINS.

Iodide method for [determination of] copper. B. PARK (Ind. Eng. Chem. [Anal.], 1931, **3**, 77—82).—In presence of much arsenic the usual iodide method for the determination of copper yields high results, but the extent to which the reaction $H_3AsO_4+2HI \longrightarrow H_3AsO_3+I_2+H_2O$ proceeds depends on the iodine and iodide concentrations and on the temperature, and increases with increase of acidity of the solution. Both experimentally and theoretically by consideration of the electrode potentials of solutions of arsenious and arsenic acid and of iodine and iodide it is found that if the p_H of the solution during titration be maintained at a value higher than 3·5 no iodine is liberated by the arsenic. Study of the reaction between the cupric and iodide ions in various buffer solutions of different p_H values shows the influence of different acids to be specific and that in certain cases low results are obtained even when a precipitate is not formed. Of a number of organic acids investigated phthalic is the most satisfactory, as the whole of the copper may be titrated if the p_H does not exceed 5·7. The following method is recommended for the determination in presence of iron and arsenic. To 30 c.c. of the solution are added sufficient ammonia to precipitate all the iron, and then, in succession, ammonium hydrogen fluoride (2 g.), potassium hydrogen phthalate (1 g.), and potassium iodide (3 g.). The solution is titrated immediately with thiosulphate, and the starch–iodide colour should not return within 30 min. All the arsenic present should be in the quinquevalent state. In presence of large amounts of iron or aluminium more ammonium hydrogen fluoride must be added.

H. F. GILLBE.

Analysis of the aluminium group. S. ATO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, **14**, 287—311).—The elements of the aluminium group are separated from those of the iron group by boiling the nitric acid solution for 5 min. with an excess of 5 c.c. of $6N$-sodium hydroxide solution, 1—5 g. of sodium peroxide, and 5 c.c. of $3N$-sodium carbonate solution. The iron group precipitate is removed and the filtrate treated with acetic acid to render it N with respect to that acid and boiled for 5 min. to precipitate titania. The filtrate is boiled with 10—20 c.c. of $3N$-lead acetate solution, the precipitate dissolved in nitric acid, the solution evaporated with sulphuric acid to remove lead, the chromium reduced with sulphur dioxide and separated from the vanadium by precipitation with sodium hydroxide, and the alkaline filtrate treated with ammonia, ammonium chloride, and hydrogen sulphide to confirm the presence of vanadium. The filtrate from the lead precipitate is treated with ammonia, the precipitate collected, and the filtrate tested for zinc; the ammonia precipitate is dissolved in nitric acid, any lead removed with hydrogen sulphide, and the solution evaporated to dryness. The residue is dissolved in 15 c.c. of 1 : 1 nitric acid and the uranium extracted with ether, three treatments being required to ensure complete separation. The aqueous layer is evaporated to dryness, the nitrates are converted into chlorides by treatment with hydrochloric acid, and the aluminium is separated from beryllium by treatment of the solution with ether and hydrogen chloride, which precipitates $AlCl_3,6H_2O$; small amounts of aluminium are more readily separated by the sodium hydrogen carbonate method. Beryllium is tested for by means of alizarin-red S in a neutral chloride solution.

A. R. POWELL.

Detection of manganese in minerals and rocks. H. LEITMEIER (Tsch. Min. Petr. Mitt., 1931, **41**, 87—94).—Manganese hydroxide, even in traces, in the presence of an acetic acid solution of benzidine gives a blue coloration. To the solution of the mineral on filter-paper a drop of potassium hydroxide is added and then the benzidine solution.

L. J. SPENCER.

Oxidation of ferrous iron by iodine in presence of phosphate, and the non-existence of a ferriphosphate complex. W. D. BONNER and H. ROMEYN, jun. (Ind. Eng. Chem. [Anal.], 1931, **3**, 85—87).—The oxidation of ferrous iron by iodine in presence of phosphate proceeds to completion, although very slowly: at $0{\cdot}1N$ concentrations in sulphuric acid solution 15 hrs. are required for completion at 40°. The velocity increases with decrease of p_H, and in neutral solution the presence of phosphate is unnecessary, as the ferric iron is precipitated as hydroxide, but the results become erratic. Completion of the reaction is rendered possible as a result of the decrease of the $Fe^{\cdots}/Fe^{\cdot\cdot}$ ratio caused by the presence of phosphate, but potentiometric titration of a ferrous–ferric salt solution with phosphoric acid shows no indication of the formation of a complex. The behaviour of such solutions is therefore attributed to the formation of a weak electrolyte which probably has a composition ranging from $FePO_4$ in solutions containing little phosphate to $Fe(H_2PO_4)_3$ in presence of an excess of phosphate.

H. F. GILLBE.

Colorimetric determination of cobalt alone and in the presence of nickel. E. S. TOMULA (Z. anal. Chem., 1931, **83**, 6—14).—The neutral cobalt solution (40 c.c.) is treated with 5 g. of ammonium thiocyanate and 50 c.c. of acetone and diluted to 100 c.c. The resulting blue colour is compared with that produced under the same conditions in a standard cobalt solution containing not less than half and not more than twice as much cobalt. The depth of the solution in the standard tube should not exceed 20 mm. and the white plate below the colorimeter tubes should be covered with a piece of glazed yellow gelatin paper if nickel is present.

A. R. POWELL.

Detection and determination of nickel with dimethylglyoxime in the presence of much cobalt. F. FEIGL and H. J. KAPULITZAS (Z. anal. Chem., 1930, **82**, 417—425).—The solution is treated with a concentrated solution of potassium cyanide until the precipitate first formed just redissolves, an excess of hydrogen peroxide is added to convert the cobalto- into cobalti-cyanide, and the solution is evaporated to one quarter its volume to destroy the excess of peroxide. On addition of dimethylglyoxime to the hot solution, followed by formaldehyde until its odour is apparent in the solution, the nickel is precipitated as the characteristic red glyoxime compound together with excess of the precipitant; the compound is purified by dissolution in hydrochloric acid and precipitation in the usual way. The method is based on the reaction $K_2Ni(CN)_4+2H\cdot CHO=Ni(CN)_2+2CN\cdot CH_2\cdot OK$. A. R. POWELL.

Arc spectrographic determination of chromium in rubies. J. PAPISH and W. J. O'LEARY (Ind. Eng. Chem. [Anal.], 1931, **3**, 11—13).—The persistence of the arc lines of chromium between 5785·8 and 3120·4 Å. has been investigated by photographing the carbon arc spectrum with from 1·0 to 0·0001 mg. of chromium trioxide placed on the electrodes. Nineteen lines suitable for the spectrographic determination of chromium are given. The smallest recognisable quantity of chromium corresponds with 0·001 mg. of chromium trioxide, but in synthetic rubies made by fusing alumina with the trioxide 0·00006 mg. may be detected. The chromium content of natural rubies, which is too small for determination by chemical means, may be determined spectrographically, and results (0·01—0·1% Cr) are given for a number of specimens. H. F. GILLBE.

Detection of chromium in minerals and rocks. H. LEITMEIER and F. FEIGL (Tsch. Min. Petr. Mitt., 1931, **41**, 95—102).—A red alcoholic solution of diphenylcarbazide turns violet in the presence of even a trace of a chromate. The mineral to be tested is first fused with sodium carbonate or sodium peroxide. L. J. SPENCER.

Detection of germanium. W GEILMANN and K. BRUNGER (Z. anorg. Chem., 1931, **196**, 312—320).—Germanium can be separated from accompanying elements by the distillation of a hydrochloric acid solution of the substance with the aid of a slow stream of carbon dioxide. The optimal concentration is 3—4*N*-hydrochloric acid; no germanium appears in the distillate when the concentration of acid is less than 0·75*N* or greater than 7·5*N*. Germanium can be detected in the distillate by spectral analysis so long as the concentration is greater than 0·001%, but a procedure is recommended for use with smaller quantities. The germanium is precipitated as sulphide by means of hydrogen sulphide and the precipitate is dissolved in a drop of 1—1·5*N*-potassium hydroxide solution, the spectrum of which is then examined. At this concentration of potassium hydroxide the precipitate is readily soluble and the spectral lines are not affected; in more concentrated solutions the lines are weakened. The method enables germanium to be detected at a concentration of $\sim\times 10^{-5}$%. Arsenic, selenium, and antimony must be removed by distillation with hydrochloric acid in a stream of chlorine. Results obtained in mineral analysis are given. E. S. HEDGES.

Determination of antimony in lead–antimony alloys of low antimony content. L. I. SHAW, C. P. WHITTEMORE, and T. H. WESTBY.—See B., 1931, 254.

Micromanipulations. E. A. HAUSER (Rev. gén. Colloid., 1930, **8**, 358—361).—A brief account of manipulation in ultramicroscopical observations. E. S. HEDGES.

Accessory apparatus to the petrographical microscope. K. H. SCHEUMANN (Tsch. Min. Petr. Mitt., 1931, **41**, 58—63).—A refractometer combined with the microscope enables the refractive index of a liquid to be determined at the moment that it is matched with an immersed mineral grain. L. J. SPENCER.

Photomicrography with the 365 μμ mercury line. A. P. H. TRIVELLI and L. V. FOSTER (J. Opt. Soc. Amer., 1931, **21**, 124—131).—An account of experimental technique is given. Photomicrography with the 365 μμ mercury line can give 19% more resolving power than the best microscopic systems can produce with the Wratten C filter. It has the advantages that the focussing is simplified, that a glass lens system can be used instead of quartz, and a mercury arc instead of a cadmium arc. C. W. GIBBY.

Polarisation apparatus for the determination of optical and magnetic rotation dispersion in the ultra-violet. A. HAGENBACH (Helv. phys. Acta, 1930, **2**, 168—179; Chem. Zentr., 1930, ii, 2805).—An apparatus for the measurement of magnetic rotation, which is attached to a Cotton and Descamps spectropolarimeter, is described. A. A. ELDRIDGE.

Modification of the Le Chatelier–Bronievski apparatus. A. REGNER (Coll. Czech. Chem. Comm., 1931, **3**, 103—110).—The apparatus has been improved by correcting the optical system and increasing the resistances of the two galvanometers to 105 and 443 ohms, and the sensitivities, at a scale distance of 75 cm., to $7\cdot3\times10^{-6}$ and $2\cdot9\times10^{-5}$ volt, respectively. The clock mechanism has been replaced by an electrical device, and temperature measurements are made with the aid of a single differential pyrometer. H. F. GILLBE.

Modified balance for approximate and quick weighing. E. KARRER (Ind. Eng. Chem. [Anal.], 1931, **3**, 112—114).—By the use of an ordinary beam balance modified by addition of a spring and extended pointer the difference between the weights of two objects may be estimated closely within 2 sec. H. F. GILLBE.

Density determinations with solids, and especially with inorganic salts. P. WULFF and A. HEIGL (Z. physikal. Chem., 1931, **153**, 187—209). —A critical study has been made of the pyknometric and flotation methods for the determination of the densities of solids and the literature relating to measurements with various halides is reviewed. Measurements with cæsium chloride show that on account of the impossibility of removing air occluded

or adsorbed by the solid, results by the pyknometric method always involve a negative error of the order of 0·1%; this view is confirmed by comparison of the densities of certain halides obtained by the pyknometric and by the X-ray and immersion methods. Accurate results, *i.e.*, with a mean error of 0·02%, may be obtained by selecting under the microscope crystals free from inclusions, washing them with an inert solvent, and floating in a mixture of suitable liquids, such as toluene and tetrabromoethane. Convenient apparatus for the determination, and for the subsequent measurement of the density of the liquid, is described. For solids having $d>3$, the displacement method, using a torsion balance, yields results with a maximum error of about 0·1%. H. F. GILLBE.

Device for estimating density of gems and small amounts of solids. E. W. BLANK (Ind. Eng. Chem. [Anal.], 1931, **3**, 9—11).—The specimen is placed in a narrow (6—8 mm.) tube previously filled with liquid to a marked level in a capillary side tube, and more liquid is then added from a weight burette in order to bring the level to a second mark. Knowing the additional weight of liquid required in absence of the solid, the displacement weight is readily calculated. Ether, despite its volatility, is a very suitable liquid for most substances. The density of 0·01 g. of material may be determined to within 0·01—0·07. H. F. GILLBE.

Glass electrode and vacuum tube potentiometers. D. H. CAMERON (J. Amer. Leather Chem. Assoc., 1931, **26**, 7—23).—Of three simple forms of glass electrodes, which are described, the MacInnes type (A., 1929, 673) is preferred because of its compactness and simplicity. Each electrode must be calibrated by means of buffer solutions of known p_H value. The suitability of the electrode is affected by the composition of the glass. The potential is measured by employing a vacuum tube potentiometer. In the apparatus described two radio tubes, UX 199 type, replace the variable resistances. The glass electrode has been used by the author for titrating some acid fractions of vegetable tan liquors in presence of pyrogallol and kindred substances. The glass electrode is not poisoned nor affected by oxidising or reducing materials. It functions as rapidly as the quinhydrone electrode. Its upper limit is p_H 9. D. WOODROFFE.

[Reproducibility of] quinhydrone electrode. I. [In air.] J. L. R. MORGAN, O. M. LAMMERT, and M. A. CAMPBELL. **II. [In nitrogen.]** O. M. LAMMERT, J. L. R. MORGAN, and M. A. CAMPBELL (J. Amer. Chem. Soc., 1931, **53**, 454—469, 597—604; cf. Biilmann and Jensen, A., 1927, 421).—I. The electrode has been investigated in $0·1N$-hydrochloric acid. Since cracks and other imperfections in the glass of the electrodes may cause deviations as great as 0·1 volt, the electrodes are annealed and then cleaned by immersion in cold chromic acid–sulphuric acid mixture which is heated at 125° and then allowed to cool to the ordinary temperature. The electrodes are washed with conductivity water, rinsed with ethyl alcohol, and then dried in a current of purified air. Short-circuiting the electrodes in pairs during the cleaning hastens the attainment of the equilibrium potential in quinhydrone solution. The reproducibility is related to the size of the metal exposed to the quinhydrone solution; very small short wires give erratic results and larger short wires yield less consistent results than foil or longer wires. The *P.D.* between two foils of dimensions greater than 1 cm.^{2} is less than 10^{-5} volt, and is little affected by the composition or age of the metal. With smaller electrodes, old roughened platinum gives more reproducible results than new platinum alone or alloyed with other metals; gold is still less efficient. The solutions should be stirred.

II. If oxygen is excluded from the electrode liquid by stirring with nitrogen, equilibrium potentials are attained very rapidly and the results are much more reproducible. Under these conditions, electrodes dried in nitrogen exhibit no improvement as compared with those dried in air, and short circuiting in pairs during pre-treatment is without effect. J. G. A. GRIFFITHS.

Glass electrode measurements by a galvanometer with condenser attachment. M. DOLE (J. Amer. Chem. Soc., 1931, **53**, 620—622).—The galvanometer system of Jones and Kaplan (A., 1928, 954) is applicable to measurements with the glass electrode (cf. MacInnes and Dole, A., 1930, 423). No drift of potential due to polarisation of the electrodes by the current charging the condenser is observed. J. G. A. GRIFFITHS.

Nephelometric titrations. I. The equal-opalesence end-point. C. R. JOHNSON (J. Physical Chem., 1931, **35**, 540—542).—The unbalanced action of certain ions, mainly multivalent, on the colloidal suspensions employed may cause differences in the light-reflecting power of the sols large enough to introduce serious constant errors in nephelometric titrations. L. S. THEOBALD.

Colour measurement and spectrophotometry. J. A. A. KETELAAR (Chem. Weekblad, 1931, **28**, 132—133; cf. Schoen, *ibid.*, 105).—There is a fundamental difference between the colour observed and the light giving rise to the colour impression; different combinations of radiations of different frequencies may give rise to the same colour effect. A method of colour measurement by comparison with a blend of three radiations of chosen frequencies is foreshadowed. S. I. LEVY.

Colour measurement. M. J. SCHOEN (Chem. Weekblad, 1931, **28**, 133).—A reply (cf. preceding abstract). Even in "synthetic" methods, as in Guild's trichromatic colorimeter, the subjective factor is important. S. I. LEVY.

Spot apparatus for colorimetric p_H determination. F. TÖDT (Chem. Weekblad, 1931, **28**, 164—165).—A reply to the criticism of Kolthoff (this vol., 325). S. I. LEVY.

Flask in two parts for vacuum evaporation, reflux distillation, and extraction. A. LUBINSKI (Chem. Fabr., 1931, 78).—The bulb of the flask is connected to the distillation head by a flanged joint made with rubber in such a way that no contact between the contents and the jointing material is possible. It is practicable by this means, for example,

to extract a substance in a Soxhlet apparatus, then without removing the liquid from the flask to distil in a vacuum. If an annular container for phosphorus pentoxide etc. is provided in the upper half of the flask the apparatus can be used as a "drying pistol" or desiccator capable of being heated. An air bath is provided for heating purposes warmed by acetone or alcohol vapour as required. C. IRWIN.

Distillation analysis [of small quantities of liquids]. H. WOLFF and J. RABINOWICZ (Chem. Fabr., 1931, 37—38).—The fractional distillation of 2—4 c.c. of liquid is accomplished by the use of a small bulb immersed in a water-bath and joined glass-to-glass to a narrow glass tube bent at two right angles. This is closed at the end, immersed in a graduated cooling vessel, and has a hole in the side to equalise pressure. Temperatures are read by a thermometer in the water-bath and a correction which is applied is determined by comparing the true initial b. p., obtained by heating the sample in a test tube, and the apparent initial b. p. in the apparatus. Curves are given which show that this micro-apparatus gives better fractionation than the usual Engler method. C. IRWIN.

Simple distilling apparatus. R. S. GIBBS (Chemist-Analyst, 1931, **20**, No. 1, 22—23).—The liquid is placed in a 300-c.c. beaker in which is suspended a 30-c.c. beaker; a 3·5-inch funnel which rests in a collar on the larger beaker has the stem cut off and the apex fused together, and is filled with ice. CHEMICAL ABSTRACTS.

[Preparation of] conductivity water. G. W. TOMPKIN (Chemist-Analyst, 1931, **20**, No. 1, 16—17).—Distilled water was fed into a distilling flask provided with a glass float valve, the steam being partly condensed in a flask submerged in a water-bath and provided with an automatic siphon.

CHEMICAL ABSTRACTS.

Laboratory thermostat for continuous operation. P. W. SCHENK (Ber., 1931, **64**, [*B*], 368—370).—An electrically heated and controlled apparatus whereby a temperature constant to within $\pm 0\cdot02°$ can be secured over long periods is figured and described. The special feature lies in the use of two relays. H. WREN.

Furnace for metallographic examination of specimens at high temperatures. B. A. ROGERS (Met. and Alloys, 1931, **2**, 9—12).—The furnace comprises a small zirconia tube wound with molybdenum wire and embedded in magnesia inside a water-jacket which is covered with a silica window. A slow current of pure hydrogen is passed through the case during use to prevent oxidation of the heating wire and of the specimen. The whole apparatus is mounted on a levelling device in a large mechanical stage of an ordinary metallurgical microscope; in this way observations of polished metal specimens may be made at a magnification of 150 diam. at temperatures up to 1000° and at 50—75 diam. at 1500°. Photographs of the surfaces of electrolytic iron and cobalt show that characteristic changes occur at the transformation points; the changes are in the nature of eruptions and sweep across the field of view abruptly at a definite temperature depending on the purity of the metal. Silicon and molybdenum raise the temperature of the A3 point in electrolytic iron, whilst manganese and chromium depress it.

A. R. POWELL.

Shaking apparatus. P. DICKENS (Chem. Fabr., 1931, 61—62).—All kinds of glass apparatus can be shaken on a round plate provided with a variety of clamps, supported on suitable guides, and shaken by an eccentric projection on a motor-driven pulley. It is possible to apply heat by means of an electric hot plate and to work with exclusion of air by a slight adaptation. A larger-scale apparatus described varies only in detail. The use of shaking apparatus is of great benefit in the precipitation of barium sulphate, calcium oxalate, and magnesium ammonium phosphate. The author also uses it in the determination of silicon and phosphorus in iron. C. IRWIN.

Analysis of gas mixtures by combustion and absorption. M. SHEPHERD (Bur. Stand. J. Res., 1931, **6**, 121—167).—The defects in design of the various parts of gas analysis apparatus of the Orsat type are discussed, and the construction and manipulation of a greatly improved form are described.

R. CUTHILL.

Apparatus for the exact analysis of gas mixtures in amounts down to 3—4 c.c. A. SCHMIDT.—See B., 1931, 186.

Polarimetry of solutions having low optical rotations. Use of the mercury-vapour lamp. H. N. NAUMANN (Biochem. Z., 1930, **229**, 269—270).—The accuracy of the methods described by the author (cf. A., 1930, 1153) is doubled or trebled if a mercury-vapour lamp in conjunction with a nickel sulphate filter is used for illumination instead of an arc lamp. A potassium dichromate filter should not be used for micro-work.

W. MCCARTNEY.

One-piece electrodialysis apparatus. L. REINER (J. Physical Chem., 1931, **35**, 423—424).—The apparatus incorporates Jena glass filter plates as a support for collodion membranes.

L. S. THEOBALD.

Use of zinc wire spiral as a Jones reductor. G. F. SMITH and J. RICH (J. Chem. Educ., 1930, **7**, 2948—2952).—A spiral of amalgamated zinc wire is used for the reduction of iron; reduction is complete in 30 min. in presence of 6—10 vol.-% of sulphuric acid. CHEMICAL ABSTRACTS.

Holder for mercuric chloride paper in Gutzeit test. G. H. DAVIS (Analyst, 1931, **56**, 30).—The paper is held over the hole (8 mm.) of a rubber bung by means of a tin screw cap arrangement cut from a "Cardboard Screw Cap Post Box" and provided with a hole to coincide with that in the bung.

A. R. POWELL.

Apparatus for the detection of traces of fluoride by the etching method. R. E. ESSERY (Analyst, 1931, **56**, 28—29).—A lead casting 2 in. high with a bottom diameter of 2 in. and a top diameter of 1½ in. is ground flat and polished on the upper surface after cutting out a cavity ½ in. diameter and 1 in. deep. The material to be tested is placed in the cavity with a few drops of sulphuric acid, a Bunsen flame

is passed over the top to warm the metal, and a waxed cover-glass is placed over the cavity so that the wax melts round the side and hermetically closes the cavity without disturbing the design previously bared on the waxed surface. After incubating overnight at 37° the slide is melted off, the wax removed with ether, and the slide examined for etching by means of a powerful lens in reflected light.

A. R. POWELL.

Apparatus for continuous leaching with suction. J. F. FUDGE (Ind. Eng. Chem. [Anal.], 1931, **3**, 114). H. F. GILLBE.

Apparatus for the extraction of solutions lighter than the solvent. E. MAMELI (Annali Chim. Appl., 1931, **21**, 38—41).—Two modified forms of the Soxhlet apparatus suitable for this purpose are described, the extraction being effected by either the liquid solvent or its vapour. The amounts of benzoic acid extracted from its dilute aqueous solution by three different solvents are greater than those extracted in other similar apparatus. T. H. POPE.

Distillation method for producing antimony-bismuth vacuum thermo-elements. H. C. BURGER and P. H. VAN CITTERT (Z. Physik, 1930, **66**, 210—217).—A vacuum distillation method for the production of small vacuum thermo-elements of antimony and bismuth is described; the sensitivity is 2·5 times that of the Moll–Burger element. The advantages and limitations of the device are discussed.

R. W. LUNT.

Preservation of silvered mirrors. H. C. BURGER and P. H. VAN CITTERT (Z. Physik, 1930, **66**, 218).—The reflective power of a silvered glass mirror may be preserved and discoloration by the atmosphere avoided by depositing an exceedingly thin film of silica over the silver surface. The technique developed by the authors for the production of thermocouples by distillation in a vacuum (cf. preceding abstract) has been developed to this end. R. W. LUNT.

Micro-absorption tube with mercury seals. R. T. K. CORNWELL (Ind. Eng. Chem. [Anal.], 1931, **3**, 4—5).—A straight tube resembling the original Pregl micro-absorption tube is fitted at each end with a hollow ground glass stopper enclosing mercury seals which can be opened by rotating the tube through 180°. The tube may readily be cleaned and can be weighed when filled with any desired gas. H. F. GILLBE.

Mill for small samples. W. H. COOK, E. P. GRIFFING, and C. L. ALSBERG (Ind. Eng. Chem. [Anal.], 1931, **3**, 102—103).—The mill described is suitable for grinding small quantities of biological materials. It consists essentially of a four-bladed rotating knife which cuts against an adjustable stationary blade; when the mill is operated at 5600 r.p.m. and with a clearance between the blades of 0·0005 in. a single charge of material, *e.g.*, several wheat leaves or five to eight wheat kernels, is reduced to pass an 80-mesh sieve within 3—4 min.

H. F. GILLBE.

Electrically heated m.-p. apparatus. C. E. SANDO (Ind. Eng. Chem. [Anal.], 1931, **3**, 65).—Within the vertical portion of a pyrex glass Thiels–Dennis m.-p. tube is sealed a small side tube which extends 1—2 in. below the point of attachment of the side arm; the latter is heated by an asbestos-covered chromel heating element. A mixture of sulphuric acid and potassium hydrogen sulphate is employed as the heating liquid, and a calcium chloride tube is fitted to prevent the ingress of water.

H. F. GILLBE.

Absorption tube for combustion analysis. W. D. TURNER (Ind. Eng. Chem. [Anal.], 1931, **3**, 63).—The stopper, into which the outlet and inlet tubes are sealed, is ground internally, and by rotation the tubes may be closed and the entry of air during disconnexion prevented. The tube is of simple and robust construction and is easy to clean.

H. F. GILLBE.

Geochemistry.

Absorption of radiation in the lower atmosphere. Determination of ozone. C. FABRY and H. BUISSON (Compt. rend., 1931, **192**, 457—461).—On plotting the coefficient of absorption of ozone for light of wave-lengths 5780—2482 Å. against the optical density of 1 km. of air at the earth's surface for the same light (cf. A., 1930, 731) it appears that atmospheric absorption is explicable as due to a layer of ozone 0·0022 cm. (at *N.T.P.*) thick per km., together with some other cause of absorption, which is independent of wave-length for values of λ greater than 2600 Å., but increases rapidly for shorter wave-lengths. It is probably due to oxygen (cf. Granath, A., 1929, 1350).

C. A. SILBERRAD.

Chemical and chemico-physical data concerning the sulphur water of S. Giorgio in Angarano (Bassano del Grappa). G. BRAGAGNOLO (Annali Chim. Appl., 1931, **21**, 12—26).—The composition and physico-chemical constants of the water and the composition of the dissolved gases are given.

T. H. POPE.

Relation between fixed residue and electrical conductivity of mineral waters. E. BOVALINI and E. VALLESI (Annali Chim. Appl., 1931, **21**, 51—75).—For a number of dilute mixed salt solutions resembling in composition natural mineral waters, determinations have been made of the fixed residue (g. per litre) and of the specific electrical conductivity at 18°. The ratio between these two magnitudes indicates in some cases the type of the water and is not greatly changed by considerable change of the concentration alone. T. H. POPE.

Biochemical formation of soda in soda lakes. W. GUBIN and W. TZECHOMSKAJA (Zentr. Bakt. Par., 1930, II, **81**, 396—401).—Mud from Siberian

soda lakes always contained iron sulphide produced as a result of the biochemical reduction of sulphates to hydrogen sulphide. The presence of sulphate-reducing organisms was demonstrated in nearly all cases. The bearing of these facts on the biological formation of soda lakes is discussed.

A. G. POLLARD.

Absorption and refraction of brown Ceylon spinel. K. SCHLOSSMACHER (Z. Krist., 1931, **76**, 370—376).—Absorption and dispersion curves for four samples of brown Ceylon spinel, determined by means of a photo-electric cell (cf. A., 1930, 1267), show that the colour is predominantly due to tervalent iron; there are slight indications of bivalent iron and of chromium (cf. following abstract).

C. A. SILBERRAD.

Colouring material of red, blue, and violet Ceylon spinel. K. SCHLOSSMACHER (Z. Krist., 1931, **76**, 377—385).—The colours of pure blue and brown Ceylon spinels are due, respectively, to bi- and tervalent iron: blue spinel 2·17—2·23% Fe (0·2% Fe^{III}), cobalt, manganese, and chromium definitely proved absent; brown spinel (cf. preceding abstract) 4·71% Fe, manganese and titanium absent, a trace of chromium in one sample; in another 1·04% Fe^{III} and 0·13% Fe^{II}. Brown crystals that luminesced in ultra-violet light contained 0·0014% Cr. Intermediate colours, *e.g.*, reddish-brown and violet, are due to mixtures.

C. A. SILBERRAD.

Genetic and crystallographic considerations of some recent barytes formations. (FRL.) BUSCHENDORF (Z. Krist., 1931, **76**, 460—462).—Recently formed occurrences of barytes in fan-shaped aggregates and in tubular stalactitic and stalagmitic forms in drusy cavities in the Silberbach mine at Stolberg (E. Harz) are described. The deposition is considered to be due to diminution in solubility of the barium sulphate on escape of carbon dioxide from the water in which it was dissolved.

C. A. SILBERRAD.

Amethyst and smoky quartz colorations. J. HOFFMANN (Z. anorg. Chem., 1931, **196**, 225—246).—The colours of amethyst and smoky quartz can be imitated by irradiating silicate- and quartz-glasses with radium rays. Amethyst quartz is free from manganese and the colour is due to iron, which is generally accompanied by titanium or zirconium. Constitutional changes in the quartz crystal cell are held to be the cause of the colour changes.

E. S. HEDGES.

Caliche in Arizona. J. F. BREAZEALE and H. V. SMITH (Arizona Agric. Exp. Sta. Bull., 1930, No. 131, 419—441).—The nature and formation of the lime hardpan ("caliche") are discussed.

A. G. POLLARD.

New radioactive mineral in Japan. S. IIMORI, T. YOSHIMURA, and S. HATA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, **15**, 83—88).—A new radioactive mineral similar to allanite has been found occurring irregularly in pegmatite in the Bijozan Range. Analysis gives the formula $4R''O,3R'''O_3,6(SiO_2,P_2O_5),2H_2O$, where R''=Ca, Fe, and [illegible] Y, Al, Fe, and Th. The name nagatelite is suggested. The mineral belongs to the epidote group; *H* 5·5, *d* 3·91.

C. W. GIBBY.

Relation between crystallisation and differentiation in basaltic magmas. E. LEHMANN (Tsch. Min. Petr. Mitt., 1931, **41**, 8—57).—Chemical analyses of rocks from Nyasaland form the basis of a discussion on the derivation of various rock types (basanite, tephrite, trachyte, phonolite, etc.) from a basaltic magma.

L. J. SPENCER.

Wearing of minerals by transportation in water. F. W. FREISE (Tsch. Min. Petr. Mitt., 1931, **41**, 1—7).—Experiments on the wearing hardness of minerals found in the gold, diamond, and monazite sands of Brazil are described. Cut cubes of the minerals were placed with water in a rotating drum and the loss of weight was determined.

L. J. SPENCER.

Geochemical and genetic classification of granite-pegmatites. A. FERSMAN (Tsch. Min. Petr. Mitt., 1931, **41**, 64—83).—A repetition of earlier papers. The magmatic, pegmatoidal, and hydrothermal phases of pegmatites are further emphasised, and twenty types are distinguished according to the predominating minerals. Schematic tables suggest the temperature ranges of the different phases and the ranges of separation of the various minerals.

L. J. SPENCER.

Transportation of constituents of [mineral] deposits by humic acids. F. W. FREISE (Metall u. Erz, 1930, **27**, 442—445; Chem. Zentr., 1930, ii, 2951).—A study of the reappearance of alluvial gold in exploited layers after a period of years. In the absence of oxygen, humic acid in small concentration (0·25—0·3%) slowly dissolves gold; the solubility is unaffected by the presence of silver or palladium. Experiments with natural waters are described.

A. A. ELDRIDGE.

Isomorphism in the hornblende group. W. KUNITZ (Neues Jahrb. Min., 1930, **A**, **60**, Beil.-b., 171—250; Chem. Zentr., 1930, ii, 3008—3009).—The formulæ anthophyllite $H_2Mg_7Si_8O_{24}$, actinolite $H_2Ca_2Mg_5Si_8O_{24}$, glaucophanite $H_2Na_2Al_2Mg_3Si_8O_{24}$, green hornblende $H_2Ca_2Mg_5Si_8O_{24}$, syntagmatitic hornblende $H_2Ca_2Mg_4Al_2Si_6O_{22}$, and arfvedsonitic hornblende $H_2Na_2Mg_4Si_2Si_6O_{22}$ can be referred to complex silicic acids. A method for the determination of the density of small quantities of material depends on the measured dilution of a heavy liquid.

A. A. ELDRIDGE.

Composition and genesis of natural ferrous sulphate. R. SCHARIZER (Z. Krist., 1930, **75**, 67—87; Chem. Zentr., 1930, ii, 3125—3126).—Römerite is formed from rhomboclase and ferrous sulphate in moist air in presence of sufficient sulphuric acid to form hydroferrisulphuric acid. Natural and artificial voltaite are apparently mixtures of a potassium ferrous salt of hydroferri-tetra- and -hepta-sulphuric acids.

A. A. ELDRIDGE.

Soils of Madagascar. H. ERHART (Ernähr. Pflanze, 1931, **27**, 77—82).

Mineralisation of humus nitrogen in low moor soils. R. REINCKE (Zentr. Bakt. Par., 1930, **II**, **81**, 210—221).—The production of nitrate and ammonia in low moor pastures at different seasons is recorded and the effect of growing plant roots on bacterial activity examined.

A. G. POLLARD.

Soil investigations at Echmiadzin. K. Mirimanian (Bull. univ. état. R.S.S. Arménie, 1930, No. 5, 45—81).—Four soils are described and analyses are recorded. Chemical Abstracts.

Soil in the Arazdajan steppe of Armenia. B. Galstian (Bull. univ. état. R.S.S. Arménie, 1930, No. 5, 5—39).—An account of soil varieties and evolution. Chemical Abstracts.

Hydrogen sulphide and the formation of petroleum deposits. A. F. von Stahl (Petroleum, 1931, **8**, 145—146).—Petroleum deposits are invariably found in the immediate neighbourhood of sulphur springs. It is assumed that hydrogen sulphide is a product of disintegration of proteins in decaying salt-water sludge and remains absorbed in the sludge. It is considered highly probable that the pressure of overlying strata liquefies the hydrogen sulphide, which penetrates and reacts on the rock and intermingles with water. E. Doctor.

Geological aspects of the formation of coal. C. S. Fox.—See B., 1931, 184.

Geological history of coal. H. G. A. Hickling (Proc. S. Wales Inst. Eng., 1931, **46**, 911—950).—A lecture. C. W. Gibby.

Organic Chemistry.

Chromic acid oxidation of organic compounds, especially nitro- and amino-compounds. F. Friedmann (Z. ges. Schiess- u. Sprengstoffw., 1929, **24**, 208—210).—The use of 2*N*-potassium dichromate and 95—96% sulphuric acid is recommended for the oxidation of organic compounds. The amount of dichromate used should be 20% in excess of the theoretical value; when the substance is unknown a preliminary trial is advised. For the treatment of difficultly oxidisable compounds the amount of sulphuric acid may be increased. E. S. Hedges.

Electrochemical oxidation of paraffin. II. I. A. Atanasiu (Ber., 1931, **64**, [*B*], 252—260).—The electrochemical oxidation of paraffin, m. p. 53°, 51°, 47°, 44°, and 38°, and of an oil, after thorough refinement with 98% sulphuric acid, has been examined in a lead cell which serves as anode and in which the material is kept stirred with sulphuric acid containing various catalysts. The lead cathode is immersed in sulphuric acid (*d* 1·2) contained in a porcelain cell. The paraffins are relatively easily oxidised in presence of a suitable catalyst such as potassium dichromate or, in particular, cerium sulphate. The action is essentially chemical, the catalyst being alternately reduced and electrochemically re-oxidised. The products of the oxidation are carbon dioxide, unsaponifiable matter, and, mainly, fatty acids. A paraffin from which the oxidised portions are periodically removed is much more easily oxidised than a fresh paraffin. Soft paraffins are easily oxidised, but give more unsaponifiable matter and difficultly separable resins than hard paraffins; most unsaponifiable matter is obtained from the oils. Since oxidation proceeds slowly, the highest yields are obtained with the smaller current densities. The absence of hydroxy-acids and the small loss in volatile products are advantages of the electrochemical process. The mixture of fatty acids varies with the nature of the paraffin, the acid value of the products lying between 150 and 200 and m. p. between 37° and 50°. The individual components of the mixtures are, in general, the same, but their relative proportions vary. H. Wren.

Production of liquid hydrocarbons from butylenes. A. Mailhe and Renaudie (Compt. rend., 1931, **192**, 429—431; cf. this vol., 60).—Δ^{α}-Butene passed over silica gel at 650—670° gives methane, propylene, benzene, toluene, and *m*-xylene, and some tar. No naphthalene or anthracene was found. β-Methylpropene gave similar products under the same conditions. With Δ^{β}-butene at 700° the products were similar, but the proportion of aromatic hydrocarbons was increased, and naphthalene and anthracene were found in the tar. It is concluded from this and previous work that a higher temperature favours cyclisation of ethylenic hydrocarbons. A. A. Levi.

Catalytic condensation of amylenes. A. Mailhe and Renaudie (Compt. rend., 1931, **192**, 561—563).—Catalytic polymerisation of γ-methyl-Δ^{α}-butene with a silica gel catalyst at 670°/1 atm. affords a gaseous product consisting of ethylenic hydrocarbons (mainly ethylene and propylene) 47%, methane 30%, and hydrogen 7%, and a liquid product containing γ-methyl-Δ^{α}-butene, benzene, toluene, and *m*-xylene. Similar polymerisation of Δ^{β}-pentene furnishes gaseous ethylenic hydrocarbons (mainly propylene and butylene) 52%, methane 34%, and hydrogen 5—6%, and the same liquid products as in the previous case. In both cases solid residues of low m. p. were obtained. J. W. Baker.

Conjugated compounds. XI. Addition of hydrogen bromide to βγ- and αδ-dimethylbutadiene. E. H. Farmer and F. C. B. Marshall (J.C.S., 1931, 129—137).—The mode of addition of hydrogen bromide to αδ- and βγ-dimethylbutadiene was investigated, and the conclusions of Bergman (A., 1922, i, 1106) and of Claisen (A., 1923, i, 1050) were shown to be incorrect. On hydrobromination of βγ-dimethylbutadiene at temperatures between −72° and −20° the sole product was the αδ-hydrobromide, m. p. −32°, b. p. 53—54°/20 mm., yielding on ozonolysis acetone and bromoacetone. The irregularity of b. p., interpreted by Claisen as due to the presence of αβ-hydrobromide, was shown to be caused by the presence of excess of hydrocarbon. αδ-Dimethylbutadiene on hydrobromination yielded a mixture of αβ- and αδ-hydrobromides, b. p. 37—47°/10 mm., which could not be separated. On ozonolysis, acetaldehyde and propaldehyde were isolated, and on oxidation with potassium permanganate followed by potassium dichromate and sulphuric acid acetic and propionic acids were obtained, together with bromo-acids, which were identified by conversion into the

nitriles and then into the malonic acids, methyl- and ethyl-malonic acid being obtained. The αβ : αδ ratio, determined by isolating the acetic and propionic acid formed, is about 9 : 1, on an isolation of the acids in 91% yield. G. DISCOMBE.

Action of magnesium on iodoform in ethereal solution. C. L. TSENG and E. J. H. CHU (Nat. Centr. Univ. Sci. Rep., **A**, 1930, **1**, 15—22).—In anhydrous ether acetylene and the compound $MgI_2,2H_2O,2Et_2O$ are formed. Only the trimagnesium compound is formed, and reacts immediately with iodoform. Chloroform and iodoform do not react similarly. CHEMICAL ABSTRACTS.

Preparation of nitromethane by Kolbe's synthesis. A. B. WANG and C. L. TSENG (Nat. Centr. Univ. Sci. Rep., **A**, 1930, **1**, 27—28).—Addition of a mol. proportion of boric acid to the sodium nitrite-chloroacetate mixture gives a 58% yield of nitromethane; loss of trichloroacetic acid by formation of sodium glycollate is thus avoided.

CHEMICAL ABSTRACTS.

Preparation of anhydrous alcohols. H. LUND and J. BJERRUM (Ber., 1931, **64**, [*B*], 210—213).—The method is based on the reactions $Mg+2EtOH \longrightarrow H_2+Mg(OEt)_2$ and $Mg(OEt)_2+2H_2O \longrightarrow Mg(OH)_2+2EtOH$. Its inception requires the use of absolute alcohol, but 96% alcohol can be used subsequently provided that an excess of ethoxide is always present. Magnesium turnings (5 g.) covered with absolute alcohol (50—75 c.c.) are heated under a reflux condenser with iodine (0·5 g.) until the halogen has disappeared. If a vigorous evolution of hydrogen has not then commenced, a further portion of iodine (0·5 g.) is added. The heating is continued until nearly all the magnesium has been converted into the ethoxide. Not more than 900 c.c. of absolute alcohol are added and ebullition is continued for half an hour, after which the product is distilled. Fractionation appears to be superfluous, but for the purest specimens only the first two thirds of the mixture should be distilled. Removal of possible volatile bases is effected by distillation over 2 : 4 : 6-tribromobenzoic acid; the procedure does not alter the electric conductivity of ethyl alcohol, but is essential for the production of electrolyte-free methyl alcohol. The following data are recorded: ethyl alcohol, d_4^{25} 0·78503; propyl alcohol, d_4^{0} 0·81925, d_4^{10} 0·81144, d_4^{15} 0·80738, d_4^{20} 0·80335, d_4^{25} 0·79934; methyl alcohol, d_4^{25} 0·78651. H. WREN.

Preparation of pentamethylethanol, and the ketol condensation of pinacolin. V. M. TOLSTOPJATOV (J. Russ. Phys. Chem. Soc., 1930, **62**, 1813—1828).—Interaction of magnesium methyl iodide with pinacolin gives a mixture of pentamethylethanol and ββγξξ-pentamethylheptan-γ-ol-ε-one, b. p. 106°/15 mm., d_0^{21} 0·8999, the latter being a condensation product of pinacolin. Condensation of pinacolin by magnesium *n*-butyl bromide gives this ketol. Dehydration by anhydrous oxalic acid gives the corresponding *ketone*, b. p. 95·5—96°/18·5 mm., d_0^{21} 0·8433 (*semicarbazone*, m. p. 117—118°; *oximes*, m. p. 116—117° and m. p. 73—92° respectively). E. B. UVAROV.

Catalytic decomposition of cetyl alcohol. C. SANDONNINI and S. BEZZI.—See this vol., 440.

αα-Dichloro- and αα-diethoxy-tertiary alcohols and the corresponding aldehyde alcohols. A. AVY (Bull. Soc. chim., 1931, [iv], **49**, 12—18).—Dichloro-tertiary alcohols, $OH{\cdot}CRR'{\cdot}CHCl_2$, are obtained by the action of Grignard reagents on ethyl dichloroacetate, but the yields are good only in the case of the lower members. The corresponding diethoxy-alcohols are similarly obtained from ethyl diethoxyacetate in good yield and on hydrolysis with hydrochloric acid afford an insoluble semiacetal from which in one case only the corresponding aldehyde alcohol was obtained. Attempts to obtain α-hydroxy*iso*butaldehyde from αα-dichloro-β-methylpropan-β-ol were unsuccessful, but in the case of αα-dichloro-β-ethylbutan-β-ol, *α-hydroxy-β-ethylbutaldehyde*, b. p. 55—57°/15 mm. [*semicarbazone*, m. p. 204—205°. from which is regenerated an aldehyde, b. p. 28°/13 mm. (*semicarbazone*, m. p. 210°; *oxime*, m. p. 62°)], is obtained by refluxing with an aqueous suspension of calcium carbonate.

The following are described: αα-dichloro-β-methylpropan-β-ol, m. p. 8°, b. p. 38°/5 mm., 52°/10 mm., d_4^{19} 1·2363, n_D^{19} 1·4598, *αα-dichloro-β-ethylbutan-β-ol*, b. p. 76°/14 mm., d_4^{21} 1·175 n_D^{21} 1·999 [together with dichloromethyl ethyl ketone, b. p. 139° (semicarbazone, m. p. 142°)]. αα-Dichloro-β-propylpentan-β-ol and αα-dichloro-β-butylhexan-β-ol could be obtained only in 15% yield. Magnesium phenyl bromide yields *diphenyldichloromethylcarbinol*. m. p. 95—96°, b. p. 200°/5 mm., together with traces of a *substance* containing C 80·47%, H 5·49%, but magnesium benzyl bromide yields dibenzyl and a viscous residue, decomp. about 220°. *αα-Diethoxy-β-methylpropan-β-ol* has b. p. 75°/19 mm., d_4^{24} 0·9277, n_D 1·41109; *αα-diethoxy-β-ethylbutan-β-ol*, b. p. 95°/18 mm., d_4^{21} 0·923, n_D^{21} 1·42555; *αα-diethoxy-β-propylpentan-β-ol*, b. p. 98°/5 mm., d_4^{22} 0·9073, 1·4285; *αα-diethoxy-β-butylhexan-β-ol*, b. p. 101°/3 mm., d_4^{20} 0·9001, n_D^{20} 1·4315; *diphenyldiethoxymethylcarbinol*, m. p. 125°, b. p. 170°/4 mm. Hydrolysis of αα-diethoxy-β-methylpropan-β-ol with hydrochloric acid for 24 hrs. at the ordinary temperature affords an insoluble *compound*,
b. p. 105°/12 mm. ββ-Diethoxy-β-ethylbutan-β-ol similarly affords a *compound*, $C_6H_{12}O_2$, b. p. 114—115°/6 mm.; with warm dilute hydrochloric acid a 65% yield of the semicarbazone of β-hydroxy-β-ethylbutaldehyde is obtained. αα-Diethoxy-β-propylpentan-β-ol with cold hydrochloric acid yields the *compound*, $C_{18}H_{36}O_4$, m. p. 87°, and αα-diethoxy-β-butylhexan-β-ol the compound, $C_{22}H_{42}O_4$, m. p. 90—91, from which *β-hydroxy-β-butylhexaldehyde*, b. p. 94—97°/6 mm., d^{22} 0·9207, n_D^{22} 1·4379, is obtained by distillation with dilute hydrochloric acid.

R. BRIGHTMAN.

Oxidations with quadrivalent lead salts. II. Oxidative fission of glycols. R. CRIEGEE (Ber., 1931, **64**, [*B*], 260—266; cf. A., 1930, 1278).—Glycols, or more generally substances containing at least two hydroxyl groups attached to two neighbouring carbon atoms are oxidised by lead tetra-acetate in accordance with the scheme $OH{\cdot}CR'R''{\cdot}CR'''R''''{\cdot}OH$

$+Pb(OAc)_4 \longrightarrow R'·CO·R''+R'''·CO·R''''+2AcOH+Pb(OAc)_2$. The following instances are cited: ethylene glycol to formaldehyde, pinacol to acetone, ethyl tartrate to ethyl glyoxylate, hydrobenzoin to benzaldehyde, *p*-αβ-dihydroxypropylanisole to anisaldehyde, *cis*- and *trans-cyclo*hexane-1 : 2-diol to adipdialdehyde. The reaction appears to be of general applicability and is specific. Among saturated alcohols and their derivatives only those are attacked which have at least two hydroxy-groups in vicinal positions. Monohydric alcohols and glycols with partly or completely masked groups are indifferent. Thus pentaerythritol is not attacked, although possessing four free hydroxyl groups. The change proceeds so readily that its quantitative nature is established by titration of glycols with a 0·1*N*-lead tetra-acetate solution in acetic acid. Δ^4-*cyclo*Pentene-1 : 2-diol and dihydroxyhydrindene reduce an excess of the reagent owing to further oxidation of the aldehyde produced. In general, reaction occurs most rapidly with glycols containing those substituents which cause greatest rate of addition at the double linking. The mechanism of the reaction does not consist in a preliminary dehydrogenation $>C(OH)·C(OH)< \longrightarrow {}^-O·C·C·O^-$, since it is not effected by dichloroquinizarinquinone, which, according to Dimroth (unpublished work), can replace lead tetra-acetate as a dehydrogenating agent. The following scheme is therefore adopted: $OH·C·C·OH \longrightarrow 2OH·C·OAc \longrightarrow 2C:O$. The applicability of the method in the study of the sugars is illustrated by the production of formaldehyde from *iso*propylideneglucose, thus confirming the furanose structure, and in that of the glycerides by the observation that the β-acetylglycerol of Bergmann and Carter contains 40% of the α-isomeride. H. Wren.

Reaction of glycerol and calcium glycerophosphate. L. Ekkert (Pharm. Zentr., 1931, 72, 85—86).—Superposition of dilute aqueous glycerol on sulphuric acid containing a little codeine gives a blue or violet ring, and after mixing, a blue or violet solution. Calcium glycerophosphate gives, similarly, a blue ring with a white precipitate and a bright blue, turbid solution. H. E. F. Notton.

Aliphatic ethers. H. Henstock (J.C.S., 1931, 371—372).—The lower aliphatic ethers, unlike many aromatic and tertiary aliphatic ethers, are not attacked by sodium, potassium, or an alloy of the two, even under pressure at 200°. n-*Propyl* iso*butyl ether*, b. p. 106°/720 mm., d^{15} 0·7549, 1·3852, and iso*propyl* n-*butyl ether*, b. p. 108°/738 mm., d^{15} 0·7594, n^{21}_{5461} 1·3889, are described. J. D. A. Johnson.

Reaction of complex esters containing a trichloromethoxyl group. IV. Action of aluminium chloride on alkyl trichloromethyl carbonates. N. N. Melnikov (J. Russ. Phys. Chem. Soc., 1930, 62, 2019—2022).—The action of aluminium chloride on methyl, ethyl, and propyl trichloromethyl carbonates gives carbon dioxide, carbonyl chloride, and the corresponding alkyl chloride. E. B. Uvarov.

ψ-Halogens. XII. Formulation. Trichloromethyl perchlorate. L. Birckenbach and J. Goubeau (Ber., 1931, 64, [*B*], 218—227; cf. A., 1930, 1564).—ψ-Halogens are defined as groups which fulfil the condition, Σ outer electrons +Σ valency electrons $=8n[+2m]-1$, where *n* is the number of atoms surrounded by octets and *m* the number of hydrogen atoms. An exact analogy of such groups of atoms with the halogens is not to be expected. Thus the isolation of the permanganate residue by the action of halogens on silver permanganate fails, since the group as such is too reactive and its proper decomposition ($MnO_4=MnO_2+O_2$) precedes the reaction of the total group. It has not been found possible to secure a solvent stable to the ClO_4 group for a study of the interaction of halogens and silver perchlorate. Pure carbon tetrachloride does not appear to react with completely anhydrous silver perchlorate, but in presence of a trace of hydrogen chloride a change proceeds slowly, probably in accordance with the scheme $AgClO_4+HCl \longrightarrow AgCl+HClO_4$ and $HClO_4+CCl_4 \rightleftharpoons CCl_3·ClO_4+HCl$. The main product is *trichloromethyl perchlorate* with about 10% each of chlorine and carbonyl chloride. The last-named compound probably results from the secondary reaction $HClO_4+CCl_3·ClO_4 \longrightarrow Cl_2O_7+COCl_2+HCl$, since the isolation of chlorine heptoxide has been effected in individual cases. Trichloromethyl perchlorate is a colourless mobile liquid, f. p. about −55°, which has not been obtained completely homogeneous. It may be preserved unchanged at a low temperature in the dark, but gradually decomposes at the ordinary temperature in the light; the change becomes vigorous at 40—50° and explosive at higher temperatures with production of chlorine and its oxides. It interacts very briskly with alcohol, benzene, and fats. Its solutions in ethylene bromide and phosphoryl chloride are unstable. It is immediately hydrolysed by water to perchloric acid and (?) trichloromethyl alcohol. H. Wren.

Esters of sulphurous acid. I. N. Voss and E. Blanke. **II. Preparation of acetals and glucosides.** W. Voss (Annalen, 1931, 485, 258—283, 283—298).—I. Symmetrical alkyl sulphites are obtained in good yield by gradual addition of thionyl chloride (1 mol.) to the dry alcohol (2·2 mols.) at the ordinary temperature in a rapid stream of carbon dioxide, and then heating until hydrogen chloride ceases to be evolved. Alkyl chlorosulphinates are formed intermediately, and may readily be isolated in good yield by addition of the alcohol (1 mol.) to thionyl chloride (1 mol.) cooled in ice and salt. The lower chlorosulphinates are immediately hydrolysed by water, and decompose, slowly on keeping, and rapidly when heated, into the alkyl halide and sulphur dioxide; the poor yields of alkyl sulphite obtained by Arbusoff (A., 1909, ii, 573) are ascribed to this ready thermal decomposition. Methyl ethyl sulphite is obtained by interaction of methyl alcohol with ethyl chlorosulphinate in presence of a suitable base, *e.g.*, pyridine. If the base is omitted a mixture of methyl, ethyl, and methyl ethyl sulphites results. The reversibility of the reactions $Et_2SO_3+2MeOH$ $MeEtSO_3+MeOH+EtOH \rightleftharpoons Me_2SO_3+2EtOH$ in presence of hydrogen chloride is established experimentally. Poor yields of alkyl sulphite are obtained

by interaction of thionyl chloride and an alcoholic solution of sodium alkoxide, on account of decomposition, $SO(OR)_2 + NaOR = R_2O + NaO{\cdot}SO{\cdot}OR$. Better results are obtained with the alcohol-free alkoxide in an indifferent medium; thus phenyl sulphite, previously isolated in an impure condition by Richter (A., 1917, i, 24), is obtained in 40% yield by interaction of dry sodium phenoxide and thionyl chloride in dry ether. The following are described: *methyl*, b. p. 35°/60 mm., d_4^{18} 1·4186; *ethyl*, b. p. 32°/16 mm., d_4^{17} 1·2826, and iso*propyl*, b. p. 34°/24·5 mm., d_4^{18} 1·2005, *chlorosulphinates*; *methyl ethyl*, b. p. 53°/20 mm., 141·5°/769 mm., d_4^{18} 1·1364, 1·41417; *n*- and *iso*-propyl; n-*butyl*, b. p. 114—115°/15 mm., d_4^{22} 0·9944, $n_{He}^{1\cdot6}$ 1·43051; iso*amyl*, b. p. 127—128°/15 mm., $d_4^{16\cdot2}$ 0·97293, 1·43547; cyclo*hexyl*, b. p. 182°/19 mm., $d_4^{17\cdot8}$ 1·0974, 1·48396, and phenyl, b. p. 143°/0·7 mm., 152°/1·8 mm., $d_4^{20\cdot2}$ 1·2404, 1·56899, sulphites. Methyl methanesulphonate is best prepared from the silver salt and methyl iodide at 100°; silver sulphite gives only a small yield. *Sodium methyl sulphite* is obtained from methyl sulphite and the calculated quantity of 5% sodium methoxide, a little methanesulphonate being also formed. It is immediately hydrolysed by acid or alkali in aqueous solution.

Propyl and the lower alkyl sulphites may be distilled unchanged at atmospheric pressure, but continued heating of the former gives traces of propyl alcohol. They are not hydrolysed by pure water. Methyl methanesulphonate is hydrolysed by water according to a unimolecular reaction, $k=2{\cdot}98\times10^{-4}$, which therefore is not catalysed by hydrogen ions; in alkaline solution hydrolysis is accelerated. In the case of methyl sulphite also alkaline hydrolysis is more rapid than acid hydrolysis; both reactions, although actually the result of two consecutive reactions, have unimolecular velocity coefficients on account of the immediate hydrolysis of the sodium methyl or methyl hydrogen sulphite formed intermediately.

Alkyl sulphites may be used as alkylating agents in other than aqueous alkaline media. Phenyl ethers are obtained in yields of 55—90% by heating the sodium phenoxide (1 mol.) with the alkyl sulphite (1·1 mols. in the case of monohydric and 3 mols. in the case of dihydric phenols; in the latter case the dialkyl ether is readily produced) in toluene or other inert solvent. Lower yields are obtained from the phenol and alkyl sulphite in presence of an anhydrous mineral acid as catalyst. Aniline is readily alkylated, and a convenient method is afforded for preparation of the higher alkylanilines. Thus from 1 mol. of aniline and 3 mols. of *iso*amyl sulphite mono- (p-*toluenesulphonyl* derivative, m. p. 76—77°) and di-*iso*amylanilines were obtained in yields of 74% and respectively. The *benzenesulphonyl* derivative of ethylaniline has b. p. 188·5°/1·5 mm. Carboxylic acids are esterified by warming with an alkyl sulphite (1·1 mols. for each carboxyl group) in presence of a little mineral acid, but the method is not applicable to acids that are not esterified by the alcohol in presence of a catalyst.

Interaction of methyl sulphite (2 mols.) with dimethylaniline (1 mol.) at 135 140° gives *phenyltrimethylammonium methanesulphonate*, m. p. 188—189°, in 99% yield (75% with 1·1 mols. of sulphite), identified by synthesis from dimethylaniline and methyl methanesulphonate. Equimolecular quantities of the reagents on long keeping at the ordinary temperature, however, give (probably) *phenyltrimethylammonium methosulphite*, m. p. 120—121° to a turbid liquid (sinters at 90°); this is recovered unchanged after heating at 135°, and evolves sulphur dioxide when treated with acids. N-*Methylpyridinium methanesulphonate*, m. p. 117—118°, and *methosulphite*, m. p. 104—107°, are similarly prepared.

II. Acetals are produced by interaction of the carbonyl compound (1 mol.) with the alcohol (2—3 mols.) and an alkyl sulphite (1·1 mols.) in presence of an acid catalyst. In common with orthoformates and orthosilicates, the sulphites are considered to act merely as dehydrating agents, thereby disturbing the equilibrium $CORR' + 2R''{\cdot}OH \rightleftharpoons C(OR'')_2RR' + H_2O$. This view is based on (1) the need of a minimum amount of alcohol, (2) the relative order of ease of acetal formation, which is also the order of ease of hydrolysis, (3) the velocity coefficients for the acid hydrolysis of sulphites and orthoformates, (4) formation of the acetal corresponding with the alcohol used and not with the sulphite (if derived from a different alcohol), and (5) the fact that acetals which are more readily hydrolysed by acid than is benzophenone dimethylacetal (*e.g.*, acetone diethylacetal) may be used in place of sulphites etc. in preparation of the latter, but such as are more slowly hydrolysed (*e.g.*, benzaldehyde dimethylacetal) are inactive. Methyl carbonate is also inactive. The following are described: n-*butaldehyde dimethyl*- and *diethyl-acetals* and *benzaldehyde* n-*butylacetal*, b. p. 149—150°, d_4^{14} 0·9289, n_D^{19} 1·4790.

Methyl- and ethyl-glucosides are similarly prepared from sugars, but the method is not applicable to the higher members on account of solubility difficulties. The product is a mixture of the α- and β-forms, of which the former preponderates. On account of the use of an acid catalyst, the method is not available for the alkylbiosides, but for the same reason it offers a convenient route to α-methylglucoside from starch.

H. A. Piggott.

Formation of sulphonium chlorides and unsaturated substances by the action of water and aqueous-alcoholic potassium hydroxide on ββ′-dichlorodiethyl sulphide. J. S. H. Davies and A. E. Oxford (J.C.S., 1931, 224—236).—ββ′-Dihydroxydiethyl sulphide (I), b. p. 130°/2 mm., d_4^{20} 1·1821 [*diphenylcarbamate*, m. p. 128·5—129·5°; p-*toluenesulphilimine* (+H_2O), m. p. 86—87°], reacts with 1, 2, or 3 mols. of aqueous ethylene chlorohydrin to give *tri-β-hydroxyethylsulphonium chloride*, m. p. 125—126°, and an oil, both being soluble in water, their solutions containing ionisable chlorine. With ββ′-dichlorodiethyl sulphide (II) I yields *sulphidobis-β-hydroxydiethyl sulphide* 1 : 3-*di-β-hydroxyethochloride*, $S[C_2H_4S(C_2H_4{\cdot}OH)_2\}Cl]_2$, m. p. 101·5—103° (*mercurichloride*, an oil; *chloroplatinate*, m. p. 133—134°), which reverts to II with hydrogen chloride at 100°. No additive compounds of II with ethyl sulphide, sulphidobis-β-hydroxydiethyl sulphide, ethylenebis-β-hydroxyethyl sulphide, 1 : 4-dithian, or

1 : 4-thioxan are obtained when mixtures of the components are heated at 80° for 6 hrs. Sulphidobis-β-hydroxydiethyl sulphide reacts with ethylene chlorohydrin at 100° to give substances presumed to be *sulphidobis-β-hydroxydiethyl sulphide* 1 : 2-*di-β-hydroxyethochloride*, m. p. 120—121·5°, 1 : 4-*dithian* 1-β-*hydroxyethochloride* (III), m. p. 175° (*mercurichloride*, m. p. 95—96°), the latter also being formed rationally from 1 : 4-dithian and ethylene chlorohydrin and from ethylenebis-β-hydroxyethyl sulphide and ethylene chlorohydrin. Hydrogen chloride and I at 100—106° give II (56%) and an undistillable residue which probably mainly consists of *oxidobis-β-chlorodiethyl sulphide*, $(C_2H_4Cl·S·C_2H_4)_2O$, since it gives a *diphenoxy*-derivative, m. p. 55—57°. Hydrolysis of II with the minimum quantity of boiling water during 6 hrs. leads to the formation of III and traces of thiodiglycol and dithian. Hydrolysis with 4 volumes of water, followed by treatment of the crude syrup with a little concentrated hydrochloric acid, leads to II and a little ethylenebis-β-chloroethyl sulphide. Treatment of the syrup with excess of concentrated hydrochloric acid leads only to II. Boiling dilute hydrochloric acid and I give a mixture of sulphonium chlorides from which III can be isolated. Hydrolysis of II with 4 mols. of 20% aqueous-alcoholic potassium hydroxide gives a mixture of divinyl sulphide (*sulphilimine*, m. p. 91—93°), β-*ethoxyethyl vinyl sulphide*, b. p. 65°/8 mm., d_4^{20} 0·9532 (*mercurichloride*, m. p. 152—153°), ββ′-diethoxydiethyl sulphide, and β-ethoxy-β′-hydroxydiethyl sulphide, but with 1 mol. of aqueous-alcoholic alkali, β-*chloroethyl vinyl sulphide* (IV), b. p. 71—72°/50 mm., 151·5—152·5/764 mm. (*sulphilimine*, m. p. 101·5—103°; ill-defined *mercurichloride*), is obtained in good yield. Hydrogen chloride converts IV into *αβ′-dichlorodiethyl sulphide* (not pure), b. p. 68—69°/9 mm. The formation of β-chloro-β′-hydroxydiethyl sulphide on hydrolysis of II (Bales and Nickelson, J.C.S., 1923, **123**, 2486) is not confirmed, the substance isolated by these authors being most probably IV. A mechanism is suggested whereby the formation of the sulphonium chlorides by hydrolysis of II may be explained.

J. D. A. Johnson.

Behaviour of certain thiophanes in heptane and naphtha solutions. R. W. Bost and M. W. Conn (Ind. Eng. Chem., 1931, **23**, 93—95).—The action of various reagents on tetramethylene and pentamethylene sulphides, ethyl sulphide, and thiophen in pure *n*-heptane and in three naphtha solutions has been studied. Mercuric chloride, potassium permanganate, hydrogen peroxide, and methyl iodide react with the thiophanes to form definite products which are easily purified and identified. Bromine and mercuric iodide form unstable products. Nitric acid gives the sulphone when *n*-heptane solutions of the sulphides are used, but no definite product when the naphthas are employed as solvents. In general, the thiophanes resemble the alkyl sulphides more than thiophen. The following *compounds* appear new: $Et_2S,2HgCl_2$, m. p. 119·5°; Et_2S,HgI_2, m. p. about 52°; Et_2SO_2, m. p. 70°; Et_2SO, m. p. 4—6°; $(CH_2)_4S,HgCl_2$, m. p. 124·5°; $(CH_2)_4S,xHgI_2$, m. p. about 78°; $(CH_2)_4SO_2$, m. p. 8—10°; $(CH_2)_4S,MeI$, m. p. 185—190°; $(CH_2)_4SBr_2$, m. p. 80°; $(CH_2)_5S,HgCl_2$, m. p. 137·5—138·5°; $(CH_2)_5S,xHgI_2$, m. p. about 79·5°; $(CH_2)_5SO_2$, m. p. 99°; $(CH_2)_5S,MeI$, m. p. 192·5°; $(CH_2)_5SBr_2$ m. p. 69·5°.

H. S. Garlick.

Methanetetrasulphonic acid. F. B. Kipping (J.C.S. 1931, 222—223).—Attempts to prepare potassium methanetetrasulphonate by the interaction of potassium sulphite and potassium di-iodomethanedisulphonate or potassium diazomethanedisulphonate (Pechmann, A., 1896, i, 14) yielded, respectively, potassium methionate and potassium methanetrisulphonate. The sulphonation of acetamide with fuming sulphuric acid containing less than 10% of sulphur trioxide yielded only potassium methionate, more concentrated acid giving potassium methanetrisulphonate. The results of Fantl and Fisch (A., 1930, 320) and of Backer and Claassens (*ibid.*, 1556) on the non-existence of hydroxymethanetrisulphonic acid are confirmed.

G. Discombe.

Electrolysis of salts of *n*-butyric acid. F. Fichter and A. Bürgin (Helv. Chim. Acta, 1931, **14**, 90—101).—*iso*Propyl alcohol, but not *n*-propyl alcohol, appears amongst the products of the electrolysis of potassium butyrate solutions under various conditions, and its formation is ascribed to the hydrolysis of *iso*propyl butyrate formed by the action of the primary electrolytic product, propylene, on butyric acid. By heating a solution of propylene in butyric acid for 50 hrs. at 130—140° in sealed tubes followed by hydrolysis a 50% yield of *iso*propyl alcohol was obtained. The electrolytic formation of the alcohol, even when the electrolyte is alkaline, is ascribed to the presence of free butyric acid at the anode.

The thermal decomposition of dibutyryl peroxide proceeds mainly as follows: $(Pr·CO·O)_2=C_6H_{14}+2CO_2$, a 62·6% yield of *n*-hexane being obtained. Exposure of the peroxide to ultra-violet light also causes decomposition in this manner, but the yield of hexane is smaller. The explosive decomposition of perbutyric acid takes place as follows: $C_4H_8O_3=C_3H_6+CO_2+H_2O$. Propylene and carbon dioxide were also found among the products of decomposition of the peracid by ultra-violet light. It is considered, therefore, that in the electrolysis of *n*-butyrates the dibutyryl peroxide is hydrolysed at the anode to butyric and perbutyric acids; the latter is then decomposed into carbon dioxide and propylene, which reacts as shown above with butyric acid. Measurements have been made of the velocity of hydrolysis of dibutyryl peroxide.

O. J. Walker.

Acetoacetic ester condensation. II. Reaction of aliphatic esters with sodium. J. M. Snell and S. M. McElvain (J. Amer. Chem. Soc., 1931, **53**, 750—760).—The reaction between sodium (2 atoms) and 1 mol. of ethyl acetate, propionate, butyrate, *iso*butyrate, and trimethylacetate has been studied in ether and benzene at the b. p. The resulting sodium salts are decomposed with 35% sulphuric acid and the products fractionated. The appropriate acylalkylcarbinols are obtained usually in 50—75% yield, together with small amounts of the corresponding diketones, higher-boiling products, and acids; the yield of diketone from ethyl trimethylacetate is

much higher than from the other esters. When the ester is used as solvent, the acetoacetic ester condensation takes place with ethyl acetate and propionate; no diketone or acylalkylcarbinol results in these cases. The yields of carbinol from ethyl butyrate, *iso*butyrate, and trimethylacetate are 7, 56, and 98%, respectively, on the sodium used; diketones, acids, and high-boiling products are also formed. There is no appreciable difference in the rates of reaction of the last three esters, and there is no necessity for special mechanisms to account for the slowness of reaction of an ester which cannot enolise. The suggestion that reaction proceeds, when possible, through the enol form (Scheibler and Emden, A., 1924, i, 42) is unnecessary. The diketone is probably an intermediate in the formation of the carbinol (cf. Egorova, A., 1929, 49). The following changes probably occur in the above reactions: $2Na + 2R{\cdot}CO_2Et \longrightarrow [CR(ONa)(OEt)]_2 \xrightarrow{2Na} (CR{\cdot}ONa)_2 + 2NaOEt$.
H. BURTON

Degradation of the salts of organic acids by *Aspergillus fumaricus*. W. THIES (Ber., 1931, 64, [*B*], 214—218).—The action of the mould on the calcium salts of gluconic, saccharic, citric, succinic, tartaric, malic, fumaric, and lactic acids, on sodium gluconate, citrate, fumarate, and lactate, potassium succinate and malate, and ammonium tartrate has been investigated. Whereas the calcium salts yield calcium carbonate, the degradation of the alkali salts terminates with the production of oxalate. A modifying influence of acidity could not be established and acidity or neutrality of the culture medium is without effect. No support is afforded to the hypothesis that the degradation of sugar to citric or fumaric acid occurs through other acids as intermediate products.
H. WREN.

Supposed asymmetry of *meso*-tartaric acid. K SCHERINGA (Pharm. Weekblad, 1931, 68, 143—145).—The configuration suggested by Boeseken (Chem. Weekblad, 1922, 207) should be associated with optical activity; this is probably compensated externally, since for every asymmetric molecule of a given orientation molecules possessing the image configuration must be present in a solution.
S. I. LEVY.

Compound uronic acids. Structure of aldobionic acid from gum arabic. S. W. CHALLINOR, HAWORTH, and E. L. HIRST (J.C.S., 1931, 258—65).—The aldobionic acid from gum arabic has the biose linking through the side-chain of galactopyranose. Complete methylation leads to *methyl heptamethylaldobionate* (*methyl* ester of *hexamethyl-6-glycuronosido-β-methylgalactoside*) (I), m. p. 86°, $[\alpha]_D^{?}$ −21° in water, $[\alpha]^{20}$ −43° in chloroform, mixed with the α-form (mixture, b. p. about 185°/0·02 mm.); the mixture when hydrolysed by 7% hydrochloric acid ... 4-*trimethylgalactose* (II) (crude, n_D^{18} 1·4727, $[\alpha]_D^{20}$ +83° in water) and 2 : 3 : 4-*trimethylglycuronic acid* (III) [crude, n_D^{18} 1·4709, $[\alpha]_D^{18}$ +58° (equilibrium value in water)]. The latter on methylation gives ... β-*methylglycuronide*, m. p. 133°, ... −38° in water, $[\alpha]_D^{21}$ −63° in chloroform, identical ... the completely methylated product of the lactone of the glycuronic acid obtainable from gum arabic. Methylation of II gives 2 : 3 : 4 : 6-tetramethyl-β-methylgalactoside, whilst oxidation with bromine water leads to 2 : 3 : 4-trimethyl δ-galactonolactone (IV), characterised by its *phenylhydrazide*, m. p. 165—167°. Oxidation of IV with nitric acid (*d* 1·42) gives, after esterification of the product, the *dimethyl* ester of 2 : 3 : 4-*trimethylmucic acid*, m. p. 98°, $[\alpha]_D$ +35° in water, which is proof that II possesses a free $\cdot CH_2\cdot OH$ group, and since I is non-reducing, establishes the fact that the union with the glycuronic acid residue is through the reducing group of the latter.
J. D. A. JOHNSON.

Highly-polymerised compounds. XLIX. Action of bases on formaldehyde solutions. H. STAUDINGER, R. SIGNER, and O. SCHWEITZER (Ber., 1931, 64, [*B*], 398—405; cf. this vol., 202).—The action of 0·05 equivalent of alkali, alkaline-earth, or thallous hydroxide on 30% formaldehyde solution yields precipitates which, after washing and electrodialysis, contain metal in amount indicating polymerisation to an extent far greater than that observed with the polyoxymethylene dimethyl ethers. Treatment of 40% formaldehyde with lithium, sodium, potassium, and rubidium hydroxide and with calcium, barium, and magnesium oxide gives precipitates increasing in quantity with increasing strength of the base, showing that polymerisation and precipitation depend on the hydroxyl-ion concentration. Marked difference in the solubility of the salts is not observed. The formaldehyde content of the precipitates lies between 98 and 99·5%, the metal oxide content between 0·1 and 0·2%. The precipitates therefore contain 0·5—1·5% of water. They are not polymerically uniform and it is not possible to determine the mol. wt. from the metal content even on the supposition that the latter is united chemically. Since the precipitates are decomposed by hydrochloric acid or sodium hydroxide at the same rates as polyoxymethylene, there is no evidence of the chemical union of the metals. With 40% formaldehyde and 0·5—1 mol. of solid potassium hydroxide, a vigorous Cannizzaro reaction occurs; with smaller quantities, polymerisation predominates, the best yields of precipitate being obtained with 1 mol. of hydroxide to 20—100 mols. of formaldehyde. Even with much smaller amounts polymerisation is observed. The precipitates have the same properties and composition whatever the amount of hydroxide used, so that a polymeric homologous series is not thus obtained.

The constitution of β-polyoxymethylenes is discussed in detail. The conclusion is reached that the ester-like union of sulphuric acid in these compounds is not firmly established.
H. WREN.

Absorption and reactivity of the ketone group. (MME.) RAMART-LUCAS and (MME.) BRUZAU (Compt. rend., 1931, 192, 427—429).—Absorption spectra measurements of some polyalkyl ketones indicate "mutual influence" between the ketone group and α-alkyl substituents. The decreased reactivity of the ketone group when the α-positions are fully alkylated is attributed to a similar cause.
A. A. LEVI.

Enolisation of ketones. V. GRIGNARD and H. BLANCHON (Bull. Soc. chim., 1931, [iv], 49, 23—42).—

Determinations of the enolisation of ketones by a modification of Zerevitinov's method, in which the ketone is treated in ethereal solution with a large excess of the magnesium alkyl halide and the hydrocarbon liberated on heating to 40° to initiate this reaction, measured in a Bunte burette, indicate that all ketones which are structurally capable of enolisation can be enolised even if under ordinary conditions there is no evidence of a keto-enol equilibrium. The enolic form is obtained when the keto-enol equilibrium is displaced in this direction by certain reagents, particularly by Grignard reagents, which produce varying degrees of enolisation and fix the enolic form as a mixed magnesium organo-enolate. Negative groups and ethylenic linkings, especially when conjugated with the enolic linking, promote enolisation, but the latter is not dependent on the presence of anomaly, although no relation has been established between the constitution of the ketone and its tendency to enolise or the stability of the enolic form. The figures in parentheses give the percentage of enolisation with magnesium *tert.*-butyl chloride for the following ketones: pulegone (100) (cf. Grignard and Savard, A., 1926, 92, 408), dibutyl ketone (20), carvone (20·5), mesityl oxide (60), dibenzyl ketone (24), acetone (30), acetophenone (31), *cyclo*pentanone (32·5), thujone (41), 4-methyl*cyclo*hexanone (46), butyrone (49), *cyclo*hexanone (50·5), menthone (51). The enolisation is generally increased about 10% by rise of temperature, but with thujone and menthone the enolisation may thus attain or exceed 60%. The effect of the Grignard reagent depends both on the nature of the halogen and on the organic radical. With dibutyl ketone at 13—14°, primary magnesium alkyl halides produce 6—8·5% enolisation, secondary, 13·5—16%, and tertiary, *e.g.*, magnesium *tert.*-butyl chloride, 19·7—20·4%. The enolising action of the chlorides is inferior to that of bromides and iodides, the latter being usually a little inferior to the bromides. Determinations of the keto-enolic equilibrium of the following ketones by Job and Reich's method (A., 1924, i, 24) has given the percentage of enol indicated: *cyclo*hexanone 8·2, 4-methyl*cyclo*hexanone 6·3, mesityl oxide 6·3. Acetone, butyrone, dibutyl ketone, dibenzyl ketone, acetophenone, *cyclo*pentanone, menthone, carvone, and thujone initially contained no enol.

The enolic forms have been isolated by conversion into the magnesium alkyl enolenate by treatment with magnesium *iso*propyl bromide in ether, initiating the reaction by warming at 40° for ½ hr., conversion of the enolenate into the acetyl derivative by treatment with acetyl chloride in ether at −5°, and hydrolysis with ice-water, using sodium hydrogen carbonate to neutralise the acetic acid liberated.

After distillation of the ether, *cyclo*hexanone yields a small fraction, 30% of enol, b. p. 60—62°/12 mm., a fraction, b. p. 75°/12 mm., n_D^{12} 1·4867, *cyclo*hexanonenyl acetate, and a fraction, b. p. 132°/12 mm., *iso*propyl*cyclo*hexyl acetate, hydrolysed to *iso*propyl*cyclo*hexanol, b. p. 125°/12 mm. Hydrolysis of the *cyclo*hexanonenyl acetate with 10% oxalic acid yields on ether extraction a 70—75% enol, n_D^{12} 1·4601 falling to 1·45451 in 10 hrs. Benzoquinone and phthalic anhydride do not stabilise the enol.

Similarly, thujone, b. p. 83—85°/12 mm., d_4^{15} 0·905, n_D^{15} 1·4471, yields a fraction, 89·5% of thujonenol, b. p. 84—86°/12 mm., d_4^{15} 0·9010, n_D^{15} 1·45401, falling to 69·9% enol, n_D^{15} 1·45261, in 1 hr. and to 4·1%, n_D^{15} 1·44731, in 15 hrs., stabilised by phthalic anhydride and oxalic acid, and a larger fraction, iso*propylthujyl acetate*, b. p. 124°/12 mm., hydrolysed to iso*propylthujol*, b. p. 115°/12 mm.

Carvone, b. p. 222°, d_4^{15} 0·965, n_D^{15} 1·503, with magnesium ethyl bromide gives a fraction, 96·5% of carvonenol, b. p. 114—115°/12 mm., d_4^{15} 0·957, n_D^{15} 1·5151, falling to 82·3% enol, n_D^{15} 1·51, in 1 hr. and to 1·5%, n_D^{15} 1·5033, in 25 hrs., the transformation being accelerated by sunlight alkali, ammonia, bromine, and mineral acids, and retarded only 5 hrs. by 1% of phthalic anhydride, together with a larger fraction, *ethylcarveol acetate*, b. p. 142°/12 mm., hydrolysed to ethylcarveol, b. p. 135°/12 mm. Mesityl oxide with magnesium *iso*propyl bromide similarly yields a fraction, 70% of enol, b. p. 134°, d_4^{12} 0·861, n_D^{12} 1·45001, falling to 50·1% enol in 1 hr., and to 6·4% in 5 hrs., phthalic anhydride and oxalic acid having no stabilising effect, a fraction, b. p. 140—145°, consisting of the enol acetate, and a fraction, b. p. 172°, containing the acetate of *βγε-trimethyl-Δ^δ-hexen-γ-ol*, b. p. 163°.

An alternative method of preparing the enols is from the chlorohydrins through the acetates. Thus pulegone, d_4^{12} 0·93, n_D^{12} 1·47392, is converted by phosphorus pentachloride into the enolic chlorohydrin, b. p. 88—89°/12 mm., d^{12} 0·995, n_D^{12} 1·49889 (cf. Klages, A., 1900, i, 44), which with alcoholic potassium acetate and decomposition with water affords the pure enol, b. p. 79—81°/3 mm., d_4^{12} 0·9130, n_D^{12} 1·48115, in 50% yield on the pulegone. Similarly, acetophenone in light petroleum with phosphorus pentachloride yields the enolic chlorohydrin, b. p. 195°/740 mm., converted in boiling alcoholic potassium acetate in 12 hrs. and treatment with ice-water into a mixture of the enol and its acetate, yielding when boiled with aqueous oxalic acid an oil, b. p. 205°, 75% hydroxyl. Acetophenonenol is completely tautomerised in 10 hrs. in the dark and in 5 hrs. in direct daylight.

The substances previously described as stabilisers, quinone, phthalic anhydride, and oxalic acid, do not appreciably retard the tautomerisation of this enol, and sunlight, sodium carbonate, ammonia, bromine, alkali hydroxides, strong acids, and sometimes even sodium hydrogen carbonate have a pronounced and even instantaneous accelerating action.

R. BRIGHTMAN.

cis- and trans-Forms of isobutylideneacetone and the isomeric βγ-unsaturated ketone. R. HEILMANN (Bull. Soc. chim., 1931, [iv], 49, 75—80).—The results obtained by Eccott and Linstead (A., 1930, 893) indicating that the semicarbazones, m. p. 126 and 160°, correspond with *trans-* and *cis*-forms of *iso*butylideneacetone appear to weaken the view previously advanced (A., 1930, 325) that the semicarbazone, m. p. 164°, is derived from β-methyl-Δ^β-hexen-ε-one. The formation of the hexenone from the residues in the preparation of 3-methyl-5-*iso*propylpyrazoline is now attributed to spontaneous oxidation of the latter to the ketazine of *iso*butylidene-

acetone, hydrolysis of the latter to a mixture of *cis*- and *trans*-*iso*butylideneacetone, and isomerisation of the *trans*-form to β-methyl-Δ^{β}-hexen-ε-one. Hydrolysis of the oxidation products of 3-methyl-5-*iso*propylpyrazoline and of the residues obtained in the preparation of this pyrazoline does not, however, yield identical results, the latter affording larger quantities of β-methyl-Δ^{β}-hexen-ε-one. It is concluded that this ketone corresponds at least in part with an initial βγ-unsaturated ketazine formed by the action of hydrazine on β-methyl-Δ^{β}-hexen-ε-one present in the *iso*butylideneacetone and that in the condensation of *iso*butaldehyde with acetone some β-methyl-Δ^{β}-hexen-ε-one is always formed with the *iso*butylideneacetone. R. BRIGHTMAN.

Constitution of homomesityl oxide. S. G. POWELL and C. H. SECOY (J. Amer. Chem. Soc., 1931, **53**, 765—768; cf. Becker and Thorpe, J.C.S., 1922, **121**, 1303).—Homomesityl oxide (improved method of preparation given) is ethyl β-methyl-Δ^{α}-butenyl ketone, since it is reduced catalytically (Adams) to ethyl β-methylbutyl ketone, b. p. 158°, d_4^{24} 0·829, n_D^{24} 1·412 [semicarbazone, m. p. 96° (lit. 102°)], which is oxidised by sodium dichromate and dilute sulphuric acid to acetic and β-methylvaleric acids. Reduction of homomesityl oxide with sodium and moist ether gives ethyl-β-methylbutylcarbinol, b. p. 155°, d_4^{24} 0·8425, n_D^{24} 1·433, obtained also from magnesium β-methylbutyl bromide and propaldehyde, which is oxidised to the above saturated ketone.

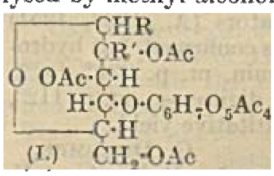
Methyl αβ-dimethylbutyl ketone, b. p. 158°, d_4^{22} 0·8295, n_D^{22} 1·412 (semicarbazone, m. p. 124—126°), is obtained by hydrolysis of ethyl methyl*sec.*-butylacetoacetate with 15% sodium hydroxide solution. H. BURTON.

Preparation of organic reagents. III. Diacetyldioxime. K. H. SLOTTA and K. R. JACOBI (Z. anal. Chem., 1931, **83**, 1—5).—An ice-cold mixture of methyl ethyl ketone (72 g.), ether (200 c.c.), and 20% methyl-alcoholic hydrochloric acid (30 c.c.) is treated with a slow stream of ethyl nitrate for 1½ hrs. The resulting diacetylmonoxime solution is treated with 1000 c.c. of water and a solution of sodium hydroxylaminodisulphonate, prepared as described below, and heated at 65—75° on the water-bath for 10 hrs., whereby the ether and excess of ethyl nitrite are slowly evaporated and diacetyldioxime separates in white crystals, which, after washing, are suitable for use without further purification. The sulphonate solution is prepared by treating 260 g. of sodium carbonate crystals in 50 c.c. of water with an excess of sulphur dioxide, adding the solution to an ice-cold solution of 138 g. of sodium nitrite in 500 c.c. of water, and saturating the mixture with sulphur dioxide at below 5°. A. R. POWELL.

Reactive form of glucoseoxime. M. L. WOLFROM and A. THOMPSON (J. Amer. Chem. Soc., 1931, **53**, 622—632).—Oximation of aldehydoglucose penta-acetate (A., 1929, 1043) gives *aldehydoglucoseoxime penta-acetate*, m. p. 99—99·5°, $[\alpha]_D^{24}$ +57·2° in chloroform, acetylated by acetic anhydride in pyridine at *aldehydoglucoseoxime hexa-acetate* (I), m. p. (labile form) 79°, resolidifying with m. p. about 119°, m. p. (stable form) 119·5°, $[\alpha]_D^{25}$ +45·9° in chloroform. Crystallographic data are given for I. Acetylation of glucoseoxime, m. p. 142—143° (lit. 138°), $[\alpha]_D^{23}$ in water −8·9⟶−1·9°, by Wohl's method (A., 1893, i, 292; cf. Behrend, A., 1907, i, 481) affords a glucoseoxime hexa-acetate, m. p. 113—115°, $[\alpha]_D^{25}$ +7·3° in chloroform (cf. *loc. cit.*), which must have the ring structure; it is designated the β-form. Deacetylation of the above penta-acetate by cold methyl-alcoholic ammonia gives β-glucoseoxime. When I is heated at 135—140° or boiled with acetic anhydride and sodium acetate, acetic acid is eliminated and penta-acetylgluconitrile, m. p. 83—84°, $[\alpha]_D$ +47·8° in chloroform, is obtained. Similar treatment of the β-hexa-acetate gives none of the nitrile. Treatment of β-glucoseoxime with acetic anhydride and sodium acetate at 75—80° (cf. Wohl, *loc. cit.*) gives penta-acetylgluconitrile and a small amount of I; it is presumed that ring fission occurs during acetylation and nitrile formation occurs by way of I. *Penta-acetylmannononitrile*, m. p. 92—93°, $[\alpha]_D^{25}$ −1·8° in chloroform, prepared from mannoseoxime, acetic anhydride, and sodium acetate at 85—90°, is not formed during any of the above reactions, indicating that ψ-oxime formation does not take place. H. BURTON.

Fall of rotatory power of solutions of polysaccharides under the action of alkali. J. EFFRONT (Compt. rend., 1931, **192**, 529—532).—The optical rotation of a 4—5% starch solution is decreased by 16% in 5·5 hrs. (no further change after 24 hrs.) by addition of an equal volume of *N*-sodium hydroxide. The rotations of solutions of maltose and dextrose are similarly reduced by 25·2% and 48·2%, respectively, in 5·5 hrs., and by 50% and 91%, respectively, in 24 hrs. These values vary only slightly with the specimen of starch used and the concentration of the solutions. Thus a decrease in optical rotation, under such conditions, of more than 52% in a solution containing dextrin, maltose, and dextrose, indicates the presence of the last-named, and in solutions of maltose and dextrose the decrease in rotation beyond the 48·2% given by maltose alone is directly proportional to the dextrose content of the mixture. The method also serves to determine approximately the amount of free maltose in the presence of soluble starch and reducing dextrins obtained by enzymolysis of malt extracts with diastase. J. W. BAKER.

Crystalline acetates of cellobiosone and the question of the formation of the γ-pyrone ring from disaccharides. K. MAURER and K. PLOTNER (Ber., 1931, **64**, [*B*], 281—289; cf. A., 1930, 1412).—2-Hydroxycellobial hepta-acetate, m. p. 125°, is readily hydrogenated in presence of palladium and glacial acetic acid to 1 : 4-*glucosidostyracitol hepta-acetate*, m. p. 187°, $[\alpha]_D^{22}$ +7·0° in chloroform, hydrolysed by methyl-alcoholic ammonia to 1 : 4-*glucosidostyracitol*, m. p. 173°, $[\alpha]_D^{17}$ +29·01° in water. Treatment of 2-hydroxycellobial hepta-acetate suspended in ether with dry chlorine gives a mixture of products from which a solid *dichloride* (I; R=R′=Cl), m. p. 158°, $[\alpha]_D^{20}$ −5·74° in chloroform,



(I.)

is isolated. It is re-converted by zinc dust and 50% acetic acid into 2-hydroxycellobial hepta-acetate and transformed by an excess of silver acetate in glacial acetic acid into *cellobiosone hydrate nona-acetate* (I; R=R′=OAc), m. p. 122—124°, $[\alpha]_D^{20}$ +38·92° in alcohol, re-converted into the hepta-acetate by pyridine and acetic anhydride. The crystalline dichloride is not affected by silver carbonate in cold or warm, moist ether, but one or more of the non-crystalline isomerides which are formed during its preparation are transformed into *cellobiosone hydrate hepta-acetate* (I; R=R′=OH), m. p. 121—138°, $[\alpha]_D^{20}$ +43·88° to +32·60° in aqueous alcohol. Treatment of this substance with acetic anhydride yields *cellobiosone hepta-acetate*, m. p. 172°, $[\alpha]_D^{20}$ +2·40° in chloroform; formation of a hydroxy-4-pyrone is not observed. Confirmation of the structure of cellobiosone hepta-acetate is deduced from its formation from cellobiosone hydrate nona-acetate and an excess of acetic anhydride. The cellobiosone acetates resemble cellobiosone in their reducing action towards cold Fehling's solution and potassium permanganate at 20°. They do not yield an osazone with phenylhydrazine. Hydrolysis with warm sodium hydroxide converts them into products which do not reduce Fehling's solution or form an osazone. A similar effect is produced by cold sodium hydroxide or methyl-alcoholic ammonia except that the syrups reduce boiling Fehling's solution. Fischer's cellobiosone behaves similarly. Hydrolysis with acids involves the glucosidic linking.

2-*Hydroxygentiobial hepta-acetate*, m. p. 130° after softening at 126°, $[\alpha]_D^{20}$ −29·04° in chloroform, prepared from acetobromogentiobiose and diethylamine in chloroform, is hydrogenated in presence of palladium to 1 : 6-*glucosidostyracitol hepta-acetate*, m. p. 152°, $[\alpha]_D^{20}$ +17·21° in chloroform, hydrolysed by methyl-alcoholic ammonia to 1 : 6-*glucosidostyracitol*, m. p. 223° (decomp.), $[\alpha]_D$ +2·44° in water. Treatment of 2-hydroxygentiobial hepta-acetate with chlorine in ether affords a non-crystalline *dichloride*, converted by silver carbonate in moist ether into a syrupy *osone hydrate*, from which kojic acid is obtained by means of pyridine and acetic anhydride.

H. WREN.

Effect of ethylene on the hydrolysis of salicin by emulsin. D. T. ENGLIS and F. A. DYKINS (J. Amer. Chem. Soc., 1931, 53, 723—726).—Ethylene has no influence on the hydrolysis of salicin by emulsin, as determined polarimetrically and by the amount of reducing sugar formed. H. BURTON.

Digitalis glucosides. III. Glucosides of *Digitalis lanata*. S. SMITH (J.C.S., 1931, 23—25).—Leaves of *D. lanata* contain digoxin (A., 1930, 583), gitoxin, $[\alpha]_{5461}^{30}$ +3·5° in pyridine, identical with that from *D. purpurea*, and other glucosides. The work of Windaus and his collaborators (A., 1928, 1251) and of Cloetta (A., 1926, 755) is confirmed, but hydrolysis of gitoxin gives gitoxigenin, m. p. 234°, $[\alpha]_{5461}^{30}$ +38·5° in methyl alcohol, and digitoxose, m. p. 112°, $[\alpha]_{5461}$ +55·7° in water, in quantitative yield.

G. DISCOMBE.

Digitalin of Nativelle and digitoxin. V. HASENFRATZ (Compt. rend., 1931, 192, 366—368; cf. Raymond-Hamet, A., 1929, 613).—Digitalin, probably $C_{41}H_{64}O_{13}$, m. p. (block) 263°, is hydrolysed by aqueous-alcoholic hydrochloric acid to digitoxose and a genin, m. p. (block) 256°, $[\alpha]_D^{20}$ +18·5° in methyl alcohol. Digitalin appears to be identical with digitoxin (Windaus and Stein, A., 1929, 71).

H. BURTON.

Synthesis of glucosides. VIII. 6-Bromoindican. A. ROBERTSON and R. B. WATERS (J.C.S., 1931, 72—76).—The synthesis of 6-bromoindican by the author's general method (A., 1927, 960) is described. The interaction of *O*-tetra-acetyl-α-glucosidyl bromide and *methyl* 6-*bromo*-3-*hydroxyindole*-2-*carboxylate* (I), m. p. 192° (*diacetyl* derivative, m. p. 151°), prepared by the action of sodium and sodium methoxide on a benzene suspension of *dimethyl* 5-*bromophenylglycine*-2-*carboxylate*, m. p. 101°, yields *methyl* 6-*bromo*-3-O-*tetra-acetyl*-β-*glucosidoxyindole*-2-*carboxylate*, m. p. 171°, $[\alpha]_D^{20}$ −59·7° in acetone, converted by hydrolysis and acetylation into 6-*bromo*-1-*acetyl*-3-O-*tetra-acetyl*-β-*glucosidoxyindole*, m. p. 151°, $[\alpha]_D^{20}$ −48·8° in acetone, which is hydrolysed by methyl-alcoholic ammonia at 0° to 6-*bromo*-3-β-*glucosidoxyindole* (6-*bromoindican*) *tetrahydrate*, m. p. 64°, $[\alpha]_D^{20}$ −6·4° in acetone. The latter is hydrolysed by hydrochloric acid and by emulsin to dextrose and 6-bromoindoxyl, which on oxidation yields 6 : 6′-dibromoindigotin. On hydrolysis in presence of isatin or of *p*-nitrobenzaldehyde, 6-*bromoindirubin*, m. p. above 340°, and p-*nitrobenzaldehyde*-6-*bromoindogenide*, respectively, are formed.

Attempts to prepare 6-bromoindoxyl by the acetylation of 6-bromoindoxylic acid obtained by the hydrolysis of I gave 6-bromo-1-acetyl-3-acetoxyindole (*hydrate*, m. p. 150—152°) in small yield.

G. DISCOMBE.

Para*iso*dextran. A. KIESEL and M. ZNAMENSKAJA (Ber., 1931, 64, [*B*], 378—383).—Successive extractions of *Polyporus betulinus* with 1·5, 3, and 6% sodium hydroxide followed by acidification of the extracts gives a material much less homogeneous than that obtained by Winterstein (A., 1895, i, 323). The fractions have $[\alpha]_D$ +219·4°, +259·6°, and +81·4° in 5% sodium hydroxide. They give reddish-brown colorations with iodine and sulphuric acid or zinc chloride and iodine. The presence of pentoses is established in the first two fractions by the orcinol reaction. Hydrolysis of all the fractions affords mannose in addition to dextrose. Acetylation and subsequent regeneration of the carbohydrate causes the three fractions to approximate more closely to one another in composition. Since the pentose content of the initial fractions remains almost unchanged, the simultaneous participation of hexose and pentose groups in the structure of the complete molecule must be assumed. The product obtained by means of 6% sodium hydroxide retains its initial properties almost unchanged and is more uniform than the other fractions; apart from its lower optical activity, it coincides most closely with Winterstein's para*iso*dextran. Treatment of the fractions with acetic anhydride and pyridine yields the corresponding triacetates; determinations of mol. wt. in freezing glacial acetic acid give results in harmony with the simple formula $C_6H_7O_5Ac_3$. H. WREN.

Starch. J. Effront (Ann. Soc. Zymol., 1930, 2, 27 pp.; Chem. Zentr., 1930, ii, 2886).—Maquenne and Roux' hypothesis that starch is composed of amylopectin and amylose is contested; these substances are, however, produced by natural starch by depolymerisation followed by repolymerisation. The polymerised product is more sensitive than natural starch to chemical and physical attack.

A. A. Eldridge.

Cellulose. XXXVIII. Morphology and chemistry of cellulose fibres. Purification of fibres in connexion with swelling, tenacity of fibre, size of crystallite, and viscosity of solutions. II. K. Hess, C. Trogus, L. Akim, and I. Sakurada (Ber., 1930, 64, [*B*], 408—427; cf. A., 1930, 1417).—A review of the literature leads the authors to the conclusion that there is at present no established method for the identification of cellulose, so that the course of purification of natural cellulose can be followed only by observation of as many properties as possible of the material at its different stages and comparison of the data thus obtained among themselves.

The crude fibre of *Boehmeria nivea* is subjected to four successive extractions with 2% sodium hydroxide in the absence of air, then bleached three times with neutral hypochlorite solution of progressively decreasing concentration, and finally treated with chlorine dioxide and sodium sulphite. The considerable loss of material during the last stage of the operations is remarkable. The fibres remain intact and exhibit no damage under the microscope. The final product cannot be regarded as 100% cellulose, but further purification is possible only through dissolution and reprecipitation. Morphological examination shows that the treatment with 2% sodium hydroxide and dilute hypochlorite removes a non-cellulose material localised on the outer layers of the fibre and that a component probably lying between the micelle series is removed by exhaustive treatment with chlorine dioxide. The extent to which this component is affected by the sodium hypochlorite cannot be stated, but the great decrease in the viscosity of the solutions after the first bleaching indicates that the treatment penetrates beyond the primary lamellæ.

As the purification progresses, the tenacity and extension of the fibres pass through a maximum which is reached with the removal of the primary lamellar material by dilute sodium hydroxide. Subsequent treatment with hypochlorite causes a considerable diminution of tenacity, which is not further affected greatly by chlorine dioxide. Röntgenographic examination shows that degradation of the crystallites does not take place during purification. Products of the nitration of the preparation according to the method of Trogus (following abstract) retain their fibrous form and yield well-defined Röntgen diagrams. The relative viscosity of solutions of the nitrated compounds in acetone diminishes very markedly as the purification progresses, as does also the dependence of viscosity on pressure. In these respects a similar behaviour is own by ramie in ammoniacal copper solution. It is considered doubtful whether the fibre properties have the expected relationship to the constitution of cellulose.

H. Wren.

Preparation of fibrous cellulose nitrates. C. Trogus (Ber., 1931, 64, [*B*], 405—407; cf. Berl and Rueff, this vol., 203).—Highly-nitrated cellulose nitrate is produced by the addition of air-dried ramie fibre to a mixture of nitric acid (*d* 1·52), glacial acetic acid, and acetic anhydride or phosphoric oxide. After 2—4 hrs. the fibre is well washed with water and stabilised with boiling 50% acetic acid. For the preparation of products containing 11—12·5% of nitrogen, a mixture of nitric acid (*d* 1·52) and glacial acetic acid is used.

H. Wren.

Composition and formation of cellulose acetate soluble in acetone. S. Iwasaki (J. Soc. Chem. Ind. Japan, 1931, 34, 9—10B).—Fractions precipitated from a cellulose acetate soluble in acetone were found to have widely different physical properties. although their acid content was practically the same. A theory of the ripening of cellulose acetate is based on these observations and on the micellar theory of Meyer and Mark.

H. Ingleson.

Lignin. V. Distillation of alkali lignin with zinc dust in an atmosphere of hydrogen. M. Phillips (J. Amer. Chem. Soc., 1931, 53, 768—774).—When lignin is heated with zinc dust in a current of hydrogen up to 400°, carbon dioxide, oil, and an aqueous distillate are obtained. The aqueous distillate contains acetone (0·36%), methyl alcohol (1·48%), and acid (as acetic, 0·24%), and gives characteristic reactions for pyrocatechol. The oil (16% of lignin used) contains guaiacol and an unidentified methoxyphenol (3 : 5-*dinitrobenzoate*, m. p. 110°). Lignin probably contains an aromatic nucleus. The production of carbon dioxide suggests the presence of a free or combined carboxyl or lactone group.

H. Burton.

Lignin, humic acids, and humins. W. Fuchs (Z. angew. Chem., 1931, 44, 111—118).—A lecture. The following appears to be new. The β-methoxyethyl alcohol derivative ("methylin," cf. A., 1929, 1282) prepared direct from pine-wood by an improved method is degraded by fusion with potassium hydroxide at 250—295° to protocatechuic acid and small amounts of pyrocatechol, *m*-hydroxy-aromatic acids, and oxalic acid. The methylin derivative may be separated by solvents into two principal and two subsidiary fractions; of the former the more readily soluble has mol. wt. about 1000, and the other about 2000. Their solubility in organic solvents is improved by methylation and still further by acetylation of the methyl derivatives, which occurs by replacement of methyl groups. The methylin residues are removed by hydrochloric acid, giving products with the properties of the original lignin. Tentative lignin and humic acid structures are formulated.

Oxidation of coal with nitric acid (*d* 1·4) at 90—95° gives, in yields of 110—120% of starting material, products with the characteristics of the dehydrohumic acids prepared from lignite (cf. B., 1928, 555). They are somewhat soluble in organic solvents, and are capable of methylation to products with the properties of ether-esters. Alcoholic potassium acetate converts them into definite potassium salts,

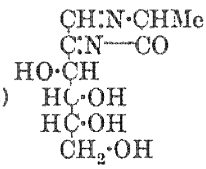
which are either soluble in water or may be obtained in water-soluble forms; the potassium is almost quantitatively replaced by treatment with ammonium chloride. H. A. PIGGOTT.

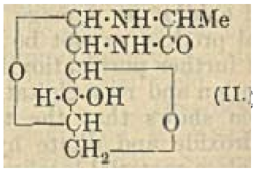
Action of formaldehyde on amino-acids. Formation of amines. L. ZELENY and R. A. GORTNER (J. Biol. Chem., 1931, **90**, 427—441).—Hydrolysis of alanine, cystine, glutamic acid, and tyrosine by 20% hydrochloric acid in presence of formaldehyde results in the appearance of 12—40% of the total nitrogen as volatile amines (including a little ammonia). Casein after removal of amide nitrogen by preliminary hydrolysis behaves similarly. The distribution of primary, secondary, and tertiary amines in the volatile distillates is essentially the same as is found when ammonium chloride is boiled with 20% hydrochloric acid in presence of formaldehyde. The non-volatile amino-nitrogen reaches a minimum value after several hours' boiling, but the non-volatile non-amino-nitrogen steadily decreases, showing that, after a few hours at least, the latter is the progenitor of the volatile nitrogen, which, except in the case of tyrosine, continually increases. Trimethylamine is the final product of the hydrolysis and no evidence of the formation of amines by decarboxylation was obtained. J. D. A. JOHNSON.

***n*-Aminobutenes.** E. GALAND (Bull. Soc. chim. Belg., 1930, **39**, 529—538).—Fuming hydrobromic acid converts γ-ethoxybutylamine (Luchmann, A., 1896, i, 544) into γ-bromobutylamine hydrobromide, converted by quinoline at 100° into Δ^{β}-butenylamine, b. p. 82—83°/757 mm., d^{20} 0·7771, n_D 1·43016, which could not be separated into geometrical isomerides either by careful fractional distillation or by fractional crystallisation of its *phenylthiourethane*, m. p. 106° (crystallographic data), or its *phenylurethane*, m. p. 130°. The same unsaturated amine is obtained by reduction of crotononitrile with zinc–copper couple in acetic acid. Similar reduction of vinylacetonitrile affords *Δ^{γ}-butenylamine*, b. p. 81—82·5°/748·5 mm., d_4^{20} 0·7735, n_D 1·42734, which differs from the amine to which Luchmann (*loc. cit.*) assigned this structure. Silver nitrite converts Δ^{β}-butenylamine into crotyl alcohol. J. W. BAKER.

Thiocholine halides. II. Thiocholine chloride and its derivatives. I. HARADA (Bull. Chem. Soc. Japan, 1931, 6, 25—28).—*Chlorocholine chloride*, m. p. 242° (decomp.) after becoming discoloured at 163°, is obtained by the interaction of trimethylamine with ethylene chloride. It reacts with 2-thiouracil at 150° to form *thiocholine chloride*, m. p. 238° (decomp.) after softening at 200°, isoelectric point at p_H 7·0, which forms a *complex* with silver chloride, m. p. about 228° (decomp.) after darkening at 70°. G. DISCOMBE.

Synthesis of peptide-like substances from amino-sugars and amino-acids. I. Glucosamine as a component. A. BERTHO, F. HOLDER, W. MEISER, and F. HUTHER (Annalen, 1930, **485**, 127—151).—The synthesis of various simple derivatives of the type of the products of enzymolysis of glucoproteins is described. Condensation of chloroacetyl chloride with glucosamine hydrochloride in the presence of sodium hydroxide gives a 5% yield of N-*chloroacetylglucosamine*, m. p. 168—169°, $[\alpha]^{25}$ +24·8° in methyl alcohol. The corresponding α-bromopropionyl derivative [which with benzoyl chloride and 50% potassium hydroxide gives a *tetrabenzoyl* derivative, m. p. 189°, $[\alpha]^{20}$ +73·75° in chloroform (crystallisation affords a sample $[\alpha]_D^{18}$ +86·7°, which, however, is not optically pure), together with a *substance*, m. p. 238°, $[\alpha]_D^{25}$ +25·87° in chloroform, possibly tetrabenzoyl *N*-(α-hydroxypropionyl)glucosamine] and α-bromo*iso*hexoylglucosamine (*tetrabenzoyl* derivative, m. p. 189°, $[\alpha]_D^{15}$ +103·1° in chloroform) (cf. Weizmann and Hopwood, A., 1913, i, 958), exhibit mutarotation and fractional crystallisation separates a specimen of higher initial rotation. The failure to obtain carbonyl derivatives with phenylhydrazine and semicarbazide is ascribed to steric effects and not to betaine formation (cf. Irvine and Hynd, J.C.S., 1913, **103**, 41). Prolonged action (3 months) of cold methyl-alcoholic ammonia on *N*-α-bromopropionylglucosamine affords, in addition to *N*-alanylglucosamine (obtained by Weizmann and Hopwood, *loc. cit.*, by similar action of aqueous ammonia), N-*alanylanhydroglucosamine anhydride*, m. p. 199°, $[\alpha]_D^{20}$ −89·8° in water, to which the structures I and II, respectively, are assigned. The latter is almost the only product when concentrated methyl-alcoholic ammonia at 100° in a sealed tube is used, and is also obtained in very small yield when aqueous ammonia is employed. These two products reduce Fehling's solution only very slowly and are formed independently in the reaction, since they could

(I.) 

 (II.)

not be interconverted. By the action of benzoylated amino-acid azides on glucosamine benzamidoacylglucosamines are obtained. Thus hippurazide and glucosamine hydrochloride afford N-*benzoylglycylglucosamine*, $C_4H_8O_3{<}{}^{O\cdot CH\cdot OH}_{CH\cdot NH}\cdot CO\cdot CH_2\cdot NHBz$, m. p. 200° (decomp.), together with a trace of a *substance*, m. p. 263—265° (decomp.), but with *p*-bromohippurazide only an amorphous *substance*, m. p. 214°, containing two bromohippuryl residues could be obtained. With benzoylalanine azide is obtained N-*benzoylalanylglucosamine*, m. p. 222° (decomp.), $[\alpha]_D^{?}$ +59·0° in water, which is a mixture of optical isomerides. The structure of these glucosamine derivatives and others in the literature is discussed. J. W. BAKER.

Resolution of synthetic *iso*leucine into four optically active components, namely, *l*(+)- and *d*(−)-*iso*leucines and *d*(−)- and *l*(+)-*alloiso*leucines. E. ABDERHALDEN and W. ZEISSET (Z. physiol. Chem., 1931, **195**, 121—131).—Treatment of α-bromo-β-methylvaleric acid with saturated aqueous ammonia during 4—5 days at 37°, evaporation of the resulting solution in a vacuum until crystallisation begins, admixture of this with alcohol whereby crystalline material is obtained, and crystallisation of this from water gives *dl*-*iso*leucine (α-amino-β-methyl-

valeric acid). The mother-liquors from this crystallisation contain *dl-alloiso*leucine (*formyl* derivative, m. p. 117—118°), isolated by way of the ethyl ester, b. p. 85—88°/15 mm., which is hydrolysed to the free acid by boiling water. Resolution of both *dl*-acids is effected by Locquin's method (A., 1907, i, 593). The following data (amongst others) are recorded for the optically active acids and their derivatives: *l*(+)-*iso*leucine, m. p. (sealed tube) 285—286° (decomp.) (lit. 280°), $[\alpha]_D^{20}$ +10·7° in water, +40·8° in 20% hydrochloric acid [formyl, m. p. 155°, $[\alpha]^{20}$ +26·6° in alcohol; benzenesulphonyl, m. p. 153° (lit. 149—150°), $[\alpha]_D^{20}$ +25·3° in alcohol; phenylcarbimide, m. p. 121°, $[\alpha]^{20}$ +37·5° in alcohol, and α-naphthylcarbimide, m. p. 178—179°, $[\alpha]^{20}$ +30·1° in alcohol, derivatives]; *d*(−)-*iso*leucine, m. p. (sealed tube) 283—284° (decomp.) (lit. 280—290°), $[\alpha]^{20}$ −10·7° in water, −41·6° in 20% hydrochloric acid (formyl, m. p. 156°, $[\alpha]_D^{20}$ −26·8° in alcohol; *benzenesulphonyl*, m. p. 153—154°, $[\alpha]_D^{20}$ −25·5° in alcohol; *phenylcarbimide*, m. p. 119—121°, $[\alpha]^{20}$ −36·3° in alcohol, and *α-naphthylcarbimide*, m. p. 177—178°, $[\alpha]_D^{20}$ −29·5° in alcohol, derivatives); l(+)-alloiso*leucine*, m. p. (sealed tube) 278° (decomp.), $[\alpha]_D^{20}$ +14·0° in water, +38·1° in 20% hydrochloric acid (*formyl*, m. p. 126°, $[\alpha]^{20}$ +24·2° in alcohol; *benzenesulphonyl*, m. p. 147—148°, $[\alpha]_D^{20}$ +30·7° in alcohol; *phenylcarbimide*, m. p. 151°, $[\alpha]_D^{20}$ +30·8° in alcohol, and *α-naphthylcarbimide*, m. p. 165—166°, $[\alpha]^{20}$ +25·1° in alcohol, derivatives); *d*(−)-*alloiso*leucine, m. p. (sealed tube) 274—275° (decomp.), $[\alpha]^{20}$ −14·2° in water, −38·0° in 20% hydrochloric acid (*formyl*, m. p. 126°, $[\alpha]^{20}$ −25·2° in alcohol; *benzenesulphonyl*, m. p. 147—148°, $[\alpha]^{20}$ −30·7° in alcohol; *phenylcarbimide*, m. p. 151°, $[\alpha]^{20}$ −30·6° in alcohol, and *α-naphthylcarbimide*, m. p. 168°, $[\alpha]^{20}$ −25·5° in alcohol, derivatives). H. BURTON.

Ethyl aminomalonate. Action of acyl chlorides on ethyl aminomalonate. *N*-Acyl derivatives of ethyl aminomalonate. R. LOCQUIN and V. CERCHEZ (Bull. Soc. chim., 1931, [iv], **49**, 42—47).—When ethyl aminomalonate is treated with acyl chlorides in pyridine ethyl *N*-acylaminomalonates are obtained in 60—80% yields. The same derivatives are obtained when the sodium derivative of ethyl aminomalonate is treated with acyl chlorides in ether and the yields are higher. Acetyl cyanide and ethyl sodioaminomalonate also yield the *N*-acetyl derivative and it is concluded that the amino-group prevents the fixation of an acyl radical on the central carbon atom. Attempts to obtain such a compound by previously blocking the amino-group failed, since ethyl *N*-formamidomalonate yields no sodium derivative.

Ethyl *N*-acetamidomalonate, m. p. 95°, b. p. 185°/20 mm., is obtained quantitatively from ethyl sodioaminomalonate and acetyl chloride in ether, or in lower yield from acetyl cyanide. Ethyl *N*-*iso*butyramidomalonate, m. p. 74°, *ethyl* N-iso*valeramidomalonate*, m. p. 49°, b. p. 185—190°/17 mm. (*diamide*, m. p. 250°); *ethyl* N-*nonoamidomalonate*, m. p. 66° (*diamide*, m. p. 229—230°), and *ethyl* N-*benzamidomalonate*, m. p. 61°, are similarly obtained by the pyridine method. R. BRIGHTMAN.

Action of carbonyl chloride on ethyl aminomalonate. Preparation of ethyl carbamidodimalonate and its hydrolysis to carbamidodiacetic acid and hydantoin-3-acetic acid. R. LOCQUIN and V. CERCHEZ (Bull. Soc. chim., 1931, [iv], **49**, 47—54).—When a 20% solution of carbonyl chloride (0·5 mol.) in toluene is added to a mixture of ethyl aminomalonate (1 mol.) and pyridine (2·5 mols.) in ether and the pyridine hydrochloride removed with water, *ethyl carbamidodimalonate*, m. p. 167°, is obtained in 80% yield; with ethyl sodioaminomalonate the yields are much lower. On hydrolysis with aqueous *N*-sodium hydroxide ethyl carbamidodimalonate is converted into carbamidodiacetic acid, m. p. 230° (decomp.), and with 10% hydrochloric acid (*d* 1·015) into hydantoin-3-acetic acid, m. p. 196°. R. BRIGHTMAN.

Optical activity of cystine preparations used for animal experiments. J. R. HAAG (J. Amer. Chem. Soc., 1931, **53**, 808—809).—The specific rotations of cystine preparations (from human hair) vary from −185·9° to −216·6° in *N*-hydrochloric acid. The majority of the samples have $[\alpha]_D^{25}$ about −210°. The variations in rotation are partly due to prolonged washing of some of the samples with hot water to remove tyrosine. H. BURTON.

Action of magnesium ethyl halides on ethyl diethylcyanoacetate. A. MAVRODIN (Compt. rend., 1931, **192**, 363—365; cf. this vol., 205).—When ethyl diethylcyanoacetate is treated with magnesium ethyl bromide or iodide, part of the ester is converted into *β-cyano-ααβ-triethyl-*n*-butyl alcohol*, b. p. 132—133°/20 mm., which reacts further with the Grignard reagent, forming some triethylcarbinol (*allophanate*, m. p. 182—183°) and α-ethylbutyronitrile. The remainder of the ester reacts as previously described (*loc. cit.*), giving, after hydrolysis, diethyl ketone, ethyl α-ethyl-*n*-butyrate, and ethyl ααγγ-tetraethylacetoacetate. These results confirm the hypothesis that in ethyl cyanoacetate and ethylcyanoacetate (A., 1929, 796) enolisation of the carbonyl group occurs. The above cyano-compound is dehydrated by thionyl chloride to *δ-cyano-γδ-diethyl-Δ^{β}-hexene*, b. p. 105°/16 mm. H. BURTON.

Diethyl dicyanoglutaconate. Y. URUSHIBARA (Bull. Chem. Soc. Japan, 1931, **6**, 29—31).—Methods are described by which *diethyl dicyanoglutaconate* (I), and not the semihydrate (A., 1927, 345, 1059), is prepared. The presence of the free ester is proved by the precipitation of the semihydrate from an alkaline extract of the reaction mixture. Ethyl hydroxymethylenecyanoacetate condenses with ethyl cyanoacetate in presence of acetic anhydride to yield I. *Ethyl chloromethylenecyanoacetate*, b. p. 105°/12 mm., condenses with ethyl chlorocyanoacetate in presence of copper and with ethylcyanoacetate in presence of pyridine to give I, whilst ethyl ethoxymethylenecyanoacetate failed to react with ethyl cyanoacetate in presence of acetic anhydride and zinc chloride. G. DISCOMBE.

Mechanism of the conversion of nitriles into amides by sulphuric acid. J. VERHULST (Bull. Soc. chim. Belg., 1930, **39**, 563—567).—The action of concentrated sulphuric acid below 25° on the

cyanohydrins of acetone, methyl propyl ketone, methyl ethyl ketone, and diethyl ketone, exact neutralisation of the solution with potassium (or sodium) carbonate, evaporation to dryness, and extraction of the residue with hot alcohol furnishes the crystalline *potassium* (or *sodium*) salts of the type OH·CRR′·(C:NH)·OSO_3K. These give no ionic reaction for sulphate in aqueous solution, but when boiled with barium chloride in dilute hydrochloric acid solution barium sulphate is precipitated and rapid cooling of the solution affords the corresponding hydroxy-acid amide more or less contaminated with the hydroxy-acid. An almost quantitative yield of the amide is obtained if the initial reaction between the sulphuric acid and the nitrile is carried out at 80—100°. The intermediate imino-sulphates from the cyanohydrins of methyl *iso*propyl and ethyl *n*-propyl ketones are less stable and could not be obtained pure, but the *amides*, m. p. 89°, and m. p. 72·2—73·2°, respectively, of α-hydroxy-αβ-dimethylbutyric and of α-hydroxy-α-ethyl-*n*-valeric acids were similarly obtained. The cyanohydrins of di-*iso*butyl ketone affords the *amide*, m. p. 101—102°, of α-hydroxy-γ-methyl-α-*iso*butyl-*n*-valeric acid. The mechanism of the hydrolysis of nitriles by sulphuric acid is therefore OH·CRR′·CN $\xrightarrow{H_2SO_4}$ OH·CRR′·C(:NH)·O·SO_3H → OH·CRR′·C(:NH)·OH → OH·CRR′·CO·NH_2. J. W. BAKER.

Carbamidosulphonic acids. P. BAUMGARTEN and I. MARGGRAFF (Ber., 1931, 64, [*B*], 301—309).—Carbamide is converted by a molecular proportion of *N*-pyridiniumsulphonic acid (cf. A., 1926, 844) at 120° into *pyridinium carbamidosulphonate*, m. p. 130° (also *monohydrate*), transformed by alkali hydroxide into the corresponding *sodium* and *potassium* salts, NH_2·CO·NH·SO_3K(Na). In acid solution the salts undergo rapid and quantitative hydrolysis to carbamide and sulphuric acid, so that the free acid could not be prepared. In neutral or alkaline solution, hydrolysis occurs more slowly with formation of ammonia, carbon dioxide, and alkali aminosulphonate. The *barium* salt is converted by an excess of barium hydroxide into the *dibarium* salt, (NH_2·CO·N·SO_3)Ba,$3H_2O$. The hygroscopic *dipotassium* salt, NH_2·CO·NK·SO_3K, is analogously prepared. Treatment of carbamide (1 mol.) with *N*-pyridiniumsulphonic acid at 140—150° yields *pyridinium carbamidodisulphonate*, CO(NH·SO_3H,C_5H_5N)$_2$, m. p. 146°; the corresponding *monohydrated potassium*, *dihydrated sodium*, and *monohydrated barium* salts are described. In acid solution, the disulphonates are rapidly hydrolysed, mainly to carbamide and sulphuric acid, but partly to carbon dioxide and aminosulphonic acid. In neutral solution they are rapidly decomposed when heated, giving exclusively carbon dioxide and aminosulphonate if the solutions are dilute, but yielding carbamide and hydrogen sulphate in minor amount if the solutions are more concentrated. In alkaline solution (as tetra-salts) they are remarkably stable. *Tetrapotassium carbamidodisulphonate*, CO(NK·SO_3K)$_2$,H_2O, and the corresponding *tetrahydrated barium* salt are described. H. WREN.

***cis-trans*-Isomerism of unsaturated aliphatic nitriles and amides.** P. BRUYLANTS (Bull. Soc. chim. Belg., 1930, 39, 572—580).—A theoretical paper in which it is emphasised that the configurations assigned to ethylenic nitriles and amides on the basis of their ultra-violet absorption spectra are untrustworthy and often opposed to chemical evidence (cf. A., 1930, 1276). J. W. BAKER.

ββ′-Diethylacrylonitrile. P. COLMANT (Bull. Soc. chim. Belg., 1930, 39, 568—571).—Magnesium ethyl bromide reacts with ethyl chloroacetate at −10° (Fourneau and Tiffeneau, A., 1907, i, 817) to give a 50% yield of a mixture containing 86% of the chlorohydrin, CH_2Cl·CEt_2·OH, converted by alcoholic potassium cyanide into β-*hydroxy*-β-*ethyl*-n-*valeronitrile*, b. p. 231—232°/766 mm., d_4^{20} 0·9562, n_D^{20} 1·45086 (50% yield), which is converted by distillation under atmospheric pressure with a few drops of concentrated sulphuric acid into a mixture of β-ethyl-Δ^{α}- and -Δ^{β}-pentenonitriles, which are only partly separated by fractional distillation (physical data of fractions recorded). Isomerisation with alcoholic sodium ethoxide affords a fraction, b. p. 177·4—178·4°, d_4^{20} 0·84248, n_D^{20} 1·44755, which contains 97% of the Δ^{α}-form, hydrolysed to the corresponding *amide*, m. p. 90—91°. J. W. BAKER.

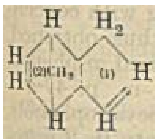
Aliphatic compounds of arsenic. W. J. C. DYKE, G. DAVIES, and W. J. JONES (J.C.S., 1931, 185—188).—Tri-*n*-propylarsine has b. p. 84°/17 mm., 92°/27 mm., and 113°/79 mm., connected by the expression $10{\cdot}2378 - \log_{10} p = 3215/(t + 273)$. The arsines were prepared by the interaction of arsenic trichloride and the appropriate Grignard reagent, and purified by distillation. On oxidation in air, the oxide is formed. *Tri*-n-*butylarsine oxide* and *tri*-n-*amyl arsine oxide* are described. The sulphides (A., 1907, i, 496) *tri*-n-*propyl sulphide* and *triisobutyl sulphide* form needles. By interaction of carbon tetrachloride solutions of the arsine and chlorine or bromine, the dichlorides or dibromides are formed, the di-iodides being obtained from solutions of the components in light petroleum. *Tri*-n-*propylarsine dichloride*, m. p. 84°; *tri*-n-*butylarsine dichloride*, m. p. 40°; *triisobutylarsine dichloride*, m. p. 130°; *tri*-n-*amylarsine dichloride*, liquid. *Tri*-n-*propylarsine dibromide*, m. p. 95°; *tri*-n-*butylarsine dibromide*, m. p. 55°; *triisobutylarsine dibromide*, m. p. 135°; *tri*-n-*amylarsine dibromide*, liquid. *Tri*-n-*propylarsine di-iodide*, m. p. about 130°; *tri*-n-*butylarsine di-iodide*, m. p. 124°; *triisobutylarsine di-iodide*, m. p. 117—119°. The dibromides react with silver sulphate to give the arsine sulphate; *tri*-n-*propylarsine sulphate*, m. p. 84°. With mercuric chloride in alcohol the arsines give double salts, R_3As,$HgCl_2$. *Tri*-n-*propylarsine mercurichloride*, m. p. 106°; *tri*-n-*butylarsine mercurichloride*, m. p. 70°; *triisobutylarsine mercurichloride*, m. p. 158°. Methiodides, from methyl iodide and the arsine in ether: *methyltriethylarsonium iodide*, m. p. 270°, *cadmi-iodide*, m. p. 283°, *mercuri-iodide*, m. p. 61°; *methyltri*-n-*propylarsonium iodide*, m. p. 204°, *chloroplatinate*, m. p. 219° (decomp.), *cadmi-iodide*, m. p. 279°, *mercurichloride*, m. p. 141°, *mercuri-iodide*, m. p. 61°; *methyltriisobutylarsonium iodide*, m. p. 254°, *chloroplatinate*, m. p. 224° (decomp.), *cadmi-iodide*, m. p. 138°, *mercuri-iodide*, m. p. 117°; *methyl tri*-n-*butylarsonium iodide*, impure, *cadmi-*

iodide, m. p. 100°, *mercuri-iodide*, m. p. 76°; *ethyltri*-n-*butylarsonium iodide*, impure, m. p. about 107°; *methyltri*-n-*amylarsonium iodide*, oil, *chloroplatinate*, m. p. 114°. G. DISCOMBE.

Mechanisms for the formation of organo-magnesium and other organometallic compounds. H. GILMAN and R. E. BROWN (Rec. trav. chim., 1931, **50**, 184—187).—Theoretical. J. W. BAKER.

Reducing action and constitution of the Grignard reagent. C. R. NOLLER (J. Amer. Chem. Soc., 1931, **53**, 635—643).—The various possibilities whereby Grignard reagents can function as reducing agents are discussed. The Grignard reagent ($c=$ about $1 \cdot 3M$) from magnesium and *iso*butyl bromide is shown by Schlenk and Schlenk's method (A., 1929, 687) to contain about 75% of magnesium di*iso*butyl. Addition of a solution of benzophenone in benzene to the Grignard reagent gives a complex, probably $(CHPh_2 \cdot O)_2Mg,MgBr_2$, also precipitated when benzophenone is treated successively with magnesium di*iso*butyl and anhydrous magnesium bromide. Solutions of magnesium di*iso*butyl which are almost halogen-free (*i.e.*, contain little magnesium *iso*butyl bromide) reduce benzophenone to benzhydrol to at least 64% of the theoretical amount. It is considered that the constitution of the Grignard reagent is best represented by the equilibrium $R_2Mg,MgX_2 \rightleftharpoons MgR_2+MgX_2$. H. BURTON.

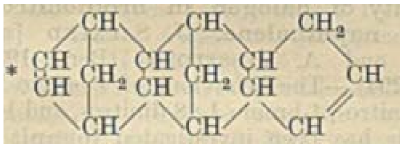
Polymerisation of cyclic hydrocarbons. I. Polymeric forms of *cyclo*pentadiene. K. ALDER, G. STEIN, and H. FINZENHAGEN (Annalen, 1931, **485**, 223—246).—The formation by di*cyclo*pentadiene of an additive *compound*, m. p. 130—131°, with phenyl azide is in better agreement with the structure (I), tentatively suggested by Wieland (A., 1906, i, 417), than with the generally accepted formula of Krämer and Spilker (A., 1896, i, 289). This view is conclusively proved by isolation (as anhydride) of *cyclo*pentane-1 : 3-dicarboxylic acid from the products of oxidation with permanganate of the dihydro-derivative; the main product, m. p. 137° (Wieland and Bergel, A., 1926, 56, give m. p. 134°), is therefore 3 : 6-*endo*methylenehexahydrohomophthalic acid (probably *trans*), the double linking in ring 1 (formula I) being the point of attack. Further evidence in favour of formula I is afforded by the existence of the hydrocarbon in a single form only, the stability to alkalis of the "ketotribromo-compound" of Wieland and Bergel (*loc. cit.*), and the existence of a second form of the oxide. Staudinger's arguments (A., 1924, i, 274) in favour of Krämer and Spilker's formula, based on the ready thermal dissociation of the dimeride into *cyclo*pentadiene, and the comparative stability of reduction products, are rebutted by the similar behaviour of *cyclo*pentadienequinone (A., 1906, i, 674) and similar compounds. The acid $C_{10}H_{10}O_4$, m. p. 232°, isolated by Bergel and Widmann (A., 1929, 53) by oxidation of the dicyclic ketone $C_{10}H_{14}O$ with permanganate is therefore *cis*-di*cyclo*pentane-1 : 3-dicarboxylic acid



(I.)

(II), derived by degradation of ring 2; it is also obtained by oxidation with nitric acid in the cold, the acid, m. p. 200°, prepared in this way by Wieland and Bergel being a mixture of II with the acid of m. p. 137°. "Di*cyclo*pentadiene monoxide" (Wieland and Bergel) is a mixture. The action of phenyl azide leads to the slow separation of an additive *compound*, m. p. 149°, presumably derived from the isomeride in which the oxygen is attached to ring 1; from the mother-liquors the isomeric *oxide*, m. p. 79—80°, may be separated, and is readily converted by palladium and hydrogen into a *dihydro*-derivative, m. p. 118—119° (the dihydro-derivative of the isomeric oxide has m. p. 98°; Bergel and Widmann give m. p. 91·5°).

It is suggested that further polymerisation occurs by 1 : 4-addition of another molecule of *cyclo*pentadiene to the reactive ethylenic linking in ring 2, proof of the structure III of tri*cyclo*pentadiene being afforded by the formation of an additive *compound*, m. p. 199—200° (decomp.), with phenyl azide. Polymerisation in this manner can continue indefinitely, on account of the highly reactive ethylenic linking (*), and accounts for the existence of each



(III.)

polymeride in one form only (cf. Staudinger and Bruson, A., 1926, 719). H. A. PIGGOTT.

Aryl chlorosulphinates and aryl sulphites. M. BATTEGAY and L. DENIVELLE (Compt. rend., 1931, **192**, 492—493).—The preparation of *phenyl chlorosulphinate*, b. p. 94—96°/13 mm., and of phenyl sulphite is described. A. A. LEVI.

Forced reaction between tetraphenylethylene and magnesium organohalides. H. GILMAN and S. A. HARRIS (Bull. Soc. chim., 1931, [iv], **49**, 10—12).—No reaction appears to take place between tetraphenylethylene and magnesium phenyl bromide when heated in toluene at 60° for 20 hrs. or at 90—100° for 6 hrs. (cf. A., 1929, 1056), 86% of the tetraphenylethylene being recovered and a little triphenylcarbinol formed. Similarly with magnesium phenyl chloride at 60° and then at 110° for 23 hrs., 85·5% of the tetraphenylethylene is recovered unchanged. R. BRIGHTMAN.

Polarisation of the ethylenic linking. G. WITTIG (Ber., 1931, **64**, [*B*], 437—444; cf. A., 1930, 762).—Examination of the criticisms of Bergmann (A., 1930, 1568) leads the authors to the conclusion that they neither prove nor disprove the interpretation of the fission of ααζζ-tetraphenylhexadiene propounded by Wittig and Leo (*loc. cit.*). Examination of ααδδ-tetraphenyl-Δ^{α}-butene, which, like ααζζ-tetraphenylhexadiene, offers two points of attack to the metal, proves that fission of the molecule occurs.

ααδδ-Tetraphenylbutadiene is converted by successive treatment with sodium–potassium alloy and methyl alcohol into ααδδ-tetraphenyl-Δ^{α}-butene,

isomerised by sodium and amyl alcohol at 150° to *ααδδ-tetraphenyl-Δ^α-butene*, m. p. 97—98°, oxidised by potassium permanganate to ββ-diphenylpropionic acid, m. p. 153—154°. Alternatively, γ-phenylbutyrolactone is converted by aluminium chloride and benzene into *γγ-diphenylbutyric acid*, m. p. 105—106°. The corresponding *methyl* ester, b. p. 190—191°/12 mm., is transformed by magnesium phenyl bromide into *ααδδ-tetraphenylbutanol*, m. p. 149—150°, dehydrated by glacial acetic acid containing a little sulphuric acid to ααδδ-tetraphenyl-Δ^α-butene, m. p. 97—98°. With sodium–potassium alloy followed by methyl alcohol the hydrocarbon gives αα-diphenyl-Δ^α-propene and diphenylmethane.

s-Tetraphenylethane can be distilled unchanged under atmospheric pressure and yields only a small proportion of diphenylmethane at 400°. ααζζ-Tetraphenyl-Δ^{αε}-hexadiene is volatile without decomposition in a vacuum, but decomposes completely when distilled under atmospheric pressure with production of αα-diphenyl-Δ^α-propene. ααδδ-Tetraphenyl-Δ^α-butene occupies an intermediate position; at 400° it gives diphenylmethane and ααδδ-tetraphenylbutadiene. H. WREN.

Reactivity of halogen in bromonitro-derivatives of naphthalene. J. SALKIND [with E. LIFSCHITZ and A. VESSELOVA] (Ber., 1931, **64**, [*B*], 289—294).—The behaviour of 4-bromo-1-nitro-, 5-bromo-1-nitro-, 4-bromo-1 : 8-dinitro-, and 1-bromonaphthalene has been investigated towards sodium ethoxide in ethyl alcohol, benzamide in presence of copper powder and nitrobenzene, piperidine, and magnesium (with which reaction does not occur). The displaced bromine is determined titrimetrically. The nitro-group very appreciably increases the reactivity of bromine in position 4. If the halogen atom is in position 5, the effect of the nitro-group is much less pronounced and the bromine atom is little more mobile than that in 1-bromonaphthalene. In the case of 4-bromo-1 : 8-dinitronaphthalene, the influence of the second nitro-group is marked only in the reaction with piperidine; the hydrolysis with sodium ethoxide proceeds only a little more rapidly than that of 4-bromo-1-nitronaphthalene. It appears that the influence of the nitro-group extends only to substituents in the same ring and that the two rings of naphthalene are considerably independent of one another with respect to reactivity of their substituents. H. WREN.

Bromination of 4-nitro-1-methylnaphthalene. J. S. H. DAVIES and A. E. OXFORD (J.C.S., 1931, 220—221).—Bromination of 4-nitro-1-methylnaphthalene in ultra-violet light yields a nuclear-substituted *monobromo-4-nitro-1-methylnaphthalene*, m. p. 137·5—138·5°, and *tetrabromo-4-nitro-1-methylnaphthalene*, m. p. 189—190° (decomp.). α-Naphthylmethyl chloride (Wislicenus and Wren, A., 1905, i, 284) separated from alcohol at −15° as a solid, m. p. 29·5—30·5°. 2 : 4-*Dinitrobenzyl bromide*, m. p. 46—47°, is formed by the interaction of sodium bromide and 2 : 4-dinitrobenzyl chloride in methyl alcohol. G. DISCOMBE.

Sulphonation of naphthalene. C. B. RADCLIFFE and W. F. SHORT (J.C.S., 1931, 220).—Sulphonation of naphthalene with 98% sulphuric acid at 40—50° yields small quantities of naphthalene-1 : 5-disulphonic acid, contrary to the statements of Euwes (A., 1909, i, 707) and other workers, since the sodium naphthalene-1-sulphonate isolated yields on fusion with potassium cyanide small quantities of naphthylene-1 : 5-dicyanide. G. DISCOMBE.

***N*-Phenyl-*N'*-diethylaminocarbamide.** R. STOLLÉ and W. BRANDT (J. pr. Chem., 1931, [ii], **129**, 206).—The compound obtained by interaction of *as*-diethylhydrazine and phenylcarbimide is found by analysis to be N-*phenyl*-N'-*diethylaminocarbamide*, and not "phenylcarbimidediethylhydrazone" as stated by Hurd and Spence (A., 1927, 232). H. A. PIGGOTT.

Sulphides and polysulphides of organic bases. T. G. LEVI (Gazzetta, 1930, **60**, 975—987).—The following compounds are described: phenyldiguanide hydrosulphide, $C_8H_{11}N_5,H_2S$, m. p. 143—147° (cf. Romani, A., 1924, i, 847); *o-tolyldiguanide hydrosulphide*, m. p. 123—126°; benzylamine polysulphide, $(CH_2Ph\cdot NH_2)_2H_2S_6$; *phenyldiguanide hexasulphide*, $(C_8H_{11}N_5)_2H_2S_6$, m. p. 130—135°; *diphenylguanidine hexasulphide*, $(C_{13}H_{13}N_3)_2H_2S,S_5$, m. p. 100—110°; *di-o-tolylguanidine heptasulphide*, $(C_{15}H_{17}N_3)_2H_2S,S_6$; *as-triphenylguanidine hexasulphide*, $(C_{19}H_{17}N_3)_2H_2S_6$, m. p. 108—112°. T. H. POPE.

Nitration of *p*-thiocyanoacetanilide. J. W. DIENSKE (Rec. trav. chim., 1931, **50**, 165—183).—Nitration of *p*-thiocyanoacetanilide with absolute nitric acid at −10° affords 2 : 6-dinitro-4-thiocyanophenylnitroamine (I), decomp. (explosively) 70°, the structure of which is proved by oxidation of the thiocyano-group to a sulphonic acid by absolute nitric acid, conversion of the nitroamino-group into hydroxyl by alkali, and finally replacement of the sulphonic acid group by a nitro-group by heating with concentrated nitric acid, picric acid being thus obtained. By the Sandmeyer reaction on diazotised *p*-phenetidine is obtained p-*thiocyanophenetole*, m. p. 47·5—48° (not obtained by ethylation of *p*-thiocyanophenol), converted by nitric acid (*d* 1·4) at 50° into its 2-*nitro*-derivative, m. p. 85° (identical with a specimen obtained by the Sandmeyer reaction from 2-nitro-4-aminophenetole), together with some *p*-nitrophenetole and picric acid. Further nitration of 2-nitro-4-thiocyanophenetole with absolute nitric acid at 0 affords 2 : 6-*dinitro-4-thiocyanophenetole*, m. p. 77°, the constitution of which is proved by its conversion into picric acid by a method similar to that used with I (above). It is converted by warm alcoholic ammonia into 2 : 6-*dinitro-4-thiocyanoaniline*, m. p. 180°. By similar methods *p*-anisidine is converted into p-*thiocyanoanisole*, m. p. 35°, 2-*nitro-4-thiocyanoanisole*, m. p. 106° (together with *p*-nitroanisole and picric acid), and 2 : 6-*dinitro-4-thiocyanoanisole*, m. p. 93° (also converted into 2 : 6-dinitro-4-thiocyanoaniline). Attempted conversion of this compound into I (by absolute nitric acid at 0°) or *vice versa* (by denitrating with phenol) was unsuccessful. The m. p. of various derivatives of the type $X\cdot C_6H_4\cdot SCN$ are compared and agree with Franchimont's rules (A., 1897, ii, 542). J. W. BAKER.

3 : 5-Dimethoxyaniline. R. SEKA and W. FUCHS (Monatsh., 1931, 57, 63—70).—Prolonged treatment of methyl 3 : 5-dimethoxybenzoate with liquid ammonia at the ordinary temperature gives 3 : 5-*dimethoxybenzamide*, m. p. 148—149°, converted by cold alkaline sodium hypobromite into 3 : 5-dimethoxyaniline, b. p. 177°/12 mm., m. p. 46° (*hydrochloride*, m. p. 210°; *chloroplatinate*, decomp. 223°; *picrate*, decomp. 165—170° after darkening at 150°; *picrolonate*, decomp. 230° after darkening at 220°; *benzoyl* derivative, m. p. 139°; *anisoyl* derivative, m.p. 119—120°). 3 : 5-*Dimethoxybenzhydrazide*, m. p. 168·5° (*hydrochloride*, m. p. 210°), is converted by the usual method into the azide, m. p. 50—51°, decomp. about 70°, which when heated with methyl alcohol furnishes *methyl* 3 : 5-*dimethoxyphenylcarbamate*, m. p. 43·5°.

H. BURTON.

Aminodiphenylamine compounds. I. G. FARBENIND. A.-G.—See B., 1931, 238.

Influence of halogens on the colour of azo-dyes. Spectral absorption of monoazo-dyes. D. G. FOSTER (J. Amer. Chem. Soc., 1931, 53, 654—660).—The absorption curves for solutions of sodium 1-*o*-, -*m*-, and -*p*-chloro-, 1-*o*-, -*m*-, and -*p*-bromo-, and 1-*o*-, -*m*-, and -*p*-iodo-benzeneazo-β-naphthol-3 : 6-disulphonates are all of the same type. The depth of the absorption band for the chloro- and bromo-derivatives increases in the order *m*, *o*, *p*, whilst the sequence for the iodo-compounds is *o*, *m*, *p*. The effect of position isomerism is the same as that recorded in the literature.

H. BURTON.

***p*-Cymene. XIV. 2-*p*-Cymylhydrazine.** A. S. WHEELER and T. L. KING (J. Amer. Chem. Soc., 1931, 53, 809—810).—The *acetate*, m. p. 63—64°, *lactate*, m. p. 134·5°, *oxalate*, m. p. 167°, and *benzoate*, m. p. 72·5°, of 2-*p*-cymylhydrazine are described; only the lactate is stable to water. m-*Nitrobenzaldehyde*-2-p-*cymylhydrazone* has m. p. 143°. 2-*p*-Cymylhydrazine is not a good reagent for the carbonyl group, since unstable products are obtained from many aldehydes and ketones.

H. BURTON.

Monosubstituted carbohydrazides, their typical derivatives, and formation of heterocyclic compounds from them. P. C. GUHA and M. A. HYE (J. Indian Chem. Soc., 1930, 7, 933—944).—Treatment of ethyl phenylcarbazinate (prepared from phenylhydrazine and ethyl chloroformate in aqueous pyridine) with hydrazine hydrate in alcohol at 120—125° gives 1-*phenylcarbohydrazide*, m. p. 154°:

$$NHPh\cdot NH\cdot CO_2Et + NH_2\cdot NH_2 \longrightarrow NHPh\cdot NH\cdot CO\cdot NH\cdot NH_2.$$

1-o-*Tolyl*-, m. p. 153°, and 1-p-*tolyl-carbohydrazides*, m. p. 148—149°, are prepared similarly from *ethyl* o-*tolyl*-, m. p. 74—75°, and p-*tolyl-carbazinates*, m. p. 89—90°, respectively. Ethyl phenylcarbazinate does not react with phenylhydrazine or *o*-phenylenediamine. 1-*Phenylcarbohydrazones* and 1-o-*tolylcarbohydrazones* of the following substances are prepared (the m. p. of the latter are given in parentheses): *benzaldehyde*, m. p. 210—211° (201—202°); o-*chlorobenzaldehyde*, m. p. 212—213° (212—213°); p-*chlorobenzaldehyde*, m. p. 197—198° (198°); m-*bromobenzaldehyde*, m. p. 196—197° (216°); o-*nitrobenzaldehyde*, m. p. 208—209° (219°); m-*nitrobenzaldehyde*, m. p. 243—244° (211—212°); *salicylaldehyde*, m. p. 222—223° (218—219°); m-*phthalaldehyde*, m. p. 266—267° (236—237° [decomp.]); *acetone*, m. p. 83° (177°); *isatin*, m. p. 281° (decomp.) (251—252° [decomp.]). Phenanthraquinone and 1-phenylcarbohydrazide in boiling acetic acid give the *compound*,

$$C_{12}H_8{<}\begin{matrix}C\cdot CO\\ C\cdot N\cdot NHPh\end{matrix}$$

m. p. 285° (decomp.); reaction is presumed to occur by cyclisation of the intermediate phenylcarbohydrazone and subsequent loss of nitrogen.

1-Phenylcarbohydrazide reacts with carbon disulphide in alcoholic potassium hydroxide at the ordinary temperature, forming *potassium* 1-*phenylcarbohydrazidodithioformate*; when the mixture is boiled, potassium hydrogen sulphide is eliminated from the salt and 6-*thiol*-3-*keto*-1-*phenyl*-1 : 2 : 3 : 4-*tetrahydro*-1 : 2 : 4 : 5-*tetrazine*, m. p. 206°, results. *Ethyl* 1-*phenylcarbohydrazidoformate*, m. p. 202—203°, prepared from phenylcarbohydrazide and ethyl chloroformate, is decomposed by hydrochloric acid to hydrazine, phenylhydrazine, alcohol, and carbon dioxide. 1-*Phenylcarbohydrazidocarbonamide*, m. p. 223° (decomp.), is formed when the hydrazide is heated with carbamide at 130—135°, or treated with cyanic acid. Nitrous acid converts 1-phenylcarbohydrazide into 4-*hydroxy*-1-*phenylsemicarbazide*, $NHPh\cdot NH\cdot CO\cdot NH\cdot OH$, m. p. 86°.

The following 1-arylcarbohydrazidothiocarbonaryl-(alkyl)amides are prepared from the requisite arylcarbohydrazide and aryl(alkyl)thiocarbimide in alcohol: 1-*phenylcarbohydrazido*-5-*thiocarbon-anilide* (I), m. 196° (decomp.), -o-*toluidide* (II), m. p. 175—176°, -p-*toluidide*, m. p. 196—197°, -m-4-*xylidide*, m. p. 179—180°, -*allylamide*, m. p. 196°, and -*methylamide*, m. p. 207°; 1-o-*tolylcarbohydrazido*-5-*thiocarbon-anilide*, m. p. 194—195° (decomp.), -o-*toluidide*, m. p. 189°, -p-*toluidide*, m. p. 213°, -m-4-*xylidide*, m. p. 186°, -*allylamide*, m. p. 197°, and -β-*naphthylamide*, m. p. 94—96°. 1-*Phenylcarbohydrazido*-5-*carbonanilide*, m. p. 218—219°, is unaffected by boiling hydrochloric acid, whilst I is similarly converted into 5-*anilino*-2-*keto*-2 : 3-*dihydro*-1 : 3 : 4-*thiodiazole*, m. p. 246°, also formed from I and ferric chloride solution. Potassium hydroxide solution converts I into 5-*anilo*-2-*keto*-2 : 3 : 4 : 5-*tetrahydro*-1 : 3 : 4-*oxdiazole*-2-*phenylhydrazone*, m. p. 244—245°. 5-o-*Toluidino*-2-*keto*-2 : 3-*dihydro*-1 : 3 : 4-*thiodiazole*, m. p. 220—221°, is prepared by the action of hydrochloric acid or ferric chloride on II.

H. BURTON.

Condensation products of phenylacethydrazide. R. SEKA and S. P. HEILPERIN (Monatsh., 1931, 57, 45—51).—*Pyruvic acid phenylacethydrazone*, m. p. 168°, is obtained in 76·6% of the theoretical amount from aqueous solutions of pyruvic acid (1 mol.) and phenylacethydrazide (1 mol.). *Lævulic acid phenylacethydrazone*, m. p. 119°, is prepared similarly in 70% yield. Galactose and the hydrazide in boiling alcohol give 58% of *galactosephenylacethydrazone*, m. p. 192—193°. Diacetyl and the hydrazide react in aqueous solution to give a mixture of the *mono*-, m. p. 138°, and *di-phenylacethydrazones*, decomp. 254°. Benzil and the hydrazide at 120°/vac. furnish a mixture of the corresponding *mono*-,

m. p. 198—199°, and *di-phenylacethydrazones*, m. p. 236—237°. A phenylacethydrazone could not be obtained from ethyl acetoacetate. In most of the above reactions a small amount of s-*di(phenylacetyl)-hydrazine*, m. p. 236—237°, is also produced.

H. BURTON.

Acyldiarylhydrazine series. II. Salt formation in the benzidine and semidine rearrangements. J. J. RITTER and F. O. RITTER (J. Amer. Chem. Soc., 1931, 53, 670—676; cf. A., 1930, 1175).—Monoacetylation of unsymmetrically substituted αβ-diarylhydrazines gives either α- or β- or mixtures of the α- and β-acetyl derivatives (cf. *loc. cit.*). The following have been prepared: α-phenyl-β-*p*-iodophenylhydrazine (α-, m. p. 135—136°, and β-, m. p. 156—157°, -*acetyl* derivatives); α-phenyl-β-*p*-carboxyphenylhydrazine (α-*acetyl* derivative, m. p. 207—208°); α-phenyl-β-*p*-ethoxyphenylhydrazine (β-*acetyl* derivative, m. p. 108°); *α-phenyl-β-*p*-acetoxyphenylhydrazine*, m. p. 117—118° (α-*acetyl* derivative, m. p. 105—106°). All m. p. are corr. Oxidation of the α-acetyl derivatives with potassium dichromate and acetic acid at the ordinary temperature gives the corresponding azo-derivatives: NRAc·NHR′⟶ NRAc·NR′·OH⟶Ac·OH+NR:NR′. Similar oxidation of the β-acetyl derivatives affords intensely coloured products (red or violet), apparently owing to the presence of the anilino-group. Various α-phenyl-β-arylhydrazines when suspended in 10% hydrochloric acid at the ordinary temperature furnish blue or violet solutions owing to atmospheric oxidation. This oxidation is parallel to the oxidation of the above acetyl derivatives, *i.e.*, the αβ-diarylhydrazines yielding β-acetyl derivatives give intensely coloured solutions, whilst those furnishing α-acetyl derivatives do not. It is assumed that salt formation occurs on either the α- or β-nitrogen atoms; the subsequent course of the reaction is the same as for the acetyl derivatives. Some of the diarylhydrazines give mixtures of salts. Analysis of the results of Jacobsen (A., 1922, i, 589, 596) suggests that similar salt formation is involved in the benzidine and semidine rearrangements. Those diarylhydrazines yielding mixtures of α- and β-acetyl derivatives give, under Jacobsen's conditions (*loc. cit.*), approximately equal amounts of diphenyl and semidine derivatives.

H. BURTON.

Oxidation of propenyl derivatives by means of diazo-compounds. A. QUILICO (Atti R. Accad. Lincei, 1930, [vi], 12, 341—344).—The mechanism suggested by Angeli and Polverini (A., 1930, 906) for oxidations by means of diazo-compounds (A., 1928, 997; 1929, 559; 1930, 82) is discussed. If the oxidation of a propenyl compound by a normal diazohydroxide proceeds according to the two schemes CHR:CHMe+Ph·N_2·OH⟶(1) CHR:N·NHPh+Me·CHO and (2) R·CHO+CHMe:N·NHPh, the aromatic aldehydephenylhydrazone and acetaldehyde formed should be accompanied by the aromatic aldehyde and acetaldehydephenylhydrazone. The latter could not be found, but the formazyl compound, NPh:N·CMe:N·NHPh, resulting from the interaction of the acetaldehydephenylhydrazone with the diazohydroxide present, is obtained. Similarly, free anisaldehyde is found among the products of the interaction of *p*-nitrobenzenediazonium sulphate and anethole, and free piperonaldehyde among those of the interaction of *p*-nitrobenzenediazonium sulphate and *iso*safrole.

T. H. POPE.

Behaviour of ketonehydrazones towards diazonium salts. M. BUSCH and K. SCHMIDT (J. pr. Chem., 1931, [ii], 129, 151—162).—The phenylhydrazones of aromatic and mixed aliphatic–aromatic ketones couple with diazonium salts in the *p*-position in the phenylhydrazone nucleus, or, if this is already substituted, in the *o*-position, but with less readiness; if both the *p*- and an *o*-position are occupied, the hydrazone residue is replaced by the diazonium salt, yielding, *e.g.*, with benzenediazonium chloride, the *p*-benzeneazophenylhydrazone and a new diazonium salt: CPhMe:N·NH·C_8H_9(2 : 4)+Ph·N_2Cl⟶ C_8H_9·N_2Cl+HCl. Nitrated diazonium salts, with some exceptions, also replace the hydrazone radical, even when unsubstituted. Thus acetophenonephenylhydrazone (and also the *p*-bromophenylhydrazone) and *p*-nitrobenzenediazonium chloride give acetophenone-*p*-nitrophenylhydrazone, but acetophenonebenzylphenylhydrazone reacts normally, as also does benzophenonephenylhydrazone, which reacts only with difficulty. Deoxybenzoinphenylhydrazone behaves like the acetophenone derivative. The reaction proceeds best in all cases in alcoholic solution or in a mixture of alcohol and benzene. The presence of water is deleterious, and tends to cause hydrolysis. No reaction occurs in alkaline solution under the conditions used by von Pechmann (A., 1894, i, 457) for the aldehydehydrazones.

The following are described: *acetophenone*-p-*benzeneazophenylhydrazone*, m. p. 161° (*hydrochloride*), -*4-bromo-2-benzeneazophenylhydrazone*, m. p. 183°, -*benzylphenylhydrazone*, m. p. 58° (diffuse), -p-*benzeneazophenylbenzylhydrazone* (*hydrochloride*), -*4-nitro-2*-p-*nitrobenzeneazophenylhydrazone*, m. p. 300° (sinters 290°) (from the *as*-*m*-xylylhydrazone and *p*-nitrobenzenediazonium chloride; a nitrobenzenediazo-group has entered the hydrazone nucleus, thus forming an exception to the general rule), -p-*nitrobenzeneazophenylbenzylhydrazone*, m. p. 130°; *benzophenone*-p-*nitrobenzeneazophenylhydrazone*, m. p. 194—196°; *deoxybenzoin-benzeneazophenylhydrazone*, m. p. 138°, and -p-*nitrophenylhydrazone*, m. p. 160°.

H. A. PIGGOTT.

Combustion of activated charcoal in the vapours of organic compounds containing oxygen. N. D. ZELINSKI and M. V. GAVERDOVSKAJA (Ber., 1931, 64, [B], 435—437; cf. A., 1928, 747).—Secondary and primary alcohols are converted into hydrocarbons by passage over activated charcoal at 300°, the yields being nearly quantitative. The following examples are cited: *cyclo*hexanol to *cyclo*hexane; *o*- and *m*-methyl*cyclo*hexanol to *o*- and *m*-methyl*cyclo*hexane; *cyclo*hexylethyl alcohol to ethyl*cyclo*hexane; phenylethyl alcohol to ethylbenzene; diphenylcarbinol to diphenylmethane. Alcoholic oxygen oxidises activated charcoal more energetically and at a lower temperature than molecular oxygen attacks ordinary charcoal; the gaseous product, as with the more easily reduced oxides, is carbon dioxide. *cyclo*Hexylmethyl alcohol is not

affected under the prescribed conditions. Benzyl alcohol behaves exceptionally, yielding toluene, benzaldehyde, carbon dioxide and monoxide, oxygen, hydrogen, and methane. The monoxide is a normal product of the reduction of carbon dioxide by activated charcoal. H. WREN.

Reactions of heterocyclic compounds with phenols. Reaction of ethylene oxide with phenol. R. A. SMITH and J. B. NIEDERL (J. Amer. Chem. Soc., 1931, **53**, 806—808).—Ethylene oxide (1 mol.) and phenol (1 mol.) react in presence of sulphuric acid (0·2 mol.) at the ordinary temperature during 1 week forming *o*-vinylphenol (I), also obtained when phenyl β-hydroxyethyl ether is treated with sulphuric acid. The following reactions probably occur:

$$\begin{matrix} CH_2 \\ CH_2 \end{matrix}\!\!>O + H_2SO_4 \longrightarrow HO{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}SO_3H \xrightarrow{Ph{\cdot}OH} H_2SO_4 + HO{\cdot}CH_2{\cdot}CH_2{\cdot}OPh \longrightarrow I.$$

H. BURTON.

Behaviour of aceto-*p*-phenetidide towards chlorine and bromine. E. BUREŠ and J. KOVAŘOVICOVA (Časopis Českoslov. Lek., 1930, **10**, 197—202, 233—239; Chem. Zentr., 1930, ii, 2775).—By the action of bromine on aceto-*p*-phenetidide 3 : 5-dibromoaceto-*p*-phenetidide is formed; dry gaseous chlorine attacks positions 2, 3, 5, and 6. The following derivatives of phenetole were prepared: 3 : 5-dibromo-4-acetamido-, m. p. 175°; 3 : 5-dibromo-4-amino-, m. p. 54° (picrate, m. p. 145°); 3 : 5-dibromo-4-dimethylamino-, m. p. 84°; 3 : 5-dibromo-4-benzamido-, m. p. 159°; 3 : 5-dibromo-4-ethylamino-, m. p. 91°; 3 : 5-dibromo-4-diacetamido-, m. p. 108°; 3 : 5-dibromo-, b. p. 267°; 3 : 4 : 5-tribromo-, m. p. 72°; 3 : 5-dibromo-4-iodo-, m. p. 99°; 4-chloro-3 : 5-dibromo-, m. p. 42—44°; 3 : 5-dibromo-4-nitro-, m. p. 128°; 3-bromo-5-nitro-4-amino-, m. p. 108°; 3 : 4 : 5-tribromo-2-nitro-, m. p. 52—53°; 3 : 5-dibromo-4-amino-, m. p. 53—54°; 2 : 3 : 5 : 6-tetrachloro-4-acetamido-, m. p. 226°; 2 : 3 : 5 : 6-tetrachloro-4-amino-, m. p. 96°; 2 : 3 : 5 : 6-tetrachloro-, m. p. 56°; 2 : 3 : 4 : 5 : 6-pentachloro-, m. p. 75°; 2 : 3 : 5 : 6-tetrachloro-4-bromo-, m. p. 81°; 2 : 3 : 5 : 6-tetrachloro-4-iodo-, m. p. 79°. 2 : 3 : 5 : 6-Tetrachlorobenzoquinone sublimes without melting. A. A. ELDRIDGE.

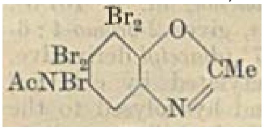
Action of bromine on phenols. G. HELLER [with W. DIETRICH, T. HEMMER, H. KATZEL, E. ROTTSAHL, and P. G. ZAMBALOS] (J. pr. Chem., 1931, [ii], **129**, 211—256).—Phenols and their derivatives are classified according to their behaviour with bromine in glacial acetic acid. The following general types of behaviour are observed: (1) no action (usually where the hydroxyl group is protected), (2) simple substitution which may or may not involve the displacement of other substituents, and, if it proceeds to completion, finally gives pentabromophenol, (3) bromination of acetamido-groups with the consequent formation of stable glyoxaline and oxazole derivatives, (4) oxidation to a quinone, sometimes followed by bromination to bromoanil, and (5) formation of tetrabromodiketo*cyclo*pentene or polybromoacetones by ring-fission. The last reaction seems characteristic of derivatives of *o*-aminophenol, corresponding derivatives of *m*- and *p*-aminophenols showing no tendency to ring-fission under the conditions employed.

4 : 6-Dinitro-3-acetamidophenyl acetate, prepared by nitration of diacetyl-*m*-aminophenol in acetic anhydride, is unaffected by bromine in acetic acid at 100°, but the corresponding *phenol*, m. p. 167·5°, obtained by alkaline hydrolysis, gives 2-*bromo*-4 : 6-*dinitro*-3-*aminophenol*, m. p. 207° (*diacetyl* derivative, m. p. 222°, completely deacetylated by cold [?] concentrated sulphuric acid, and hydrolysed to the -*acetamidophenol*, m. p. 223·5°, by dilute sodium hydroxide). This is converted by nitric acid (*d* 1·42), or by diazotisation and decomposition of the diazo-compound, into 2-*bromo*-4 : 6-*dinitroresorcinol*, m. p. 192·5—193°. Bromination of 4-nitro-2-acetamidoresorcinol gives the 6-*bromo*-derivative, m. p. 173—174°. 6-Nitro-3-acetamidophenol is converted at 100° into 2-*bromo*-, m. p. 230°, and 2 : 4-*dibromo*-6-*nitro*-3-*aminophenol*, m. p. 199—200°, bromination ceasing at the dibromo-stage; the products were identified by elimination of the amino-group (diazo-reaction). The preparation of 4 : 6-dibromo-2-nitrophenol, m. p. 117°, by Goldstein's method (J. Russ. Chem. Soc., 1878, **10**, 354) presented difficulties, but it was readily formed by bromination of *o*-nitrophenol in the usual way. Bromination of 3 : 5-dinitro-4-acetamidophenol at the ordinary temperature gives 2 : 6-*dibromo*-3 : 5-*dinitro*-4-*acetamidophenol*, decomp. 274·5°; the corresponding *aminophenol*, m. p. 138°, obtained by deacetylation with concentrated sulphuric acid at 100°, gives on further bromination bromoanil. From 4-nitro-3-acetamidophenol, the 6-*bromo*-derivative, m. p. about 295° (decomp.), is readily produced; it is hydrolysed by aqueous-alcoholic potassium hydroxide to 6-*bromo*-4-*nitro*-3-*aminophenol*, m. p. 244° (decomp.) (*potassium* salt), identified by conversion into 2-bromo-4-nitrophenol. More drastic bromination of the original substance gives 2 : 6-*dibromo*-4-*nitro*-3-*acetamidophenol*, m. p. 192—195°, and -3-*aminophenol*, m. p. 162·5°; the latter is produced from the former by alkaline hydrolysis, and from 6-bromo-4-nitro-3-aminophenol by bromination, and is readily converted into 2 : 6-dibromo-4-nitroresorcinol by the diazo-reaction. Exhaustive bromination of 4-nitro-3-acetamidophenol gives tetrabromophenol, m. p. 140° (Benedict, A., 1880, 246), which in presence of ferric chloride at 60° may be brominated to pentabromophenol.

5-Bromo-, m. p. 192°, and 6-*bromo*-2 : 4-*dinitroresorcinol*, m. p. 89°, and 2-bromo-4 : 6-dinitroresorcinol are the products of bromination of the corresponding nitroresorcinols, accompanied by tetrabromoresorcinol in the case of the 2 : 4-dinitro-compound. 6-Nitro-4-acetamidoresorcinol gives the 2-*bromo*-derivative, m. p. 226° (decomp.), and (under vigorous conditions) a small amount of a *substance*, m. p. 82—84°. The preparation of *tetrabromopyrocatechol* and *tetrabromo-o-benzoquinone* from 3- and 4-nitropyrocatechol is described. 3-Nitro-4-acetamidophenol and its acetate are similarly brominated to pentabromophenol, but 3-nitro-4-aminophenol gives bromoanil.

By graduated bromination of 2 : 4-diacetamidophenol 6-*bromo*-, m. p. 215° (I), and 5 : 6-*dibromo*-2 : 4-*diacetamidophenol* (II), m. p. 208° (+2H_2O, m. p. 188·5°), 3 : 5 : 6 - *tribromo* - 2 - *acetamidobenzoquinone*, golden-yellow, m. p. 198° (readily reduced by sul-

phurous acid to the corresponding *quinol*, m. p. 212°), the *substance* III, decomp. indef. above 180°, and tetrabromodiketo*cyclo*pentene (IV), are produced. By



(III.)

oxidation with dilute nitric acid 6-*bromo*-, m. p. 183°, and 5 : 6-*dibromo*-2-*acetamidobenzoquinone*, m. p. 213°, the former of which is oxidised smoothly by an excess of bromine in acetic acid to IV. The compound III gives with 2*N*-sodium hydroxide at the ordinary temperature 5 : 6-*dibromo*-4-*acetamido*-1-*methylbenzoxazole*, m. p. 245°, which is readily reconverted into III by bromine in acetic acid, is hydrolysed by fuming hydrochloric acid to II, and is oxidised by nitric acid (*d* 1·4) to 5 : 6-dibromo-2-acetamidobenzoquinone. A similar series of changes is undergone by 2 : 6-*diacetamidophenol*, m. p. 170° (from the diaminophenol hydrochloride, sodium sulphite, and acetic anhydride), the following being isolated: 3 : 5(?)-*dibromo*-2 : 6-*diacetamidophenol*, m. p. 208°, a *monobromo*-compound, m. p. 215° (decomp.), and 3 : 4 : 5-*tribromo*-6-*acetamido*-1-*methylbenzoxazole*, m. p. 226° [*perbromide* (analogous to III), m. p. about 161—163° (decomp.)]. 2 : 6-*Diacetamidobenzoquinone*, orange, m. p. 270° (decomp.) (*anilide*, bluish-black, m. p. 202°), is produced by oxidation either of 2 : 6-diacetamido- or 2 : 4 : 6-*triacetamido-phenol*, m. p. 265°, with nitric acid (*d* 1·5) at a low temperature. 2 : 4 : 6-Triacetamidophenol gave no halogen derivative on bromination. 6-Nitro-2 : 4-diacetamidophenol gives 3 : 5 : 6-tribromo-2-acetamidobenzoquinone (above) and, under more vigorous conditions, IV.

6-*Bromo*-2 : 4-*dinitro*-3-*aminophenol* (*mono*-, decomp. 221°, and *di-acetyl* compounds, m. p. 161°) is converted by further bromination into bromoanil, by diazotisation or by nitric acid (*d* 1·5) in the cold into 6-bromo-2 : 4-dinitroresorcinol (above), and by nitric acid (*d* 1·42) in the warm into styphnic acid. Bromoanil is the sole bromination product of 2 : 6-dinitro-4-acetamidophenol and 2 : 5-dinitroquinol.

Nitration of 2-nitro-4-acetamidophenol according to the directions of Meldola and Hay (J.C.S., 1909, **95**, 1381) gave, not a dinitro-, but 2 : 3 : 5-*trinitro*-4-*acetamidophenol*, m. p. 171° [+β-naphthol, m. p. 181° (*loc. cit.*)]. The corresponding free aminophenol, obtained by hydrolysis with concentrated sulphuric acid, is converted by bromination into 5-*bromo*-2-*nitro*-4-*diazo*-1-*keto*-1 : 4-*dihydrobenzene*,

$CBr{<}\begin{matrix}CH{-}{-}CO\\ C(:N_2)\cdot CH\end{matrix}{>}C\cdot NO_2$, decomp. 186° (explodes).

It couples with β-naphthol to a red dye, and a solution in hydrochloric acid effervesces violently when boiled with cuprous chloride, and deposits a *substance*, m. p. 80°. A similar substance, exploding at 170°, is obtained from the acetyl compound; it appears to be different from the above, giving a *substance*, m. p. 122°, when boiled with cuprous chloride and hydrochloric acid. With a large excess of bromine the acetyl compound gives bromoanil. A similar behaviour appears to be shown by 3 : 5 : 6-*trinitro*-2-*aminophenol*, decomp. explosively about 167° (the *acetamido*-compound, m. p. 151°, is prepared by nitration of 5-*nitro*-2-*acetamidophenol*, m. p. 258—259°), the *diazo-keto*-compound exploding at 180°, and forming a cherry-red dye with alkaline β-naphthol; the acetyl derivative, however, appears to decompose on bromination, a *bromo*-compound, m. p. 218° (decomp.), being isolated in small amount.

Bromination of 4-*nitro*-2-*acetamidophenol*, decomp. 267°, gives the 6-*bromo*-derivative, m. p. 206° (decomp.), which, on further bromination, gives 3 : 5 : 6-*tribromo*-2-*aminobenzoquinone* 4-*dibromide* (?), m. p. 216° (decomp.) (*acetyl* derivative, m. p. 208°), and IV. The first is synthesised by partial reduction of 6-bromo-2 : 4-dinitrophenol, and acetylation of the 6-*bromo*-4-*nitro*-2-*aminophenol*, m. p. 162° (*ammonium* salt), thus produced. 4 : 6-Dinitro-2-acetamidophenol (by nitration of *o*-acetamidophenol) is decomposed by bromine to IV.

Diazotisation of 3 : 5 : 6-trinitro-2-aminophenol in moderately concentrated sulphuric acid gives 3 : 5 : 6-*trinitro*-2-*diazo*-1-*keto*-1 : 2-*dihydrobenzene* (explosive), which is decomposed by boiling alcohol to 3 : 5 : 6-trinitrophenol, and forms a reddish-violet crystalline dye with β-naphthol: short heating with alcohol gives 5 : 6-*dinitro*-3-*ethoxy*-2-*diazo*-1-*keto*-1 : 2-*dihydrobenzene*, m. p. 166° (decomp.), which gives a red dye with β-naphthol. Bromination of 5-nitro-2-acetamidoquinol (cf. this vol., 488) gives 5 : 6-dibromo-2-acetamidobenzoquinone (above), *tribromo*-2-*acetamidobenzoquinone*, m. p. 189—190° (decomp.), and IV. 2 : 5-*Diacetamidotetra-acetoxybenzene*, m. p. 216° (decomp.), gives 2 : 5-diacetamidodihydroxybenzoquinone (A., 1888, 943), whilst 3 : 4-diacetamidophenol gives successively the 6-*bromo*-, decomp. 258°, and 2 : 6-*dibromo*-derivative, m. p. 223° (decomp.), and 4 : 6-*dibromo*-5-*hydroxy*-2-*methylbenziminazole* (*hydrobromide*).

2 : 6-*Diacetamidobenzoquinone*, m. p. 295°, is obtained by oxidation with air in alkaline solution, or with ferric chloride, of the *quinol*, m. p. 240° (decomp.), itself prepared by acetylation of the reduction product of 2 : 6-dinitroquinol. Both it and the quinol give 3-*bromo*-, m. p. 225° [*quinol*, m. p. 198° (decomp.)], and 3 : 5-*dibromo*-2 : 6-*diacetamidobenzoquinone*, m. p. 201° [*quinol*, m. p. 213° (decomp.)], and, with a large excess of bromine, hexabromoacetone. Nitroaminotetrahydroxybenzene (cf. A., 1885, 779) (*di*-, decomp. about 214°, and *penta-acetyl* derivative, m. p. 194°) gives with bromine in acetic acid a yellow additive *compound*, from which it is readily regenerated; an excess of bromine yields a *substance*, $C_6H_3O_4NBr_2$, and ammonium bromide, and, under still more drastic conditions, dibromotetrahydroxybenzene, polybromoacetone, and bromoform.

Improved methods for the preparation of *o*-acetamidophenyl acetate and 3-nitro-2-aminophenol are given. From the latter by bromination in the usual way 6-*bromo*-, m. p. 233°, and 4 : 6-*dibromo*-3-*nitro*-2-*aminophenol*, m. p. 182°, 4 : 5 : 6-*tribromo*-3-*nitro*-1-*dibromomethyl*-, m. p. 233°, and -1-*tribromomethyl*-*benzoxazoles*, m. p. 172°, are obtained; the last two compounds may also be prepared by bromination of 3-nitro-1-methylbenzoxazole and 3-nitro-2-acetamidophenyl acetate, respectively. A new aniline derivative of IV, probably 4 : 5-*dibromo*-2 : 2-*dianilino*-3-*anilocyclopentan*-1-*one*, m. p. 261° (decomp.), is described.

H. A. PIGGOTT.

4-Nitro-4′-methoxystilbene. A correction. J. T. Hewitt and W. Lewcock (J.C.S., 1931, 444).—This compound has m. p. 132° and not 162° as previously stated in error (Hewitt and others, J.C.S., 1912, **101**, 608). J. W. Baker.

Naphthalene series. III. Preparation of 3-amino-2-naphthyl methyl ether. G. B. Jambuserwala, S. Holt, and F. A. Mason (J.C.S., 1931, 373—377).—Methyl sulphate and 20% sodium hydroxide convert 2-hydroxy-3-naphthoic acid into the 2-methoxy-acid (96% yield), from which by treatment with thionyl chloride the acid chloride is obtained, and the latter converted by dry ammonium carbonate in dry benzene into 2-methoxy-3-naphthoamide. Conversion of this into 3-amino-2-naphthyl methyl ether by the Hoffmann reaction under various conditions gives unsatisfactory yields (5—20%), but satisfactory results are obtained by the Curtius method. Ethyl 2-methoxy-3-naphthoate, b. p. 298°/18 mm. (Auwers and Frühling, A., 1921, ii, 230, give b. p. 208°/18 mm.), is converted by hydrazine hydrate into the *hydrazide*, m. p. 121—124°, converted by 2-methoxy-3-naphthoyl chloride in benzene into *di-(2-methoxy-3-naphth)hydrazide*, m. p. 248—250° (corr.), and by the appropriate aldehyde into *benzylidene-*, m. p. 222·5° (corr.), m-, m. p. 223—224° (corr.), and o-, m. p. 185—186° (corr.), *-nitrobenzylidene-*, and *4′-hydroxy-2 : 2′-dimethoxybenzylidene-*, m. p. 211—212° (corr.), *-3-naphthhydrazide*. The original monohydrazide is converted by ethyl nitrite and anhydrous hydrogen chloride in warm absolute alcohol into *ethyl 2-methoxy-3-naphthylcarbamate*, m. p. 104—105° (corr.), which is hydrolysed by boiling 40% aqueous potassium hydroxide to 3-amino-2-naphthyl methyl ether in 92% yield. The last-named is converted by the Sandmeyer reaction into *3-chloro-2-naphthyl methyl ether*, m. p. 78·5°, hydrolysed by hydriodic acid to 3-chloro-β-naphthol. J. W. Baker.

Naphthalene series. IV. Preparation and properties of β-naphthol-3-sulphonic acid. S. Holt and F. A. Mason (J.C.S., 1931, 377—381).—Diazotisation of 3-amino-β-naphthyl methyl ether and treatment of the diazonium solution with an excess of sulphur dioxide and chemically prepared copper affords *2-methoxynaphthalene-3-sulphinic acid*, m. p. 133—134°, which condenses in warm alcoholic solution with 2 : 4-dinitrochlorobenzene to give *- : 4-dinitrophenyl-2-methoxy-3-naphthylsulphone*, m. p. 213—214°, which is oxidised by potassium permanganate in acetone suspension to *2-methoxynaphthalene-3-sulphonic acid* (*potassium* salt; *sulphonyl chloride*, m. p. 137—138°; *amide*, m. p. 113°; and *anilide*, m. p. 173—174°). This does not couple with diazonium salts, but is readily hydrolysed by dilute hydrochloric ac (1 : 1) to *β-naphthol-3-sulphonic acid* [*sodium* $+H_2O$, *aniline*, m. p. 241—242°, and *α-naphthylamine*, m. p. 247—248°, salts; *amide*, m. p. 110°, and *anilide*, m. p. 112° (decomp.), not obtained pure], which with nitrous acid affords *1-nitroso-β-naphthol-3-sulphonic acid*, decomp. 268°. β-Naphthol-3-sulphonic acid couples with diazotised amines and thus are obtained the *azo*-dyes from aniline, *p*-nitroaniline, *m*-xylidine, α-naphthylamine, and dianisidine, which dye wool somewhat deeper shades than does the corresponding 2 : 6-sulphonic acid, the peaks of the absorption curves being shifted a little in the direction of longer wave-lengths compared with those in the latter acid. J. W. Baker.

Preparation of *iso*eugenol from clove oil. R. Priester (Riechstoffind., 1930, **5**, 83—85, 108—109; Chem. Zentr., 1930, ii, 3206).—Glycerol and ethylene glycol are suitable diluents. Eugenol (30 g.), water (50 g.), potassium hydroxide (15 g.), and glycerol (10 g.) are heated for 45 min. at 180° and then for 15 min. not above 186°; only 1 g. of resin is produced and good conversion is effected, the product having n_D^{20} 1·5744. A. A. Eldridge.

Bromo*iso*vanillin. H. Pauly (Ber., 1931, **64**, [*B*], 503; cf. A., 1916, i, 150).—A reply to Henry and Sharp (A., 1930, 1602). H. Wren.

Relative directive powers of groups of the forms RO and RR′N in aromatic substitution. IX. Nitration of *p*-cetyloxyanisole and *p*-benzyloxyanisole. J. C. Smith (J.C.S., 1931, 251—258).—The action of methyl-alcoholic sodium methoxide on a boiling acetone solution of cetyl iodide and quinol monomethyl ether gives *4-cetyloxyanisole*, m. p. 67·9°, nitrated with nitric (*d* 1·42) and acetic acids at 0° or 25° to a mixture of 2- (dimorphous), m. p. 62·5° (prisms) and 63·9° (needles), and 3-, m. p. 49·5°, *-nitro-4-cetyloxyanisole*, containing 67·9% of the latter. The composition of the product was determined by thermal analysis, the 2- and 3-nitro-compounds being synthesised by similar methods from 3- and 2-nitro-4-methoxyphenol, respectively. They are resistant to alkaline hydrolysis and form a complex binary system, the curve indicating the existence of a compound of the type AB. *4-Benzyloxyanisole*, m. p. 69·7° (plates, unstable) and 71·5° (needles), is similarly prepared, using benzyl chloride at 90°, and by nitration under similar conditions affords a mixture of 2-, m. p. 59·8°, and 3-, m. p. 61·3°, *-nitro-4-benzyloxyanisole* (similarly synthesised) containing 51% (at 28°) and 51·4% (at 14°) of the 3-nitro-isomeride. These nitro-compounds give a normal m.-p. curve. On the basis of these data the values of the relative directive powers of the cetyloxy- and benzyloxy-groups are, respectively, 210 and 107 (OMe=100: cf. Robinson and Smith, A., 1926, 397), and the results are in agreement with the requirements of the theory of Allan, Oxford, Robinson, and Smith (*ibid.*, 397). J. W. Baker.

Phenyl ethers. M. Oesterlin (Monatsh., 1931, **57**, 31—44).—*p*-Bromoanisole and potassium phenoxide condense in presence of copper-bronze (Naturkupfer *C*) at 200—210° to give *p*-methoxydiphenyl ether, b. p. 163—165°/14 mm., which is brominated with a bromide–bromate mixture in presence of dilute sulphuric acid and carbon disulphide to *4-bromo-4′-methoxydiphenyl ether*, m. p. 85°, and demethylated by aluminium chloride in benzene to *p-hydroxydiphenyl ether*, m. p. 84°. This condenses (as above) with *p*-bromoanisole, forming *4-phenoxy-4′-methoxydiphenyl ether*, m. p. 82°, demethylated by the above method to *4-hydroxy-4′-phenoxydiphenyl ether*, m. p. 87°. Quinol monomethyl ether and *p*-bromoanisole afford *4 : 4′-dimethoxydiphenyl ether*, m. p. 102°, demethylated by aluminium chloride in xylene to

the 4 : 4′-dihydroxy-derivative, m. p. 160°. Quinol monomethyl ether and *p*-dibromobenzene furnish *quinol di*-p-*methoxyphenyl ether*, m. p. 136—137° (also formed from quinol monomethyl ether and 4-bromo-4′-methoxydiphenyl ether), convertible into *quinol di*-p-*hydroxyphenyl ether*, m. p. 188°. 4 : 4′-*Di*-p-*methoxyphenoxydiphenyl ether*, m. p. 164°, is prepared from 4 : 4′-dibromodiphenyl ether and quinol monomethyl ether. *p*-Nitrodiphenyl ether, prepared from potassium phenoxide and *p*-chloronitrobenzene in presence of copper powder at 130—160°, is reduced by iron powder and acetic acid to *p*-aminodiphenyl ether. The acetyl derivative, m. p. 131° (lit. 127°), of this gives with nitric (*d* 1·52) in acetic acid 3-*nitro*-4-*acetamidodiphenyl ether*, m. p. 104°, hydrolysed by aqueous-alcoholic barium hydroxide to 3-*nitro*-4-*aminodiphenyl ether*, melts partly at 47—48° and re-solidifies with m. p. 81°, and reduced by sodium hyposulphite in 50% alcohol to 3-*amino*-4-*acetamidodiphenyl ether*, m. p. 124°. 3 : 4-*Diaminodiphenyl ether*, m. p. 67° (*hydrochloride*, m. p. 216°), and 3 : 3′-dinitrobenzil in alcohol give 6-*phenoxy*-2 : 3-*di*-p-*nitrophenylquinoxaline*, m. p. 195—196°. *p*-Hydroxydiphenyl ether and *p*-chloronitrobenzene afford 4-*nitro*-4′-*phenoxydiphenyl ether*, m. p. 194°, reduced by stannous chloride and hydrochloric acid to 4-*amino*-4′-*phenoxydiphenyl ether*, m. p. 84° (*acetyl* derivative, m. p. 148°). 3-*Nitro*-4-*acetamido*-4′-*phenoxy*- and 3 : 4-*diamino*-4′-*phenoxy*-*diphenyl ethers* have m. p. 124° and 95°, respectively. 4-*Nitro*-4′-*methoxydiphenyl ether*, m. p. 111—112° (from quinol monomethyl ether and *p*-chloronitrobenzene), is reduced by iron powder and acetic acid to 4-*amino*-4′-*methoxydiphenyl ether*, m. p. 81—82° (*hydrochloride*, m. p. 212°; *sulphate*, m. p. 220°), convertible by way of its *acetyl* derivative, m. p. 131°, into 3-*nitro*-4-*acetamido*-4′-*methoxydiphenyl ether*, m. p. 106° (free *base*, m. p. 76—77°). 3 : 4-*Diamino*-4′-*methoxydiphenyl ether* has m. p. 105°. 4 : 4′-Dihydroxydiphenyl ether and *p*-chloronitrobenzene (2 mols.) afford 4 : 4′-*di*-p-*nitrophenoxydiphenyl ether*, m. p. 136°, reduced by iron powder and acetic acid to 4 : 4′-*di*-p-*aminophenoxydiphenyl ether*, m. p. 109° (*diacetyl* derivative, m. p. 265—266°).

Phenol and *p*-hydroxydiphenyl ether could not be condensed with 4-bromo-2-nitroaniline at low temperatures; at higher temperatures, resinification occurred. H. BURTON.

Nitrogen derivatives of primary phenylethyl alcohol. S. SABETAY, J. BLEGER, and (MME.) Y. DE LESTRANGE (Bull. Soc. chim., 1930, [iv], 49, 3—7).—Nitration of β-phenylethyl alcohol in acetic anhydride in presence of a few drops of sulphuric acid with nitric acid (*d* 1·49) at 35—40°, and hydrolysis of the mixed β-nitrophenylacetates with 2% methyl-alcoholic hydrogen chloride affords a mixture of β-*p*-nitrophenylethyl alcohol and β-o-*nitrophenylethyl alcohol*, b. p. 144—147°/1·3 mm., d^{22} 1·253, n^{22} 1·562 (*benzoate*, m. p. 55°). The latter is separated by vacuum distillation of the oil filtered from the solid *p*-isomeride. Reduction with zinc dust in presence of calcium chloride gives an 83% yield of β-o-*aminophenylethyl alcohol*, b. p. 147—148°/3·5 mm., n^{19} 1·5849 [*hydrochloride*, m. p. 126·5° ($+H_2O$, m. p. 80°); N-*acetate*, m. p. 103—103·5°, hydrolysed quantitatively by 0·5*N*-benzyl-alcoholic potassium hydroxide], which when dehydrated with potassium hydroxide yields *o*-aminostyrene, b. p. 104—105°/15 mm., d^{20} 1·019, 1·6101 (*N*-acetyl derivative, m. p. 94·5°; lit. 129°). R. BRIGHTMAN.

Halogenation of optically active phenylmethylcarbinol in the presence and in the absence of pyridine, by thionyl chloride and the chlorides and oxychloride of phosphorus. J. KENYON, H. PHILLIPS, and F. M. H. TAYLOR (J.C.S., 1931, 382—389).—As in the case of ethyl *l*-mandelate (Kenyon, Lipscomb, and Phillips, A., 1930, 598), *l*-phenylmethylcarbinol, $[\alpha]_{5461}$ −51·7°, which is converted by thionyl chloride in the absence of pyridine into *l*-α-chloroethylbenzene, $[\alpha]_{5461}$ −63·3° (McKenzie and Clough, J.C.S., 1910, 97, 2564), affords a product of opposite sign when the reaction is carried out in the presence of pyridine or quinoline. When the chlorides or oxychloride of phosphorus are used in the presence of pyridine, the signs of rotation of the α-chloroethylbenzene obtained are the same as in its absence, but the magnitudes of the rotations are greater. Potassium carbonate is without effect. Thus pyridine facilitates the occurrence of the reactions which lead to change of sign of rotation which are considered (*loc. cit.*) to be indicative of a change of configuration. Thus *l*-phenylmethylcarbinol with 2 mols. of phosphorus trichloride and 1 mol. of pyridine affords *d*-α-chloroethylbenzene, $[\alpha]_{5461}$ +64°, and hence, if the reaction with thionyl chloride (above) is unattended by racemisation, the reaction with phosphorus trichloride and pyridine occurs with complete inversion of configuration. These results, which are discussed in detail, are consistently explained by the mechanism previously suggested in the case of ethyl *l*-mandelate (*loc. cit.*). In the absence of pyridine the decomposition of the intermediate compound $CHMePh{\cdot}O{\cdot}PCl_2{\cdot}O$ is initiated by the separation of a phenylmethylcarbonium cation with simultaneous production of a chlorine anion, and thus accounts for the observed formation of styrene, optically active αα-diphenyldiethyl ether, and almost inactive α-chloroethylbenzene. *dl*-α-Chloroethylbenzene has n_D 1·5280, 1·5269, 1·5264, 1·5253, and 1·5230 at 20°, 22·0°, 22·8°, 24·8°, and 28°, respectively. J. W. BAKER.

Derivatives of optically active triarylcarbinols and their halochromic salts. E. S. WALLIS (J. Amer. Chem. Soc., 1931, 53, 812—813).—*l*-Phenyldiphenylyl-α-naphthylmethylthioglycollic acid (I), $[\alpha]_{D}^{20}$ −13·63° in carbon tetrachloride (cf. A., 1930, 773), forms halochromic compounds with sulphuric and perchloric acids and mercuric chloride, which are decomposed by water to phenyldiphenylyl-α-naphthylcarbinol. The coloured compound from I and titanium tetrachloride in chloroform is decomposed by water to the *dl*-acid, whilst that from ferric chloride is similarly converted into the original optically active acid. The last observation is evidence against quinonoid formulation for the explanation of colour. H. BURTON.

Reduction of triphenylmethane dyes and related substances with the formation of free radicals. J. B. CONANT and N. M. BIGELOW (J.

Amer. Chem. Soc., 1931, **53**, 676—690).—Short treatment of *p*-dimethylaminotriphenylcarbinol with chromous or vanadous chloride in acetic acid in an atmosphere of nitrogen and addition of the reaction mixture to aqueous sodium acetate gives *s-pp'*-tetramethyldiaminohexaphenylethane, readily oxidised in ethereal solution to p-*dimethylaminotriphenylmethyl peroxide*, m. p. 145—150° (decomp.) according to the rate of heating. The ethane and 1% sodium amalgam in ether give the unstable sodium *p*-dimethylaminotriphenylmethyl, converted by carbon dioxide into *p*-dimethylaminotriphenylacetic acid (*methyl* ester, m. p. 141°). Prolonged reduction of the carbinol with chromous or titanous chloride in acetic acid affords *p*-dimethylaminotriphenylmethane, also formed when the above ethane is reduced with titanous chloride or when an acetic acid solution is kept in absence of air. These results are readily understandable by postulating the intermediate formation of the free radical *p*-dimethylaminotriphenylmethyl, which subsequently dimerises to the ethane or undergoes the change $2R\cdot + H\cdot \longrightarrow R\cdot H + R\cdot$. Reduction of the carbinol by chromous chloride in acetone and hydrochloric acid affords the *compound* $C_{42}H_{40}N_2$, m. p. 165°, which probably possesses a constitution of the type of *p*-benzhydryltetraphenylmethane (substances of this type are termed Tschitschibabin compounds). Malachite-green is reduced rapidly by vanadous or titanous chloride in acetic acid and sodium acetate in nitrogen, forming *s-ppp'p'*-octamethyltetra-aminohexaphenylethane, which with sodium amalgam in ether gives only a transient coloration (*pp'*-tetramethyldiaminotriphenylmethane is isolated from the reaction mixture), is readily decomposed by acids, and is reduced by titanous chloride to *pp'*-tetramethyldiaminotriphenylmethane. The last-named compound is also produced when malachite-green is reduced by vanadous chloride in acetic acid and sodium acetate for a long time. The Tschitschibabin *compound*, $C_{46}H_{50}N_4$, from malachite-green has m. p. 231—232°.

p-Dimethylaminobenzhydrol is reduced by chromous chloride in acetone and hydrochloric acid to a mixture of αβ-*diphenyl*-αβ-*di*-p-*dimethylaminophenylethane*, m. p. 206—207° (also prepared by the action of sodium-potassium alloy on the corresponding ethylene), and an *isomeride*, m. p. 264—267°. *p*-Dimethylaminophenyl*iso*propylcarbinol is similarly reduced to two isomeric *compounds*, $C_{24}H_{36}N_2$, m. p. 174° and 239—240°, whilst *pp'*-tetramethyldiaminobenzophenone chloride and tetra-*p*-dimethylaminophenylethylene glycol are reduced to tetra-*p*-dimethylaminophenylethylene. H. BURTON.

Cholesterol. XIII. Action of phosphorus pentasulphide. E. MONTIGNIE (Bull. Soc. chim., 1931, [iv], **49**, 73—75).—When refluxed with phosphorus pentasulphide in carbon disulphide, cholesterol is converted into *thiocholesterol*, $C_{27}H_{45}\cdot SH$, m. p. 191°, $[\alpha]_D$ 39° (in ether) (*bromide*, m. p. 152—153°; *nitro*-derivative, m. p. 125°). With white phosphorus in benzene in a current of oxygen at 60°, cholesterol yields a *phosphorate*, $C_{27}H_{46}O_5P_2$, m. p. 120—123°, which is decomposed by boiling water, yielding an *acid*, $C_{27}H_{?0}O_7P_2$ (*acetate*, m. p. 250°, decomp. about 200°; *salts*). R. BRIGHTMAN.

Preparation of aromatic acid amides. C. H. KAO and S. Y. MA (J.C.S., 1931, 443—444).—The method used for the preparation of benzamide (this vol., 220) is applied with satisfactory results to the preparation of the amides of *m*- and *p*-nitro- and *p*-chloro-benzoic, benzilic, phenylacetic, and β-phenylpropionic acids (some dehydration to the nitrile in the last two cases), and succinimide. Poor yields are obtained with *o*-nitrobenzoic and cinnamic acids, and none with salicylic acid. J. W. BAKER.

***N*-Acyl derivatives of alanine. Resolution of externally compensated *m*-nitrobenzoylalanine.** W. M. COLLES and C. S. GIBSON (J.C.S., 1931, 279—285).—Condensation of *dl*-alanine with *m*- and *o*-nitrobenzoyl chloride affords dl-m-, m. p. 163—164° (*ethyl*, m. p. 89°, and *methyl*, m. p. 110—111°, esters; *amide*, m. p. 189—190°; *silver* salt) (91), and dl-o-, m. p. 165—166° (47), -*nitrobenzoylalanine*, reduced by ferrous sulphate and barium hydroxide (Simonsen) to dl-o-*aminobenzoylalanine*, not melting at 270°, and dl-m-*aminobenzoylalanine hydrochloride*, m. p. 150—152° (decomp.), respectively. By similar methods are obtained dl-p-*toluoyl*-, m. p. 188—189° (95); dl-m-*nitrobenzenesulphonyl*-, m. p. 158·5—159° (21); dl-4-*nitrotoluene-2-sulphonyl*-, m. p. 125·5—126·5° (2), and dl-*cinnamoyl*-, m. p. 196—197° (92), -*alanine*. The figures in parentheses give the percentage hydrolysis by constant b.-p. hydrochloric acid in 3 hrs., the corresponding values for benzoyl-, phthalyl-, *p*-nitrobenzoyl-, benzenesulphonyl-, α- and β-naphthalenesulphonyl-, and *p*-toluenesulphonyl-alanine being 96, 76, 97, 14, 66, 18, and 17, respectively. Resolution of *dl-m*-nitrobenzoylalanine is effected by the half-molecule method, addition of quinine to a boiling solution of the sodium salt affording crystals of the *quinine* salt, $+2H_2O$ and anhydrous, converted into a glass at 125°, $[\alpha]^{20}_{5461}$ −137·1° in alcohol, of l-m-*nitrobenzoylalanine*, m. p. 158°, $[\alpha]^{20}_{5461}$ −44·7° (as its ammonium salt in water), and +5·87° in ethyl alcohol (*ethyl* ester, m. p. 104—105°, $[\alpha]^{20}_{61}$ +6·91° in alcohol). The acid recovered from the original mother-liquor contains 90·4% of the *d*-acid and is converted by brucine into the *brucine* salt, $+3\cdot5H_2O$ and anhydrous, $[\alpha]^{20}_{61}$ −9·1° in alcohol, of d-m-*nitrobenzoylalanine*, m. p. 158°, $[\alpha]^{20}_{5461}$ +44·7° (as ammonium salt in water), −5·62° in alcohol (*methyl* ester, m. p. 126°, $[\alpha]^{20}_{5461}$ −12·7° in alcohol; *amide*, m. p. 193—194°, $[\alpha]^{20}_{5461}$ +24·2° in alcohol). The relative rotatory powers of the acids and their derivatives in water and alcohol are discussed.

J. W. BAKER.

Esters of 2 : 4 : 6-trinitrobenzoic acid. I. Phenyl and nitrophenyl esters. P. P. SCHORIGIN and M. S. BELENKI (J. Russ. Phys. Chem. Soc. 1930, **62**, 2027—2032).—The *phenyl* ester, m. p. 170·5—171·5°, is prepared by heating 2 : 4 : 6-trinitrobenzoyl chloride with phenol in pyridine. Nitration of the phenyl ester under different conditions gives the p-*nitrophenyl*, m. p. 186—187°, 2 : 4-*dinitrophenyl*, m. p. 168—169·5°, and 2 : 4 : 6-*trinitrophenyl*, m. p. 224—225°, esters. E. B. UVAROV.

Esters of orthophenylacetic acid. P. P. T. Sah, S. Y. Ma, and C. H. Kao (J.C.S., 1930, 305—307).—By prolonged action of the appropriate alcohol on phenylacetimido-ethyl and *-methyl* ether hydrochlorides (prepared in usual manner) at the ordinary temperature the following orthophenylacetates, $CH_2Ph\cdot C(OR)(OR')_2$, have been prepared in 40—45% yields: trimethyl, b. p. 216—218°, d_4^{20} 1·0651, n_D^{20} 1·5075; dimethyl ethyl, b. p. 217—219°, d_4^{20} 1·0640, n_D^{20} 1·5080; *diethyl methyl*, b. p. 224—226°, d_4^{20} 1·0356, n_D^{20} 1·5000; *triethyl*, b. p. 225—227°, d_4^{20} 1·0308, n_D^{20} 1·4997; *di*-n-*propyl methyl*, b. p. 239—242°, d_4^{20} 1·0109, n_D^{20} 1·4950; *diisopropyl methyl*, b. p. 227—229°, d_4^{20} 1·0079, n_D^{20} 1·4913; *di*-n-*propyl ethyl*, b. p. 238—241°, d_4^{20} 1·0094, n_D^{20} 1·4967; *diisopropyl ethyl*, b. p. 228—230°, d_4^{20} 1·0030, n_D^{20} 1·4908; *di*-n-*butyl methyl*, b. p. 254—257°, d_4^{20} 0·9953, n_D^{20} 1·4911; *diisobutyl methyl*, b. p. 245—248°, d_4^{20} 0·9929, n^{20} 1·4898; *di*-n-*butyl ethyl*, b. p. 254—257°, d_4^{20} 0·9974, n_D^{20} 1·4916; *diisobutyl ethyl*, b. p. 248—251°, d_4^{20} 0·9867, n_D^{20} 1·4883; *diisoamyl methyl*, b. p. 260—265°, d_4^{20} 0·9880, n_D^{20} 1·4900, and *ethyl*, b. p. 260—265°, d_4^{20} 0·9867, n_D^{20} 1·4887, *orthophenylacetates*. J. W. Baker.

Asymmetric induction, in particular the optical activity of cinnamic acid. L. Ebert and G. Kortüm (Ber., 1931, 64, [B], 342—358).—A critical review of the literature leads the authors to the conclusion that, although asymmetric induction must be recognised as fundamentally probable and necessary in theory, almost all the quantitative measurements point to an action of very small magnitude. A marked effect of asymmetric induction appears to be found most convincingly in Erlenmeyer's observations of the activation of cinnamic acid, whereas other investigations have yielded results which are either negative or capable of explanation in another manner.

Measurements are recorded of the solubility of potassium hydrogen *d*- and *l*-tartrate in water and in a 0·5*N*-solution of *d*-mannitol and of *d*- and *l*-camphorsulphonic acid in benzene and in 0·25*N*-solutions of *d*- and *l*-camphor in benzene. Within the limits of experimental error, *d*-mannitol has the same influence on the *d*- and *l*-tartrate and the effect of the camphor antipodes is the same for either camphorsulphonate. Changes in the relative surface tensions of *N*- and 0·5*N*-aqueous solutions of sodium *d*- and *l*-camphorsulphonate are not observed when these solutions are saturated with strychnine nitrate, *d*-pinene, *d*-camphor, menthol, menthone, menthene, methyl camphorate, propyl *d*-tartrate, or menthyl acetate.

Repetition of Erlenmeyer's work confirms the observation that the cinnamic acids produced by heating storax or synthetic cinnamic acid or their anhydrides with *d*-tartaric acid at 168—170° are optically active. Crystallisation of the activated acids from much water at 75° results in the separation of optically inactive crystals and concentration of the activity in the residue obtained by evaporation of the filtrates to dryness. Fractional extraction of the activated acid with water shows that the solubility of the active component varies between fairly wide limits and that the material is probably not homogeneous. The residues obtained from the various fractions evolve cinnamic acid at about 130°, become brown between 130° and 140°, form brown drops of liquid at 143—148°, and finally melt indefinitely at 152—155°. When heated in a vacuum at 100° they give a sublimate of cinnamic acid and a compound, m. p. above 160°. The ratio C : H in them is invariably much lower than in cinnamic acid. Repeated fractional extraction of the activated acid until optical activity has ceased to appear in extract or residue yields further extracts which give a residue in which the percentage of carbon is much less than that in cinnamic acid, thus indicating the presence of inactive or feebly active impurities. It is regarded as established that the observed activity is not associated with a substance with the analytical composition of cinnamic acid. The presence of tartaric acid in the active component of the preparations is established by prolonged treatment of the residues from the aqueous extracts with sodium hydroxide. The residues obtained by evaporation of the solutions to dryness are feebly dextrorotatory in aqueous solution and exhibit the very characteristic small dispersion of the tartrates and increased magnitude after addition of boric acid. The existence of an optically active cinnamic acid in preparations from molten tartaric acid is regarded as extremely improbable.

H. Wren.

Derivatives of salicylic acid. II. 3-Nitro-5-sulpho- and 5-nitro-3-sulpho-salicylic acids. A. N. Meldrum and N. W. Hirve. **III. 3-Sulphosalicylic acid.** N. W. Hirve (J. Indian Chem. Soc., 1930, 7, 887—892, 893—897).—II. Salicylic acid (20 g.) is dissolved in sulphuric acid (*d* 1·8, 100 g.) and after 1 hr. the mixture is treated with nitric acid (*d* 1·4, 21 g.) below 20°; *3-nitro-5-sulphosalicylic acid* ($+4H_2O$) [*barium* ($+H_2O$), *barium hydrogen* ($+2·5H_2O$), *potassium hydrogen* ($+H_2O$), *potassium* ($+H_2O$), and *tripotassium* ($+H_2O$), salts] is thereby produced. The acid is also prepared by nitrating 5-sulphosalicylic acid with a mixture of nitric acid (*d* 1·4) and acetic anhydride and by the method of Sakellarios (A., 1922, i, 1144) (in this case, some dinitrosalicylic acid is also produced); it could not be prepared by Hirsch's method (A., 1901, i, 84) or by sulphonation of 3-nitrosalicylic acid. *Methyl* and *ethyl 3-nitro-5-sulphosalicylates* (*potassium* salts; *barium* salts; *dibarium* salts) are prepared by the usual methods. *5-Nitro-3-sulphosalicylic acid* ($+2H_2O$) [*barium, silver, potassium hydrogen, potassium* ($+2·5H_2O$), and *tripotassium* (anhydrous and $+3H_2O$) salts] is obtained when 5-nitrosalicylic acid is sulphonated with fuming sulphuric acid (19% SO_3). *Methyl* and *ethyl 5-nitro-3-sulphosalicylates* (*potassium* salts; *barium* salts; *dibarium* salts) are also described.

III. *5-Amino-3-sulphosalicylic acid* (—1 and $3H_2O$), decomp. 353° *sodium* ([$+3H_2O$) and *barium* salts], prepared by sulphonating 5-aminosalicylic acid with fuming sulphuric acid (20% SO_3) or reducing 5-nitro-3-sulphosalicylic acid with iron powder and hydrochloric acid, is converted by way of *5-diazo-3-sulphosalicylic acid*, decomp. 166° (rapid heating) or 216 (slow heating) [*potassium hydrogen* ($+H_2O$), decomp. violently at 210°; *sodium hydrogen* ($+0·5H_2O$), decomp. violently at 205°; *sodium*, and *barium* ($+H_2O$), salts], into *3-sulphosalicylic acid* ($+5H_2O$; 3 mols.

are lost when it is kept in a desiccator), m. p. 152·5° [*potassium hydrogen, sodium hydrogen* (+1·5H_2O), and *barium* (+1·5H_2O) salts]. Nitration of this gives 5-nitro-3-sulphosalicylic acid, whilst bromination of the potassium salt in water affords 5-*bromo-3-sulphosalicylic acid*, m. p. (+4H_2O) 98—100°, m. p. (+2H_2O) 174° (*potassium hydrogen* salt, also formed when potassium hydrogen 5-diazo-3-sulphosalicylate is treated with hydrobromic acid and copper powder). Desulphonation of the last-named acid with superheated steam furnishes 5-bromosalicylic acid.

H. BURTON.

Reaction of mutual displacement of phenylacetic and salicylic acids from their compounds with β-naphthylamine. A. P. OBUCHOV (J. Russ. Phys. Chem. Soc., 1930, **62**, 1919—1931).—Salicylic acid (15%) and phenylacetic acid (85%) give a simple eutectic at 65°. Phenylacetic acid and β-naphthylamine form an equimolecular *compound*, m. p. 71·5° (decomp.); a transition point corresponds with 50% of phenylacetic acid. A eutectic point at 42° between phenylacetic acid and the compound corresponds with 33·8 mol.-% of β-naphthylamine. The ternary system consists of five surfaces, two triple transition points, and one triple eutectic. E. B. UVAROV.

Reaction of mutual displacement of β-naphthylamine and *m*-phenylenediamine from their compounds with salicylic acid. D. E. DIONISIEV (J. Russ. Phys. Chem. Soc., 1930, **62**, 1933—1946).—Both bases form equimolecular compounds with salicylic acid. Salicylic acid and β-naphthylamine form a stable binary system with a eutectic at 77°, corresponding with 24·7% of β-naphthylamine. The ternary system consists of 5 unequal surfaces meeting in 3 triple points. The binary system *m*-phenylenediamine–β-naphthylamine gives a eutectic at 54°, corresponding with 87·6 mol.-% of *m*-phenylenediamine. E. B. UVAROV.

Nitration of 6-methoxy-*m*-toluic acid. J. L. SIMONSEN (J.C.S., 1931, 444).—The neutral product obtained by nitration of the above acid is 5-nitro-*o*-tolyl methyl ether, m. p. 69—70° (not 63°), and not the 6-nitro-compound as previously stated (J.C.S., 1918, **113**, 781; 1915, **107**, 834). J. W. BAKER.

Optically active mandelonitrile. I. A. SMITH (Ber., 1931, **64**, [*B*], 427—434).—Hydrolysis of amygdalin with sulphuric acid under somewhat modified conditions (cf. Walker and Krieble, J.C.S., 1909, 95, 1369) gives *d*-mandelonitrile, m. p. 28·5—29·5°, $[\alpha]_{5461}^{15}$ +5·27° in benzene (among other values), hydrolysed by concentrated hydrochloric acid to *l*-mandelic acid. The nitrile is readily racemised by water, very readily by alcoholic alkali hydroxide. Treatment of *d*-mandelonitrile with magnesium phenyl bromide, short boiling of the product, and its subsequent treatment with ice and concentrated hydrochloric acid affords an aqueous solution from which *l*-benzoin, $[\alpha]_D^{18.5}$ −119° in acetone, slowly separates (cf. McKenzie and Wren, J.C.S., 1908, **93**, 310), whilst small amounts of highly active material are isolated from the ethereal solution after removal of diphenyl. The process is applicable to the crude *d*-mandelonitrile obtained directly from amygdalin. Treatment of the homogeneous *d*-nitrile with the Grignard reagent followed by decomposition with ice and sulphuric acid and extraction of the product with ether yields a product racemised to an extent which inhibits the isolation of homogeneous *l*-benzoin. H. WREN.

Local anæsthetics. F. KONEK [with A. LOCZKA and J. DOKTAY] (Mat. Nat. Anz. Ungar. Akad. Wiss., 1929, **46**, 348—360; Chem. Zentr., 1930, ii, 2892—2893).—Methyl 3-methoxysalicylate, m. p. 64° (the acid has m. p. 148°), with *m*-nitrobenzoyl chloride at 100° affords methyl 3-methoxy-*m*-nitrobenzoylsalicylate, m. p. 45°, which on reduction with tin and hydrochloric acid gives *methyl* 3-*methoxy*-m-*aminobenzoylsalicylate hydrochloride*, m. p. 204° (decomp.), which produces local anæsthesia. 5-Nitro-3-methoxysalicylic acid, m. p. 220°, obtained by nitration of methyl 3-methoxysalicylate in acetic acid below 5° and then at 80° (red barium salt; methyl ester, m. p. 137·5—138·5°), is readily converted (as the methyl ester) into the benzoyl derivative, m. p. 112—118°, and thence into *methyl 3-methoxy-5-amino-2-benzoylsalicylate hydrochloride*, which is a local anæsthetic. 3-Ethoxysalicylic acid has m. p. 157°.

A. A. ELDRIDGE.

Preparation of phenylmalonic acid, *o*- and *p*-chlorophenylmalonic acids. D. IVANOV and A. SPASSOV (Bull. Soc. chim., 1931, [iv], **49**, 19—23). —When magnesium phenylacetate chloride, $CH_2Ph{\cdot}CO_2{\cdot}MgCl$, is treated with 1 mol. of magnesium ethyl bromide, and after the evolution of ethane is complete, the dimagnesium derivative is treated with carbon dioxide at 0°, phenylmalonic acid is obtained in 62·5% yield on hydrolysis. With magnesium *iso*propyl chloride the yield is 65·6%; with other Grignard reagents the yields are as follows: magnesium *iso*propyl bromide 48·9%, propyl chloride 45%, butyl bromide 42·2%, *cyclo*hexyl bromide 40%, *o*-tolyl bromide, 50·6%, α-naphthyl bromide 53·3%, benzyl chloride 3·1%. Magnesium methyl iodide gives practically no evolution of gas. Magnesium *o*- and *p*-chlorophenylacetate chlorides behave similarly. o-*Chlorophenylmalonic acid*, m. p. 139°, is obtained in 46·2% yield with magnesium *iso*propyl chloride and in 52·8% yield with magnesium phenyl bromide. p-*Chlorophenylmalonic acid*, m. p. 163°, is obtained in 56·4% yield with magnesium *iso*propyl chloride and in 48·3% yield with magnesium *o*-tolyl bromide. Phenylmalonic acid and *o*-chlorophenylmalonic acid are determined by heating in a pyrex flask with an air condenser in a current of air at 150—160° for 10—15 min. and absorbing and weighing the carbon dioxide evolved. R. BRIGHTMAN.

Dibenzylsuccinic acids. P. CORDIER (Compt. rend., 1931, **192**, 361—363).—Dibenzylidenesuccinic acid is reduced by Stobbe's method (A., 1904, i, 673) to a dibenzylsuccinic acid, m. p. 203°, which when treated with acetic anhydride for a short time at 100° (bath) gives the corresponding anhydride, m. p. 104°. More prolonged treatment affords the *anhydride*, m. p. 125°, of r-*dibenzylsuccinic acid*, m. p. 172°, resolved by strychnine into d-, α_D +22·8°, and

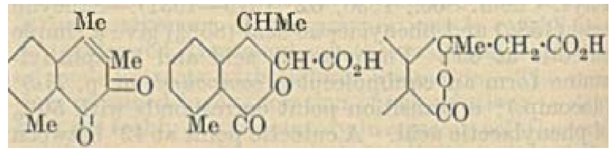
l-*isomerides*, α_D −29·5°, both of which have m. p. about 130°. The dibenzylsuccinic acid, m. p. 204°, and anhydride, m. p. 155°, obtained by Stobbe (*loc. cit.*) could not be prepared. H. BURTON.

Synthesis of 2 : 4 : 5-trimethoxyphenylalanine. T. SZEKI and E. LAKOS (Acta chem. min. phys., 1929, **1**, 157—166; Chem. Zentr., 1930, ii, 1539—1540).—Condensation of asarylaldehyde with hippuric acid, or with hydantoin followed by hydrogenation and fission, gives 2 : 4 : 5-trimethoxy-*N*-benzoylphenylalanine, from which free 2 : 4 : 5-trihydroxyphenylalanine could not be obtained. The following compounds are described: 2-*Phenyl*-4 : 2′ : 4′ : 5′-*trimethoxybenzylideneoxazol*-5-*one*, m. p. 210°; α-*benzamido*-β-2 : 4 : 5-*trimethoxyphenylacrylic acid*, m. p. 204°; α-*benzamido*-β-*asarylpropionic acid*, m. p. 191°; 2 : 4 : 5-*trimethoxyphenylpyruvic acid*, m. p. 145°; 2 : 4 : 5-*trimethoxyphenylacetic acid*, m. p. 104°; 2 : 4 : 5-*trimethoxybenzylidenehydantoin*, m. p. 274° (decomp.) [*bromo*-derivative, $C_{13}H_{15}O_5N_2Br$, m. p. 254° (decomp.)]; 2 : 4 : 5-*trimethoxybenzylhydantoin*, m. p. 234°; dl-2 : 4 : 5-*trimethoxyphenylalanine*, by hydrolysis of the foregoing substance with barium hydroxide, m. p. 217° (decomp.) (*ethyl* ester *hydrochloride*, $C_{14}H_{22}O_5NCl$, m. p. 181°). A. A. ELDRIDGE.

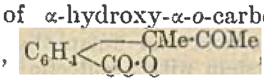
Opianic acid. I. Fission of opianic acid (and other hydroxycarboxylic acids and their ethers and esters) by heating with water under pressure. P. SCHORIGIN, V. ISSAGULIANZ, and V. BELOV (Ber., 1931, **64**, [*B*], 274—280, and J. Russ. Phys. Chem. Soc., 1930, **62**, 2039—2045).—Opianic acid passes when heated with water at 190—200° during 4—5 hrs. into 3-hydroxy-4-methoxybenzaldehyde (yield about 38%). The hypothesis that the mobility of one methyl group is due to the influence of the vicinal carboxyl is supported by the observations that *o*-methoxybenzoic acid passes when similarly treated into carbon dioxide, methyl alcohol, and phenol (yield about 23%), whilst methyl *o*-methoxybenzoate is produced in minor amount; *o*-dimethoxybenzene and *m*- and *p*-methoxybenzoic acid are unchanged by this treatment. Methyl salicylate is decomposed by water at 200—210° into salicylic acid and phenol; methyl *o*-methoxybenzoate yields phenol and *o*-methoxybenzoic acid, whilst salicylic acid is almost quantitatively transformed into phenol. The reaction is attributed to the intermediate formation by addition of water of an oxonium complex which decomposes into acid and methyl alcohol.

Treatment of *iso*vanillin with potassium hydroxide and ethyl *p*-toluenesulphonate in methyl alcohol yields 4-*methoxy*-3-*ethoxybenzaldehyde*, m. p. 51—52°; 3 : 4-dimethoxybenzaldehyde has m. p. 47—48°. H. WREN.

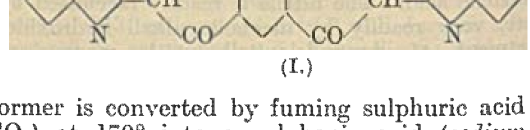
Congo copal oil. II. Oxidative degradation of the naphthalene hydrocarbon $C_{13}H_{14}$ from Congo copal oil. L. WESTENBERG and J. P. WIBAUT (Rec. trav. chim., 1931, **50**, 188—199).—Oxidation of the trimethylnaphthalene obtained by catalytic dehydrogenation of Congo copal oil (Westenberg, A., 1929, 818) with chromic oxide affords 3-acetyl-*o*-toluic acid [*oxime*, m. p. 162°; methyl ester, m. p. 68° (Heilbron and Wilkinson, this vol., 80, give m. p. 47—48°)], which has also been obtained by similar oxidation of the trimethylnaphthalene obtained from squalene (Heilbron and Wilkinson, *loc. cit.*). It is also converted by further oxidation with potassium permanganate into hemimellitic acid, and by iodine and 10% sodium hydroxide into toluene-2 : 3-dicarboxylic acid identical with a specimen synthesised from *m*-toluic acid. When a smaller proportion of chromic oxide is used in the original oxidation the trimethyl-β-naphthaquinone (I), darkens at 120° (*quinoxaline*, m. p. 142°), is obtained. This is further oxidised by chromic and acetic acids to the lactonic acid, $C_{12}H_{12}O_4$, m. p. 201°, obtained by Westenberg (*loc. cit.*), to which structure II or IIa is assigned. This is further oxidised by



(I.) (II.) (IIa.)

potassium dichromate and sulphuric acid, or, better, by potassium permanganate, to an *acid*, $C_{12}H_{10}O_6$, probably by oxidation of a methyl group to a carboxyl group. The substance $(C_4H_4O)_n$, m. p. 69°, also obtained (Westenberg, *loc. cit.*) in the original chromic acid oxidation of the trimethylnaphthalene is now assigned the constitution of the *lactone* (*oxime*, m. p. 116°) of α-hydroxy-α-*o*-carboxyphenylethyl methyl ketone,  which is considered to be identical with the oxidation product, m. p. 70—71°, obtained by Heilbron and Wilkinson (*loc. cit.*) and to which these authors assigned the structure 5 : 8-diacetoxy-1 : 6-dimethylnaphthalene. This lactone is oxidised by hydrogen peroxide in alkaline solution, by iodine and methyl-alcoholic sodium hydroxide, or by dilute potassium permanganate to the *lactone* $(+H_2O)$, m. p. 74°, of α-hydroxy-α-(*o*-carboxyphenyl)-propionic acid. These results accord well with the view that the original hydrocarbon is 1 : 2 : 5-trimethylnaphthalene. J. W. BAKER.

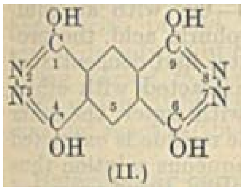
Pyromellitic acid. Diketobenzohydrindene and benzodipyridazine derivatives. R. SEKA, H. SEDLATSCHEK, and H. PREISSECKER (Monatsh., 1931, **57**, 86—96).—When pyromellitic anhydride is heated with 2-methylquinoline at 250°, a mixture of the *hydrindene* (I), decomp. 265°, and a *substance*, $C_{20}H_{11}O_6N$, decomp. about 125°, is produced; the



(I.)

former is converted by fuming sulphuric acid (50% SO_3) at 170° into a sulphonic acid (*sodium* salt), which dyes wool and silk yellow (similar to quinoline-yellow). Pyromellitic anhydride and alcoholic hydrazine hydrate give the cyclic *dihydrazide*, decomp. about 450° (*tetra-acetyl* derivative, m. p. 235—238°), of pyromellitic acid, which is considered to be

1 : 4 : 6 : 9 - tetrahydroxybenzodipyridazine (II).



4 : 9 - *Dihydroxy* - 1 : 6-*diphenylbenzodipyridazine*, chars at 445°, is prepared similarly from 2 : 5 - dibenzoylterephthalic acid, whilst 4 : 6-*dihydroxy* : 9-*diphenyl*-, decomp. 430°, and 4 : 6-*dihydroxy*-1 : 9 - *dixylyl* - *benzodipyridazine* are obtained from 4 : 6-dibenzoyl*iso*phthalic and dixyloylbenzenedicarboxylic acid (A., 1927, 360), respectively. Pyromellitic anhydride and α-naphthylamine at 200° give *pyromellitdi-α-naphthylimide*, m. p. 431°. 2-Benzoylanthraquinone-3-carboxylic acid and alcoholic hydrazine hydrate at 120° afford the corresponding *hydrazide*, decomp. 374°. *Methyl* and *phenyl pyromellitates*, m. p. 138° and 179·5°, respectively, are prepared from pyromellityl chloride and sodium methoxide and phenoxide, respectively, in benzene. H. BURTON.

Manufacture of aromatic amino-aldehyde compounds. I. G. FARBENIND. A. G.—See B., 1931, 335.

Homologues of cinnamaldehyde. I. α-Alkyl substituted homologues of cinnamaldehyde. P. SCHORIGIN, V. ISSAGULIANZ, E. SMOLIANINOVA, K. BOGATCHEVA, and S. SKOBLINSKAYA (J. Russ. Phys. Chem. Soc., 1930, **62**, 2033—2038).—The following α-alkyl substituted homologues and derivatives of cinnamaldehyde are described: *ethyl*, b. p. 122—123°/13 mm., d^{20} 1·0384 (*semicarbazone*, m. p. 199—200°); iso*propyl*, b. p. 139—140°/15 mm., d^{22} 1·0112 (*semicarbazone*, m. p. 191—192°); n-*hexyl*, b. p. 174—176°/15 mm., m. p. 4°, d^{14} 0·9500 (*semicarbazone*, m. p. 111—112°). The molecular refraction of the aldehydes shows considerable exaltation.

E. B. UVAROV.

Salt-forming characteristics of doubly- and singly-linked elements of the oxygen group. II. Nitration of benzaldehyde and acetophenone in sulphuric acid solution. J. W. BAKER and W. G. MOFFITT (J.C.S., 1931, 314—318).—The conclusions reached from physical data (this vol., 486) concerning the existence of benzaldehyde and acetophenone as oxonium salts in sulphuric acid solution have been confirmed by a study of the proportions of the *m*-nitro-derivatives (determined by Flürscheim and Holmes' method, A., 1928, 403, after oxidation to the mixed nitrobenzoic acids) formed by nitration at 5° of these substances with nitric acid (*d* 1·53) in the presence of sulphuric acid of various concentrations. The presence of the positive charge on the cation $Ph{\cdot}\overset{\oplus}{C}R{:}OH$ of the salt form causes a considerable increase in the proportion of *m*-nitration observed under these conditions. Thus in sulphuric acid containing 7·3% of free sulphur trioxide benzaldehyde and acetophenone afford 90·8 and 90·0% of the *m*-nitro-isomeride, respectively. The proportion decreases gradually as the concentration of the sulphuric acid is diminished until in 80% sulphuric acid the values are 83·9 and 83·1% of *meta*, respectively. Moreover, in all cases, the addition of ammonium sulphate to the nitrating medium causes a depression in the amount of *m*-isomeride formed, comparable in both magnitude (4—5%) and type with that observed in the case of the ψ-base benzylidene-*m*-nitroaniline (Baker and Ingold, A., 1930, 594), thus proving that substitution occurs mainly through the cation of the oxonium salt. With nitric acid (*d* 1·53) alone at −10°, benzaldehyde affords 72·1% of the *m*-nitro-isomeride, and the formation of a loose salt-like complex even in nitric acid alone is suggested by the slight fall in the proportion of *m*-nitration of acetophenone from 70% in nitric acid d^{15} 1·53 (Camps, A., 1902, i, 294, found only 55%) to 66·9% in nitric acid d^{15} 1·485, that is, as the dilution of the acid is increased.

J. W. BAKER.

Condensation of phenolic aldehydes with methyl *n*-propyl and *n*-butyl ketones. K. IWAMOTO and T. KATO (Sci. Rep. Tohoku, 1930, **19**, 689—693).—Methyl *n*-propyl and *n*-butyl ketones condense with 1 mol. of a *p*-, or with 2 mols. of a *m*-hydroxy- or -methoxy-benzaldehyde in the same way as methyl ethyl ketone (A., 1927, 566). The formation of styryl methyl or of distyryl ketone depends therefore on the position of the substituent in the benzaldehyde. The ketones are formed from the dialkyl ketone and the corresponding benzaldehyde in presence of hydrogen chloride; p-*hydroxy-α-ethylstyryl methyl ketone*, m. p. 120—121°; p-*hydroxy-α-*n*-propylstyryl methyl ketone*, m. p. 100—101° (*oxime*, m. p. 119·5—121·5°); p-*methoxy-α-ethylstyryl methyl ketone*, b. p. 171—172°/12 mm. (*oxime*, m. p. 93—94·5°); p-*methoxy-α-*n*-propylstyryl methyl ketone*, b. p. 183—184°/14 mm. (*oxime*, m. p. 91—92°). mm′-*Dihydroxy-α-ethyldistyryl ketone*, mm′-*dihydroxy-α-*n*-propyldistyryl ketone*, and the corresponding *methoxy*-compounds are brick-red or yellow amorphous solids. G. DISCOMBE.

Inner-complex salts of hydroxyaldimines and hydroxyketimines. P. PFEIFFER, E. BUCHHOLZ, and O. BAUER (J. pr. Chem., 1931, [ii], **129**, 163—177).—Complex *zinc* and *nickel* compounds of *salicylaldimine* are obtained by action of ammoniacal zinc and nickel acetates on salicylaldehyde; the copper complex isolated by Ettling (Annalen, 1840, **35**, 265; cf. Delepine, A., 1900, i, 177) is also of this type, which may be represented by the formula $M\left(<\begin{matrix}O—C_6H_4\\NH{:}CH\end{matrix}\right)_2$ (where M is a bivalent metal). The zinc complex takes up 2 mols. of pyridine on crystallisation from this solvent. *o*-Vanillin readily gives a *nickel* complex of the imine, but with zinc the *compound* $\begin{matrix}C_6H_3O{\cdot}O\\CH{=\!=}O\end{matrix}>Zn<\begin{matrix}O{\cdot}C_6H_3O\\NH{=}CH\end{matrix}$ is formed. The corresponding *calcium* ($+2H_2O$) and *magnesium* ($+2H_2O$) derivatives of salicylaldehyde, similarly prepared, appear to be the simple aryloxides.

With *o*-hydroxyacetophenone and its substitution products nickel acetate and dilute ammonia give complex salts of the ketone which are capable of combining with pyridine or aniline; these are converted by concentrated aqueous ammonia into complex compounds of the corresponding ketimines, which are also formed by use of higher concentrations of ammonia in the original preparation, and (with one exception) no longer have the power of adding solvent molecules. The *nickel* ($+2C_5H_5N$; $+1\frac{1}{2}PhNH_2$) and *copper* ($+2C_5H_5N$; $+2PhNH_2$) compounds of 2-hydroxy-

4-methoxyacetophenone in the pure state (cf. Pfeiffer and Golther, A., 1927, 362) are described, as also are the *nickel* complexes of *o*-hydroxyacetophenone ($+2C_5H_5N$), *o*-hydroxy- ($+1NH_2Ph$), 2-hydroxy-4-methoxy-, and 2-hydroxy-5-methoxy-acetophenone-imines, and 2-hydroxy-4-methoxyphenyl styryl ketimine. H. A. PIGGOTT.

Salt-forming characteristics of doubly- and singly-linked elements of the oxygen group. I. Carbonyl group in benzaldehyde and acetophenone. J. W. BAKER (J.C.S., 1931, 307—314).—By analogy with Schiff's bases (Baker and Ingold, A., 1930, 594) it is suggested that the intensely coloured solutions formed by benzaldehyde and acetophenone in concentrated or fuming sulphuric acid are due to the formation of oxonium salts of the type $\overset{\oplus}{Ph{\cdot}CR{:}OH}\}HSO_4$, the ions of which are in equilibrium with the colourless pseudo salt-form $Ph{\cdot}CR(OH)(OSO_3H)$ (cf. Kendall and Carpenter, A., 1915, i, 15). When benzaldehyde is partitioned, at the ordinary temperature, between light petroleum and sulphuric acid containing 7·3% of free sulphur trioxide, 100, 90, and 80% sulphuric acid, only 0·5, 0·81, 0 83, and 1·77% of the benzaldehyde (determined as its *p*-nitrophenylhydrazone), respectively, is found in the petroleum layer, indicating that the equilibria $Ph{\cdot}CR{:}O+HO{\cdot}SO_3H = Ph{\cdot}CR(OH)(O{\cdot}SO_3H) \rightleftharpoons \overset{\ominus}{O{\cdot}SO_3H}+\overset{\oplus}{Ph{\cdot}CR{:}OH}$ are displaced largely towards the right. Addition of ammonium sulphate to the acid layer causes a repression of the ionic dissociation, followed, in turn, by a further decomposition of the pseudo-salt into sulphuric acid and free benzaldehyde and in this case 1·4, 1·03, 8·7, and 30·8%, respectively, of the latter is retained in the petroleum layer. By colorimetric measurements it is shown that solutions of these two carbonyl compounds in 100% sulphuric acid do not obey Beer's law, the specific colour value (s) decreasing with decreasing concentration of the carbonyl compound (c equiv. per litre) more slowly than this law requires, whilst, in agreement with the view that decreasing the concentration of the carbonyl compound results in an increased ionisation of the colourless pseudo-salt into the coloured carbonium–oxonium ion, the molecular equivalent colour value ($1000s/c$) increases with increasing dilution in a manner analogous to the similar increase in the equivalent conductivity in solutions of electrolytes. The colour values (corrected for differences in total volume of the solutions) of solutions of benzaldehyde in 100, 90, 80, and 70% sulphuric acid in which the mol. ratio $Ph{\cdot}CHO/H_2SO_4$ is constant (1/89) are, respectively, [100], 85, 45, and 21, indicating that, of the amount of oxonium salt present in 100% sulphuric acid, 15, 55, and 79%, respectively, suffers hydrolysis in the presence of the same molecular quantity of sulphuric acid, but in 90, 80, and 70% dilution, respectively. Similar results are obtained with acetophenone. J. W. BAKER.

Preparation of phenylglyoxal. C. NEUBERG and E. HOFMANN (Biochem. Z., 1930, **229**, 443—445; cf. this vol., 68).—Oximinoacetophenone dissolved in dry dioxan to which water is added is oxidised first at 0—5° and then at about 40—60° with an equimolecular amount of nitrosylsulphuric acid, the product being then diluted with water and concentrated in a vacuum. The residue is extracted with ether, the ethereal solution is washed with water, the ether is removed by distillation, and the residue is extracted with boiling water. When the aqueous solution thus obtained is filtered, concentrated in a vacuum, and cooled to 0° phenylglyoxal crystallises and can be purified by dissolution in the minimum quantity of warm ether, filtration of the ethereal solution, and addition at 0° of an equal volume of light petroleum (d 0·71—0·72). Yield up to 50%, m. p. 73°. W. McCARTNEY.

Catalytic esterification of alcohols in alkaline solution. I. J. HOUBEN and W. FISCHER (Ber., 1931, 64, [*B*], 240—247).—In the presence of a small proportion of alkali metal or alkoxide, trichloromethyl ketones react with alcohols, yielding esters and chloroform: $R{\cdot}CO{\cdot}CCl_3+R'{\cdot}OH=[R{\cdot}C(OR')(OH){\cdot}CCl_3] \longrightarrow R{\cdot}CO_2R'+CHCl_3$. Reaction is generally effected at the ordinary temperature or at 0° and can be applied to primary, secondary, and tertiary alcohols, hydroxy- and polyhydroxy-compounds. The following examples are cited: trichloroacetophenone into methyl, ethyl, or *iso*propyl benzoate; *p*-trichloroacetophenetole into ethyl *p*-ethoxybenzoate; trichloroacetocarvacrol into *methyl* 4-*hydroxy*-5-*methyl*-2-iso*propylbenzoate*, b. p. 153—154°/1·5 mm.; trichloroacetothymol into *methyl* 4-*hydroxy*-2-*methyl*-5-iso*propylbenzoate*, m. p. 97—98°; 4-trichloroacetyl-2-methylphenetole into *methyl* 4-*ethoxy*-3-*methylbenzoate*, b. p. 178—179°/43 mm., m. p. 33°; trichloroacetophenone into benzyl benzoate, linalyl benzoate, mono- and di-benzoylglycol, menthyl benzoate, ethyl benzoyl-lactate, glyceryl di- and tri-benzoate. H. WREN.

Preparation of cyclic non-saturated ketones with more than nine ring-members. SOC. ANON. M. NAEF ET CIE.—See B., 1931, 290.

4-*p*-Tolylthiosemicarbazide and its reactions with ketones. R. W. BOST and W. F. SMITH (J. Amer. Chem. Soc., 1931, 53, 652—654).—4-*p*-Tolylthiosemicarbazide, m. p. 137° (*hydrochloride*, m. p. 173°), is obtained in 90% of the theoretical amount from hydrazine hydrate and *p*-tolylthiocarbimide. 4-p-*Tolylthiosemicarbazones* were prepared from the following ketones: methyl ethyl ketone, m. p. 75°; ethyl acetoacetate, m. p. 107°; *cyclo*hexanone, m. p. 125°; acetophenone, m. p. 165°; benzophenone, m. p. 158°; benzoylacetone, m. p. 126°; benzoin, m. p. 161°; benzil, m. p. 164°, and carvone, m. p. 147°. *Acetylacetone*-4-p-*tolylthiosemicarbazone*, m. p. 100°, when boiled with alcohol, gives 3 : 5-dimethylpyrazole and ethyl anilinothioformate. H. BURTON.

Some reactions of phenyl propenyl ketone with semicarbazides and thiosemicarbazides. A. Y. LIVINGSTONE and F. J. WILSON (J.C.S., 1931, 335—337).—Phenyl propenyl ketone reacts with δ-phenylsemicarbazide and δ-phenylthiosemicarbazide to give only its *δ-phenylsemicarbazone*, m. p. 212°, and *δ-phenylthiosemicarbazone*, m. p. 140°, whilst *p*-methoxyphenyl propenyl ketone similarly affords only its

δ-*phenylsemicarbazone*, m. p. 249°. On the other hand, with phenyl propenyl ketone and thiosemicarbazide only addition to the ethylenic linking occurs, giving *phenyl thiosemicarbazidopropyl ketone*, m. p. 140°, which, although it yields an *oxime*, m. p. 165°, does not react further with thiosemicarbazide.

J. W. BAKER.

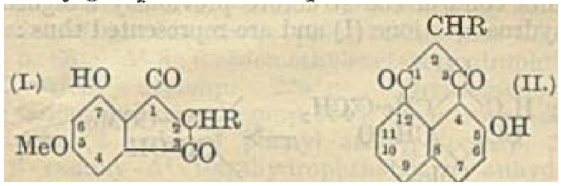
Heteropolar compounds. XIII. Effect of the nitro-group on the colour of salts of positive ions. W. DILTHEY, C. BLANKENBURG, W. BRANDT, W. BRAUN, R. DINKLAGE, W. HUTHWELKER, and W. SCHOMMER (J. pr. Chem., 1931, [ii], **129**, 189—205).—The bathochromic influence on halochromism of a nitro-group as substituent in the phenyl nucleus attached to a carbonyl group (cf. A., 1929, 1300) is confirmed by observations of the colour of further chalkones, Ar·CH:CH·CO·Ar, and benzophenone derivatives in concentrated sulphuric acid. Halochromism is also shown by the former in the presence of small proportions only of acid, *e.g.*, with sulphuric acid in acetic acid, or perchloric acid in acetic anhydride, but the shades are lighter than in sulphuric acid, and deepen on warming; this difference in behaviour is still more marked with the benzophenone derivatives, presumably on account of their lower basicity. The effect of the nitro-group on shade is not, however, conditioned by the decreased basicity, as this is also shown in cases where it has a hypsochromic action. The following nitro-compounds are prepared by interaction of the appropriate acyl chloride with diphenyl, diphenyl ether, diphenyl sulphide, etc., reduction to the corresponding amino-compounds being effected by stannous chloride and hydrochloric acid in acetic acid: *4′-nitrophenyl 4-diphenylyl ketone*, m. p. 164°; 4-p-*nitrophenylthiolacetophenone*, m. p. 119°; 4-p-*nitrobenzoyl*-, m. p. 121—122°, 4-m-*nitrobenzoyl*-, m. p. 87—88°, 4-m-*aminobenzoyl*- (isolated as *hydrochloride*, m. p. 200—206°; *benzoyl* derivative, m. p. 127°; *azo*-β-*naphthol* derivative, orange-red), 4 : 4′-*di*-p-*nitrobenzoyl*-, m. p. 226°, 4 : 4′-*di*-p-*aminobenzoyl*-, m. p. 177—178° (*hydrochloride*; *azo*-β-*naphthol* derivative), 4 : 4′-*di*-m-*nitrobenzoyl*-, m. p. 175°, and 4 : 4′-*di*-m-*aminobenzoyl-diphenyl ether*, m. p. 150—151° (*azo*-β-*naphthol* derivative); 4-m-*nitrobenzoyl*-, m. p. 128—129°, 4 : 4′-*di*-m-*nitrobenzoyl*-, m. p. 229—230°, 4 : 4′-*di*-p-*nitrobenzoyl*-, m. p. 2?8°, and 4′-*nitro-4-benzoyl-diphenyl sulphide*, m. p. 145°; 4 : 4′-*di*-m-*nitrobenzoyl*-, m. p. 221—222°, and 4 : 4′-*di*-p-*nitrobenzoyl-diphenyl selenide*, m. p. 267—268°. Interaction of 4-*p*-nitrophenylthiolacetophenone with the appropriate aldehyde in ethyl alcohol in presence of sodium methoxide gives 4-p-*nitrophenylthiolchalkone*, m. p. 142°, followed by resolidification and further fusion at 180°, and its 4-*methoxy*-, m. p. 154°, and 3′ : 4′-*methylenedioxy*-, m. p. 174°, -derivatives. Condensation of sodium thiophenoxide with *p*-chloronitrobenzene in alcoholic solution gives, not the expected *p*-nitrodiphenyl sulphide (cf. A., 1897, -?), but p-*azodiphenyl sulphide*, m. p. 121—122°.

H. A. PIGGOTT.

Stereochemical structure. II. Optically active α- and β-methylhydrobenzoins. R. ROGER (Biochem. Z., 1931, **230**, 320—329).—$d(-)$-Acetylphenylcarbinol with magnesium phenyl bromide gives the *α-form* of $d(+)$-methylhydrobenzoin, m. p. 92—93°, α^{20}_{5893} +31·1° in acetone, +40·6° in ethyl alcohol. This is compared with a sample of the β-form obtained by the action of magnesium methyl iodide on $d(-)$-benzoin, which gives m. p. 80—81°, α^{20}_{5893} +30·9° in acetone, +21·3° in ethyl alcohol. Admixture of the α- with the β-form of $d(+)$-methylhydrobenzoin depresses the m. p. to 50—70°, and the m. p. of the α-form on keeping for 2 months fell from 92—93° to 84—89°. By the action of magnesium phenyl bromide on ethyl $d(+)$-lactate, β-methyl-αα-diphenylethylene glycol is obtained, m. p. 92—93°, α^{20}_{H} +133° in acetone. The substance is therefore readily distinguished from the methylhydrobenzoins by its high rotation (cf. A., 1930, 211).

P. W. CLUTTERBUCK.

Syntheses of antiseptic derivatives of indan-1 : 3-dione. I. Interaction of malonyl chloride and of alkylmalonyl chlorides with the methyl ethers of resorcinol and β-naphthol. R. BLACK, H. SHAW, and T. K. WALKER (J.C.S., 1931, 272—279).—Malonyl chloride (best prepared by the action of phosphorus pentachloride on malonic acid, Staudinger and Bereza's method, A., 1909, i, 83, being unsatisfactory) and various alkylated malonyl chlorides condense with resorcinol dimethyl ether and β-naphthyl methyl ether in the presence of aluminium chloride in nitrobenzene to give indandiones of types I and II, respectively, demethylation only of the methoxy-group in the *ortho*-position to the carbonyl

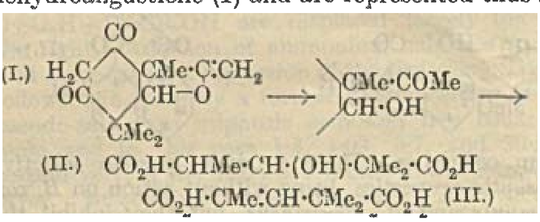


group occurring. These products possess selective antiseptic properties, being without action on *B. coli communis* and *B. pyocyaneus*, but they inhibit the growth of *Bacterium C*, the values of x, the inhibiting concentration (1 g. in x c.c.), being given in parentheses after each compound. The following were prepared: *7-hydroxy-5-methoxy*-, m. p. 217° (22,000); *7-hydroxy-5-methoxy-2-methyl*-, m. p. 225—226° (10,000), *-2-ethyl*-, m. p. 192·5° (8300), and -2-n-*propyl*-, m. p. 190·5° (12,500), [the -2-n-*butyl* derivative (20,000) was not obtained pure], -*indan*-1 : 3-*dione*: *5-hydroxy*-, m. p. 276—280° (16,600); *5-hydroxy-2-ethyl*-, m. p. 215° (66,400), -2-n-*propyl*-, m. p. 181° (166,000), and 2-n-*butyl*-, m. p. 185° (277,000), -peri*naphthindan*-1 : 3-*dione*. Introduction of an alkyl group in the 2-position of the resorcinol derivative lowers the antiseptic power, but this depressing effect is counterbalanced as the length of the substituent alkyl chain is increased. The lowering effect of alkyl groups is absent in the derivatives of β-naphthol.

J. W. BAKER.

Essential oil of *Backhousia angustifolia*. III. Constitution of angustione and dehydroangustione. R. S. CAHN, C. S. GIBSON, A. R. PENFOLD, and J. L. SIMONSEN (J.C.S., 1931, 286—294).—Oxidation of angustione with potassium hypobromite converts it quantitatively into l-ααγ-trimethylglutaric acid. Oxidation with potassium permanganate in acetone at 0° affords a liquid ketonic acid, probably $CO_2H{\cdot}CMe(COMe){\cdot}CH_2{\cdot}CMe_2{\cdot}CO_2H$, since it is further

oxidised smoothly to *l*-$\alpha\alpha\gamma$-trimethylglutaric acid with sodium hypobromite. Although only 80% of the hydrogen required for one ethylenic linking is absorbed, reduction of dehydroangustione with hydrogen and palladised norite in alcohol affords a homogeneous product of dl-*angustione*, b. p. 127°/14 mm., d_{20}^{20} 1·083, n_D^{20} 1·5087 (*copper* derivative, m. p. 203—204°), isolated by the action of ammonia on the alcoholic solution as dl-*aminoangustione*, m. p. 138—139°, and converted by hydroxylamine into dl-*anhydroangustione*-4(or 6)-*oxime*, m. p. 57—58°. Hence the original sample of dehydroangustione contained 26% of angustione, the presence of which accounts for the formation of $\alpha\alpha\gamma$-trimethylglutaric acid in the products of the oxidation of dehydroangustione with sodium hypobromite (A., 1930, 921). The neutral product, $C_8H_{10}O_3$, m. p. 88·5°, obtained in the latter oxidation (*loc. cit.*) is the anhydride of *cis*-$\alpha\alpha\gamma$-trimethylglutaconic acid (III), since it is readily hydrated to this acid [converted by bromine, not into a dibromide as stated by Perkin and Smith (J.C.S., 1904, **85**, 157), but into the *lactone*, m. p. 147—148°, of β-bromo-γ-hydroxy-$\alpha\alpha\gamma$-trimethylglutaric acid], whilst a small yield of *trans*-β-hydroxy-$\alpha\alpha\gamma$-trimethylglutaric acid (II) [Perkin and Smith (*loc. cit.*); reduced by hydriodic acid (*d* 1·7) and red phosphorus at 170—180°, followed by sodium and amyl alcohol, to $\alpha\alpha\gamma$-trimethylglutaric acid] is also isolated. These results confirm the structure previously assigned to dehydroangustione (I) and are represented thus :

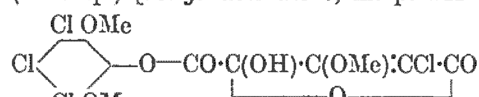


Hydrobromic acid (*d* 1·5) at 100° converts natural or *dl*-angustione into 1 : 1 : 3-trimethyl*cyclo*hexane-4 : 6-dione, whilst dehydroangustione is similarly converted into 1 : 1 : 3-trimethyl-Δ^2-*cyclo*hexene-4 : 6-dione, oxidised by sodium hypobromite to *cis*-$\alpha\alpha\gamma$-trimethylglutaconic acid, and an unstable *substance*, $C_8H_{12}O_2$, m. p. 85—86°, probably $CMe_2{<}^{CO-CO}_{CH_2\cdot CHMe}$ or its dienol, which has phenolic properties and with bromine affords a red bromide, decomposed by water into the substituted glutaconic acid. Dehydroangustione is converted by *p*-toluidine and zinc chloride at 140—150° into p-*toluidinodehydroangustione*, m. p. 63—65°.

[With O. J. Evans and F. G. Soper.] The parachors of *dl*-angustione and dehydroangustione at 20° are, respectively, 442, and 435, and possible explanations of the negative anomalies from the calculated values (462·1 and 439·5, respectively) are discussed. J. W. Baker.

Quinone formation from nitroacetamidoquinol. G. Heller and T. Hemmer (J. pr. Chem., 1931, [ii], **129**, 207—210).—2 : 5-Dinitroquinol (Nietzki, A., 1883, 465) is more conveniently prepared from its diacetate by hydrolysis with 5% sulphuric acid than with alkali. It is reduced by the calculated quantity of stannous chloride in hydrochloric acid to 2-*nitro*-5-*acetamidoquinol*, decomp. 226° without melting (*diacetate*, m. p. 183—184°), readily hydrolysed to 2-*nitro*-5-*aminoquinol*, decomp. 154°. The acetyl compound is oxidised by fuming nitric acid in acetic acid to 2-*nitro* 5-*acetamido*-3 : 6-*dihydroxybenzoquinone*, m. p. 164° (decomp.), an unstable substance, decomposed by heating with the commoner solvents, but capable of recrystallisation, with care, from ethyl acetate. Careful oxidation with chromic in place of nitric acid gives a small quantity of a somewhat impure substance, decomp. indefinitely above 140°, probably 2-*nitro*-5-*acetamido*-3-*hydroxybenzoquinone*. Both of these hydroxyquinones readily give with aniline in alcohol 5-*nitro*-2-*acetamido*-3 : 6-*dianilinobenzoquinone*, decomp. 260°. H. A. Piggott.

New type of oxidation product derived from quinones. W. H. Hunter and M. M. Sprung (J. Amer. Chem. Soc., 1931, **53**, 700—711).—The colourless compound formed during the oxidation of trichloropyrogallol 1 : 3-dimethyl ether with chromic oxide in acetic acid (A., 1926, 839) has m. p. 187·4—187·8° (decomp.), and is also formed by similar oxidation of 3 : 5-dichloro-6-methoxy-2-(3′ : 4′ : 5′-trichloro-2′ : 6′-dimethoxyphenoxy)-*p*-benzoquinone. It furnishes an *acetyl* derivative, m. p. 135—136° (decomp.), and is decomposed by boiling 6% potassium hydroxide solution to the original trichloropyrogallol dimethyl ether. Its production from the above quinone probably involves fission of the quinone ring, loss of one carbon atom, and subsequent hydroxylactone formation; the compound is given the structure I. The analogous compound, m. p. 206—206·6° (decomp.) [*acetyl* derivative, m. p. 141—144°



(I.)

(decomp.)] (cf. *loc. cit.*), from tribromopyrogallol 1 : 3-dimethyl ether, is also formed by oxidation of 3 : 5-dibromo-6-methoxy-2-(3′ : 4′ : 5′-tribromo-2′ : 6′-dimethoxyphenoxy)-*p*-benzoquinone. It appears to be an anhydro-compound formed by loss of 1 mol. of water from 2 mols. of an intermediate of type I (where Cl=Br); during acetylation a simpler compound (type I) is produced. The possible mechanism of formation of these colourless substances is discussed. H. Burton.

Reaction occurring in place of the Beckmann transformation with certain aromatic diketonemonoximes. II. R. Scholl, K. Stephani, and E. Stix. III. R. Scholl and J. Donat (Ber., 1931, **64**, [*B*], 315—318, 318—321; cf. this vol., 357).—II. Phenyl 1-anthraquinonyl ketoxime, m. p. 230° when rapidly heated, 223° after darkening when slowly heated, is converted by concentrated hydrochloric acid at 175° into anthraquinone-1-carboxylic acid, aniline, a little anhydro-oxime, and phenyl 1-anthraquinonyl ketone; under similar conditions the last-named substance is unchanged. With ethyl-alcoholic hydrochloric acid at 150° the oxime affords the corresponding *ethyl ether*, m. p. 154—156° after softening, also prepared from the oxime, alcoholic sodium ethoxide, and ethyl iodide. Antimony penta-

chloride in chloroform, benzenesulphonyl chloride in pyridine, and phosphorus pentachloride in acetyl chloride are without action. Phenyl 1-anthraquinonyl ketoxime is transformed into the anhydride by treatment with concentrated sulphuric acid at 100°, with glacial acetic acid at 230—240°, with boiling glacial acetic acid containing potassium iodide, or, most advantageously, by treatment with boiling nitrobenzene containing a little hydrogen chloride. *m*-Xylyl 1-anthraquinonyl ketoxime is converted into its anhydride by treatment with potassium iodide in boiling glacial acetic acid, with boiling nitrobenzene even in the absence of hydrogen chloride, and with hydrogen chloride in boiling glacial acetic acid.

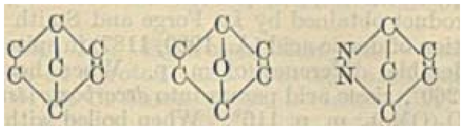
III. The possibility has been suggested (*loc. cit.*) that the anhydro-compounds are derivatives of phthalylphenanthridine, possibly formed through the *N*-aryl ethers of anthraquinone-1-aldoxime. These compounds are found to be incapable of transformation into their anhydrides and to isomerise, as expected according to Beckmann, into acid anilides. There is at present no support for the hypothesis that the anhydro-oximes are phthalylphenanthridines. Phthalic anhydride, suspended in a mixture of benzene and ether, is converted by magnesium *o*-tolyl bromide into *o*-2-toluoylbenzoic acid, m. p. 128—129°, almost quantitatively converted by fuming sulphuric acid into 1-methylanthraquinone. Oxidation of the last-named substance with manganese dioxide and sulphuric acid affords anthraquinone-1-aldehyde, transformed by β-phenylhydroxylamine into *anthraquinone*-1-*aldoxime phenyl ether*, m. p. 219—219·5°. Treatment of the ether with boiling nitrobenzene or with a mixture of glacial acetic and sulphuric acids affords, respectively, anthraquinone-1-carboxyanilide and anthraquinone-1-carboxylic acid. 4-*Chloroanthraquinone*-1-*aldoxime* N-*phenyl ether*, m. p. 214—215°, behaves analogously to the non-chlorinated compound. H. WREN.

Aminohydroxyanthraquinones and substitution products. I. G. FARBENIND. A.-G.—See B., 1931, 195.

Potentials and decomposition reactions of o-quinones in acid solution. L. F. FIESER and M. A. PETERS (J. Amer. Chem. Soc., 1931, 53, 793—805).—It is shown by potentiometric analysis that β-naphthaquinone decomposes in dilute acid solution, forming equal amounts of β-naphthaquinhydrone and 2-hydroxy-1 : 4-naphthaquinone; the reaction is unimolecular. It is suggested that slow addition of 1 mol. of water to the β-quinone occurs, forming 1 : 2 : 4-trihydroxynaphthalene, which then reacts rapidly with a further molecule of the β-quinone. Phenanthrene-3 : 4-quinone behaves similarly. The values for the normal oxidation–reduction potentials of the systems 1 : 2-dihydroxyphenanthrene–phenanthrene-1 : 2-quinone, pyrocatechol–*o*-benzoquinone, and 3 : 4 : 3′ : 4′-tetrahydroxy-1 : 1′-dinaphthyl–1 : 1′-dinaphthyl-3 : 4 : 3′ : 4′-diquinone have been redetermined using the discontinuous titration method (this vol., 1,2). H. BURTON.

[**1-Hydroxyphenanthraquinone.**] K. BRASS (Ber., 1931, 64, [*B*], 503; cf. A., 1930, 1589).—*o*-Methoxy-benzoin and -benzil have been described previously by Asahina and Terasaka (A., 1923, i, 1023). H. WREN.

Graduated additive powers of unsaturated ring systems. K. ALDER, G. STEIN, and H. FINZENHAGEN (Annalen, 1931, 485, 211—222).—Derivatives of the ring systems represented by the skeletal formulæ :



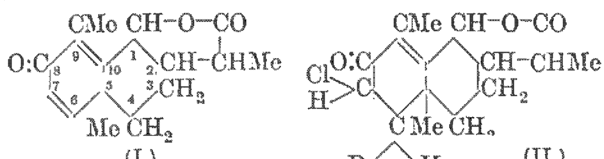
are characterised by the ready addition of phenyl azide and similar substances at the ordinary temperature. This property is not destroyed by substitution of the six-membered ring (including fusion of a saturated ring); addition does not occur, however, to unbridged *cyclo*hexene, nor when the bridge consists of more than a single atom (di*cyclo*octane). Two mols. of phenyl azide are readily taken up by bis*cyclo*pentadienequinone (Albrecht, A., 1906, i, 674), which has two 1 : 4-*endo*methylene*cyclo*hexene rings in its molecule. The underlying cause of this behaviour is regarded as stereochemical, the corresponding saturated rings being highly strained in those cases where additive power exists, but free from strain in cases where it is absent. The following additive *compounds* are described : phenyl azide with santene, m. p. 86°; Δ^4-3 : 6-*endo*methylenetetrahydrophthalic anhydride, decomp. 225°; dihydromono*cyclo*pentadienequinone, decomp. 194°; bis*cyclo*pentadienequinone (2 mols. of phenyl azide), decomp. 258°; 3 : 6 - *endo*oxy - Δ^4 - tetrahydrophthalic anhydride, decomp. 200°, and *NN′*-dicarbethoxy-3 : 6-*endo*methylenetetrahydropyridazine, m. p. 126° : dihydromono*cyclo*pentadienequinone with benzyl azide, m. p. 141°, and ethyl diazoacetate, m. p. 177° (decomposition points are determined with " rapid heating "). Δ^4-3 : 6-*endo*Ethylenetetrahydro- and Δ^4-tetrahydro-phthalic anhydrides, bis*cyclo*hexadiene, dihydromono*cyclo*hexadiene-, dihydromonobutadiene-, and bisbutadiene-quinones do not react with phenyl-azide. H. A. PIGGOTT.

Linear pentacene series. XX. Optical absorption of pentacene derivatives. G. MACHEK (Monatsh., 1931, 57, 201—224).—Extinction curves are given for the following pentacene derivatives : pentacene-6 : 13-quinone; pentacene-5 : 7 : 12 : 14-diquinone; 1 : 8- and 6 : 13-dihydroxy-; 1 : 8-, 1 : 11-, 2 : 9-, and 6 : 13-dibromo-; 1 : 8- and 1 : 11-dinitro- and 1 : 8- and 1 : 11-diamino-pentacene-5 : 7 : 12 : 14-diquinones. Measurements were made usually in benzene and pyridine solution; the molar extinction is higher in the latter solvent. The results for the 1 : 8-disubstituted derivatives in pyridine show that the displacement towards the red is in the order nitro->amino->hydroxy->bromo-. All the compounds show the same type of curve. Substituents in the 6 : 13-positions cause the appearance of a new band, thus enabling a distinction to be made between the 6 : 13- and the 1 : 8-, 1 : 11-, and 2 : 9-derivatives. H. BURTON.

Rotenone, the active component of the *Derris* root. VI. Constitution of derric acid and rissic acid. S. Takei, S. Miyajima, and M. Ōno (Ber., 1931, 64, [*B*], 248—252; cf. A., 1930, 1044).—Rotenone is converted by a modification of Butenandt's method (A., 1928, 1017) into derrisic acid, m. p. 153°, which is oxidised by permanganate in alkaline solution to *rissic acid*, $C_9H_6O_5(OMe)_2$, m. p. 256° (decomp.) (*methyl* ester, m. p. 86°), regarded as identical with the product obtained by La Forge and Smith by the oxidation of derric acid (A., 1930, 1187) in spite of the considerable difference of m. p. When heated at 255—260°, rissic acid passes into *decarboxyrissic acid*, $C_8H_6O_3(OMe)_2$, m. p. 116°. When boiled with dilute nitric acid, rissic or decarboxyrissic acid is transformed into a *nitrodimethoxybenzoic acid*, m. p. 209° (*methyl* ester, m. p. 146°). Fusion with potassium hydroxide transforms rissic acid into quinol. Rissic acid is therefore regarded as hydroxy-2 : 5-dimethoxyphenylmalonic acid and decarboxyrissic acid as 2 : 5-dimethoxyphenylglycollic acid. Derric acid is considered to be most probably α-hydroxy-α-2 : 5-dimethoxyphenylsuccinic acid. The resolution of derric and decarboxyrissic acids into their optical antipodes has been effected. H. Wren.

Constitution of aloins. E. Léger (Bull. Soc. chim., 1931 [iv], 47, 70—72).—A reply to Gibson and Simonsen (A., 1930, 609). Low yields in the decomposition of barbaloin into aloemodin and *d*-arabinose with sodium peroxide and alcoholic hydrogen chloride are attributed to oxidation of the products, especially arabinose, by the peroxide and to the formation of furfuraldehyde, which yields humic products or with the aloemodin gives amorphous substances. Léger's observations (A., 1917, i, 276) do not agree with the assumption that the bromobarbaloin obtained by the action of bromine water on barbaloin has the formula $C_{16}H_{15}O_7Br_3$, and the low halogen results are again attributed to loss of halogen in recrystallisation. Chlorobarbaloin, $C_{20}H_{14}O_9Cl_4$ (Cl 25·17%), gives a chloroaloemodin, $C_{15}H_6O_5Cl_4$, of correct chlorine content, and the formation of 1 mol. of the latter together with *d*-arabinose (1 mol.) from a compound $C_{16}H_{15}O_7Cl_3$ would be inexplicable. The compound $C_{20}H_{15}O_9Br_3$ may have a much greater mol. wt. than corresponds with the formula, since its solution in boiling alcohol deposits nearly insoluble crystals. R. Brightman.

Santonin series. XV. Position of the double linkings in santonin; halogeno-derivatives of santonin and the so-called "δ-hydroxysantonin." E. Wedekind and K. Tettweiler (Ber., 1931, 64, [*B*], 387—398; cf. A., 1930, 347).—The position of



(I.) (II.)

the double linkings in the structure I assigned to santonin by Clemo and others (A., 1930, 919, 1442; this vol., 227) is established.

Re-examination of the "monochlorosantonin," $C_{15}H_{19}O_4Cl$, obtained by Wedekind and Koch (A., 1905, i, 212, 529) by the action of freshly-prepared chlorine water on powdered santonin, shows that it must be regarded as santonin chlorohydrin (II; R=OH), since it may also be obtained by the use of hypochlorous acid containing no free chlorine. The hypothesis that addition and not substitution has occurred is strengthened by the observations that α-tetrahydrosantonin is stable towards hypochlorous acid and that the chlorohydrin is hydrogenated in presence of platinum to *dihydrosantonin chlorohydrin*, $C_{15}H_{21}O_4Cl$, decomp. 214°. *Santonin bromohydrin*, decomp. 216°, is described. The hydroxyl group of the chlorohydrin cannot be detected by the usual methods except that of Zerevitinov. The chloro- or bromo-hydrin is transformed by methyl-alcoholic potassium hydroxide at 50—60° into *santonin oxide*, m. p. 214°, identical with the δ-hydroxysantonin of Wedekind and Koch (*loc. cit.*). The substance does not contain a hydroxyl group, since it does not yield methane with magnesium methyl iodide. It is hydrogenated to *α-dihydrosantonin oxide*, m. p. 142—143° (*oxime*, decomp. 225°), and small amounts of *β-dihydrosantonin oxide*, m. p. 169° [*oxime*, m. p. 189—190° (decomp.)]. When similarly treated, dihydrosantonin chlorohydrin yields α-dihydrosantonin oxide. Since the last-named substance is stable towards Caro's acid and therefore does not contain the $\cdot CO\cdot CH_2\cdot$ group, it follows that the oxide ring is attached to the carbon atoms 6 and 7.

The action of concentrated hydrochloric acid on santonin oxide gives iso*santonin chlorohydrin*, $C_{15}H_{19}O_4Cl$, decomp. 210°, quantitatively re-converted by pyridine or boiling water into santonin oxide and catalytically hydrogenated to *dihydro*iso*santonin chlorohydrin*, m. p. 175° (decomp.), also prepared from α-dihydrosantonin oxide. The presence of the hydroxyl group is established by Zerevitinov's method, but it cannot be vicinal to the keto-group, since the compound does not yield an osazone. The *iso*-compound is probably stereoisomeric with santonin chlorohydrin. During the action of concentrated hydrochloric acid on santonin oxide, *dichlorosantonin* (II; R=Cl), decomp. 173—174°, is obtained, also prepared from dry chlorine and santonin in chloroform and regarded by Wedekind and Koch (*loc. cit.*) as a substitution product. The presence of one double linking is established by hydrogenation to *dichlorodihydrosantonin*, decomp. 145—146°, obtained also from α-dihydrosantonin oxide and concentrated hydrochloric acid. Treatment of dichlorosantonin with boiling alkali solution or, preferably, with aniline affords monochlorosantonin (I; Cl in position 7), decomp. 224° (cf. Rödiger, Diss., Tübingen, 1908), hydrogenated to *chloro-α-tetrahydrosantonin*, $C_{15}H_{21}O_3Cl$, decomp. 215°. The same product is obtained by chlorination of α-tetrahydrosantonin in chloroform. The probability that the chlorine atom is attached to a carbon atom vicinal to one of the two ketonic groups is supported by the observation that halogenation does not occur with *deoxy-α-tetrahydrosantonin*, m. p. 153—154°, and the allocation of it to position 7 follows from the inactivity of chloro-α-tetrahydrosantonin to Caro's acid. Hydrogenation of dichlorosantonin to dichlorodihydrosantonin and subsequent removal of hydrogen chloride by aniline gives a *chlorodihydrosantonin*,

decomp. 160°, catalytically hydrogenated to chloro-α-tetrahydrosantonin. H. WREN.

Tephrosin. I. Composition of tephrosin and its relation to deguelin. E. P. CLARK (J. Amer. Chem. Soc., 1931, **53**, 729—732).—Deguelin, m. p. 171°, and a substance, m. p. 198° (corr.) (termed tephrosin), have been isolated from the leaves of *Cracca vogelii*, derris root, and the root of *Lonchocarpus nicou* (cf. A., 1930, 967; this vol., 357). Deguelin and tephrosin form a difficultly separable mixture, which is apparently identical with the tephrosin of Hanriot (A., 1907, ii, 292). Deguelin can be removed from such mixtures by selective oxidation with chromic and acetic acids. Tephrosin, $C_{21}H_{16}O_5(OMe)_2$, is probably a hydroxydeguelin, since, when it is warmed with sulphuric and acetic acids, dehydrodeguelin is produced. Oxidation of tephrosin with potassium permanganate in acetone at the ordinary temperature gives *tephrosindicarboxylic acid*, $C_{23}H_{20}O_{11}$, m. p. 221° (decomp.). H. BURTON.

Rotenone. XI. Relation between *iso*rotenone and rotenone. H. L. HALLER (J. Amer. Chem. Soc., 1931, **53**, 733—737).—In an attempt to isomerise rotenonic acid by treatment with acetic and sulphuric acids, the alkali-insoluble β-*dihydrorotenone*, $C_{23}H_{24}O_6$, m. p. 156°, $[\alpha]_D^{25}$ —26·5° in chloroform, was obtained. This is converted by alcoholic potassium hydroxide into β-*dihydrotubaic acid*, m. p. 175—176° (decomp.) (also formed by fusion with potassium hydroxide at 225°), and oxidised by chromic and acetic acids to a *diketone*, $C_{23}H_{20}O_7$, m. p. about 310° (decomp.). Oxidation with alkaline potassium ferricyanide gives *dehydro-β-dihydrorotenone*, m. p. 269°, converted by zinc dust and alcoholic potassium hydroxide into *dehydrodihydroxy-β-dihydorotenonic acid*, m. p. 149°, which is oxidised by alkaline hydrogen peroxide to derric acid. Treatment of β-dihydrorotenone with iodine in alcoholic potassium acetate affords β-*dihydrorotenolone*, m. p. 274° (*acetyl* derivative, m. p. 224°), dehydrated by alcoholic sulphuric acid to dehydro-β-dihydrorotenone.

The isomerisation of rotenone to *iso*rotenone (by treatment with sulphuric and acetic acids) probably involves the migration of a double linking from an *iso*propylene group to an αβ-position with respect to the lactone group. The double linking becomes part of a conjugated system which is reduced only with difficulty. β-Dihydrorotenone appears to be a saturated lactone; its production from rotenonic acid is accompanied by the disappearance of the double linking. H. BURTON.

Sapogenin of guaiacum bark. I. E. WEDEKIND and W. SCHICKE (Z. physiol. Chem., 1931, **195**, —138).—The saponin is hydrolysed with 5% sulphuric acid first at the b. p. and then at 155°. The resulting *sapogenin* (termed *guagenin*), $C_{29}H_{46}(OH)(CO_2H)$ (*methyl* ester, m. p. 196°, $[\alpha]_D^{15}$ + 60° in chloroform), has m. p. 310° after sintering at 304°, $[\alpha]^{17}$ —77·4° in chloroform, when regenerated from its *acetyl* derivative, m. p. 268°, $[\alpha]_D^{15}$ +74·5° in chloroform (*methyl* ester, m. p. 220°, $[\alpha]^{17}$ +69·2° in chloroform). H. BURTON.

Ursolic acid. C. E. SANDO (J. Biol. Chem., 1931, 90, 477—495).—Malol (Sando, A., 1923, i, 990), prunol (Power and Moore, J.C.S., 1910, 97, 1099), and urson (van der Haar, A., 1924, i, 643) are shown to be identical ($C_{30}H_{48}O_3$) and the name ursolic acid is proposed. The formation of already known derivatives is described in detail and the conclusion is reached that the acid is a hydroxy-acid. *Methyl phthalylursolate*, m. p. 214—215°, *phthalylursolic acid*, m. p. 264—265°, and *phenacyl ursolate*, m. p. 199—200°, are described. J. D. A. JOHNSON.

Carotene. III. Hydrogenation and optical properties of carotene and hydrogenated derivatives. J. H. C. SMITH (J. Biol. Chem., 1931, **90**, 597—605).—Carotene has $[\alpha]^{15}$ —63°± 17% in carbon disulphide. In ethereal solution with aluminium amalgam it gives *dihydrocarotene*, a viscous oil, $[\alpha]_D^{18}$ +41·9 in ether, $[\alpha]_D^{18}$ +38·0° in alcohol, the absorption spectrum of which is very different from that of carotene. *Octadecahydrocarotene*, b. p. 276°/1 mm., $d_4^{20\cdot2}$ 0·8828, n_D^t 1·4962—0·000367*t*, $[\alpha]_D^{14}$ +7·56° in carbon disulphide, is obtained from carotene in a mixture of acetic acid and *cyclo*hexane by catalytic hydrogenation in presence of platinum oxide. With an excess of catalyst, *eicosahydrocarotene*, b. p. 206°/10^{-4} mm., $d_4^{21\cdot2}$ 0·8748, $n_D^{21\cdot2}$ 1·4821, $[\alpha]_D^{20}$ +0·337°, was produced. The decrease in [α] as carotene is hydrogenated is held to show that progressive hydrogenation symmetrises the molecule, and since the linkings most difficult to hydrogenate are in such positions as to produce asymmetry, the presence of an unsaturated or a dicyclic ring is inferred. An explanation of the colour of carotene is advanced.

J. D. A. JOHNSON.

Carotenoids. III. Degradation of carotene by ozone. R. PUMMERER, L. REBMANN, and W. REINDEL (Ber., 1931, **64**, [*B*], 492—502; cf. A., 1929, 906).—Carotene has been subjected to ozonisation in carbon tetrachloride (1) with 4% ozone followed by removal of the solvent in a vacuum and hydrogenation of the ozonide in glacial acetic acid and (2) with 1·5% ozone followed by decomposition of the product with boiling water. The most characteristic substances obtained are a neutral oil, b. p. 104°/1·5 mm., also derived from β- but not from α-ionone, ε-keto-αα-dimethylheptaldehyde, ε-keto-αα-dimethylheptoic acid, and glyoxal. Considerations of the results from a quantitative viewpoint strongly support Karrer's formula for carotene with two terminal β-ionone residues.

Carotene in carbon tetrachloride is readily oxidised by oxygen with production of glyoxal. H. WREN.

Conjugated double linkings. XVI. Violaxanthin, the xanthophyll of the yellow pansy [*Viola tricolor*]. R. KUHN and A. WINTERSTEIN (Ber., 1931, **64**, [*B*], 326—332).—The dried blossoms are extracted with light petroleum at the ordinary temperature in an atmosphere of carbon dioxide and the violaxanthin ester thus obtained is hydrolysed with sodium ethoxide in a mixture of light petroleum and alcohol. *Violaxanthin*, m. p. 199—199·5° (corr., decomp.), is thus obtained in brownish-yellow prisms. On the basis of elementary analyses the formula $C_{40}H_{56}O_4$ is assigned to it. According to the Zerevitinov method, all four oxygen atoms are present in

hydroxyl groups. It has $[\alpha]^{20}_{D}$ +35° in chloroform. The absorption spectra of zeaxanthin, lutein, and violaxanthin in carbon disulphide, chloroform, ethyl alcohol, light petroleum, and methyl alcohol are described in detail as well as the colour reactions. The behaviour of violaxanthin towards dilute mineral acids is particularly characteristic. Hydrogenation of violaxanthin in presence of alcohol and platinum oxide affords *perhydroviolaxanthin*, $C_{40}H_{78}O_4$, a colourless, viscous liquid, $[\alpha]^{20}_{D}$ −18° in chloroform. The alkaline, methyl-alcoholic mother-liquor from violaxanthin contains a lipochrome pigment which has not been caused to crystallise. H. WREN.

Conjugated double linkings. XVII. Polyene pigments of the azafran root. R. KUHN, A. WINTERSTEIN, and H. ROTH (Ber., 1931, **64**, [*B*], 333—341; cf. Liebermann and others, A., 1911, i, 391; 1913, i, 889; 1916, i, 56).—The powdered root is extracted with chloroform and the extracts are concentrated and cooled, whereby the bulk of the azafrin, mixed with some resin, separates. It is purified by dissolution in *N*-alcoholic potassium hydroxide, precipitation with acetic acid, and crystallisation from toluene. It has m. p. 212° (corr., decomp.), $[\alpha]^{23}_{C}$ −75·5° in alcohol. Elementary analyses of azafrin and many of its derivatives indicate with certainty the presence of only four oxygen atoms in the molecule and point to the formula $C_{28}H_{40}O_4$. Three active hydrogen atoms appear to be present. Azafrin is converted by sodium hydroxide and methyl sulphate into azafrin methyl ester, m. p. 192·8—193·2° (corr.), $[\alpha]^{20}_{C}$ −30° in chloroform, −147° in nitrobenzene; *azafrin ethyl* ester has m. p. 182° (corr., decomp.). Catalytic hydrogenation transforms azafrin into *perhydroazafrin*, a colourless, viscous liquid, $[\alpha]^{20}_{D}$ −6·7° in alcohol, 7 mols. of the gas being absorbed. It resembles crocetin in this respect and in its behaviour towards bromine which indicates the presence of 3·5—4 double linkings. *Perhydroazafrin methyl* ester, $C_{29}H_{56}O_4$, has $[\alpha]^{20}_{D}$ −9·0° in alcohol. Two of the oxygen atoms of azafrin are present in a carboxyl group, since the pigment can be titrated as a monobasic acid in alcohol in presence of thymol-blue. The remaining oxygen atoms are present in hydroxyl groups which probably are tertiary, since their acylation has not been accomplished. The optical activity of azafrin and its perhydro-derivative appears to be connected with the two hydroxyl groups, since it disappears completely when the last-named substance is treated with alcoholic hydrogen chloride and subsequently hydrolysed. Azafrin is therefore an optically active, seven-fold unsaturated, monocyclic, dihydroxymonocarboxylic acid, the colour of which is explicable by the assumption of an uninterrupted conjugation of the seven double linkings among themselves and with the carboxyl group. When the methyl ester is reduced with aluminium amalgam, a sulphur-yellow, very auto-oxidisable *dihydro*-compound, m. p. about 60°, is produced. Oxidation of azafrin with chromic acid yields acetic acid in amount pointing to the presence of five isoprene residues. The constitution $C_{10}H_{17}(OH)_2{\cdot}[CH{:}CH{\cdot}CMe{:}CH]_3{\cdot}CH{:}CH{\cdot}CO_2H$ is suggested. H. WREN.

Isoprene and caoutchouc. XXXII. Constitution of caoutchouc. H. STAUDINGER (Kolloid-Z., 1931, **54**, 129—140).—The molecular size of complex chain-like compounds is given by determination of the terminal groups if the mol. wt. does not exceed 10,000, but is too inaccurate for caoutchouc or cellulose. The mol. wt. of caoutchouc in solution, determined from the viscosity, lies between 50,000 and 200.000. The caoutchouc molecule probably consists of at least 1000 isoprene units in a chain, and is of colloidal size in one dimension only. Viscous solutions of caoutchouc and of other substances of very high mol. wt. are intermediate between gels and solutions; probably the effective volume of the long molecule is greater than the volume of surrounding liquid. The thermal and chemical sensitivity of caoutchouc is due to the unsaturation and length of the molecule. E. S. HEDGES.

Caoutchouc micelle or macromolecule ? H. LOEWEN (Kautschuk, 1931, **7**, 12—14).—A reply to Staudinger (this vol., 93). The arguments in favour of the macromolecule are not convincing and rubber in solution is probably present in the form of micelles. D. F. TWISS.

Linalool from coriander oil. I. I. VANIN and A. A. TSCHERNOJAROVA (J. Russ. Phys. Chem. Soc., 1930, **62**, 2013—2017).—Linalool was prepared from coriander oil by fractionation. The *chloride*, b. p. 120—127°/8 mm., d_4^{20} 1·0304, was obtained by the action of hydrogen chloride. The action of nickel carbonate on the chloride gave a monocyclic *terpene*, b. p. 165—167°, d_4^{20} 0·8333. E. B. UVAROV.

Tribornyl borate and its use in separation of borneol from camphor. P. SCHORIGIN and Y. MAKAROV-ZEMLIANSKI (J. Russ. Phys. Chem. Soc., 1930, **62**, 2047—2049).—Borneol is converted almost quantitatively into tribornyl borate by the action of benzene or xylene and boric acid. A method for separating borneol from camphor is based on this. E. B. UVAROV.

Sesquiterpenes from the turpentines of *Pinus sylvestris*. B. A. ARBUSOV (J. Russ. Phys. Chem. Soc., 1930, **62**, 2023—2026).—A new *sesquiterpene* isolated from turpentine has b. p. 126·5—128·5°/8 mm., d^{13} 0·933, α_D −30·45° (*dioxide*, b. p. 134—136°/5·5 mm., d_0^{20} 1·0175). E. B. UVAROV.

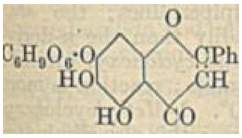
Pin*iso*sylvic acid. O. ASCHAN [with O. M. GADD] (Fenno-Chem., 1929, **1**, 18—27; Chem. Zentr., 1930, ii, 3142).—*Pinisosylvic* acid, $C_{20}H_{30}O_2$, m. p. 80° (sinters 60°) (*sodium* and *silver* salts), is obtained by heating pinabietic acid dihydrobromide with alcoholic alkali; bromination in chloroform affords the *tetrabromide*, $C_{20}H_{30}O_2Br_4$, m. p. 87°. The dihydrobromide, m. p. 192°, is identical with pinabietic acid dihydrobromide. Reduction of this with zinc and acetic acid affords *dihydropinisosylvic acid*, m. p. 92° (*hydrobromide*, m. p. 163—165°; dibromide, m. p. 92°). A. A. ELDRIDGE.

Spectrochemistry of furan and its derivatives. E. C. HUGHES and J. R. JOHNSON (J. Amer. Chem. Soc., 1931, **53**, 737—746).—The densities and refractive indices (for various wave-lengths) of furan and 20 of its derivatives are recorded. The exaltation in the molecular refraction for furan and the

2-substituted derivatives which do not contain a double linking on the atom attached to the ring is negative, whilst those compounds containing a double linking in the 2-position as part of a conjugated system give positive values. Isomeric 2- and 3-substituted furans can be distinguished from each other by von Auwers' formula (cf. A., 1921, ii, 73). Absorption spectra curves are given for 8 furan derivatives. Calculations of the wave-lengths of the absorption maxima for 5 of them by the Sellmeir dispersion formula (cf. Hunter, J.C.S., 1923, **123**, 434, 1671) gives results agreeing with those determined. Various electronic formulæ for furan are discussed. H. BURTON.

Homochromanone. S. G. POWELL and L. ANDERSON (J. Amer. Chem. Soc., 1931, **53**, 811).—Treatment of γ-phenoxybutyric acid (1 g.) with phosphoric oxide in benzene (cf. A., 1924, i, 287) gives impure homochromanone (oxime, m. p. 99°; *semicarbazone*, m. p. 228—229°). H. BURTON.

Orientation of glycuronic acid in baicalin. K. SHIBATA and S. HATTORI (Acta Phytochim., 1930, **5**, 117—118; cf. Shibata, Iwata, and Nakamura, A., 1923, i, 591).—Baicalin monomethyl ether gives a violet-brown colour with ferric chloride, indicating



ortho-related hydroxyl and carbonyl groups in the benzopyrone nucleus. By analogy with the behaviour of primetin (Nagai and Hattori, A., 1930, 784), the green colour given by baicalin with ferric chloride, and its oxidation by pentamminocobalt salts are regarded as evidence of free 5 : 6-dihydroxy-groups. It is therefore concluded that glycuronic acid is linked through the 7-hydroxyl group of baicalein (annexed formula). A. COHEN.

Spectrography of the flavone series. III. Constitution of wogonin. S. HATTORI (Acta Phytochim., 1930, **5**, 99—116; cf. A., 1928, 1020).—Further investigation of wogonin (cf. Shibata, Iwata, and Nakamura, A., 1923, i, 591) shows that it is 5:7-dihydroxy-8-methoxyflavone (+H_2O), m. p. 201°. The ferric chloride colour reaction indicates a 5-hydroxyl group. Hydrolysis gives acetophenone and benzoic acid. It yields a *diacetyl* derivative, m. p. 152—153°, and a *dimethyl ether* (+H_2O), m. p. 167—168°, different from 5 : 6 : 7-trimethoxyflavone, m. p. 163—164° (lit. 165°), obtained by methylation of baicalein with methyl sulphate or diazomethane. Treatment of 2 : 3 : 4 : 6-tetramethoxyacetophenone (Chapman, Perkin, and Robinson, A., 1928, 183) with aluminium chloride affords a product which is identified as 2-*hydroxy*-3 : 4 : 6-*trimethoxyacetophenone*, m. p. 112—113° (*oxime*, m. p. 164°), since, on interaction with benzoic anhydride and sodium benzoate, it yields 5 : 7 : 8-*trimethoxyflavone*, m. p. 167—168°, identical with wogonin dimethyl ether. Demethylation of the latter gives 5 : 7 : 8-*trihydroxyflavone*, m. p. 226—227° (*diacetyl* derivative, m. p. 212—213°; *triacetyl* derivative, m. p. 172—173°), identical with the demethylation product of the former. These relationships are confirmed by spectrographs. A. COHEN.

Colouring matters of flowers and fruit. P. SISLEY (Bull. Soc. chim., 1931, [iv], **49**, 101—117).—A lecture.

Condensation of catechin tannin. M. BERGMANN and G. POJARLIEFF (Naturwiss., 1930, **18**, 1114).—The facility with which catechin and catechin tannins condense to form insoluble products such as tannin-red and phlobaphen is attributed to the presence of a double linking in the 2 : 3-positions of the pyran nucleus and a hydroxyl group in the 5-position, and suggests that the phenolic hydroxyl groups are not essential in this connexion, since catechin tetramethyl ether also readily undergoes analogous condensation. W. R. ANGUS.

Condensation of aldehydes and phenols. V. *m*-Chlorobenzylidenedi-β-naphthol [*m*-chlorophenyldi-2-hydroxy-α-naphthylmethane]. O. DISCHENDORFER and H. MANZANO (Monatsh., 1931, **57**, 20—30).—*m*-Chlorobenzaldehyde and β-naphthol condense in presence of acetic and hydrochloric acids at the ordinary temperature forming m-*chlorophenyldi*-2-*hydroxy*-α-*naphthylmethane* (+AcOH), m. p. (solvent-free) 178—179° after slight previous sintering (*monosodium* salt; *diacetate*, m. p. 216—217°; *dibenzoate*, m. p. 164° after sintering at 162°; *monomethyl ether*, m. p. 168°), converted by treatment with warm acetic and sulphuric acids into ms-m-*chlorophenyldinaphthopyran* (9-m-*chlorophenyl*-1 : 2 : 7 : 8-*dibenzoxanthen*), m. p. 191—192°. This pyran is also formed when the initial condensation is carried out in the warm. Oxidation of the methane with aqueous-alcoholic sodium hypobromite gives *dehydro*-m-*chlorobenzylidenedi*-β-*naphthol*, m. p. 199°, whilst oxidation of the pyran with manganese dioxide and hydrochloric acid in acetic acid and treatment of the resulting solution with ferric chloride gives ms-m-*chlorophenyldinaphthopyrylium chloride ferrichloride*, m. p. 225—226° after darkening. This is decomposed by aqueous acetone to ms-m-*chlorophenyldinaphthopyranol* (9-m-*chlorophenyl*-1 : 2 : 7 : 8-*dibenzoxanthhydrol*), m. p. 254—255° after darkening at 250° [*chloride mercurichloride*, m. p. 272° after darkening from 225°; *perbromide*, $C_{27}H_{16}OClBr_3$, m. p. 205—206° (decomp.) after slight previous sintering; *perchlorate*, m. p. 285° (decomp.) after darkening from 260°; *ethyl ether*, m. p. 215—216° after slight sintering, prepared by the action of alcohol on the above ferrichloride; *methyl ether*, m. p. 217—218° after slight sintering]. H. BURTON.

Third *o*-hydroxynaphthaldehyde; isomeric benzocoumarins. T. BOEHM and E. PROFFT (Arch. Pharm., 1931, **269**, 25—37).—2-Acetoxy-3-naphthoyl chloride, m. p. 99—100° (cf. Graff, A., 1909, i, 665) is hydrogenated by Rosenmund's method (A., 1918, i, 300) to 2-*acetoxy*-3-*naphthaldehyde*, m. p. 100—101° (p-*nitrophenylhydrazone*, m. p. 213—214°; *semicarbazone*, m. p. 211—212°; *oxime*, m. p. 202—203°), hydrolysed by alkali to 2-*hydroxy*-3-*naphthaldehyde*, yellow, m. p. 99—100° [*phenylhydrazone*, m. p. 246—248°; p-*nitrophenylhydrazone*, m. p. 271—273°; *semicarbazone*, m. p. above 270°; *oxime*, m. p. 207° (decomp.); *anil*, m. p. 158—159°]. This gives normal condensation *products*, m. p. 207—208°; m. p. 188—189°; m. p. 162—163°, and m. p. 112—113° (*acetyl* derivative, m. p. 142—143°), respectively, with 1 mol.

of acetone, acetophenone, ββ-diketopentane, and ethyl oxaloacetate. With acetic anhydride and sodium acetate at 180° for 3 hrs. it gives 6 : 7-*benzocoumarin*, m. p. 163—164°, which is also obtained by heating its 3-carboxylic acid (below). The compound to which von Pechmann and Welsh (A., 1884, 1346) ascribed this formula was probably 7 : 8-benzocoumarin. β-Naphthol, malic acid, and sulphuric acid yield only 5 : 6-benzocoumarin. The hydroxyaldehyde with aniline and malonic acid in alcohol affords 6 : 7-*benzocoumarin-3-carboxylic acid*, m. p. 258—259°. In presence of piperidine it gives with ethyl malonate, *ethyl* 6 : 7-*benzocoumarin-3-carboxylate*, m. p. 157—158°, with ethyl acetoacetate, 3-*acetyl*-6 : 7-*benzocoumarin*, m. p. 209—210° (p-*nitrophenylhydrazone*, m. p. 266—267°), with methyl benzoylacetate, 3-*benzoyl*-6 : 7-*benzocoumarin*, m. p. 225°, and with ethyl cyanoacetate, 3-*cyano-4-cyanocarbethoxymethyl*-3 : 4-*dihydro*-6 : 7-*benzocoumarin*, m. p. 158—159°

H. E. F. NOTTON.

Closing of heterocyclic rings in indigoid dyes. I. S. IOFFE and R. F. MAZEL (J. Russ. Phys. Chem. Soc., 1930, **62**, 2001—2012).—The action of chlorosulphonic acid on acetylenedithiosalicylic acid produces closure of heterocyclic rings giving thioindigotin. Under analogous conditions ethylenedianthranilic and ethylenedithiophenolcarbonic acids were unchanged.

E. B. UVAROV.

Syntheses of pyrroles and dipyrrylethanones. H. FISCHER and P. VIAUD (Ber., 1931, **64**, [*B*], 193—200).—2 : 4-Dimethylpyrrole is transformed by trichloroacetonitrile and hydrogen chloride in chloroform through the *ketimine hydrochloride* into 5-*trichloroacetyl*-2 : 4-*dimethylpyrrole*, m. p. 108—109°, stable towards boiling alcohol but converted by zinc dust and glacial acetic acid into 5-acetyl-2 : 4-dimethylpyrrole, m. p. 119—120°. 3-*Bromo-5-trichloroacetyl*-2 : 4-*dimethylpyrrole*, m. p. 145—146°, is described. The following compounds, including the non-analysed ketimine hydrochlorides, are analogously prepared: *ethyl* 3-*trichloroacetyl*-2 : 4-*dimethylpyrrole-5-carboxylate*, m. p. 173—174°; 5-*trichloroacetyl*-2 : 4-*dimethyl-3-ethylpyrrole*, m. p. 101—102°, whence 5-*acetyl*-2 : 4-*dimethyl-3-ethylpyrrole*, m. p. 111—112°; 5-*trichloroacetyl*-2 : 3 : 4-*trimethylpyrrole*, m. p. 114—115°, whence 5-acetyl-2 : 3 : 4-trimethylpyrrole, m. p. 135—136°; 3-*acetyl*-5-*trichloroacetyl*-2 : 4-*dimethylpyrrole*, m. p. 145—146°; 3-*bromo-5-chloroacetyl*-2 : 4-*dimethylpyrrole*, m. p. 184—186°. 2 : 4-Dimethylpyrrole is converted by ethyl cyanoformate and hydrogen chloride in chloroform into *ethyl* 2 : 4-*dimethylpyrrole-5-glyoxylate*, m. p. 60—61°, readily hydrolysed to the corresponding *acid*, m. p. 164—165° (decomp.). Propaldehyde and 3-acetyl-2 : 4-dimethylpyrrole in presence of a little hydrochloric acid afford *ethyldi*-3-*acetyl*-2 : 4-*dimethylpyrrylmethane*, m. p. 208—209°; analogously, *n*-butaldehyde gives *propyldi*-3-*acetyl*-2 : 4-*dimethylpyrrylmethane*, m. p. 213—214°, whereas crotonaldehyde gives only a small amount of material, m. p. 236—238°. Addition of 2 : 4-dimethylpyrrole and 5-chloroacetyl-2 : 3 : 4-trimethylpyrrole in ether to an ethereal solution of magnesium ethyl bromide gives 3 : 4 : 5-*trimethylpyrryl*-3′ : 5′-*dimethylpyrryl*-2 : 2′-*ethan-α-one*, m. p. 168°. The following compounds are prepared analogously: 3 : 5-*dimethylpyrryl*-3′ : 5′-*dimethyl*-4′-*ethylpyrryl*-2 : 2′-*ethan-α-one*, m. p. 162—163°, and possibly a *dimeride*, m. p. 229° (corr.); 3 : 5-*dimethyl-4-ethylpyrryl*-3′ : 5′-*dimethylpyrryl*-2 : 2′-*ethan-α-one*, m. p. 156°; 3 : 4 : 5-*trimethylpyrryl*-3′ : 5′-*dimethyl*-4′-*ethylpyrryl*-2 : 2′-*ethan-α-one*, m. p. 157°; *di*-3 : 5-*dimethylpyrryl*-2 : 2′-*ethan-α-one*, m. p. 179° (corr.). According to the amount of reagent used, 5-chloroacetyl-2 : 4-dimethyl-3-ethylpyrrole is converted by sulphuryl chloride in ether into a *substance* $C_{10}H_{13}ONCl_2$, m. p. 123—125°, or 5-chloroacetyl-4-methyl-3-ethylpyrrole-2-aldehyde, m. p. 113—114°. 2 : 4-Dimethylpyrrole-3-propionic acid and chloroacetonitrile afford *chloroacetylcryptopyrrolecarboxylic acid*, $C_{11}H_{14}O_3NCl$, m. p. 212—213°. 5-*Anilinoacetyl*-2 : 3 : 4-*trimethylpyrrole*, m. p. 194—196°, 5-*anilinoacetyl*-2 : 4-*dimethylpyrrole*, m. p. 207°, 3-*bromo*-5-*anilinoacetyl*-2 : 4-*dimethylpyrrole*, m. p. 205—210° (decomp.), and 5-*anilinoacetyl*-2 : 4-*dimethyl-3-ethylpyrrole*, m. p. 181—183°, are described.

H. WREN.

Reaction of organic halides with piperidine. I. Alkyl bromides. J. SEMB and S. M. MCELVAIN (J. Amer. Chem. Soc., 1931, **53**, 690—696).—Piperidine (2 mols.) reacts with *n*- and *sec.*-alkyl bromides and aralkyl bromides (1 mol.) in light petroleum at 90° forming usually 1-alkylpiperidines; the *sec.*-bromides react much less readily than the *n*-derivatives. *tert.*-Alkyl bromides and *cyclo*hexyl bromide undergo loss of hydrogen bromide; reaction is more rapid at 125—135° than at 90°. 1-*Methyl*cyclo*hexyl bromide* has b. p. 65—66°/19 mm.; this also eliminates hydrogen bromide.

H. BURTON.

Hydrogenation of α-picoline under pressure in presence of pairs of catalysts. Comparative action of osmium and nickel in presence of rare earths. V. S. SADIKOV and P. I. ASTRACHANTZEV (J. Russ. Phys. Chem. Soc., 1930, **62**, 2071—2090).—Hydrogenation was carried out in autoclaves, using as catalyst osmium oxide, osmium and cerium oxides, osmium and lanthanum oxides, and osmium and zirconium oxides, and was repeated using nickel instead of osmium. The products of hydrogenation in each case were investigated, and the action of the various catalysts used is discussed.

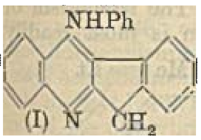
E. B. UVAROV.

Two isomeric cyanoketophenylmethylpyridines. N. TROCCOLI (Annali Chim. Appl., 1931, **21**, 41—45).—The *sodium*, *potassium*, *barium*, *copper*, *nickel*, and *cobalt* salts of 5-cyano-6-keto-4-phenyl-2-methyldihydropyridine and 5-cyano-6-keto-2-phenyl-4-methyldihydropyridine (cf. Issoglio, A., 1905, i, 609) have been prepared.

T. H. POPE.

Synthesis of quinoline compounds from arylamides of carboxylic acids. II. J. VON BRAUN, A. HEYMONS, and G. MANZ (Ber., 1931, **64**, [*B*], 227—235; cf. this vol., 236).—It appears that every straight-chained aliphatic and fatty-aromatic acid is capable, under suitable conditions, of conversion into the 4-anilino-derivative of a 2- and 3-alkylated quinoline. Polycyclic compounds are obtained from the dianilides of pimelic and *o*-phenylenediacetic acid in good yield, whereas the reaction is less successful with adipic and hexahydro-*o*-phenylenediacetic acids

and fails with sebacic and succinic acids. *n*-Butyranilide is converted by phosphorus pentachloride into *4-anilino-3-ethyl-2-propylquinoline*, m. p. 90—92° (*hydrochloride*, m. p. 234°), whilst heptanilide affords *4-anilino-3-n-amyl-2-n-hexylquinoline*, b. p. 216—220°/0·3 mm. (*hydrochloride*, m. p. 183°; *picrate*, m. p. 107°). Stearanilide gives *4-anilino-3-n-hexadecyl-2-n-heptadecylquinoline*, m. p. 53—54° (*hydrochloride*, m. p. 107°). Adipdianilide is converted into *4-anilino-2 : 3-trimethylenequinoline*, $C_6H_4<\begin{matrix}C(NHPh):CH\cdot CH_2\\N:CH\cdot CH_2\end{matrix}>CH_2$, decomp. 173° (*hydrochloride*, decomp. about 320° after darkening at 200°), in addition to compounds formed by condensation of several molecules. Pimeldianilide is converted with great readiness into *anilinotetrahydroacridine*, m. p. 232° (*hydrochloride*, m. p. 252°), transformed by alcohol and an excess of sodium into *as*-octahydroacridine, m. p. 83°. Treatment of the anilino-derivative with concentrated hydrochloric acid at 190—200° affords *tetrahydroacridone*, not molten below 360°, converted by distillation over lead oxide into acridone, m. p. 348°, and by subsequent treatment with zinc dust into acridine, m. p. 105°. With phosphoryl chloride and phosphorus pentachloride, tetrahydroacridone yields ms-*chlorotetrahydroacridine*, m. p. 68°, transformed by an excess of piperidine at 160° into ms-*piperidinotetrahydroacridine*, m. p. 112°. Succindianilide and sebacdianilide yield mainly non-crystalline, viscous products; occasionally, succinanil and (?) the cyclic *amidine* $\begin{matrix}CH_2\cdot C(:NPh)\\CH_2\cdot CO\end{matrix}>NPh$, m. p. 138°, can be obtained from the former compound. *o-Phenylenediacetdianilide*, m. p. 230°, gives *4-anilino-o-phenylenequinolylenemethane* (I), m. p. 242—244°.



cis- and trans-*Hexahydro-o-phenylenediacetdianilide*, m. p. 289—290° and 291—295°, respectively, appear to be converted into the same 4-anilinohexahydro-*o*-phenylene-α-quinolylenemethane, m. p. 204—206° (*hydrochloride*, m. p. 291° after darkening above 275°). H. WREN.

Dyes derived from thiohydantoin. I. G. P. PENDSE and S. DUTT (J. Indian Chem. Soc., 1930, 7, 953—956).—Thiohydantoin condenses with aromatic nitroso- and oximino-compounds in acetic anhydride, forming readily hydrolysable acetyl derivatives of 5-aryliminothiohydantoins and 5-arylaminoiminothiohydantoins (from nitrosoamines). Thus, thiohydantoin and nitrosobenzene give *5-anilothiohydantoin*, m. p. above 300°; with phenylmethylnitrosoamine, *5-phenylmethylaminoiminothiohydantoin*, m. p. 156°, results. The following are described: 5-p-*hydroxyanilo-*, m. p. above 300°; 5-β-*hydroxynaphthylimino-*, m. p. 184° (from nitroso-β-naphthol), 5-4′-*hydroxy-methyl*-3′-iso*propylanilo-*, m. p. above 300°; 5-2′ : 4′-*dihydroxyanilo-*, m. p. 278°; 5-p-*dimethylaminoanilo-*, m. p. 212°; 5-p-*diethylaminoanilo-*, m. p. 162°; 5-*phenylethylaminoimino-*, m. p. 174°; 5-*diphenylaminoimino-*, m. p. 191°; 5-*phenyl*-α- and -β-*naphthylaminoimino-*, m. p. above 300°, respectively; 5-β-*naphthylmethylaminoimino-*, m. p. above 300°; 5-N-*carbazolylimino-*, m. p. above 300°; 5-p-*dimethylamino-o-hydroxyanilo-*, m. p. above 300°; 5-p-*diethylamino-o-hydroxyanilo-*, m. p. above 300°, and 5-*phenylhydroxylaminoimino-thiohydantoins*, m. p. above 300°. Similar condensation *products*, all of which have m. p. above 300°, are prepared from thiohydantoin and oximinocamphor, oximino-1-phenyl-3-methylpyrazolone, violuric acid, benzilmonoxime, and phenanthraquinonemonoxime; it is presumed that these oximino-compounds are first converted into nitroso-derivatives. Most of the above compounds dye wool and silk from a slightly alkaline bath with a brown (light–dark) shade. H. BURTON.

3 : 5-Diketopyrazolidine derivatives. I. T. TSUMAKI (Bull. Chem. Soc. Japan, 1931, 6, 1—9).—Hydrazobenzene on acylation gives sometimes acylhydrazobenzene and sometimes acylbenzidines (Stern, A., 1884, 1015; Bischoff, A., 1889, i, 278; Biehringer and Busch, A., 1903, ii, 296; Kaufmann, B., 1927, 155). Hydrazobenzene reacts with malonyl chloride in ether to form benzidine hydrochloride and *1 : 2-diphenyl-3 : 5-diketopyrazolidine* (I), m. p. 178° (*oximino*-derivative, m. p. 163—164°; *ammonium* salt, m. p. 138—139°), hydrated by dilute hydrochloric acid to *1 : 2-diphenyl-3 : 4-dihydroxy-5-pyrazolidone*, m. p. 160—162°, and condensing with aldehydes and ketones at 100° to form 4-alkylidene derivatives (*benzylidene* derivative, m. p. 160—165°; *furfurylidene*, m. p. 157—158°; *cinnamylidene*, m. p. 190—192°; iso*propylidene*, m. p. 113°; *α-phenylethylidene*, m. p. 148—149°; *diphenylmethylene* derivative, m. p. 269°), which with alkali regenerate the carbonyl compound and I. Hot alcoholic potassium hydroxide destroys I. Carbon suboxide and hydrazobenzene in ethereal solution give some diphenyldiketopyrazolidine. G. DISCOMBE.

Thio-orotic [2-thiouracil-4(6)-carboxylic] acid. M. BACHSTEZ (Ber., 1931, 64, [*B*], 322—326; cf. A., 1930, 781).—Ethyl oxalacetate is condensed with thiocarbamide in the presence of alcohol containing a little hydrochloric acid and the unstable ester thus produced is immediately hydrolysed by alcoholic potassium hydroxide to *2-thiouracil-4(6)-carboxylic acid*, $CS<\begin{matrix}NH\cdot C(CO_2H)\\NH-\!\!-\!\!-CO\end{matrix}>CH$, decomp. 322° (corr.), which is more strongly acidic than orotic acid. The *sodium*, *potassium*, and *ammonium*, *mono-*, *di-*, and *tri-silver*, *lead*, *copper*, and *mercury* salts are described. The action of hydrogen chloride on the acid suspended in methyl alcohol leads to the formation of the *O-methyl* derivative, $C_6H_6O_3N_2S$, m. p. 261° (corr., decomp.). Treatment of the disilver salt of thio-orotic acid with methyl iodide in methyl alcohol at 100° affords the *O*-methyl derivative of orotic acid, m. p. 298—300° (corr., decomp.), identical with the product described previously (*loc. cit.*), hydrolysed to orotic acid. Thio-orotic acid is unchanged by treatment with alcoholic sodium ethoxide and ethyl chloroacetate. Conversion of thio-orotic acid into its sodium salt followed by treatment with benzyl chloride gives the N-*benzyl* compound, $C_{12}H_{10}O_2N_2S$, m. p. 264° (decomp.). H. WREN.

Organic catalysts. V. Fission of α-ketonic acids. W. LANGENBECK, R. HUTSCHENREUTER, and R. JUTTEMANN (Annalen, 1931, 485, 53—61).—The catalytic decomposition of phenylglyoxylic acid in presence of aniline (cf. A., 1930, 714) is accompanied

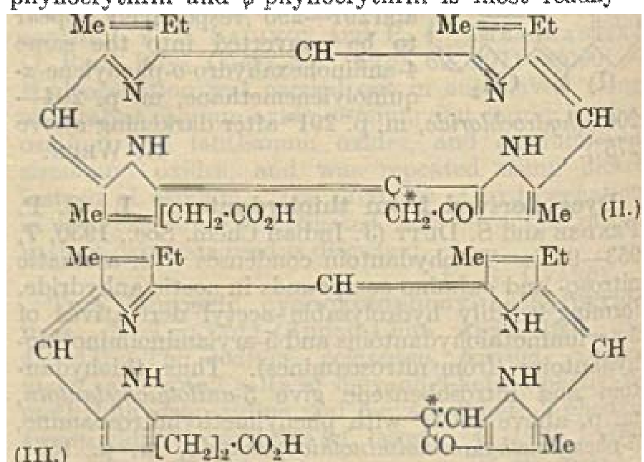
by formation of 1 : 2 : 3 : 4 : 5-*pentaphenyldihydroglyoxaline* (+$2H_2O$, not evolved at 150° in a vacuum) [*perchlorate*; *periodide* (decomp. 250° in a vacuum with evolution of iodine); *perbromide*; *hydrochloride*], the constitution of which is assumed from its formation by interaction of benzoinanilanilide with benzaldehyde; it is also formed by successive treatment of desyl chloride with aniline and benzaldehyde. By an empirical method, starting from methylamine, and studying the effects of substitution on the activity of the products as catalysts, the following series was realised: methylamine<glycine<phenylaminoacetic acid<3-aminoindoxyl. The last was prepared by hydrogenation of isatin-3-oxime in presence of platinum oxide (cf. Baeyer and Knop, Annalen, 1866, **140**, 37). H. A. Piggott.

Synthesis of 1 : 2 : 4-triazoles. I. T. N. Ghosh and M. V. Betrabet (J. Indian Chem. Soc., 1930, **7**, 899—903).—Ethyl acetamidoformate (acetylurethane) and *p*-nitrophenylhydrazine react in presence of xylene and phosphoric oxide at 125—130°, forming *acetylurethane*-p-*nitrophenylhydrazone*, m. p. 241° (isolated from the xylene), and 5-*keto*-1-p-*nitrophenyl*-3-*methyl*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*, m. p. 259° (isolated from the phosphoric acid residue). The triazole reacts with anthranilic acid in phosphorus trichloride to give 5-o-*carboxyanilo*-1-p-*nitrophenyl*-3-*methyl*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*, m. p. 308°, and the *quinazolone*, $C_6H_4<^{CO\cdot N\cdot CMe:N}_{N=C\text{——}N\cdot C_6H_4\cdot NO_2}$ m. p. 293°. Acetylurethane and phenylhydrazine afford *acetylurethanephenylhydrazone*, m. p. 142—143°, and 5-*keto*-1-*phenyl*-3-*methyl*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*, m. p. 166—167°, whilst 4-phenylthiosemicarbazide and the urethane give a mixture of *α-phenylthiocarbamido-γ-carbethoxyacetamidine*, m. p. 178° (corresponding α-p-*tolyl* derivative, m. p. 203°), and 5-*keto*-3-*methyl*-2 : 5-*dihydro*-1 : 2 : 4-*triazole*-1-*thiocarbonanilide*, m. p. 243° (corresponding p-*toluidide*, m. p. 228°, and *allylamide*, m. p. 201°). The first-named amidine is oxidised by ferric chloride to the *compound*, NHPh·CS·N:N·CMe:N·CO_2Et, m. p. 225° (decomp.). Acetylurethane and thiosemicarbazide give 5-*keto*-3-*methyl*-2 : 5-*dihydro*-1 : 2 : 4-*triazole*-1-*thiocarbonamide*, m. p. 222°, as the sole product. H. Burton.

Analogy in the chemistry of pyrazole and tetrazole. F. Konek (Math. Nat. Anz. Ungar. Akad. Wiss., 1929, **46**, 340—345; Chem. Zentr., 1930, ii, 2902; cf. A., 1920, i, 880; Stollé, A., 1929, 828).—A discussion. The formation of mercuridithiobisantipyrine by shaking dithiobisantipyrine with mercury depends on radical dissociation of the sulphur atoms. A. A. Eldridge.

Complex formation between caffeine and salicylic acid. R. Labes (Arch. exp. Path. Pharm., 1930, **158**, 42—52).—The constant of the reaction in which sodium salicylate and caffeine combine to form a complex is found, by a partition coefficient method, to be between 30 and 40. A. Cohen.

Chlorophyll. XV. Phyllo- and pseudo-phyllo-erythrin. H. Fischer, O. Moldenhauer, and O. Süs (Annalen, 1931, **485**, 1—25; cf. this vol., 102).—*ψ*-Phylloerythrin (A., 1930, 1194) is identical with natural phylloerythrin in all respects except the ability to take up chloroform of crystallisation; it becomes identical in this respect also after treatment with fuming sulphuric acid. It is unaffected by heating with formic acid, or by bromine in acetic acid; chlorination with hydrogen peroxide and hydrochloric acid gives a yellow amorphous product which yields rhodoporphyrin and unchanged *ψ*-phylloerythrin on reduction with hydriodic acid and red phosphorus in acetic acid at 100°. The same final result is obtained by oxidation with hydrogen peroxide in sulphuric acid. Phyllo- and *ψ*-phyllo-erythrin have a carboxyl and a carbonyl group, which together account for all the oxygen present. They are reduced by sodium ethoxide and hydrazine hydrate at 165—170° (Wolff–Kishner) to *deoxyphylloerythrin* [*methyl* ester, m. p. 264° (*iron* and *copper* salts)], in which the carbonyl group has been completely reduced to methylene. This is also formed by heating phylloerythrinsemicarbazone with alcoholic sodium ethoxide at 165°. Of the possible structures for phylloerythrin suggested by its decomposition by alkalis (*loc. cit.*), that of 6-aldehydo-1 : 3 : 5 : 8-tetramethyl-2 : 4-diethylporphin-7-propionic acid is improbable on account of the marked differences between the spectra of 1 : 3 : 5 : 6 : 7-*pentamethyl*-2 : 4-*diethylporphin*-8-*propionic acid* (I, see below) and deoxyphylloerythrin, which should then be the isomeride in which the groups in the 7- and 8-positions are interchanged. The alternatives II and III are advanced as most probable, a lower homologue with a *cyclo*butene ring in place of the *cyclo*pentene ring of II being rejected on spatial and other considerations. It is considered that action of alkali first leads to fission between the C* and its adjacent carbonyl group. The isomerism of phylloerythrin and *ψ*-phylloerythrin is most readily



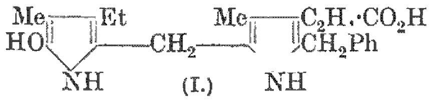
explained on formula II, the former being assigned the ketonic and the latter the enolic structure.

The following derivatives of phylloerythrin are described: *potassium* salt, *semicarbazone* [*methyl* ester, m. p. 270° (decomp.)], *hydrazone*, and *oxime* (*methyl* ester). In addition to the semicarbazone and oxime (methyl ester), the *zinc* and *iron* salts of *ψ*-phylloerythrin are prepared (derivatives of the ester being in every case prepared from the ester). Fusion of 5-bromo-3 : 4′-dimethyl-4 : 3′-diethyl-5′-bromomethylpyrromethene and 3 : 3′ : 4′ : 5′-tetramethyl-

pyrromethene-4-propionic acid hydrobromides (A., 1928, 76) with methylsuccinic acid at 120—160° or with succinic acid at 210° gives I (isolated as *methyl* ester, m. p. 242°), accompanied by small amounts of meso- and ætio-porphyrins. Diacetyldeuteroporphyrin dimethyl ester (*dioxime*; *disemicarbazone*) is reduced by the Wolff–Kishner method to a mixture of hæmo- and meso-porphyrins (identified spectroscopically). A green crystalline *substance* (oxime?) obtained by interaction of chloroporphyrin e_5 with hydroxylamine is described, as also is the hydrolysis of the trimethyl ester of chlorin e to a crystalline form of the acid and a small amount of a monomethyl ester.

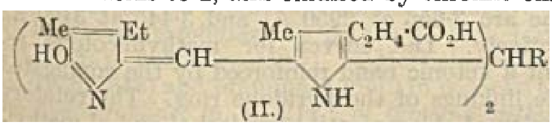
H. A. PIGGOTT.

Bile pigments. X. Neo- and neoxanthobilirubic acids and partial synthesis of mesobilirubin and mesobilirubinogen (urobilinogen). H. FISCHER and R. HESS (Z. physiol. Chem., 1931, 194, 193—228).—Treatment of mesobilirubin with boiling resorcinol for 30 sec. gives *neoxanthobilirubic acid* (probably *5'-hydroxy-3 : 4'-dimethyl-3'-ethyl-4-β-carboxyethylpyrromethene*), yellow, m. p. 229° {*bromo*-derivative, not melted at 350° after darkening at 171°, sintering when heated further, and then swelling at 213°; *phthalide*, m. p. 298°; *methyl* ester, m. p. 190° [*benzeneazo*-derivative *dihydrochloride*, m. p. 193° (decomp.)]}, oxidised by nitric acid (*d* 1·39) to methylethylmaleimide. Prolonged treatment of the acid with boiling hydriodic and acetic acids gives cryptopyrrole and hæmopyrrolecarboxylic acid, whilst reduction with hydriodic and acetic acids at 100°, sodium amalgam and aqueous alkali, or hydrogen in presence of colloidal palladium and dilute alkali affords *neobilirubic acid*, m. p. 184°, which is the corresponding pyrromethane (colourless). The *benzylidene* derivative, m. p. 248°, of this appears to be identical with benzylidenebilirubic acid (A., 1924, 1092), whilst *methyl benzylideneneobilirubate*, m. p. 212°, is identical with methyl benzylidenebilirubate (*loc. cit.*). Reduction of the benzylidene derivative with hydriodic and acetic acids at 100° gives *benzylneobilirubic acid* (I), m. p. 189°, identical with the compound described by Fischer and Niemann (A., 1925, i, 1198), which when treated with bromine in acetic acid is converted into benzylideneneobilirubic acid. Condensation of neoxanthobilirubic acid with benzaldehyde in presence of



(I.)

alkali or, better, with 25% hydrochloric acid gives the *compound* (II, R=Ph), m. p. 257°, reduced by hydriodic and acetic acids to I, and oxidised by chromic oxide



(II.)

in acetic acid to benzoic acid and oily products. Condensation *products*, similar to II, are also prepared from the following aldehydes: *o*-nitrobenzaldehyde, m. p. -59°; *p*-dimethylaminobenzaldehyde, m. p. 239°; ethyl 2-aldehydo-4-methylpyrrole-3 : 5-dicarboxylate, m. p. 246°, and acetaldehyde, m. p. 267°. When condensation is effected with acetone, the resultant *compound*, m. p. 250°, is formed by way of the first produced mesityl oxide. Condensation of neoxanthobilirubic acid with formaldehyde gives K-*mesobilirubin* (II, R=H), m. p. 310° (*methyl* ester *dihydrochloride*, m. p. 190°), which is probably identical with mesobilirubin. Reduction of this with sodium amalgam and water affords K-*mesobilirubinogen*, m. p. 192°, which appears to be crystallographically identical with natural mesobilirubinogen. Reduction of *K*-mesobilirubin with hydriodic and acetic acids gives bilirubic and neobilirubic acids, whilst treatment with boiling resorcinol affords neoxanthobilirubic acid.

H. BURTON.

Structure of hæmocyanin. I. Isolation of "hæmocuprin," the copper-containing component of hæmocyanin from *Octopus vulgaris*. A. SCHMITZ (Z. physiol. Chem., 1931, 194, 232—247). —A more detailed account of work previously reviewed (A., 1930, 1304).

H. BURTON.

Zerevitinov determination with hæmins and pyrrole dyes. IV. H. FISCHER and P. ROTHEMUND (Ber., 1931, 64, [*B*], 201—210; cf. A., 1928, 903).—The use of a Grignard solution more concentrated than that recommended by Zerevitinov (cf. Haurowitz and Zirm, A., 1929, 334) appears disadvantageous, since a portion of the compound separates from the solution which must then be heated before being measured, whilst eventual reseparation increases the difficulty of securing uniform conditions.

Treatment of hæmin with magnesium phenyl bromide in presence of nitrogen or oxygen yields diphenyl in amount much greater than that formed in blank experiments. Reaction is considered to occur in accordance with the scheme $2{>}Fe'''Cl+2MgPhBr=2{>}Fe''+2MgBrCl+Ph{\cdot}Ph$. Confirmation of this view is obtained spectroscopically, but the large quantity of diphenyl which is produced requires the assumption that the main action of the hæmin is catalytic. Deuterohæmin similarly yields diphenyl in quantity far exceeding the "blank value," whereas with ætioporphyrin I and mesoporphyrin Iα dimethyl ester only a slight excess is observed. Hæmatoporphyrin hydrochloride yields an excess of diphenyl and phæophorbid *a* behaves essentially in the same manner as hæmin. It thus appears that the Zerevitinov determination is not in a position to give constant values with hæmin and, possibly, with all hæmins. The results are more consistent with porphyrins, but variable with chlorophyll derivatives. Complex salts of the porphyrins give non-uniform results. The silver salts, which on account of their spectroscopic identity with zinc and copper salts are regarded as containing bivalent silver, yield variable results. The occasional disclosure of one active hydrogen atom instead of the theoretical none is attributed to the catalytic properties of the porphyrin molecule; this view is supported by the high value for active hydrogen obtained with chlorophyll-porphyrin copper salts.

H. WREN.

ψ-Bases in the *iso*oxazole series. IV. E. P. KOHLER and W. F. BRUCE (J. Amer. Chem. Soc., 1931, 53, 644—651).—The product from 3-phenylbenz*iso*oxazole and ethyl sulphate at 130—140° is converted

by successive treatment with 6*N*-hydrochloric acid and ferric chloride into 3-*phenyl-2-ethylbenz*isooxa*zolinium ferrichloride*, m. p. 134° (corresponding *chloride*, m. p. 95—97°; *mercurichloride*, m. p. 119—120°; *picrate*, m. p. 132—133°; *perchlorate*, m. p. 183—184°). Decomposition of the initial reaction mixture with alkali hydroxide gives the ψ-*base*, $C_6H_4Bz(O·NHEt)$-*o*, m. p. 79—80° [*oxime*, m. p. 135·6° (decomp.); *phenylcarbimide* derivative, m. p. 128° (*oxime*, decomp. 145—150° according to the rate of heating]), which can be used for the preparation of the above salts. The ψ-base passes on keeping (or when heated to 95°/vac.) into 4-*phenyl-2-methyl*-5 : 6-*benzometoxazine*, $C_6H_4<\begin{matrix}CPh:N\\O—CHMe\end{matrix}$, b. p. 177°/11 mm., m. p. 33—35° (*hydrochloride*, m. p. 104°, decomp. slowly at 110°; *ferrichloride*, m. p. 139—140°; *picrate*, m. p. 128—129°; *mercurichloride*, m. p. 180—181°), degraded by dilute acid or phenylhydrazine to ammonia, acetaldehyde, and *o*-hydroxybenzophenone. Methylation of I with methyl sulphate and treatment of the product with ferric chloride and hydrochloric acid gives 4-*phenyl*-2 : 3-*dimethyl*-5 : 6-*benzometoxazinium ferrichloride*, m. p. 119—120°, readily hydrolysed by water to acetaldehyde, methylamine, and *o*-hydroxybenzophenone. H. BURTON.

Thiazoles. XVI. Synthesis of aminotoluthiazoles and derivatives from 2 : 5-diaminotoluene-4-thiosulphuric acid. M. T. BOGERT and M. G. SEVAG (J. Amer. Chem. Soc., 1931, **53**, 660—669).—2 : 5-*Diaminotoluene-4-thiosulphuric acid*, k_{25}—$5·56\times10^{-6}$, is prepared from 2 : 5-diaminotoluene by a slight modification of Bernthsen's method (A., 1889, 775). Condensation of the acid with *o*- and *m*-nitrobenzaldehydes gives 6-*amino*-2-o-*nitrophenyl*-, m. p. 144° (corr.), and 6-*amino*-2-m-*nitrophenyl-5-methylbenzthiazoles*, m. p. 233·5° (corr.). With *p*-nitrobenzaldehyde, 6-p-*nitrobenzylideneamino*-2-p-*nitrophenyl-5-methylbenzthiazole*, m. p. 279° (corr.), results. This is unaffected by boiling hydrochloric or 30% sulphuric acid, but is reduced by tin and hydrochloric acid to 6-*amino*-2-p-*aminophenyl-5-methylbenzthiazole*, m. p. 255·5° (corr.). 6-*Amino*-2-op-*dinitrophenyl-5-methylbenzthiazole*, m. p. 239·2° (corr.), is reduced similarly to the corresponding *triamino*-compound, m. p. 285·5°. 6-*Amino*-2-o-*aminophenyl-5-methylbenzthiazole*, m. p. 251° (corr.), and the isomeric *p*-aminophenyl derivative are converted by sulphonation and subsequent oxidation with sodium hypochlorite into dyes of the Columbia-yellow type. A thiosulphuric acid could not be prepared from 2 : 4-diaminotoluene. H. BURTON.

Monosubstituted carbohydrazides, their typical derivatives and formation of heterocyclic compounds from them. P. C. GUHA and M. A. HYE.—See this vol., 457.

Glutathione. VI. Preparation of oxidised glutathione. H. L. MASON (J. Biol. Chem., 1931, **90**, 409—416).—The conclusion of Hopkins (A., 1929, 1491) that aerial oxidation of glutathione leads to loss of nitrogen and sulphur is shown to be incorrect, the low analytical figures for these elements in the product being due to the presence of alcohol (approx. 1 mol. of glutathione : 2 mols. of alcohol), which is lost with difficulty even at 111° in a vacuum. Under the latter conditions some change takes place whereby carboxyl and amino-groups (in the ratio of 2 : 1) disappear. Quantitative oxidation of glutathione with ferricyanide or iodine in excess of iodide suggests the oxidation of the thiol group to disulphide. J. D. A. JOHNSON.

New lead iodide double salt of trigonelline. K. LENDRICH and F. MAYER (Z. Unters. Lebensm., 1930, **60**, 569—575).—Trigonelline has been isolated from coffee beans as the *plumbi-iodide*, $C_7H_7O_2N,PbI_2$, m. p. 217° (decomp.). J. GRANT.

Alkaloids of *Anabasis aphylla*. L. I. A. OREKHOV and G. MENSCHIKOV (Ber., 1931, **64**, [*B*], 266—274).—The dried plant is percolated with 95% alcohol containing 2% of ammonia. After removal of solvent the residue is treated with hydrochloric acid, from which the bases are liberated with sodium hydroxide and extracted with ether. The crude alkaloidal mixture (2·33% of the plant) is distilled under diminished pressure, giving fractions b. p. 136—138·5/12 mm. and about 200°/12 mm., of which the first has been investigated. Treatment of it with benzoyl chloride and sodium hydroxide affords lupinene, m. p. 68—69°, b. p. 265—266°/760 mm., $[\alpha]_D^{20}$ −23·62° in water (hydrochloride, m. p. 211·5—212·5°; chlorolupinan, b. p. 113°/7 mm., $[\alpha]_D^{20}$ −33·19° and its picrate, m. p. 146—147°), a little *O*-benzoyl-lupinine hydrochloride, and *benzoylanabasine*, $C_{17}H_{18}ON_2$, m. p. 82—83°, b. p. 222°/2 mm., $[\alpha]_D^{20}$ −127·23° in alcohol. *Anabasine* (probably 2-*piperidyl-3-pyridine*) is a pale yellow liquid, b. p. 104—105°/2 mm., 276°/760 mm., d^{20} 1·0455, n_D^{20} 1·5430, $[\alpha]^{20}$ −82·2°; the hygroscopic *hydrochloride*, $[\alpha]_D^{20}$ +9·23° in dilute hydrochloric acid, *picrate*, m. p. (indef.) 200—205°, and *nitrosoanabasine*, b. p. 176°/4 mm., d_{20}^{20} 1·1777, n_D^{14} 1·5698, $[\alpha]_D^{20}$ −155·0°, are described. The alkaloid is oxidised by permanganate to pyridine-3-carboxylic acid. Dehydrogenation of anabasine by silver acetate according to Tafel or by treatment with zinc dust results in the removal of six hydrogen atoms and yields a product, b. p. 292—294° (picrate, m. p. 151—152°), which appears to be identical with 2 : 3′-dipyridyl. H. WREN.

Nicotine and its derivatives. III. Chloronicotine and methylnicotone. T. M. LOWRY and H. K. GORE (J.C.S., 1931, 319—323).—The molecular extinction coefficients of nicotine and chloronicotine (Karrer and Takahashi, A., 1926, 626) show maxima at log ε=3·37 at 2600 Å. and 3·55 at 2700 Å., respectively; the corresponding values for methylnicotone (Karrer and Widmer, A., 1925, i, 1084) in water and *cyclo*hexane are 3·656 at 2950 Å. and 3·445 at 3100 Å., respectively. The curves for methylnicotone represent a ketonic band reinforced by the conjugated double linkings of the pyridone ring. The rotatory dispersion of chloronicotine in alcohol and of methylnicotone in water and ethyl acetate is simple. H. BURTON.

Lupin alkaloids. III. G. R. CLEMO, R. RAPER, and C. R. S. TENNISWOOD (J.C.S., 1931, 429—437).—*dl*-Lupanine and *d*-camphorsulphonic acid in acetone give d-*lupanine* d-*camphorsulphonate* (+$2H_2O$), m. p. 108—110°, $[\alpha]_D$ +45·5° in water, converted by

aqueous potassium iodide into the *hydriodide* ($+2H_2O$), m. p. 189°, $[\alpha]_D$ +45·5° in water, of *d*-lupanine, b. p. 185—186°/0·08 mm., m. p. 40° (lit. 44°), $[\alpha]_D$ +61·4° in acetone. The base from the above mother-liquors gave with *l*-camphorsulphonic acid the l-*camphorsulphonate* ($+2H_2O$), m. p. 110—113°, $[\alpha]_D$ −45·3°, of *l*-lupanine, b. p. 186—188°/1 mm., $[\alpha]_D$ −61° in acetone [*hydriodide* ($+2H_2O$), m. p. 190°, $[\alpha]_D$ −43·6°]. Reduction of *d*-lupanine with phosphorus and hydriodic acid gives *l*-sparteine, b. p. 130—135°/1 mm., $[\alpha]_D$ −11·3° in alcohol (cf. Willstatter and Marx, A., 1904, i, 613). Similar reduction of *l*-lupanine affords d-*sparteine*, b. p. 133—135°/1 mm., $[\alpha]_D$ +15·9° (*picrate*, m. p. 205—206°; *monohydriodide*, m. p. 229°).

Treatment of lupinine with phosphorus pentabromide in benzene yields bromolupinane, b. p. 103°/1 mm. [*methiodide*, m. p. 226—228° (decomp.)], converted by aqueous sodium acetate at 170—180° into lupinine and by boiling methyl-alcoholic alkali into a mixture of lupinine methyl ether, b. p. 84—85°/1 mm. (*methiodide*, m. p. 177—178°; *picrate*, m. p. 81—82°), and *l*-ψ-anhydrolupinine. The Hofmann degradation of ω-lupinyltrimethylammonium chloride as carried out by Karrer and Vogt (A., 1930, 1454) gives a base resembling ψ-anhydrolupinine rather than anhydrolupinine. The base, which contains some ω-*dimethylaminolupinane*, b. p. 95°/0·5 mm., $[\alpha]_D$ −37·7° in acetone (*dimethiodide*, m. p. 308°), affords a picrate, m. p. 152°, $[\alpha]_D$ −53° in ethyl acetate, the m. p. of which is not depressed by ψ-anhydrolupinine picrate; the crystalline forms of the picrates are not, however, always identical.

Chlorolupinane, potassium phthalimide, and a trace of copper powder at 210—220° give N(11)-*lupinylphthalimide*, m. p. 165°, reduced electrolytically in 20% sulphuric acid to N-*lupinyldihydroisoindole*, m. p. 88°, and hydrolysed by Ing and Manske's method (A., 1926, 1132) to 11-aminolupinane, b. p. 98°/1 mm. (*benzoyl* derivative, m. p. 131—132°). This base absorbs carbon dioxide readily, reacts with methyl succinate at 160—190°, forming *dilupinylsuccinamide*, m. p. 225—226°, and N(11)-*lupinylsuccinimide*, m. p. 137° (*methiodide*, m. p. 293—294°), and gives with methyl glutarate at 180° a mixture of *dilupinylglutaramide*, m. p. 193—195°, and *methyl* N(11)-*lupinylglutaramate*, m. p. 75—76°. The last-named compound could not be converted into lupinylglutarimide and it has not been possible to effect ring closure by elimination of water between the methylene group of the lupinyl residue and the carbonyl group of the amide or imide residue. Electrolytic reduction of lupinylsuccinimide as above gives N(11)-*lupinylpyrrolidine*, b. p. 155°/1 mm. [*dimethiodide*, m. p. 302° (decomp.)]. α-Methyloxysparteine (A., 1929, 1318) and bromine (1 mol.) in benzene afford the *hydrobromide*, m. p. 214°, of *bromo-α-methyloxysparteine*, m. p. 142°, which is unaffected by potassium hydroxide at 180°, hydrobromic acid, or boiling pyridine.

H. BURTON.

Lupin alkaloids. IV. Synthesis of octahydropyridocoline. G. R. CLEMO and G. R. RAMAGE (J.C.S., 1931, 437—442).—Distillation of lupinine acid with soda-lime (cf. Schopf and others,

A., 1928, 1144) gives basic and non-basic products. Reduction of the basic material (hydrogen; acetic acid; palladium) affords a *base* (I), $C_9H_{17}N$, b. p. 43—45°/0·5 mm. [*picrate*, m. p. 193—194°; *methiodide*, m. p. 333—335° (decomp.); *chloroaurate*, m. p. 166—167°], and material of b. p. 55—60°/0·5 mm. The non-identity of I with octahydropyridocoline (see below) indicates that lupinine has not the structure suggested by Karrer and others (A., 1929, 200) or that structural changes occur during the formation of I (cf. von Bruchhausen and Bersch, A., 1930, 1600; Winterfeld and Holschneider, this vol., 370).

Ethyl piperidine-2-carboxylate, γ-bromobutyronitrile, and potassium carbonate at 100° (bath) give γ-2-*carbethoxypiperidinobutyronitrile*, b. p. 170°/12 mm. (the use of an excess of the nitrile produces a quaternary salt, m. p. 184°), converted by alcoholic hydrogen chloride into *ethyl* γ-2-*carbethoxypiperidinobutyrate*, b. p. 169°/14 mm. This by the Dieckmann reaction gives *ethyl* 1-*keto-octahydropyridocoline*-2-*carboxylate*, b. p. 155°/15 mm., hydrolysed by 20% sulphuric acid to 1-*keto-octahydropyridocoline*, b. p. 107°/14 mm. (*semicarbazone*, m. p. 215°; *methiodide*, m. p. 210°). Reduction of this with sodium amalgam and alcohol gives 1-*hydroxyoctahydropyridocoline*, b. p. 120°/13 mm., m. p. 65—68°, whilst Clemmensen reduction affords *octahydropyridocoline*, b. p. 43°/0·5 mm., 75°/14 mm. [*picrate*, m. p. 213° (decomp.); *methiodide*, m. p. 283°; *chloroaurate*, m. p. 170°].

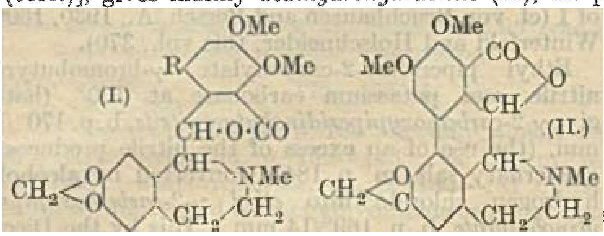
H. BURTON.

Mechanism of the oxidation of laudanosine. V. K. BHAGWAT, D. K. MOORE, and F. L. PYMAN (J.C.S., 1931, 443).—The compound $C_{14}H_8(OMe)_4$, m. p. 231° (corr.), obtained by oxidation of laudanosine with manganese dioxide and sulphuric acid (Pyman, J.C.S., 1909, **95**, 1266) or with mercuric acetate (Gadamer, A., 1916, i, 736) is 2 : 3 : 6 : 7-tetramethoxy-9 : 10-dihydroanthracene ($+0·5H_2O$ and $+0·5C_6H_6$), m. p. (anhydrous) 227° (Robinson, J.C.S., 1915, **107**, 267). Gadamer's assumption that the substance is tetramethoxydibenzyl, formed by dimerisation of free dimethoxybenzyl radicals, is invalid.

H. BURTON.

Synthesis of hydrastine. I. E. HOPE, F. L. PYMAN, F. G. P. REMFRY, and R. ROBINSON (J.C.S., 1931, 236—247; cf. Proc. C.S., 1912, **28**, 17).—Hydrastinine and nitromeconine in boiling alcohol give 80—90% of the theoretical amount of a mixture, m. p. about 160—170°, of *anhydrohydrastininemeconines* (*nitrohydrastines*) (I, $R=NO_2$), which is rapidly decomposed by hot acetic acid, regenerating the starting materials; trituration of the mixture with 10% hydrochloric acid affords a *hydrochloride*, m. p. 137—138°. Reduction of the mixture with tin, stannous chloride, and hydrochloric acid in acetic acid below 25° yields dl-*aminohydrastine*-a, m. p. 216—217° (corr.) [dihydrochloride, m. p. 267—268°; tartrate, m. p. 201—203° (corr.); *acetyl* derivative, m. p. 208—211°], and dl-*aminohydrastine*-b, m. p. 196—197° (corr.), separable through the sparing solubility of the above hydrochloride. Reduction of the diazonium chloride from aminohydrastine-*a* with stannous chloride and hydrochloric acid gives *hydrazinohydrastine*-a, m. p. 175° (corr.) [hydrogen oxalate, m. p. 225° (decomp.); *iso*propylidene deriv-

ative, m. p. 190°], oxidised by copper acetate in dilute acetic acid to *hydrastine*-a (I, R=H), m. p. 137—138° (corr.) [hydrochloride, decomp. above 165°; *picrate*, m. p. 219° (decomp.); d-*camphorsulphonate* (+0·5H_2O), m. p. 145° (corr.; decomp.) after sintering at 135°; *hydrogen* d-*tartrate* (+3·5H_2O), m. p. 108—110° (corr.; decomp.)]. Similar oxidation of *hydrazinohydrastine*-b (+$CHCl_3$), m. p. (solvent-free) 183—184° (corr.) [iso*propylidene* derivative, m. p. 217—218° (corr.)], gives mainly *dedihydrohydrastine* (II), m. p.



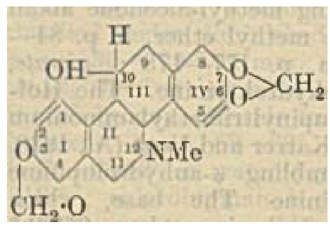
183° (corr.), together with a small amount of *hydrastine*-b, m. p. 150—151° (corr.). Oxidation of hydrastines-*a* and -*b* and *l*-hydrastine (*picrate*, m. p. 184°) with manganese dioxide and 15% sulphuric acid affords, in each case, a pale greenish-brown fluorescent solution, which on successive treatment with sodium carbonate and potassium cyanide yields cyanodihydrohydrastinine. Similar oxidation of II affords an intense cherry-red solution which becomes pale brown when treated with sodium carbonate; the cyano-compound could not be isolated. Hydrastinine is formed when hydrastine-*a* or *l*-hydrastine is oxidised with dilute nitric acid at 75°; similar oxidation of II gives no hydrastinine.

Treatment of hydrazinohydrastine-*a* with copper chloride in dilute hydrochloric acid furnishes *chlorohydrastine*-a (I, R=Cl), m. p. 152°, which when treated with aluminium amalgam in boiling alcohol gives a small amount of hydrastine-*a*. Aminohydrastine-*a* is converted by the usual method into *iodohydrastine*-a (I, R=I), m. p., 172°, also formed together with *iodohydrastine*-b, m. p. 194—195° (corr.), from hydrastinine and iodomeconine in boiling methyl alcohol. Reduction of iodohydrastine-*a* with aluminium amalgam in boiling alcohol or 6% sodium amalgam and aqueous alcohol yields hydrastine-*a*. Hydrastinine and bromomeconine give a small amount of a bromohydrastine, m. p. 170—171° (corr.) [hydrobromide, m. p. 287—288° (decomp.)].

4-*Acetoxy*-, m. p. 127—128° (corr.); 4-*benzoyloxy*-, m. p. 135—136° (corr.); m-*nitrobenzoyloxy*-, m. p. 192—193° (corr.), and *p*-nitrobenzoyloxy-3-methoxyphthalides, m. p. 202—203°, prepared by the usual methods from normeconine methyl ether, do not condense with hydrastinine. Normeconine methyl ether and hydrastinine in boiling alcohol give the *hydrastininium salt* (?), m. p. 334° (corr.), of the ether.

H. Burton.

Constitution of chelidonine. E. Späth and F. Kuffner (Ber., 1931, 62, [*B*], 370—378).—Oxidation of *N*-acetylanhydrochelidonine with nitric acid affords benzene-1 : 2 : 4-tricarboxylic acid; the absence of benzene-tetracarboxylic or -pentacarboxylic acid shows the invalidity of the constitution assigned to chelidonine by Gadamer (A., 1924, i. 1227). Further insight into the structure of the alkaloid is sought by examination of the base, m. p. 136°, isolated by Gadamer and Stichel from crude sanguinarine to which the formula $C_{18}H_{17}N$ has been assigned. The base can be obtained from pure sanguinarine, which is closely allied to chelidonine. It has the composition $C_{17}H_{11}N$ and is identical with α-naphthaphenanthridine described by Graebe (A., 1905, i, 82). The skeleton structure of chelidonine and sanguinarine is thus established. Oxidation of chelidonine by potassium permanganate gives a mixture of hydrastic and 3 : 4-methylenedioxybenzene-1 : 2-dicarboxylic acid, isolated as the ethylimides. Each of the two methylenedioxy-groups must therefore be united to a benzene nucleus to which two carbon atoms are attached and the alcoholic hydroxyl group of chelidonine cannot be attached to either of these nuclei. The results of a study of the action of acetic anhydride and of the Hofmann degradation exclude the possibility of its presence in ring II, so that it must be assigned to ring III, as assumed by von Bruchhausen and Bersch (A., 1930, 1600). Reasons are advanced in favour of the view that it occupies position 10. The authors' experiments in conjunction with the observations of von Bruchhausen and Bersch (*loc. cit.*) and Schwarz (Diss., Marburg, 1928) allow the constitution I to be assigned to chelidonine.



On purely chemical grounds it is not possible to maintain the hypothesis of a near relationship between morphine, dionine, thebaine, and chelidonine indicated by their ultra-violet absorption spectra.

Bulbocapnine is oxidised by permanganate in feebly alkaline solution to 4 : 5-methylenedioxybenzene-1 : 2 : 3-tricarboxylic acid, m. p. 205—207° (decomp.) (*methyl* ester, m. p. 125—127°).

H. Wren.

***Strychnos* alkaloids. LVIII. Formation of diketonucine dihydrate and its reduction.** H. Leuchs and F. Kröhnke (Ber., 1931, 64, [*B*], 455—462).—Brucine can be oxidised by chromic acid to the Hanssen acid, $C_{19}H_{22}O_6N_2$, which is therefore regarded as an intermediate product of the oxidation of the alkaloid to the Wieland acid, $C_{17}H_{22}O_6N_2$ (2 : 3-diketonucine hydrate) (for nomenclature see A., 1930, 1456). The preparation of the Wieland acid from the substance $C_{17}H_{22}O_5N_2$, considered previously as 2 : 3 : 4-trihydroxynucine, is explained by the observation that 2 : 3-diketonucine dihydrate when acted on by sodium amalgam absorbs 2 atoms of hydrogen and loses 1 mol. of water, thus being reconverted into the compound $C_{17}H_{22}O_5N_2$. The last-named compound must therefore be 3-hydroxy-2-ketonucine hydrate. The alkaloid $C_{17}H_{20}O_3N_2Br_2$ (cf. A., 1929, 1320) is 2 : 2-dibromo-3-hydroxynucine or, more probably, 2 : 3-dibromo-2-hydroxynucine. It is considered that the acetyl derivative of the so-called trihydroxynucine (*loc. cit.*) is the diacetate of the monoacetylated anhydride of the compound $C_{17}H_{22}O_5N_2$ with 1 mol. of water of crystallisation.

2 : 3-Diketonucine dihydrate is transformed by acetic anhydride followed by treatment of the

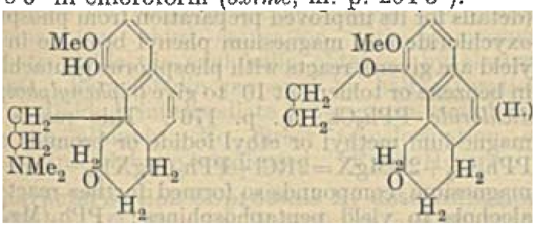
product with perchloric acid in methyl alcohol into 2 : 3-*diketonucine perchlorate*, $C_{17}H_{18}O_4N_2,HClO_4$, $[\alpha]^{15}$ $+53\cdot3°/d$, which appears to pass successively into the mono- and di-hydrate in aqueous solution.

Criticism is passed on the communication of Spath and Bretschneider (this vol., 242). H. WREN.

Ionisation constant of codeine. H. BAGGESGAARD-RASMUSSEN and I. MARTINS (Arch. Pharm., 1931, **269**, 1—8).—Determinations using the quinhydrone electrode of the p_H of solutions of codeine and codeine hydrochloride give values of $6\cdot7\times10^{-9}$ and $7\cdot9\times10^{-7}$ for the acid and basic ionisation constants, respectively, of codeine. The activity coefficient of codeine from its solubility in 0·0—1·0*N*-sodium chloride and its partition coefficient between water and chloroform is also given. In the determination of codeine in syrups by dilution and extraction with chloroform, sodium hydroxide should be added to decrease its solubility in the aqueous phase.

H. E. F. NOTTON.

Sinomenine. XXIV. Degradation of sinomenine to *l*-thebenone. K. GOTO, R. INABA, and H. SHISHIDO (Annalen, 1931, **485**, 247—257).—Demethoxydihydrosinomenine methiodide (cf. A., 1930, 230) when heated with 25% potassium hydroxide gives *de*-N-*methyldemethoxydihydrosinomenine* (I), m. p. 182°, $[\alpha]_D^{20}$ $-54\cdot94°$ in chloroform, the methiodide (not characterised) of which is converted by similar treatment into trimethylamine and l-*dehydrothebenone* (II), m. p. 113° (sinters at 104°), $[\alpha]_D^{18}$ $-206\cdot87°$ in chloroform. Reduction of II (hydrogen and palladised charcoal) gives l-*thebenone*, m. p. 134°, $[\alpha]_D^{18}$ $-78\cdot6°$ in chloroform (*oxime*, m. p. 204·5°).

(I.)  (II.)

Dihydrode-N-*methyldemethoxydihydrosinomenine*, m. p. 156·5°, $[\alpha]_D^{18}$ $+67\cdot82°$ in chloroform [the optical antipode of the dihydrode-*N*-methyldihydrothebanione of Wieland and Kotake (A., 1925, i, 1093)], prepared by reduction of I (hydrogen–palladium–charcoal) forms a *methiodide*, m. p. 226—229°, which with hot alkali gives *l*-thebenone and trimethylamine. Those compounds described above which have a double linking in the 9 : 10-position show strong halochromism, deepened by the presence of a keto-group, in concentrated sulphuric acid.

H. A. PIGGOTT.

Arsinic acids of fluorene and its derivatives. F. E. CISLAK and C. S. HAMILTON (J. Amer. Chem. Soc., 1931, **53**, 746—749).—The *acetyl* derivative, m. p. 250—253° (corr.), of 7-nitro-2-aminofluorene (prepared by reduction of 2 : 7-dinitrofluorene with alcoholic ammonium sulphide) is reduced by zinc dust and alcohol containing a little aqueous calcium chloride to 7-*amino-2-acetamidofluorene*, m. p. 188—192° (corr.; decomp.). This is converted into 2-*acetamidofluorene-7-arsinic acid*. *Fluorene*- and *fluorenone-2-arsinic acids* are also prepared. H. BURTON.

10-Chloro-5 : 10-dihydrophenarsazine and its derivatives. XIV. Chloro-derivatives. L. A. ELSON and C. S. GIBSON (J.C.S., 1931, 294—305; cf. A., 1926, 1162).—The following substituted diphenylamines are prepared by (*a*) Ullmann's method (A., 1907, i, 842) and (*b*) Chapman's method (A., 1929, 550): (*a*) o-*chlorodiphenylamine* (I), b. p. 174—175°/12 mm., m. p. 15—16°; 2 : 5-*dichlorodiphenylamine* (II), b. p. 195°/17 mm.; 3 : 4-*dichlorodiphenylamine*, b. p. 218—220°/20 mm., m. p. 69° (obtained from 3 : 4-*dichlorodiphenylamine-2′-carboxylic acid*, m. p. 178°); 3 : 5-*dichlorodiphenylamine*, b. p. 200°/12 mm. (from the 2′-*carboxylic acid*, m. p. 245°); 3 : 4 : 5-*trichlorodiphenylamine*, b. p. 248°/20 mm., m. p. 85° (2′-*carboxylic acid*, m. p. 238°), and 5-*chloro-2-methyldiphenylamine*, b. p. 205—207°/23 mm. (2′-*carboxylic acid*, m. p. 200°); (*b*) 3 : 4′-*dichlorodiphenylamine*, b. p. 235°/25 mm., m. p. 63—64° (from N-3-*chlorophenylbenzimino-4-chlorophenyl ether*, m. p. 77°); 3 : 3′-*dichlorodiphenylamine*, b. p. 225—230°/18 mm.; 3′-*chloro-2-methyldiphenylamine*, b. p. 203°/20 mm. (the N-*benzoyl* derivative, m. p. 106°, is obtained by isomerisation of *N*-*o*-tolylbenzimino-3-chlorophenyl ether at 290°); 4′-*chloro-2-methyldiphenylamine*, b. p. 200—205°/20 mm. (from N-4-*chlorophenylbenzimino*-o-*tolyl ether*, m. p. 65°); 2′ : 4′-*dichloro-2-methyldiphenylamine* (III), b. p. 205°/20 mm., m. p. 48° (from N-o-*tolylbenzimino*-2 : 4-*dichlorophenyl ether*, m. p. 53°). *Benzoyl-2′-chloro-2-methyldiphenylamine*, m. p. 132°, which could not be hydrolysed, is obtained by isomerisation of N-o-*tolylbenzimino-2-chlorophenyl ether*, m. p. 64°, at 290°. All the above diphenylamines except I, II, and III (and 2 : 4-dichlorodiphenylamine) condense with arsenious chloride yielding derivatives of 10-chloro-5 : 10-dihydrophenarsazine. The non-condensation of 2-chlorodiphenylamines supports the view (cf. A., 1930, 1601) that chelation occurs between the 2-chlorine and imino-hydrogen atoms, thus restricting the motion of the latter atom. When only one dihydrophenarsazine derivative is produced from a 3-chlorodiphenylamine, it is probable that this is the 1-chloro-derivative (possibility of chelation); the compound from *m*-chlorodiphenylamine and arsenious chloride is 1 : 10-dichloro-5 : 10-dihydrophenarsazine (cf. A., 1926, 1162). When two condensation products are isolated, the more fusible form is considered to be the 1-substituted isomeride, *i.e.*, the chelated form.

3 : 4-Dichlorodiphenylamine and arsenious chloride give a mixture of 1 : 2 : 10-, m. p. 220° after shrinking at 205°, and 2 : 3 : 10-*trichloro*-5 : 10-*dihydrophenarsazines*, m. p. 265—268°, also formed (with m. p. 230—235° and 273—274°) when 3 : 4-*dichlorodiphenylamine-6′-arsinic acid*, m. p. 150°, prepared by the Ullmann method from 3 : 4-dichloroaniline and *o*-bromophenylarsinic acid, is reduced with sulphur dioxide in presence of hydrochloric acid and a trace of iodine. 3 : 4′-Dichlorodiphenylamine affords a mixture of 1 : 8 : 10-, m. p. 240—242°, and 3 : 8 : 10-*trichloro*-5 : 10-*dihydrophenarsazines*, m. p. 292°. 3 : 5-Dichlorodiphenylamine yields 1 : 3 : 10-*trichloro*-5 : 10-*dihydrophenarsazine*, m. p. 251—252°, oxidised by hydrogen peroxide in acetic acid to 1 : 3-*dichlorophenarsazinic acid*, not melted at 280°. 1 : 2 : 3 : 10-*Tetrachloro*-5 : 10-*dihydrophenarsazine*, m. p. 260°

(from 3 : 4 : 5-trichlorodiphenylamine) is oxidised similarly to 1 : 2 : 3-*trichlorophenarsazinic acid*, not melted at 290°. 1 : 9 : 10- or 1 : 7 : 10- or 3 : 7 : 10-*Trichloro*-5 : 10-*dihydrophenarsazine*, m. p. 298°, is obtained in small yield from 3 : 3′-dichlorodiphenylamine. 4-, 3′-, and 4′-Chloro-2-methyldiphenylamines give 2 : 10-*dichloro-4-methyl*-, m. p. 245° (decomp.), 1(or 3) : 10-*dichloro-6-methyl*-, m. p. 262° (decomp.), and 2 : 10-*dichloro-6-methyl*-, m. p. 199°, -5 : 10-*dihydrophenarsazines*, respectively.

H. BURTON.

Derivatives of phenylboric acid, their preparation, and action on bacteria. W. SEAMAN and J. R. JOHNSON (J. Amer. Chem. Soc., 1931, **53**, 711—723).—Nitration of phenylboric acid, m. p. 210·6—212·6° (all m. p. are corr.), m. p. (block) 221°, with nitric acid (d 1·5, free from nitrous acid) below −9° gives a mixture of approximately 85% of *m*-, m. p. 273° (decomp.), m. p. (block) 319°, and 15% of o-*nitrophenylboric acid*, m. p. 139·2—140·8°, m. p. (block) 147·5° (cf. Ainley and Challenger, A., 1930, 1457). A suspension of the acid in acetic anhydride gives with nitric acid (d 1·5) first at −15° to −7° and then at 20°, a mixture (65% yield) of about 95% of o- and 5% of p-*nitrophenylboric acid*, m. p. 305·5° (decomp.), m. p. (block) above 360°. The positions of the nitro-groups are determined by conversion of the acids into bromonitrobenzenes. m-*Aminophenylboric acid*, m. p. 92·8—93·8° resolidifying with m. p. about 200° with darkening, m. p. (block) 176° [*acetyl* derivative, m. p. 274—275°, m. p. (block) about 160° with immediate resolidification; *benzoyl* derivative, m. p. 290°, m. p. (block) about 200° with immediate resolidification], is prepared by a modification of the method of Jacobs, Heidelberger, and Rolf (A., 1919, i, 50) from the *m*-nitro-compound. o-*Benzamidophenylboric acid* (the amino-acid could not be isolated) has m. p. 283—284°, m. p. (block) 319·5° with darkening. The nitrophenylboric acids are more bacteriostatic towards *Staphylococcus aureus* and *B. typhosus* than is phenylboric acid; *m*-aminophenylboric acid and its derivatives are inactive.

H. BURTON.

Alkali-organic compounds. IX. Reactions of alkali metal alkyls with mercury and mercuric chloride. K. ZIEGLER (Ber., 1931, **64**, [*B*], 445—448; Ziegler and Colonius, A., 1930, 590).—Mainly a reply to Bergmann (A., 1930, 1568). Sodium diphenylmethyl in ether is converted by mercuric chloride at the ordinary temperature into ααββ-tetraphenylethane; at −80° the change proceeds similarly but more slowly. Lithium benzyl is transformed by mercuric chloride or mercury into mercury dibenzyl, m. p. 110—111°. H. WREN.

Structure of compounds produced by the addition of mercuric salts to olefines. II. E. GRIFFITH and C. S. MARVEL (J. Amer. Chem. Soc., 1931, **53**, 789—792; cf. A., 1926, 747).—Treatment of *d*-bornyl cinnamate, b. p. 200—202°/6—7 mm., $[\alpha]_D^{27}$ +32·9° in ethyl acetate, with mercuric acetate in methyl alcohol gives d-*bornyl* β-*methoxy*-α-*acetoxymercuri*-β-*phenylpropionate*, m. p. 90—100°, converted by methyl-alcoholic sodium bromide into two d-*bornyl* β-*methoxy*-α-*bromomercuri*-β-*phenylpropionates*, m. p. 131—132°, $[\alpha]^{25}$ +17·3° in ethyl acetate, and m. p. 147—148°, $[\alpha]_D^{25}$ +14·9° in ethyl acetate. Unstable or low-melting mercury derivatives were obtained from *cinnam*-l-*methylamide*, m. p. 158—159°, $[\alpha]_D^{25}$ −82·9° in methyl alcohol, and d-, b. p. 174—177°/5 mm., $[\alpha]^{30}$ +42·4° in ethyl acetate, and l-β-*octyl cinnamates*, b. p. 175—180°/6 mm., $[\alpha]^{27}$ −43·3° in ethyl acetate. H. BURTON.

Alkali-organic compounds. X. Ready preparation of lithium benzyl. K. ZIEGLER and F. DERSCH (Ber., 1931, **64**, [*B*], 448—452).—Lithium benzyl is conveniently prepared by treating an ethereal solution of magnesium benzyl chloride with lithium phenyl, whereby lithium chloride and, probably, magnesium phenyl benzyl are produced; the last-named compound is converted by further addition of lithium phenyl into lithium benzyl, thus obtained in 0·2—0·4M solutions which contain magnesium phenyl. Magnesium *iso*propyl chloride and lithium phenyl afford *lithium* iso*propyl*, converted by *as*-diphenylethylene into the *compound* $CPh_2Li{\cdot}CH_2Pr^\beta$, which with carbon dioxide gives αα-*diphenyl*-γ-*methylvaleric acid*, m. p. 131—133°. H. WREN.

Magnesium *p*-methoxybenzyl bromide. H. GILMAN and E. A. ZOELLNER (Bull. Soc. chim., 1931, [iv], **49**, 7—9).—Details are given for preparing magnesium *p*-methoxybenzyl bromide, which reacts normally with carbon dioxide. R. BRIGHTMAN.

Magnesium derivatives of dichlorotriphenylphosphine, and pentaphosphines. V. GRIGNARD and J. SAVARD (Compt. rend., 1931, **192**, 592—595).—Triphenylphosphine oxide, m. p. 155—157° (details for its improved preparation from phosphorus oxychloride and magnesium phenyl bromide in 65% yield are given), reacts with phosphorus pentachloride in benzene or toluene at 10° to give *triphenylphosphine dichloride*, PPh_3Cl_2, m. p. 176°. This reacts with magnesium methyl or ethyl iodide or bromide thus: $PPh_3Cl_2+2RMgX=2RCl+PPh_3(MgX)_2$, and the magnesium, compounds so formed further react with alcohols to yield pentaphosphines: $PPh_3(MgX)_2+2ROH=2MgX(OH)+PPh_3R_2$, and thus are obtained (15—20% yield) *triphenyl-dimethyl*-, m. p. 163—166°; -*diethyl*-, m. p. 172°, and -*di*-n-*propyl*-, m. p. 179—182°, -*pentaphosphine*. The different type of reaction which occurs with dichlorophenylphosphine and the Grignard reagent, $PPhCl_2+2RMgX=PPhR_2+2MgXCl$, indicates that the chlorine in tervalent phosphorus compounds behaves differently from that which saturates the remaining two valencies in quinquevalent phosphorus derivatives.

J. W. BAKER.

ββ′-Dichlorodiethyl ether. II. Heterocyclic compounds containing two members of the oxygen group in the ring. 1 : 4-Selenoxan. C. S. GIBSON and J. D. A. JOHNSON (J.C.S., 1931, 266—272).—ββ′-Dichloro- (m. p. −44°) and di-iodo- (m. p. −19°) -diethyl ether react with aqueous sodium selenide to give 1 : 4-*selenoxan*, $O{<}^{CH_2{\cdot}CH_2}_{CH_2{\cdot}CH_2}{>}Se$ (I), m. p. −21·5°, b. p. 66°/22 mm., 167·5—168·5°/763 mm., d_4^t 1·597—0·00135t, n_D^{20} 1·5480; parachor 245·2, isolated as its *dibromide* (II) (yellow), m. p. 132° (decomp.), which is formed

by the action of bromine on I in carbon tetrachloride. The *dichloride*, colourless, m. p. 127—129° (decomp.), and *di-iodide*, deep violet, m. p. 106—107°, are formed similarly. The *mercurichloride*, m. p. 179°, *methiodide*, m. p. 171°, *chloroplatinate* $(C_4H_8OSeCl)_2PtCl_6$, m. p. 149° (decomp.), and *chloroaurate*, decomp. 142—144°, of I are described and their electronic formulæ discussed. Treatment of II with moist silver oxide gives an oily hydroxide, which on treatment with concentrated nitric acid furnishes the *hydroxy-nitrate* $C_4H_8OSe(OH)\cdot NO_3$, decomp. 140—141°, also formed by the action of concentrated nitric acid on I. In benzene solution, II gives with dry ammonia an *ammino*-derivative, $C_4H_8OSeBr_2,2NH_3$, which froths at 93° and turns brownish-yellow at 130°.

J. D. A. JOHNSON.

Reduction of organic mercury compounds by stannous salts as a method of synthesis of organic tin compounds. K. A. KOTSCHESCHKOV and A. N. NESMEJANOV (J. Russ. Phys. Chem. Soc., 1930, **62**, 1795—1812).—Reduction takes place giving stannic compounds of the type R_2SnX_2, but deviations from this may occur according to the organic radical, stannous salt, and solvent. *Stannic* compounds of the following were synthesised: di-*p*-tolyl dibromide, m. p. 74°; di-α-naphthyl dichloride, m. p. 137—137·5°; di-β-naphthyl dichloride, m. p. 110—111°; di-β-naphthyl dibromide, m. p. 114—115°; also p-*tolylstannic acid*. E. B. UVAROV.

Chemical individuality of serum-proteins. G. ETTISCH and H. SACHSSE (Biochem. Z., 1931, **230**, 129—135).—The affinity of proteins for copper, determined by *E.M.F.* methods, has been used to investigate the chemical individuality of the serum-proteins. One third saturation with ammonium sulphate yields the euglobulin obtained by electrodialysis. Paraglobulin prepared by half saturation is an individual intermediate between the euglobulin and the albumin. No direct transformation of albumin into globulin is indicated. F. O. HOWITT.

Characterisation of proteins by determination of affinity. G. ETTISCH, H. SACHSSE, and W. BECK (Biochem. Z., 1931, **230**, 68—92)—*E.M.F.* measurements have been made on protein solutions in presence of the biuret test reagents. Equilibrium between alkali and protein is established in 24 hrs. (shown by *E.M.F.*, depolarisation, viscosity, and light absorption). Globulin from serum-protein (electrodialysis) is distinct from the albumin fraction, especially as regards the electrochemical behaviour at high protein concentrations. The results indicate that the degree of affinity and number of affinity centres for copper are greater in globulin than in albumin.

F. O. HOWITT.

Hydrolysis of caseinogen by acids and alkalis. S. YAITSCHNIKOV (J. Russ. Phys. Chem. Soc., 1930, 62, 1871—1878).—Curves are given expressing the yields of protein, peptone, ammonia, amino-, and basic nitrogen produced at various times during the acid or alkaline hydrolysis of caseinogen.

R. TRUSZKOWSKI.

Denaturation of albumin. W. D. BANCROFT and RUTZLER, jun. (J. Physical Chem., 1931, **35**, 161).—Heat-coagulated egg-white sols can be peptised by potassium iodide or thiocyanate, carbamide, ammonium thiocyanate and sodium hydrogen carbonate, formaldehyde, and sucrose, whilst sodium hydroxide peptises (some hydrolysis) heat-coagulated albumin. Ether does not denature albumin and egg-white sols can be prevented from coagulating by extraction with ether, which probably removes a coagulant which (cf. crude lecithin from egg-yolk) confers heat stability. The "denaturation" by ether which sometimes occurs is due to removal of adsorbed water. Coagulated egg-white repeptises in boiling water, especially when it contains traces of ether. The sodium nitroprusside test for "denatured" egg-albumin is untrustworthy. Measurements of iso-electric point and immunobiological teats indicate that coagulated and repeptised egg-white sols are identical with the original sol. L. S. THEOBALD.

Heat-coagulable protein from gelatin. S. E. SHEPPARD, J. H. HUDSON, and R. C. HOUCK (J. Amer. Chem. Soc., 1931, **53**, 760—765).—Gelatins from calf-skin, bone, hide, etc. contain 0·2—0·6% of a coagulable protein, separable by adjusting the p_H of a gelatin solution to 4·7 and then heating at 80—100°. The isoelectric point of the coagulated protein (N about 14%, S about 0·8%) is (electro-endosmotic method) about p_H 4. The isoelectric point of egg-albumin, denatured by heat, is p_H 4·7. The coagulable protein appears to be identical with the "insoluble gelatin fractions" of Knaggs, Manning, and Schryver (A., 1923, i, 1144) and of Kunitz and Northrop (A., 1929, 458). H. BURTON.

Vegetable proteins. II. Typhoidin, the alcohol-soluble protein of *Pennisetum typhoideum*. D. NARAYANAMURTI and C. V. R. AIYAR (J. Indian Chem. Soc., 1930, **7**, 945—952).—The sun-dried grain contains water (7·92%), ash (2·34%), ether-soluble material (6·3%), crude fibre (2·3%), crude protein (9·27%), and carbohydrate (by difference, 71·87%). Details are given for the extraction of a prolamine (termed *typhoidin*) (C 56·8, H 5·56, N 14·3, S 0·605%) from the grain by cold 70% alcohol. The nitrogen distribution in the protein is similar to that in other prolamines. The protein contains relatively high quantities of cystine and tryptophan; the cystine content does not account for the total sulphur. H. BURTON.

Iodination of peptone. P. BRUNO (Giorn. Farm. Chim., 1930, **79**, 308—309; Chem. Zentr., 1930, ii, 3299).—Peptone (360 g.) is heated with iodine (100 g.) and water (350 g.) below 100°; the product is readily soluble in water to give a clear solution and contains no free iodine.

A. A. ELDRIDGE.

Elimination of sulphur in carbon determinations by direct combustion. W. H. BLATCHLEY (Ind. Eng. Chem. [Anal.], 1931, **3**, 13).—Additions to the usual number of absorption tubes in the train used for carbon determinations are unnecessary if the outlet end of the combustion tube is packed loosely with ignited asbestos; after a few combustions with red lead a sublimate of this substance forms on the asbestos, and oxidises to trioxide and fixes as lead sulphate the whole of the sulphur dioxide evolved.

H. F. GILLBE.

Micro-determination of carboxyl. S. Tsurumi and Y. Sasaki (Sci. Rep. Tohoku, 1930, **19**, 681—688).—A micro-modification of the Fuchs–Hunter–Edwards method for the determination of carboxyl groups (Fuchs, A., 1889, ii, 463; Hunter and Edwards, A., 1913, ii, 535), with an accuracy of 1%, is described. The acid (2—3 mg.) is dropped into a solution of potassium hydrogen sulphide saturated with hydrogen sulphide, and the evolved gas measured. The method fails with excessively weak acids, with those acids the alkali salts of which are insoluble in the sulphide solution, with *p*-nitrophenols, monohalogenodihydric phenols, and with keto-phenols such as methylphloroglucinol. G. Discombe.

Detection of tartaric acid in presence of citric acid by photo-catalysis. T. Pavolini (Giorn. Farm. Chim., 1930, **79**, 310—311; Chem. Zentr., 1930, ii, 3319).—The solution is treated with uranyl acetate and exposed for at least 30 min. to sunlight or intense artificial light; tartaric acid alone among the α-hydroxy-aliphatic acids affords glyoxal, which is detected by means of phenylhydrazine or its *p*-sulphonic acid. A A. Eldridge.

Identification of halides as 3 : 5-dinitrobenzoates. I. C. L. Tseng and E. J. H. Chu (Nat. Centr. Univ. Sci. Rep., **A**, 1930, **1**, 9—14).—In Mulliken's method, dry benzene is substituted for alcohol. Diphenylmethyl chloride gives diphenylmethyl 3 : 5-dinitrobenzoate, m. p. 142°.
Chemical Abstracts.

Modifications of Mulliken's system for the identification of compounds of Order I. C. L. Tseng (Nat. Centr. Univ. Sci. Rep, **A**, 1930, **1**, 1—3).—The first four genera are arranged in the order: aldehydes, acids, phenolic compounds, carbohydrates. Additional tests for solubility in water and acidity (Congo-red) are recommended. Chemical Abstracts.

Microchemical identification of cryogenin (*m*-benzamidosemicarbazide). G. Denigès (Bull. Pharm. Soc. Bordeaux, 1930, **68**, 49—51; Chem. Zentr., 1930, ii, 2680).—Characteristic hexagonal crystals are obtained from a solution in a mixture of alcohol and chloroform (1 : 2). A solution in 1% potassium chlorate solution becomes orange on addition of hydrochloric acid and violet when made alkaline with sodium hydroxide. A. A. Eldridge.

Colorimetric determination of cryogenin. G. Deniges (Bull. Soc. Pharm. Bordeaux, 1930, **68**, 51—52; Chem. Zentr., 1930, ii, 2680; cf. preceding abstract).—The above reaction is employed quantitatively. A. A. Eldridge.

System for microchemical identification of alkaloids. J. F. H. Amelink (Pharm. Weekblad, 1931, **68**, 159—185, 211—216, 221—229).—A tabulation is made of the microchemical reactions between platinic chloride and iodide, gold chloride and bromide, mercuric chloride, potassium ferro- and ferri-cyanide, potassium bismuth iodide and periodide, potassium hydroxide, and picrolonic acid, and 78 selected alkaloids. Accounts are given of the preparation of the reagents and the methods of making the tests; a great number of photomicrographs of crystalline products are reproduced. The reactions of percaine (the hydrochloride of the condensation product of α-butylhydroxycinchoninic acid and diethylethylenediamine), diocaine (diallylhydroxyethylenediphenyldiamidine), harmine (banisterine), and harmaline (dihydroharmine) with the selected reagents are described. The crystalline precipitate with gold bromide is characteristic for harmine, and that with platinic chloride for harmaline; the latter gives a blood-red coloration with acetaldehyde and its homologues. S. I. Levy.

Biochemistry.

The oxidation process in red blood-corpuscles. K. Zeile and H. von Euler (Z. physiol. Chem., 1931, **195**, 35—38).—The work of Michaelis and Salomon (A., 1930, 1053) is confirmed. A. Renfrew.

Active iron. VI. Characterisation by benzidine-peroxidase and catalase reactions. A. Simon and T. Reetz.—See this vol., 439.

Influence of the chlorophyll content of fodder on the formation of blood-corpuscles. A. Zih (Pflüger's Archiv, 1930, **225**, 728—736; Chem. Zentr., 1930, ii, 3434).—Seasonal variations in the corpuscle content of the blood of rabbits are due to variations in the amount of chlorophyll ingested.
A. A. Eldridge.

Quantity of free water in red blood-corpuscles. E. Schiødt (Biochem. J., 1930, **25**, 8—10; cf. Gough, A., 1924, i, 583; Ege, A., 1927, 892; Krevisky, A., 1930, 942).—The volume values of blood-corpuscles in isotonic, hypotonic, and slightly hypertonic salt solutions when inserted in the equation for the van 't Hoff–Boyle–Mariotte law yield values of about 65% for the quantity of free water. The same blood in highly hypertonic solutions of the same salt gives lower values for the quantity of free water—down to 35%. S. S. Zilva.

Determination of water in blood and serum. M. Dolch and E. Poechmueller (Z. physiol. Chem., 1931, **195**, 28—34).—To 15 c.c. of blood or serum, 100 c.c. of alcohol are added and the mixture is boiled for 10 min. To 20 c.c. of the clear supernatant liquid are added 20 c.c. of xylene and the separation temperature of the xylene–aqueous alcohol mixture is determined. The water content of the blood or serum is then read from a graph. The results are about 2% higher than those obtained by the ordinary method. A. Renfrew.

Glycolysis in blood. II. The pyrophosphate fraction and glycolysis. H. K. Barrenscheen and B. Vásarhelyi (Biochem. Z., 1931, **230**, 330—346).—The pyrophosphate fraction of the bloods of the animals investigated increases in the following order: horse $<$ ox $<$ dog $<$ rabbit $<$ guinea-pig $<$ man $<$ pig.

With the exception of pig's blood, the pyrophosphate fraction of the different bloods increases with increasing glycolytic power. During glycolysis, a small increase of pyrophosphate fraction is accompanied by a decrease in inorganic phosphorus. Acceleration of glycolysis with sulphate causes a decrease of the "pyrophosphate fraction." Attempts to isolate pyrophosphate as such from erythrocytes were unsuccessful, the pyrophosphate being organically combined. Whole blood, corpuscles, and to a smaller extent serum and plasma contain an enzyme which hydrolyses pyrophosphate and is inhibited by fluoride.

P. W. CLUTTERBUCK.

Glycolysis in blood. III. Inhibition of glycolysis. H. K. BARRENSCHEEN and K. BRAUN (Biochem. Z., 1931, **231**, 144—172).—The restriction or inhibition of glycolysis in human erythrocytes (in the experiments with ether rabbit erythrocytes were used) caused by hæmolysis, fluoride, oxalate, ether, chloroform, monochloro-, monobromo-, or monoiodoacetic acid leads always to the conversion of organic into inorganic phosphate in the erythrocytes, the chief source of the inorganic phosphate thus produced being the organic phosphate, which is easily hydrolysed by acid (the pyrophosphate fraction). When hydrolysis is inhibited by fluoride or by the halogenated acetic acids a difficultly hydrolysable hexosediphosphate is produced. Since after glycolysis has been inhibited by hæmolysis the inhibition can be suppressed by the action of phosphate, hydrogen carbonate, or borate, it follows that the glycolytic process is independent of the maintenance of the structure of the cells. From these results and the facts that fermentation with yeast poor in, or free from, co-enzyme is slightly activated by the pyrophosphate fraction from erythrocytes and that when glycolysis has been inhibited by hæmolysis, by fluoride, or by monohalogenoacetic acids, addition of hexosediphosphoric acids leads to accumulation of methylglyoxal, it is concluded that the pyrophosphate fraction contains either the co-enzyme required for glycolysis or the activator of the co-enzyme. W. MCCARTNEY.

Hagedorn–Jensen method for the determination of blood-sugar. H. KRAMER and A. STEINER (Biochem. J., 1931, **25**, 161—165).—The equivalent of 20—30 mg. of sugar per 100 c.c. is derived from reducing substances other than sugar. There is also a retention of 4—22 mg. of fermentable sugar per 100 c.c. in the cotton plugs employed for filtration. Hagedorn and Jensen's table for the calculation of the sugar is criticised. S. S. ZILVA.

Cholesterol metabolism. I. Determination of free and combined cholesterol in small amounts of blood. R. MANCKE (Biochem. Z., 1931, **231**, 103—109).—The author's modification 1927, 275) of the method of Windaus (A., 1909, i, has now been applied to the determination of free and combined cholesterol in 1·0—0·5 c.c. of blood-serum. W. MCCARTNEY.

Influence of lecithin on the stability of serum-p teins. S. WENT and F. FARAGÓ (Biochem. Z., 1931, **230**, 238—244).—The phenomenon of lecithin orming clear solutions in plasma was investigated. n mixtures of aqueous lecithin emulsions and serum there exists a marked reciprocal relationship between the amounts of euglobulin and pseudoglobulin I on the one hand and of pseudoglobulin II and albumin on the other. Each of these pairs of proteins appears to form a complex with lecithin and intermediately situated are serum-protein dispersoids, the stability of which also depends on the amount of lecithin present. F. O. HOWITT.

Globulin and albumin fractions of serum. II. Distribution of lipins, precipitinogens, and bacterial agglutinins amongst the various fractions of cattle-serum. B. LUSTIG and R. KATZ (Biochem. Z., 1931, **231**, 39—44; cf. A., 1930, 1607).—Each of the fractions into which the proteins can be divided by the authors' methods exhibits specificity as regards content of lipins. This content is highest in the albumins and lowest in the euglobulins. Of the eu- and pseudo-globulin fractions those which are soluble in sodium chloride solutions have the highest, those which are soluble in water the lowest, content of total lipins and lecithin. The amount of specific precipitinogens is highest in those eu- and pseudo-globulin fractions which are soluble in sodium chloride solution and lowest in the first and second albumin fractions. Normal agglutinins are found chiefly in the euglobulin fractions and are absent from the albumin fractions. Of the globulin fractions those which are soluble in sodium carbonate solution have the highest, those which are soluble in sodium chloride solution the lowest, content of agglutinins. W. MCCARTNEY.

Refractometric investigation of serum-proteins. III. Specific refraction of the total protein, and the refraction of the non-protein constituents of horse-serum. IV. Specific refraction of the protein fractions of horse-serum. D. VON DESEO (Biochem. Z., 1931, **230**, 373—382, 383—394).—III. Values of $n^{17·5}$ and $d^{17·5}$ of normal and immune sera and the protein content are determined. The figures so obtained are used for calculation of the constants which determine the magnitude of the refractive index and the specific gravity (cf. A., 1930, 359).

IV. Tables summarise a large number of results obtained for $n^{17·5}$, $d^{17·5}$, the protein and ammonium sulphate contents (determined gravimetrically) for serum-proteins precipitated by varying degrees of saturation with sulphate and for their filtrates and for solutions of albumin, globulin, and mixtures of these.

P. W. CLUTTERBUCK.

Determination of the p_H of blood-serum with the quinhydrone electrode. M. E. HANKE (Proc. Soc. Exp. Biol. Med., 1930, **27**, 972—973).—An apparatus having a total capacity of about 1 c.c., and employing 0·2 c.c. of serum, is described.

CHEMICAL ABSTRACTS.

Antimony and hydrogen electrodes [for determination of p_H of blood-serum]. M. VERAIN and TOUSSAINT (Compt. rend. Soc. Biol., 1930, **103**, 611—612; Chem. Zentr., 1930, ii, 2289).—Concordant results were obtained.

A. A. ELDRIDGE.

Determination of urea in small quantities of blood. M. FIORENTINO (Riforma Med., 1929, No.

38, 21 pp.; Chem. Zentr., 1930, ii, 2926).—Blood (0·25 c.c.) is mixed with water (1·5 c.c.) and 50% trichloroacetic acid (0·25 c.c.), kept for 2 min. at 100°, and centrifuged; 1·6 c.c. are then treated with trichloroacetic acid solution (0·2 c.c.) and acetic acid (3 c.c.), 5 c.c. of 5% xanthhydrol solution in acetic acid being added dropwise. After 10 min. the mixture is centrifuged and decanted; 4—5 drops of methyl alcohol are added to the residue and centrifuged after mixing, the procedure being repeated with alcohol and then with ether. The precipitate is then dissolved in 5 c.c. of 0·1*N*-potassium dichromate (containing sulphuric acid) and 5 c.c. of sulphuric acid, the treatment being repeated; after dilution to 45 c.c. with sulphuric acid the liquid is kept for 15 min. with intermittent mixing. After dilution with water (200 c.c.) and cooling, potassium iodide is added and the iodine titrated with *N*/40-thiosulphate.

A. A. Eldridge.

Fate of choline in the blood. F. Wrede and E. Bruch (Z. physiol. Chem., 1931, **195**, 255—259).—About 80% of the choline added to defibrinated ox-blood or to sheep's serum can be recovered after 7 hrs. at 37° by the method previously described (A., 1929, 1191). This is contrary to the findings of Page and Schmidt (A., 1930, 1614). H. Burton.

Action of blood on uric acid. A. Rowinska (Acta Biol. Exp., Warsaw, 1930, **6**, 37—44).—Hæmolysed human or avian blood destroys uric acid. The velocity of decomposition is retarded by diminution of oxygen supply. Unhæmolysed blood does not catalyse the oxidation of uric acid.

R. Truszkowski.

Changes, caused by ultra-violet irradiation, in the distribution of chlorine in blood. J. Glass (Biochem. Z., 1931, **231**, 45—53).—In the blood of rabbits which are exposed for 2—4 hrs. to powerful ultra-violet radiation the ratio of the chlorine content of the corpuscles to that of the plasma is increased. A similar increase is found after 24 hrs. in the blood of men who have been exposed to the radiation for 3—8 min. It follows that such irradiation alters the acid–base equilibrium of the blood, producing acidosis. W. McCartney.

Reciprocal influence of the inorganic constituents of blood-serum on their physical condition. H. G. Scholtz (Biochem. Z., 1931, **231**, 135—143).—Experiments with horse- and ox-serum to which approximately isotonic potassium, sodium, calcium, or magnesium salts were added, the mixtures being subsequently subjected to ultrafiltration, and on cats to which some of the salts were administered, show that calcium–phosphate and magnesium–phosphate complexes can be produced in the serum. The formation of the complexes is more pronounced *in vitro* than *in vivo*. Addition of calcium chloride to serum increases the amount of potassium which can be separated by ultrafiltration. Similarly, addition of magnesium chloride increases both *in vitro* and *in vivo* the amount of calcium which can be separated by ultrafiltration. The results support the view that serum contains colloidal potassium compounds and point to analogy with the permutit reaction.

W. McCartney.

Determination of the physical state of the mineral constituents of serum by electro-ultrafiltration. R. Spiegler (Biochem. Z., 1931, **230**, 253—258).—Methods are described whereby serum is subjected to ultrafiltration and the residue to electro-ultrafiltration for varying lengths of time, and it is claimed that quantitative fractional separation of the mineral constituents is attained.

P. W. Clutterbuck.

Serum-electrolyte in normal and pathological conditions. D. W. Atchley and E. M. Benedict (J. Clin. Invest., 1930, **9**, 265—294).—Serum-electrolyte partitions were made in normal and pathological conditions. If hydrogen carbonate, chloride, protein, phosphate, sulphate, and ketones were measured, the so-called "undetermined acids" were negligible. The normal mean total base was 151·9 and the total acid 151·7 mille-equiv. per litre. Variations in pathological conditions are recorded.

Chemical Abstracts.

Hydrotropic solution of calcium, in relation to the solution of calcium in serum. A. von Kuthy and H. Banga (Biochem. Z., 1931, **230**, 458—465).—The similarity of the hydrotropic solution of calcium in sodium salicylate solutions and the state of solution of calcium in serum is emphasised, the calcium in both cases being present partly in the ionised condition and partly as a negatively-charged non-diffusible complex. P. W. Clutterbuck.

Micro-determination of calcium and phosphorus in blood and tissues. G. Widmark and B. Vahlquist (Biochem. Z., 1931, **230**, 245—252).—The use of a new filter enables the usual methods to be somewhat simplified. The calcium in 2 c.c. of plasma can be determined with an accuracy of 2—3% and the phosphatide-phosphorus in 1 c.c. of plasma and the acid-soluble phosphorus in 2 c.c. of plasma with an accuracy of 1%. The same accuracy is obtained in determinations in tissues when the calcium content is of the order of 0·2—0·3 mg. and the phosphorus content 0·05—0·1 mg.

P. W. Clutterbuck.

Phosphorus distribution, sugar, and hæmoglobin in the blood of fish, eels, and turtles. C. M. McCay (J. Biol. Chem., 1931, **90**, 497—505).—The blood of pike and carp contains about four times as much phosphorus as cow's blood, eel blood being intermediate. The plasma-phosphorus and blood-sugar of the pike are higher than the corresponding values for the carp. Turtle blood has low values for plasma constituents. Between spawning and death, the blood changes of the lamprey-eel consist mainly of losses of hæmoglobin and dextrose.

A. Cohen.

Physico-chemical properties of crocodile blood (*Crocodilus acutus*, Cuvier). D. B. Dill and H. T. Edwards (J. Biol. Chem., 1931, **90**, 515—530).—The serum-protein, hæmoglobin content, and buffer value of crocodile blood are lower, and the effect of acid in reducing the affinity of hæmoglobin for oxygen is greater, than in man. A. Cohen.

Relation between blood-sugar and -coagulation time. A. Partos (Pflüger's Archiv, 1930, **224**, 448—450; Chem. Zentr., 1930, ii, 3308).—In normal or

depancreatised cats rise of blood-sugar is accompanied by a rise in the coagulability of the blood, and conversely. Hyperglycæmic substances (morphine, adrenaline) increase the blood-coagulability proportionally to the rise in blood-sugar; similarly, retardation of coagulation by novirudin is accompanied by low blood-sugar values. A. A. ELDRIDGE.

Effect of reduction of atmospheric pressure on the resistance of red blood-corpuscles to the action of hypotonic sodium chloride solutions. C. NAEGELI (Biochem. Z., 1931, **231**, 95—102).—The resistance to the action of hypotonic sodium chloride solutions of the erythrocytes of the blood of rabbits is greatly influenced by the pressure of the air in which they live. After periods from 144 to 192 hrs. at pressures of 260—340 mm. the concentration of the salt solution which just fails to produce hæmolysis is much lower and that of the salt solution which is just sufficient to produce complete hæmolysis is much higher than in the case of erythrocytes from the blood of rabbits living in air at ordinary pressures. W. McCARTNEY.

Hæmolytic action of potassium cyanide and its neutralisation by certain carbohydrates. P. MORETTI and G. MUSCOLINO (Arch. Farm. sperim., 1931, **51**, 167—171).—In certain concentrations and at temperatures above 37°, potassium cyanide exerts *in vitro* a hæmolytic action on the red corpuscles of ox-blood. This effect is weakened when the salt combines with carbohydrates capable of neutralising its toxic action. Strict parallelism is observed between the antitoxic and antihæmolytic actions of the different carbohydrates (cf. A., 1930, 1618). T. H. POPE.

Anti-ricin. F. REUTER (Biochem. Z., 1931, **231**, 175—232).—By means of experiments with blood-serum containing anti-ricin the conditions under which the latter can best be purified by adsorption on purified kaolin or on aluminium hydroxide and subsequent elution with phosphate buffer solutions have been investigated. Provided that sera which do not contain too much anti-ricin are used the degree of purification of the latter is increased if the adsorption is preceded by fractional salting out and electrodialysis. The anti-ricin content of the dried sera and of the electrodialysates increases when these materials are preserved. Anti-ricin is not attacked by either activated trypsin or activated pepsin. W. McCARTNEY.

Chemical and immunological study of egg-protein obtained under restricted diets. L. GERBER and R. H. CARR (J. Nutrition, 1930, **3**, —256).—Ammonia-nitrogen (4·75 and 8·40% of total nitrogen, respectively, for eggs of pigeons fed on rye and barley) showed the largest deviations; the total nitrogen content was fairly constant. Feeding with hemp, soya beans, and wheat increased the monoamino-nitrogen, with kafir the diamino-nitrogen, or with maize and kafir the non-amino-nitrogen. Immunological relationships were investigated. Embryo development was assisted by egg-proteins from hemp, soya-bean, and wheat diets more than that from maize or oats. CHEMICAL ABSTRACTS.

Cholesterol of protoplasm. V. Investigation of the suprarenal glands of the ox. G. PFEIFFER (Biochem. Z., 1931, **230**, 439—445).—A method is outlined for the hydrolysis of suprarenal gland substance with 2% sodium hydroxide and for the isolation of the cholesterol fractions. The large cholesterol content obtained is regarded as due to the accumulation of cholesterol during the breakdown of erythrocytes in the formation of the gland hormone (cf. A., 1930, 945, 1204). P. W. CLUTTERBUCK.

Cholesterol compounds in protoplasm. VI. Cholesterol compounds of the spleen in cattle. G. PFEIFFER (Biochem. Z., 1931, **231**, 239—243).—The amount of cholesterol and its derivatives in the spleens of cattle is similar to that in their livers (calculated, in both cases, on the dry weight), the similarity being particularly pronounced in the case of the material which can be precipitated by digitonin. There is practically no difference between the amount of oxycholesterol in the spleen and that in the erythrocytes. It is concluded that the accumulation of cholesterol in the spleen is, in part, a consequence of the decomposition of red blood-corpuscles which takes place there. W. McCARTNEY.

Presence and rôle of cholesterol in the shells of Lamellibranchs. A. DE WAELE (Natuurwetensch. Tijds., 1931, **13**, 51—56).—The shell of *Anodonta cygnea* contains 0·1047 g. of cholesterol per kg., which by its affinity for water enables the impervious shell to retain enough moisture to allow elimination of carbon dioxide. Owing to the presence of the sterol, the shell cannot be dried by heating to 105°, but must be first extracted with ether, the residue after evaporation of which must be allowed for in the analysis. S. I. LEVY.

Decomposition of cholesterol by X-rays. A. H. ROFFO and L. M. CORREA.—See this vol., 443.

Effect of X-irradiation on cholesterol and its fatty acid esters *in vitro* and *in vivo*. R. HUMMEL.—See this vol., 443.

Variations in sign of double refraction in myelinic and similar figures. J. NAGEOTTE (Compt. rend., 1931, **192**, 584—586).—The positive double refraction of a fresh ethereal extract of brain or pure lecithin immersed in water becomes negative when oxidation occurs. This is due to the formation of hydrates favoured by oxidation. In the absence of water, glass-mounted specimens of fresh or oxidised material show no change of sign. A. COHEN.

Biological significance and distribution of fat in the pregnant uterus of the bat. M. KADIMURA (Keijo J. Med., 1930, **1**, 475—494; cf. A., 1930, 1609).—The distribution of fat in different uterine tissues of the pregnant bat has been studied microscopically. Fat is stored in the placenta during the early stages of pregnancy and functions in a similar manner to glycogen (*loc. cit.*), serving later as a nutrient for the fœtus during its development. A. COHEN.

Fatty acids of the cat's kidney. I. K. TURNER (Biochem. J., 1931, **25**, 49—56).—The fatty acids consist of palmitic, stearic, oleic, and linoleic acids together with at least two new liquid saturated acids.

A comparison is made between the simple glyceride and phospholipin fraction from cat and ox kidneys.

S. S. ZILVA.

Specificity of lens-protein with special reference to the precipitin content. J. KUNIFUSA (Keijo J. Med., 1930, 1, 409—427).—Lens-protein possesses not only organ- but also species-specificity. The precipitin content, rather than the titre, is of especial significance with regard to specificity; on it depends the difference between the chief and the subsidiary reactions. Urea and dextrose appear to prevent the combination of precipitinogens with precipitins; under the influence of these substances the species-specificity is emphasised. A. COHEN.

Micro-determination of reduced and total glutathione in the liver. J. KUHNAU (Biochem. Z., 1931, **230**, 353—372).—An iodide titration method is described for determination of reduced glutathione and used also for total glutathione, the oxidised form being first converted into the reduced by means of cyanide. The determination is carried out on 0·5 g. of liver with an accuracy of $\pm 4\%$. The influence of dilution factors, acidity, and temperature on the iodine-combining power of glutathione is investigated and the reducing action of sodium cyanide on oxidised glutathione is measured. P. W. CLUTTERBUCK.

Relation between cystine yield and total sulphur in kemp and outer-coat animal fibres. C. RIMINGTON (Biochem. J., 1931, **25**, 71—73).—The entire sulphur in Scotch blackface kemp, Welsh mountain wool kemp, and lamb's birth-coat can be accounted for as cystine. In the case of two separate samples of camel hair, both true hair (inner coat) and coarse outer-coat fibres contained more sulphur than could be accounted for as cystine. The brownish-red pigment present in these samples may account, in part at any rate, for the discrepancy.

S. S. ZILVA.

Iodine content of the bile and thyroid gland of the ox under the influence of seasonal variations in fodder. G. PFEIFFER (Biochem. Z., 1931, **230**, 290—298).—An increase in weight of the thyroid gland is obtained from winter to summer in oxen of all ages. The relative and absolute iodine contents of the thyroid increase with increasing age and gland weight and reach maximal values in the fifth to sixth year. Change from the naturally iodine-deficient winter fodder to the iodine-rich fodder of the summer months does not affect the thyroid iodine content. Secretion of bile increases with increasing age. The iodine content of the bile is increased in the summer months by 120% over the winter months.

P. W. CLUTTERBUCK.

Iodine content of normal and pathological thyroid glands. N. VON HEDRY (Arch. klin. Chir., 1929, **154**, 611—622; Chem. Zentr., 1930, ii, 3050).—Normal thyroid glands contain 0·014% of iodine (average); goitres after removal contained 0·00087% of iodine, the total iodine content being approximately normal. The condition of thyroid gland function was independent of the iodine content.

A. A. ELDRIDGE.

X-Ray analysis of bone and teeth. H. H. ROSEBERRY, A. B. HASTINGS, and J. K. MORSE (J. Biol. Chem., 1931, **90**, 395—407).—*X*-Ray spectrograms of powdered bone and tooth enamel indicate that they possess a crystal structure similar to that of dahlite and other members of the apatite series, and that the calcium salts present in bone and enamel are represented by the formula $CaCO_3,nCa_3(PO_4)_2$, n being 2 or 3. From Laue photographs it is concluded that enamel has a close-packed hexagonal lattice, a_0 20·8, b_0 12, c_0 8·82 Å., referred to orthorhombic axes. A. COHEN.

Equilibrium between cerebrospinal fluid and blood-plasma. III. Distribution of calcium and phosphorus between cerebrospinal fluid and blood-serum. IV. The calcium content of serum, cerebrospinal fluid, and aqueous humour at different levels of parathyroid activity. H. H. MERRITT and W. BAUER (J. Biol. Chem., 1931, **90**, 215—232, 233—246).—III. In normal individuals the average calcium content of the serum is 10 mg. per 100 c.c., varying from 9·35 to 10·6 mg., and of the cerebrospinal fluid, 5 mg. per 100 c.c., varying from 4·5 to 5·23 mg. The ratio of the cerebrospinal fluid-calcium to the serum-calcium varies from 45 to 53% with an average of 50%. There is no significant change in this ratio with changes in the serum-protein content, although both serum-calcium and cerebrospinal fluid-calcium tend to vary directly with the serum-protein content. In various non-suppurative diseases of the central nervous system there is no change in the serum- and cerebrospinal fluid-calcium, but in cases of meningitis a slight diminution of serum-calcium and an increase of cerebrospinal fluid-calcium occurs. In pulmonary tuberculosis there is a slight decrease in the serum- and cerebrospinal fluid-calcium content. Water-drinking during the antidiuretic action of vasopressin causes a decrease in the serum- and cerebrospinal fluid-calcium. Towards the end of pregnancy reduction of the cerebrospinal fluid-calcium occurs. The amniotic fluid-calcium content varies between 5·4 and 8·8 mg. per 100 c.c. with an average of 6·59 mg. per 100 c.c. In cats the content of the cerebrospinal fluid and aqueous humour of the eye averages 54 and 60%, respectively, of the serum-calcium content. In non-suppurative diseases of the central nervous system, the cerebrospinal fluid-phosphorus content varies between 31 and 45% of the serum-phosphorus with an average of 38%. In suppurative diseases of the nervous system, the ratio of cerebrospinal fluid-phosphorus to serum-phosphorus varies between 0·35 and 1·23 with an average of 0·40.

IV. When the serum-calcium of man or of animals is raised by the administration of parathyroid extract, very little change occurs in cerebrospinal fluid-calcium. This is likewise little altered during parathyroid tetany. W. O. KERMACK.

Determination of total sterol and ergosterol in cow's milk. H. HENTSCHEL and O. BACHMANN. **Comparative values for milk of different origin.** O. BACHMANN (Z. ges. exp. Med., 1930, **71**, 744—754; Chem. Zentr., 1930, ii, 2322).—Potassium hydroxide is added to the milk, and the fat extracted with ether; after saponification, the unsaponifiable fraction is extracted with ether and treated with

digitonin solution. The factor is 0·2431. The following sterol contents of milk (mg. per litre) are recorded: Rosenheim 77, Allgau 57, Berlin 60, Central Germany 101. Corresponding values for inactive ergosterol were: 0·19, 0·13, 0·10, —. The spectrum of the fourth sample suggested the presence of activated ergosterol. A. A. ELDRIDGE.

Influence of fodder containing vitamin-*D* on milk. ROEMELE and STOHR (Milchwirt. Forsch., 1930, **10**, 413—423; Chem. Zentr., 1930, ii, 3433).—Admixture of a vitamin-*D* preparation with maize meal did not affect the vitamin-*D*, fat, or calcium content of the milk, its quantity, or the f. p. of the fat. A. A. ELDRIDGE.

Human milk. VI. Vitamin potency as influenced by supplementing the maternal diet with yeast. S. S. MCCOSH, I. G. MACY, and H. A. HUNSCHER (J. Biol. Chem., 1931, **90**, 1—13).—The vitamin-*B* contents of the milks of three women were inversely proportional to the quantity of milk secreted daily. The addition of 10 g. of yeast daily to the diet resulted in the secretion in the milk of some factor which whilst not increasing the appetite favoured more economic utilisation of the food consumed by the experimental animals.
W. O. KERMACK.

Milk peroxidase. W. GRIMMER and H. ENGEL (Milchwirt. Forsch., 1930, **10**, 273—296; Chem. Zentr., 1930, ii, 3585).—Precipitation with various reagents does not separate the peroxidase from the milk-albumin. In pancreatin digestion the residual albumin exhibits a marked increase in peroxidase activity. The peroxidase is not identical with the albumin; it may exhibit similar precipitation reactions, or be attached to the albumin molecule complex.
A. A. ELDRIDGE.

Action of peptone on the gastric secretion. I. TESSIERI (Semana med., 1930, II, 1579—1586).—The quantity, acidity, and duration of gastric secretion are increased. CHEMICAL ABSTRACTS.

Excretion of sodium salicylate in the bile. B. HALPERT, M. T. HANKE, and G. M. CURTIS (J. Clin. Invest., 1930, **9**, 359—362).—Oral ingestion of a medicinal dose of sodium salicylate in biliary disease is not followed by its appearance in the bile.
CHEMICAL ABSTRACTS.

Composition of bile following the relief of biliary obstruction. C. H. GREENE, W. WALTERS, FREDRICKSON (J. Clin. Invest., 1930, **9**, 29?—310).—The output of bilirubin was constant. The formation of bile acids is inhibited by biliary obstruction, with rapid return to normal in absence of liver injury. Bile-chloride is higher than blood-serum-chloride; bile-urea varies directly with blood-urea. CHEMICAL ABSTRACTS.

Polarimetric determination of bile acids in body-fluids and organs. M. JENKE (Arch. exp. Path. Pharm., 1931, **159**, 180—182; cf. Rosenthal, this vol., 251).—Rosenthal's modification of the polarimetric method of the author for the determination of bile acids is likely to introduce considerable error. The polarimetric determination of bile acids is essentially inapplicable to blood, organs, and urine which contain only very small amounts.
W. O. KERMACK.

Determination of urobilin in urine. E. LEIKOLA (Acta Soc. Med. Fenn. Duodecim, 1929, **11**, 9 pp.; Chem. Zentr., 1930, ii, 3446).—The light absorption of the urine is measured at 530, 490, and 450 mμ, whence the quantity of urobilin may be calculated, since the extinction-coefficient curve of urine is regular in the absence of foreign colouring matters. For the determination of urobilinogen the urine is treated with hydrogen peroxide, and the urobilin content is again determined. A. A. ELDRIDGE.

Solubility, dissociation, and tension of carbonic acid in urine. F. MAINZER and M. BRUHN (Biochem. Z., 1931, **230**, 395—410).—A method for determination of the carbon dioxide tension of urine depends on the use of the Henderson–Hasselbalch equation and requires, therefore, the determination of the solubility coefficient ($\alpha_{38°}$) and the apparent dissociation constant (or its negative logarithm, $p_{K'}$) of carbonic acid. The values for 20 urines are for $\alpha_{(CO_2,\ 38)}$ between 0·441 and 0·514, for $p_{K'}$ between 5·81 and 6·30, and for the tension $p_{(CO_2,\ 38)}$ between 13·3 and 242·4 mm. mercury. P. W. CLUTTERBUCK.

Determination of purine bases in urine. FISCHER and HUPPMANN (Süddeut. Apoth.-Ztg., 1930, **70**, 465—466; Chem. Zentr., 1930, ii, 2680).—Precipitation by Kruger and Schmid's method is preferred. A. A. ELDRIDGE.

Statistical analysis of the laws governing urea excretion in man. E. J. CONWAY (Proc. Roy. Irish Acad., 1931, **35 B**, 574—594).—A large quantity of data relating to urea excretion in man has been analysed statistically with reference to the diffusion secretion formula of the author (cf. Amer. J. Physiol., 1929, **88**, 1). W. O. KERMACK.

Fading of tropeolin-OO in the titration of organic acids in urine. K. L. MCCLUSKEY (J. Biol. Chem., 1931, **90**, 197—201).—The fading of the indicator occasionally observed when pathological urine is titrated for organic acids by the method of Van Slyke and Palmer (A., 1920, i, 459; ii, 131) is due to the presence of an unidentified substance (which presumably converts the azo- into the hydrazo-compound) which is readily oxidised in acid solution. Its effect may be eliminated by aeration of the urine in presence of hydrochloric acid. Urine as the result of aeration may give results up to 5% lower than the untreated urine. This difference is not due to loss of volatile acids, to incomplete removal of the carbonates, to changes in the uric acid, creatinine, and creatine, or to the salt effect on the indicator, but may be due to pigment content.
W. O. KERMACK.

Electrolyte equilibrium in blood in experimental acidosis. H. N. HARKINS and A. B. HASTINGS (J. Biol. Chem., 1931, **90**, 565—595).—The effects of hydrochloric acid injection into anæsthetised dogs on the concentrations of blood-constituents are described and discussed. Injection is followed by an immediate and temporary low p_H, anuria, and increased rate of respiration. Since the p_H remains

low after the respiration returns to normal, the p_H does not control respiration. The distribution of diffusible ions between cells and serum in experimental acidosis *in vivo* may be accounted for by the same laws as operate *in vitro*. A. COHEN.

Hæmoglobin production. II. Relief of anæmia due to milk diet by feeding amino-acids. D. L. DRABKIN and H. K. MILLER (J. Biol. Chem., 1931, **90**, 531—543; cf. Drabkin and Waggoner, this vol., 247).—Rats suffering from anæmia on a milk diet containing iron recovered when the diet was supplemented by arginine, glutamic acid, and their salts. Partial recovery was observed with tryptophan, pyrrolidonecarboxylic acid, and proline (72% purity), and sodium aspartate caused temporary relief followed by relapse. Alanine, alanine hydrochloride, histidine dihydrochloride, and hydrochloric acid failed to effect hæmoglobin regeneration. All materials were free from copper and contained insignificant traces of iron. The active substances are regarded as possible sources of pyrrole radicals which may be utilised in the synthesis of hæmoglobin. A. COHEN.

Ineffectiveness of manganese in nutritional anæmia. W. E. KRAUSS (J. Biol. Chem., 1931, **90**, 267—277).—Rats suffering from nutritional anæmia as the result of feeding on a milk diet were not cured by the addition to the diet either of manganese (0·1 mg. per day) alone or along with iron (0·5 mg. per day), whilst the addition of copper brought about recovery. The conclusions of Titus, Cave, and Hughes (A., 1929, 206) that manganese has a curative action in nutritional anæmia are therefore erroneous. W. O. KERMACK.

Nitrogen and sulphur metabolism in Bright's disease. I. Retention in nephrosis. G. P. GRABFIELD (J. Clin. Invest., 1930, **9**, 311—318).—Considerable retention of nitrogen and sulphur, a high urinary nitrogen : sulphur ratio, and a low ratio in the retained protein were observed. CHEMICAL ABSTRACTS.

Lactic acid in the blood of cancer patients treated with X-rays and with radium. E. LIVERANI (Arch. Farm. sperim., 1931, **51**, 177—188).—Radium or X-ray treatment of 15 individuals suffering from neoplasms resulted, in most cases, in a diminution of the lactic acid content of the blood; such diminution was not observed in 8 non-neoplastic cases. T. H. POPE.

Effect of fermentation poisons on experimental tumours. I—III. L. KARCZAG (Biochem. Z., 1931, **230**, 411—419, 420—434, 435—438).—I. By means of a yeast-zymin test, a large number of substances, chiefly dyes, are divided into enzyme poisons (inhibition of zymin but not of yeast), protoplasm poisons (inhibition of yeast only), and those substances which are both protoplasm and enzyme poisons or have no action at all. With substances acting as enzyme poisons, the nitrogen of the molecule appears to play a decisive role, especially the position of nitro- and cyano-groups in the side-chain. None of the investigated enzyme and protoplasm poisons has any beneficial influence on tumours in mice.

II. [With C. SELLEI.] The inhibitory effect on the glycolysis of tumour cells *in vitro* and on respiration of the following fermentation poisons decreases in the order given; ethyl-red, chrysoidin, Magdala-red, *iso*quinoline-red, Martius-yellow. The substances acting as protoplasm poisons to the yeast cell are not protoplasm poisons to the tumour cell and the effect is due to enzymic inhibition only. Whereas the action of cyanide on glycolysis is reversible, that of these poisons is irreversible. The fermentation poisons of yeast cells are also poisons of *B. coli* fermentations.

III. Rous sarcoma powder is able to ferment sugar slowly with formation of gas. P. W. CLUTTERBUCK.

Fat-soluble vitamins in tumour tissues. M. SUMI and W. NAKAHARA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, **15**, 69—74).—The oils obtained by extraction with ether of the dried tissue of transplantable tumours of four types are described; 12—16% of cholesterol is present, and the presence of admixed ergosterol may be demonstrated spectrographically. The presence of vitamin-*D* in the oils is shown by the cure of rickets in rats by doses of 1—2 drops daily. Colour reactions for vitamin-*A* were negative. R. K. CALLOW.

Chinese antidiabetics. N. SUGIHARA. **I, II. Effect on blood-sugar of rabbits.** P. MIN (Folia Pharmacol. Japon., 1930, **11**, No. 1, 11—21, 21—33).—Of all the drugs examined, aqueous extracts of *Rehmannia lutea* only reduced the blood-sugar without preliminary hyperglycæmia. CHEMICAL ABSTRACTS.

Blood-volume and plasma-electrolyte changes in the dehydration of infants. R. MCINTOSH, L. KAJDI, and D. MEEKER (J. Clin. Invest., 1930, **9**, 333—357).—Determinations with infants suffering from diarrhœa-dehydration are recorded. The serum-chloride, -hydrogen carbonate, and -total fixed base were usually decreased. CHEMICAL ABSTRACTS.

Metabolism in experimental yellow fever in *Macacus rhesus*. A. M. WAKEMAN and C. A. MORRELL (Arch. Int. Med., 1931, **47**, 104—115).—Intravenous injection of dextrose in monkeys with yellow fever does not alleviate the hypoglycæmia which is manifested as early as 24 hrs. before death. Disturbance of carbohydrate metabolism precedes that of deamination and urea formation. With a blood-sugar content of less than 45 mg. per 100 c.c. little glycogen is found in the liver of infected monkeys, although symptoms of hypoglycæmic shock are not readily produced. P. G. MARSHALL.

Distribution of nitrogen and sulphur in the urine during conditions of increased catabolism. D. P. CUTHBERTSON (Biochem. J., 1931, **25**, 236—244; cf. A., 1930, 1310).—The catabolic loss of nitrogen and sulphur which results from tissue injury (bone fractures, minor operations) reached a maximum about the third to eighth day following the injury. The maximum daily loss of nitrogen might even exceed 20 g. The increase in nitrogen was due to a practically proportionate increase in urea excreted and the increase in sulphur to a slightly greater proportionate increase in the excretion of inorganic sulphates. The excretion of ammonia fluctuated;

that of amino-acids and uric acid generally rose. Ethereal sulphate tended to diminish slightly. Creatinine and neutral sulphur remained practically constant, any increase not being proportional to the total increase of nitrogen or sulphur, respectively. Traces of creatine were observed particularly during phases of increased catabolism. Traces of heat-coagulable protein were occasionally found, particularly during the time of the maximum excretion of the nitrogenous catabolites. S. S. ZILVA.

Blood-calcium during the healing of fractures. C. LORETO (Arch. Farm. sperim., 1931, **51**, 145—164, 189—192, 217—227).—The blood-calcium does not vary appreciably as the result of a fracture, but during the healing of the fracture, from the twentieth to the ninetieth day, the calcium content of the fractured bone is greater than that of the other normal homonymous bone. T. H. POPE.

Iodine theory of goitre. C. A. HELLWIG (Klin. Woch., 1930, **9**, 1913—1916; Chem. Zentr., 1930, ii, 2911).—Rats kept for a long period on a diet poor in iodine (barley and distilled water) did not develop a goitrous thyroid; in fact the thyroid became markedly atrophied. A diet rich in calcium (the drinking water contained 2% of calcium chloride), however, caused true epithelial hyperplasia.
A. A. ELDRIDGE.

Extent of goitre in Hungary and its connexion with the iodine content of drinking water. J. STRAUB (Z. Hyg., 1930, **111**, 472—479).—No relation has been found. CHEMICAL ABSTRACTS.

Brown pigment in hæmatochromatosis. M. JACOBY (Biochem. Z., 1931, **230**, 225—227).—The pigment was insoluble in alcohol, ether, acetone, chloroform, benzene, phenol, toluene, and carbon tetrachloride. Extraction by 0·85% sodium chloride and then water gave a solution which contained only traces of hæmoglobin and methæmoglobin. The pigment was isolated by precipitation by saturated ammonium sulphate. Analysis indicated a ratio 4N : Fe. F. O. HOWITT.

Terminal hypoglycæmia. E. G. SCHMIDT [with T. N. CAREY] (Arch. Int. Med., 1931, **47**, 128—134).—From 33 non-diabetic cases only 6 showed a pronounced terminal hypoglycæmia which was not manifested prior to death, whilst at least an equal number of cases actually showed a rise in blood-sugar. Little change occurs in the blood-sugar, -chlorides, or -urea within 1 hr. of death, although the carbon dioxide-combining power decreases somewhat. P. G. MARSHALL.

Effect of experimental obstructive icterus in the dog on blood-bile salts, -bilirubin, and -cholesterol. B. V. FUENTES, E. APOLO, and J. ESCULIES (Z. ges. exp. Med., 1930, **73**, 412—421; Chem. Zentr., 1930, ii, 2796).—Values for cholesterol diminished; for bile salts they were after 7 days 4—5 times the normal which they later approached, whilst for bilirubin a maximal value was attained after 3—7 days and afterwards maintained.
A. A. ELDRIDGE.

Cholesterol partition of the blood-plasma in parenchymatous diseases of the liver. E. Z. EPSTEIN (Arch. Int. Med., 1931, **47**, 82—93).—In acute parenchymatous diseases of the liver the level of cholesteryl esters, which is low or even absent in the early stages, rises to normal during recovery, which is facilitated by a diet high in carbohydrates and low in fat. The cholesterol balance is not disturbed during atrophic cirrhosis brought on by alcoholism.
P. G. MARSHALL.

Lipuria; lipæmia. H. PECKER (J. Pharm. Chim., 1931, [viii], **13**, 197—199).—In a case of lipoid nephritis a mild lipuria (0·52 g. per litre) and a marked lipæmia (blood-lipins 1·81%) were observed. The latter also occurred in the case of a diabetic (blood-lipins 2·64%). F. O. HOWITT.

Blood-lipins in nephrosis and chronic nephritis with œdema. L. LICHTENSTEIN and E. Z. EPSTEIN (Arch. Int. Med., 1931, **47**, 122—127).—In varying types of nephrosis and in seven cases of chronic glomerulo-nephritis with œdema a marked increase in cholesterol, cholesteryl esters, and phosphatides was found. The ester fraction may be 80—90% of the total cholesterol. There is no correlation between lipinæmia and decrease in serum-protein content, which occurs chiefly at the expense of the albumin fraction. P. G. MARSHALL.

Potassium content of the heart in œdematous and non-œdematous conditions. L. C. SCOTT (Arch. Int. Med., 1931, **47**, 116—121).—The water content of the heart is remarkably constant whatever the cause of death, whilst both the sodium and potassium contents may vary widely without relation to the presence or absence of œdema, and either of these elements may predominate.
P. G. MARSHALL.

Rickets. I. Protracted observation of calcium and phosphorus metabolism in infants. E. ROMINGER, H. MEYER, and C. BOMSKOV (Z. ges. exp. Med., 1930, **73**, 343—381; Chem. Zentr., 1930, ii, 2798—2799).—In the first stage of rickets a small or negative phosphate balance and a good calcium balance are observed; in the second stage both balances are slightly positive or negative, whilst in the third stage there is a high phosphate balance, the calcium balance also becoming abnormally high in the fourth stage. Administration of "vigantol" improves at first the retention of phosphate and then that of calcium. Therapeutic doses do not appear to affect the metabolism of normal children.
A. A. ELDRIDGE.

Acid-base equilibrium of blood in pathological conditions. I. Toxæmias of pregnancy. E. MUNTWYLER, N. LIMBACH, A. H. BILL, and V. C. MYERS (J. Biol. Chem., 1931, **90**, 607—617).—A decreased plasma-hydrogen carbonate was observed in cases of toxæmia of pregnancy. The average ante-partum blood-p_H was 7·47 and the total base concentration was lower than normal. Considerable post-partum increases in the hydrogen carbonate and total base were found, with smaller increases in total acid, protein, and p_H of the blood. The lowered plasma-hydrogen carbonate is not due to abnormal acids, but to hyperventilation. A. COHEN.

Lactic acid in the blood in acute infections. E. LIVERANI (Arch. Farm. sperim., 1931, **51**, 245—

265).—An increase of the lactic acid content of the blood is observed in the acute stages of a number of infections, particularly when toxæmia is marked. This is due to several causes—increase of general metabolism, functional insufficiency of the liver, deficient oxygenation of the tissues, and increased absorption from the intestine as a result of increased fermentation. R. K. CALLOW.

Alcohol utilisation by man at high altitudes. A. BORNSTEIN and A. LOEWY (Biochem. Z., 1931, **230**, 51—67; cf. A., 1928, 197).—Following the administration of alcohol the blood-alcohol rises more rapidly at high than at low altitudes, whilst the rate of recovery is the same in both cases. The *R.Q.*, normally higher in elevated regions, is lowered to a greater extent, frequently to the level of pure alcohol combustion, but its return to the normal is more rapid. No specific dynamic action is found on administration of alcohol alone, but simultaneous carbohydrate ingestion results in an action markedly stronger than in the corresponding experiments at low levels. F. O. HOWITT.

Fate of lævulose in the animal. II. Do digestive juices convert lævulose into dextrose? W. W. OPPEL (Biochem. Z., 1931, **230**, 269—284; cf. A., 1929, 462).—Incubation of lævulose for a short time (1—5 hrs.) with digestive juices (gastric, intestinal, and pancreatic) in the absence of toluene and for a longer time (20 hrs.) in presence of toluene at varying physiological p_H did not bring about any conversion of the sugar into dextrose.
P. W. CLUTTERBUCK.

Intermediary carbohydrate metabolism. VI. Sugar assimilation, phosphorus and water metabolism on continuous intravenous injection of dextrose, lævulose, and galactose. M. WIERZUCHOWSKI, W. PIESKOW, and E. OWSIANY. **VII. Production of lactic acid on continuous intravenous injection of dextrose, lævulose, and galactose.** M. WIERZUCHOWSKI and M. ŁANIEWSKI. **VIII. Respiratory metabolism on intravenous injection of dextrose, lævulose, and galactose.** M. WIERZUCHOWSKI (Biochem. Z., 1931, **230**, 146—172, 173—186, 187—224; cf. A., 1928, 197).—VI. In dogs having normal fasting blood-sugar averaging 0·091—0·104% (of which 0·054—0·067% was due to dextrose), during the first hour of dextrose (2 g. per kg. per hr.) injection the blood-dextrose increases, and then sinks in the course of the next 2 hrs., indicating a diphasic action. Such an action does not occur with lævulose or galactose. The final dextrose level is below that of the original. Lævulose follows a somewhat parallel course, but with galactose the assimilation is much slower, as shown by the blood and urine values. With simultaneous insulin administration the diphasic action of dextrose disappears, whilst the assimilation of dextrose and galactose, but not of lævulose, is increased, the influence of the hormone being greatest on the galactose assimilation. Injection of lævulose or galactose does not increase the blood-dextrose, and with insulin administration actually decreases it. Dextrose or lævulose injection fails to increase the non-dextrose reducing substances of the blood. No relation exists between the blood- or urine-phosphate values and any phase of the sugar metabolism investigated. The blood dilution is greatest for continuous injection of galactose and least with lævulose. Where insulin increases assimilation there is a concurrent state of anhydræmia. The amount of urine excreted is related to the sugar excretion.

VII. The lactic acid production following injection of the sugars at the rate of 2 g. per kg. per hr. was investigated in fasting dogs, the blood concentration and hourly excretion of lactic acid of which were 0·007—0·025% and 1·4—5·1 mg., respectively. For each sugar the increase in blood-lactic acid and the simultaneous excretion of the acid are characteristic and follow parallel courses. Lævulose gives rise to greater amounts of lactic acid than dextrose, whilst the production from galactose varies between the two values. The blood-lactic acid during injection of the sugars reaches a level equal to that produced by muscular work. Simultaneous administration of insulin leads to increased lactic acid formation by all three hexoses. Parallel with but not stoicheiometrically related to the lactic acid increase is the resulting condition of acidosis.

VIII. Injection into dogs at the rate of 2 g. per kg. per hr. results in values of *R.Q.* of 0·23 (dextrose), 0·24 (lævulose), and 0·13 (galactose), these values being increased to 0·26, 0·30, and 0·18 on simultaneous administration of insulin. The specific dynamic action is greatest for galactose and least for dextrose, the greatest increase in heat production being during the second and third hour of injection. The extent of the increase in heat production due to simultaneous administration of insulin depends on the glycæmic level. The maximum sugar oxidation is 0·5 g. per kg. per hr. With a condition of hyperglycæmia insulin increases the oxidation of injected dextrose by 15%, that of lævulose by 24%, and that of galactose by 87%. A quantitative relationship exists between the specific dynamic action of the hexoses and their oxidation, the quotients of which are 3·04 for dextrose, 2·48 for lævulose, and 1·82 for galactose. The heat production and increase in *R.Q.* during the maximum rate of oxidation indicate that the utilisation of all three sugars is inversely proportional to the concentration of the injected hexose in the blood. The blood-lactic acid does not run parallel to the heat production, but for a definite amount of assimilated sugar the specific dynamic action and the oxidation of the introduced sugar are the greater the more lactic acid the organism produces from the sugar assimilated.
F. O. HOWITT.

Carbohydrate metabolism. II. Dextrose-lactic acid cycle in diabetes. H. E. HIMWICH, W. H. CHAMBERS, Y. D. KOSKOFF, and L. H. NAHUM (J. Biol. Chem., 1931, **90**, 417—426).—In depancreatised and phloridzinised dogs the lactic acid content of the blood of the femoral and portal veins is significantly higher than that of the blood of the femoral artery and hepatic vein, respectively. The dextrose content shows the reverse relationships. In the diabetic animal, therefore, the same cycle exists as in the normal animal (A., 1930, 368), whereby lactic acid formed by muscle is removed by the liver which liberates dextrose into the blood. A. COHEN.

Various methods of sugar degradation in the animal organism. II. E. Bumm and K. Fehrenbach (Z. physiol. Chem., 1931, **195**, 101—112).—The work of Ashford and Holmes (A., 1929, 1194) on the role of phosphate in the glycolysis of brain substance is amplified. Neither co-zymase nor hexokinase accelerates the production of lactic acid during this glycolysis. Co-enzyme-*T* (A., 1928, 1274) increases the formation of lactic acid by 40—90%. Arsenate has no effect. Glycolysis in retina substance appears to be independent of phosphate.

A. Renfrew.

Equilibrium between glycogen and lactic acid. W. D. Bancroft and G. Bancroft (J. Physical Chem., 1931, **35**, 194—214).—The theories concerning the chemical changes which occur in muscle during fatigue and recovery are discussed.

L. S. Theobald.

Glycogen formation in rats. II. E. M. Greisheimer and O. H. Johnson (J. Nutrition, 1930, **3**, 297—302).—Liver-glycogen was significantly higher with a high-sucrose diet, and lower when 87% of the calories was given as lard or caseinogen. Comparative diet values are: McCollom No. 1, 1; sucrose 1·85; caseinogen 0·61; fat 0·44.

Chemical Abstracts.

Significance of raw egg-yolk for glycogen deposition in the liver. I. Abelin (Klin. Woch., 1930, **9**, 1759—1761; Chem. Zentr., 1930, ii, 3310).—A favourable effect was observed.

A. A. Eldridge.

Glycogen content of the liver after administration of mineral (sodium sulphate) water. W. Arnoldi (Z. ges. exp. Med., 1930, **73**, 452—457; Chem. Zentr., 1930, ii, 2797).—Experiments with rabbits and rats led to an increase in the glycogen content of the liver. On administration of Franzensbad water with a diet high in carbohydrate the diminution in glycogen is less marked than normally; with a diet rich in protein and fat the liver-glycogen decreases. A. A. Eldridge.

Conversion of fat into carbohydrate in the organism. M. Henze (Z. physiol. Chem., 1931, **195**, 248—254).—Hexan-γ-ol-$\beta\epsilon$-dione (I) (A., 1930, 1022; this vol., 69), prepared from acetoacetic acid and methylglyoxal, is oxidised by cold alkaline potassium permanganate solution to pyruvic acid. It is, therefore, possible to convert a C_1 into a C_3 chain (and thence into sugar). When I is fed to rabbits about 2 g. are decomposed, the remainder being excreted in the urine. Treatment of I with liver-pulp causes complete decomposition. H. Burton.

Significance of conjugated bile-acids for fat resorption. IV. F. Verzar and A. von Kuthy (Biochem. Z., 1931, **230**, 451—457).—A much larger amount of fat is resorbed from a washed tied-off loop of intestine in the living animal in presence of a known amount of bile-acid than can be made diffusible in experiments *in vitro*. It is suggested that the bile-acids are adsorbed by the epithelial cells of the intestinal mucous membrane and are there used repeatedly in the formation of the water-soluble fat complex (A., 1929, 466, 1194).

P. W. Clutterbuck.

Biochemistry of muscle. A. Palladin (Bull. Soc. Chim. biol., 1931, **13**, 13—28).—A lecture.

Significance of arginine-phosphoric acid in the metabolism of active crustacean muscle. E. Lundsgaard (Biochem. Z., 1931, **230**, 10—18).—Crab (*Maia squinado*) muscle is much less sensitive to iodoacetic acid than frog-muscle. Following inhibition of lactic acid formation, the total activity of the muscle changes in a manner similar to that of frog muscle. Arginine-phosphoric acid plays the same role in the metabolism of the former as creatinine-phosphoric acid does in the latter (cf. Meyerhof and Lohmann, A., 1928, 1277), and hence the degradation of arginine-phosphoric acid in crustacean muscle is an energy-providing reaction similar to that of creatinine-phosphoric acid in vertebrate muscle.

F. O. Howitt.

Amino-nitrogen of blood, muscle, and proteins and its role in chemical processes of the working muscle. T. Mann (Acta Biol. Exp., Warsaw, 1930, **6**, 45—52).—The amino-group content of the blood-proteins of three persons was the same before and after exertion and, similarly, no difference was found in isolated symmetrical frog-muscles, one resting and the other stimulated to exhaustion. The amino-groups of blood and muscle proteins are not involved in the chemical processes of muscular exertion.

R. Truszkowski.

Production of ammonia in and ammonia content of muscle and their connexion with function and change of condition. VIII. Supposed changes in the amino-nitrogen content of the proteins of blood and muscle occurring during the chemical processes which accompany muscular work. T. Mann (Biochem. Z., 1931, **231**, 33—38).—Neither in human blood nor in isolated frog-muscle do changes in the amount of amino-nitrogen accompany the metabolic processes which occur during muscular work. It follows that the theory of Bliss (A., 1929, 339) must be rejected.

W. McCartney.

Intermediary metabolism of histidine. III. S. Edlbacher and J. Kraus (Z. physiol. Chem., 1931, **195**, 267—272; cf. A., 1926, 1171; 1930, 1619).—The low value for the amount of ammonia formed during the enzymic decomposition of histidine found by Kauffmann and Mislowitzer (A., 1930, 1619) is due to their use of sodium carbonate for its liberation. During the hydrolysis of histidine an intermediate is produced which is not hydrolysed by acid or carbonate. Formamide and glutamine are not hydrolysed by sodium carbonate but are hydrolysed by acid. H. Burton.

Intermediary metabolism of tryptophan. Y. Kotake. **I. Kynurenine, an intermediate metabolic product.** Y. Kotake and J. Iwao. **II. Fission of kynurenine with barium hydroxide solution.** Y. Kotake and M. Kiyokawa. **III. Fission of kynurenine with sodium hydrogen carbonate solution.** Y. Kotake and G. Schichiri. **IV. Mechanism of formation of kynurenic acid in the organism.** Y. Kotake. **V. Formation of kynurenic acid from kynurenine by micro-organisms.** G. Schichiri and M. Kiyokawa. **VI.**

Excretion of kynurenic acid in bile and its stability in the organism. Y. KOTAKE and K. ICHIHARA. **VII. Site of formation of kynurenic acid in the organism.** K. ICHIHARA, S. OTANI, and J. TSUJIMOTO [with Y. OKAGAWA and T. KIYOMATSU]. **VIII. Origin of urochrome.** Y. KOTAKE and H. SAKATA [with Y. SHIRABE and S. OTANI]. **IX. Action of trytophan in experimental anæmia and its relation to the spleen.** Y. OKAGAWA and M. TATSUI. **X. *dl*-Indolyl-lactic acid and its use in nutrition.** K. ICHIHARA and N. IWAKURA. **XI. Action of methyltryptophan in experimental anæmia and in nutrition.** Z. MATSUOKA and T. NAKAO (Z. physiol. Chem., 1931, **195**, 139—147, 147—152, 152—158, 158—166, 166—171, 171—179, 179—184, 184—191, 192—202, 202—207, 208—214).—I. After subcutaneous injection of tryptophan into rabbits fed on polished rice, the urine contains kynurenic acid and a *substance* (termed *kynurenine*), probably (o)-NH_2·C_6H_4·C(CO_2H):CH·CH(NH_2)·CO_2H, m. p. 190° (decomp.) after colouring at 170° and sintering at 180°, $[\alpha]_D^{17}$ $-28\cdot5°$ in water, which is isolated as the *sulphate*, darkens at 165° and becomes black at 180°, $[\alpha]_D^{18}$ $+10\cdot7°$ in water, by the following process. The urine is acidified with sulphuric acid, the kynurenic acid filtered off, the filtrate evaporated to small bulk, and then mixed with alcohol, whereby kynurenine sulphate and inorganic salts separate; the sulphate is then extracted with 60% alcohol. Kynurenine gives the ninhydrin reaction, affords a (?) *diethyl ester* (*dihydrochloride*), and treatment of the sulphate with bromine water furnishes the *lactam dibromide*, $\mathrm{NH}{<}^{\mathrm{C}}_{\mathrm{CO}}$ r·CHBr·CH(NH_2)·CO_2H, m. p. 206—207° (decomp.) after darkening about 200°. When kynurenine is fed to a rabbit, 20—40% is excreted in the urine as kynurenic acid.

II. Kynurenine is stable towards boiling 25% sulphuric acid, but is readily decomposed by boiling 1% barium hydroxide solution to ammonia, carbon dioxide, *o*-aminoacetophenone [*hydrochloride*, m. p. 264—265° after becoming red at 160°; acetyl derivative, m. p. 75—76° (*bromo*-derivative, m. p. 157—158°)], kynurenic acid, and a small amount of an amorphous yellow substance.

III. Kynurenine is decomposed by boiling with 2% sodium hydrogen carbonate solution to ammonia, a small amount of *o*-aminoacetophenone, about 20% of kynurenic acid, and an unstable orange-yellow substance (*A*), m. p. 80—160° (according to the time of the boiling). Further treatment of *A* with sodium hydrogen carbonate or barium hydroxide solution gives some *o*-aminoacetophenone. *A* dissolves partly in warm water; extraction of the resulting solution with ether in presence of charcoal affords "*kynurenine-yellow*," m. p. 182°, which gives Ehrlich's diazo-reaction and Jaffé's kynurenic acid reaction. When an ethereal solution of "kynurenine-yellow" is kept in air, kynurenic acid is slowly deposited. The results of the alkaline fission of kynurenine support the formula assigned.

When a mixture of kynurenine and aqueous phenylhydrazine hydrochloride is made alkaline with sodium hydrogen carbonate solution, the mixture boiled for several min., and then treated with sulphuric acid, a blue coloration is produced. This test can be used for the detection of kynurenine; the blue colour is ascribed to the formation of a pyrazole.

IV. Kynurenic acid is probably formed from tryptophan as follows: tryptophan⟶α-amino-β-2-hydroxy-3-indolylpropionic acid⟶α-amino-α′-*o*-aminophenylglutaric acid⟶kynurenine⟶β-*o*-aminobenzoylpyruvic acid⟶kynurenic acid.

V. Kynurenic acid is produced when *Oidium lactis* and *Willia anomala* are grown on media containing sucrose, inorganic salts, and kynurenine. Secondary products are a substance, m. p. 122°, and a water-soluble green compound, respectively. The green compound has properties similar to those of the urochromogen of Weiss (A., 1923, i, 417).

VI. Kynurenic acid is isolated in considerable amount from fistula bile of dogs after subcutaneous injection of an aqueous suspension of tryptophan. Bile obtained similarly from rabbits contains no kynurenic acid; the acid is present in the urine. Subcutaneous injection of kynurenic acid (as the sodium salt) into dogs with gall-bladder fistulas is followed by the excretion of the total amount in the bile and urine; the major part is in the urine. Similar experiments with rabbits show that excretion is slower, but the whole of the acid can be isolated from the urine (a small amount may be excreted in the bile). The results show that kynurenic acid is not an intermediate, but is an end-product, in the metabolism of tryptophan.

VII. Little or no kynurenic acid is found in the blood or urine of dogs from which the liver has been extirpated when injected (subcutaneously or intravenously) with tryptophan. Perfusion of the surviving liver with blood (diluted with Ringer's solution) containing kynurenine gives kynurenic acid. These results and those of Matsuoka and Takemura (A., 1923, i, 72) show that kynurenic acid is formed mainly in the liver. Excretion of kynurenic acid in fistula bile of dogs increases after splenectomy.

VIII. Ingestion of tryptophan results in an increase in the urochrome fraction of the urine; the results of Tani (Med. Ges. Osaka, 1925, **24**, 1457) are thereby confirmed. Kynurenine has a similar action.

IX. Injection of tryptophan into dogs with experimental anæmia (phenylhydrazine hydrochloride) accelerates their recovery, particularly with regard to the hæmoglobin content. This action of tryptophan cannot be noticed for a time if the animals have previously undergone splenectomy. The tryptophan contents of the liver and kidney of the dog do not alter during 40 days after splenectomy; the amount in the liver does increase, however, after 80—120 days.

X. *dl*-α-Hydroxy-β-indolylpropionic acid, m. p. 145—146° [*barium* salt (+3H_2O)], prepared from the *l*-acid and barium hydroxide solution at 150—160°, when subcutaneously injected into the rabbit results in the excretion in the urine of some unchanged material, *l*-α-hydroxy-β-indolylpropionic acid, and a small amount of kynurenic acid. Rats fed on a tryptophan-free diet undergo normal growth when the diet is supplemented by *dl*-α-hydroxy-β-indolylpropionic acid; the *l*-acid and α-keto-β-indolylpropionic acid are not able to replace tryptophan.

XI. 2-Methyltryptophan has the same action as tryptophan in experimental anæmia, but it cannot replace tryptophan in the diet. H. BURTON.

Formation of uric acid in birds. Intermediary reserve material in the liver of birds. G. PUPILLI (Arch. Fisiol., 1928, **26**, 27 pp.; Chem. Zentr., 1930, ii, 3596).—Uric acid is synthesised from lactic acid and urea under aerobic conditions in presence of birds' liver extract. Fresh hen's or goose's liver affords a crystalline compound resembling hydroxypyruvic or formylglyoxylic acid; it is an oxidation product of lactic acid and a link in the synthesis of uric acid. A. A. ELDRIDGE.

Meat in nutrition. I. Beef-muscle. P. M. NELSON, M. H. IRWIN, and L. J. PEET. **II. Dietary factors influencing lactation. III. Hæmoglobin formation.** L. J. PEET, P. M. NELSON, and E. A. SMITH (J. Nutrition, 1930, **3**, 303—311, 313—323, 325—330).—I. Growth and reproduction, but not lactation, of rats were adequately maintained on a meat diet; addition of yeast, salt mixture, or protein was ineffective.

II. Diet modifications supporting lactation are described.

III. Hæmoglobin formation was favoured by addition to a meat diet of autoclaved yeast, yeast, tikitiki, lemon juice, or wheat-germ oil. CHEMICAL ABSTRACTS.

Food requirements for the growth of the rat. VI. Influence of food consumption and efficiency quotient of the animal. L. S. PALMER and C. KENNEDY (J. Biol. Chem., 1931, **90**, 545—564).—Yeast and wheat embryo extract have the same influence as vitamin-B_1 and -B_2 on the growth of rats having equal food intake and efficiency of food utilisation. The stimulant effect on growth exerted by fresh lettuce, liver, and carrots combined with yeast appears to be due to their effects on food consumption. The differences in growth rate of the two sexes, and between individuals on the same diet, are largely determined by differences in the efficiency index deduced from the efficiency of food utilisation. A. COHEN.

Effects of vitamin deficiency on the coefficients of digestibility of protein, fat, and carbohydrate. R. ST. JULIAN and V. G. HELLER (J. Biol. Chem., 1931, **90**, 99—110).—The coefficient of digestibility ([amount ingested—amount in fæces]/amount ingested) of fats, carbohydrates, and proteins has been determined in rats fed on a complete diet and on one lacking vitamin-A, -B_1, -B_2, or -D and in guinea-pigs on a complete diet and on one lacking vitamin-C. The vitamin deficiency did not in any instance significantly affect the coefficients of digestibility. W. O. KERMACK.

Physiological effects of diets rich in egg-white. H. T. PARSONS (J. Biol. Chem., 1931, **90**, 367).—Rats fed on a diet of high protein content and containing all the known accessory factors developed in a few days a general disturbance in health characterised by digestive disturbances and hæmaturia and usually soon ending fatally provided that the protein consisted of egg-white, raw or cooked, commercial dried or fresh, but not when other types of protein such as caseinogen or beef powder were used. Dried liver protects the animals, the addition of 1% to the egg-white for 1 week being apparently about the minimum dose. 5% of dried liver fed for 3 days before the egg-white diet also protects. When the animals which have been partly protected so as to survive the first few weeks of feeding on a diet rich in egg-white are allowed to continue on this diet a second type of disease sets in characterised by dermal and neural symptoms. The addition of 20% of dried liver completely protects against this late manifestation, but 10% or less is usually insufficient. The early symptoms brought about by egg-white markedly resemble the effects of overdosage with cystine, whilst the later symptoms are not dissimilar to those of pellagra. W. O. KERMACK.

Nutrient requirements of poultry. G. SCOTT-ROBERTSON, J. B. ORR, J. H. PRENTICE, and A. J. MACDONALD (Scot. J. Agric., 1930, **13**, 410—415).—A supplement of sodium chloride (up to 1% of the ration) to a grain-soya bean meal ration increased the rate of growth of poultry and the number of eggs laid; transference of the birds to fresh pasture corrected the salt-deficiency of the ration. Under the conditions of the experiment, sulphur, iron, and potassium iodide were omitted from the mineral supplement without effect. A. G. POLLARD.

Effect of a diet of sweet clover on the serum-calcium. C. Y. CANNON and D. GREENWOOD (J. Dairy Sci., 1930, **13**, 424—431).—The serum-calcium of young rabbits was decreased, becoming again normal, on a lucerne diet. The diminution is associated with failure of blood to clot; the surface tension of the blood may be raised so that the platelets fail to rupture, thus interfering with the formation of thrombin. CHEMICAL ABSTRACTS.

Calcium and phosphorus metabolism of heavily milking cows. C. F. HUFFMAN, C. S. ROBINSON, and O. B. WINTER (J. Dairy Sci., 1930, **13**, 432—448).—Positive calcium and phosphorus balances of heavily milking cows can be maintained on a diet of lucerne, silage, and grain, or of timothy hay, silage, and grain supplemented by bone flour. Calcium and phosphorus are somewhat more efficiently utilised during high than during low milk production. The total intake is more significant than the ratio in food. CHEMICAL ABSTRACTS.

Resorption and effect of calcium gluconate. E. ROTHLIN (Z. ges. exp. Med., 1930, **70**, 634—657; Chem. Zentr., 1930, ii, 2154).—Oral administration of calcium gluconate or chloride leads to a longer continued increase in blood-calcium than intravenous administration; the effects of subcutaneous and intravenous administration are intermediate. A. A. ELDRIDGE.

Biochemistry of aluminium. II. Excretion and absorption of aluminium in the rat. K. MACKENZIE (Biochem. J., 1931, **25**, 287—291).—Rats receiving aluminium in their diet do not absorb it. The metal is excreted entirely by the alimentary canal. S. S. ZILVA.

Magnesium absorption in dogs. J. E. WINTER and C. H. RICHEY (J. Pharm. Exp. Ther., 1931, **41**,

245—254).—The absorption of magnesium chloride and oxide given by the mouth was investigated in fasting dogs the normal serum-magnesium of which ranged from 0·00065 to 0·00223%. The stomach appears to be the main site of absorption.

F. O. Howitt.

Manganese metabolism of the rat. J. T. Skinner, W. H. Peterson, and H. Steenbock (J. Biol. Chem., 1931, **90**, 65—80).—The average concentration of manganese in rats fed on the Steenbock ration was highest at birth, decreased during the first 12 days, rose to a second maximum at 21 days, and then decreased. The average total quantity of manganese in the rats was 0·0015 mg. at birth and 0·0676 mg. at 180 days of age. The manganese content of the newly born rat was increased 40% by adding extra manganese (as manganese sulphate) to the diet of the mother during gestation. During the first 12 days while the rats were receiving only mother's milk the storage of manganese was slow and could not be increased by adding manganese to the mother's ration. Addition of manganese to the rations of the young rats increased the rate of storage. The element is stored chiefly in the liver, muscle, bone, and hide, and by the addition of manganese to the ration, the amounts in bone, hide, liver, and kidney were increased by 191, 79, 29, and 29%, respectively. On a stock ration, adult rats excreted 80% of the manganese in the fæces, but with addition of manganese to the diet this increased to 99%. Addition of copper and iron, either singly or together, decreased the retention of manganese.

W. O. Kermack.

Iron requirement in early childhood. M. S. Rose, E. McC. Vahlteich, E. Robb, and E. M. Bloomfield (J. Nutrition, 1930, **3**, 229—235).—A normal diet, uncontaminated with iron, afforded insufficient iron for the needs of a girl aged 31 months. The intake of copper, about 0·2 of that of iron, was sufficient.

Chemical Abstracts.

Metabolic changes associated with pigmentary effector activity and pituitary removal in *Xenopus lævis*. I. Respiratory exchange. II. Calcium and magnesium content of the serum. E. Charles (Proc. Roy. Soc., 1931, B, **107**, 486—503, 504—510).—I. The factors controlling the metabolic rate of *X. lævis* have been investigated. Removal of the whole pituitary gland, or of the anterior lobe only, significantly decreases the rate of respiratory exchange, the pulmonary rate being depressed more than the dermal rate. Hypophysectomised animals have a significantly higher respiratory quotient than normal animals. The rate at which oxygen is absorbed through the lungs by *X. lævis* is 2—3 times as great as that at which it is absorbed through the skin.

II. The average calcium content of the serum of *X. lævis* was 7·61±0·25 mg. and 9·82±0·13 mg. for males and females, respectively. The corresponding values for the average magnesium content were 1·60±0·09 mg. and 2·35±0·10 mg. Excision of the whole pituitary or of the anterior lobe alone caused a fall in these values. No certain correlation could be detected between calcium and magnesium content and pigmentary effector activity.

W. O. Kermack.

Fate in the organism of sulphur parenterally administered. R. Meyer-Bisch and F. Techner (Biochem. Z., 1931, **231**, 110—112).—Intramuscular administration of sulphur emulsions to dogs and rabbits has no effect either on the total sulphur content of their livers or on the amount of sulphuric acid which can be liberated from the livers by hydrolysis. The liver probably does not play an important part in the changes in sulphur metabolism which follow parenteral administration of sulphur.

W. McCartney.

Permeability of the heart to sodium and potassium ions. H. P. Kryśka and W. R. Witanowski (Acta Biol. Exp., Warsaw, 1930, **6**, 53—57).—The dried frog's ventricle contains 0·28% Na and 1·25 K; similar values are found for human and rabbit heart muscle. A surviving frog's heart gives up potassium ions to, and takes up sodium ions from, Ringer's solution; the amount of sodium removed from the fluid is, however, less than equivalent to the amount of potassium lost by the heart.

R. Truszkowski.

Action of trypaflavin on metabolism. G. Monasterio (Arch. exp. Path. Pharm., 1931, **159**, 172—179).—The administration of small doses of trypaflavin to various animals (rabbits, dogs, mice, and rats) results in a hyperglycæmia which is caused by an increased production of adrenaline and is accompanied by a decrease in liver-glycogen and disturbances in the gaseous metabolism. Administration of larger doses of trypaflavin brings about a hypoglycæmia which may result in convulsions and death. In the depancreatised dog the effect is still exerted but to an inconstant degree. The hypoglycæmic action does not occur as a result of an increase in the rate of polymerisation or of oxidation of dextrose.

W. O. Kermack.

Experimental hyperglycæmia and the reticulo-endothelial system. R. Messina (Arch. Farm. sperim., 1931, **51**, 229—240, 267—292).—The blood-sugar level of rabbits is raised by continued intravenous injection of trypan-blue, but not of basic iron saccharate. Death ultimately results in each case. In rabbits treated with either substance the hyperglycæmia which follows injection of dextrose becomes progressively more intense and more prolonged. This is attributable to the blocking of the reticulo-endothelial system. The hyperglycæmic effect of the injection of adrenaline becomes progressively less, owing to the exhaustion of glycogen reserves. The part played by endocrine disturbances is uncertain. The mechanism of the participation of the reticulo-endothelial system in carbohydrate metabolism is discussed.

R. K. Callow.

Guanidine structure and hypoglycæmia. II. F. Bischoff and M. L. Long (J. Pharm. Exp. Ther., 1931, **41**, 127—137; cf. A., 1929, 468).—Diphenetyl- and dianisyl-guanidines administered enterally are more toxic (as measured by changes in the carbamide- and amino-acid-nitrogen of the blood) than ditolylguanidine. Their action is accompanied by albuminuria and transient hyperglycæmia. Administration of benzthiazole-, benziminazole-, and benzoxazole-guanidines results in varying degrees of

kidney damage, but not in a rise of the amino-acid-nitrogen of the blood. The oxazole derivative alone effects a mild hypoglycæmia, whilst the thiazole and iminazole derivatives produce no effect and an increase in the blood-sugar, respectively.

F. O. HOWITT.

Action *in vivo* of synthalin on cell oxidation. O. KAUFFMANN-COSLA and O. VASILCO (Arch. exp. Path. Pharm., 1931, **159**, 154—162).—The administration of synthalin in mild diabetes may result in the disappearance of dextrose from the urine, but the place of the reducing sugar is taken by other carbon-containing compounds such as lactic acid and acetaldehyde. Synthalin therefore does not possess the same property as insulin of stimulating cell oxidation.

W. O. KERMACK.

Influence of colloids on the action of histamine. B. BEHRENS (Biochem. Z., 1931, **231**, 92—94).—Since histamine is only very slightly adsorbed by kaolin or talc and since the action of the base on the surviving intestine or uterus is scarcely if at all influenced by the presence of these substances the results and explanation of Bernfeld (A., 1930, 1472) cannot be accepted. W. MCCARTNEY.

Comparative changes in gastric acidity and urinary reaction after injection of histamine. M. J. MATZNER and I. GRAY (Arch. Int. Med., 1931, **47**, 202—205).—Following subcutaneous injection of histamine into patients as a gastric stimulant, free hydrogen chloride was found in the gastric secretion in about 50% of cases, and in not more than 50% of these did the urine show an alkaline tide.

A. COHEN.

Pharmacological effect of the substitution of methyl in the β-carbon group of methylamino-*p*-hydroxyphenylcarbinol. RAYMOND-HAMET (Compt. rend., 1931, **192**, 450—452).—The substitution causes the manifestation of properties resembling those of adrenaline, which the parent substance itself does not possess. P. G. MARSHALL.

3 : 4-Dihydroxy-ephedrine and -*nor*ephedrine. RAYMOND-HAMET (Compt. rend., 1931, **192**, 300—302; cf. this vol., 120).—The physiological action of 3 : 4-dihydroxy-ephedrine and -*nor*ephedrine resembles that of adrenaline rather than that of ephedrine. Thus, as with adrenaline, but not with ephedrine, their hypertensive action is sensitised by cocaine, they do not become hypotensive in large doses, and they have a strong and lasting inhibitive effect on the intestinal functions. It is concluded, therefore, that the physiological action is not modified by the introduction of a methyl group on the β-carbon atom of the side-chain, but is profoundly affected by the substitution of two phenolic hydroxyl groups in the 3 : 4-positions. J. W. BAKER.

Influence of nicotine on the blood-sugar. R. TOPPNER (Arch. exp. Path. Pharm., 1931, **159**, 223—23-).—Subcutaneous injection of nicotine (3 mg. of nicotine tartrate per kg. body-weight) into rabbits or the inhalation of tobacco smoke by healthy men results in a rise of blood-sugar during the first ½—1 hr. followed by a fall to somewhat below the normal level after about 3 hrs. When hyperglycæmia results from administration of dextrose or from pancreatic disease is present, the hyperglycæmic action of nicotine is less marked but the hypoglycæmic effect is rather more pronounced. W. O. KERMACK.

Pharmacological properties of the alkaloids of *Helleborus*. G. FRANZEN (Arch. exp. Path. Pharm., 1931, **159**, 183—201).—The properties of the alkaloids of *H. viridis*, celliamine, sprintillamine, and sprintilline, resemble those of cevadine, aconitine, and delphinine, but, unlike the latter group, they exert a stimulating action on the respiratory centre of warm-blooded animals. W. O. KERMACK.

***Panax ginseng*. V. Toxicity of nerve poisons in rats fed on *P. ginseng*. VI. Comparison of composition and action of *P. ginseng* and *P. quinquefolius*.** N. SUGIHARA and P. MIN. **VII. and VIII. Pharmacological actions of "panaxic acid" and "panacene."** N. SUGIHARA and K. KIN (Keijo J. Med., 1930, **1**, 685—710, 711—772; cf. A., 1930, 1617).—V. The effect of feeding *Panax* extract to rats is antagonistic to that of adrenaline and atropine, but hastens the appearance of convulsions and death caused by physostigmine and pilocarpine.

VI. *P. ginseng*, which is richer in active constituents, is more effective than *P. quinquefolius* in causing curvature of the tail and convulsions in mice.

VII. An account of the pharmacology of "panaxic acid," a mixture of saturated and unsaturated fatty acids obtained by alkaline hydrolysis of the ethereal *Panax* extract.

VIII. A parallel study of "panacene," the oil obtained by steam-distillation of the ethereal *Panax* extract. A. COHEN.

Santonin. I. Excretion of santonin. H. W. KNIPPING and H. SEEL (Arch. exp. Path. Pharm., 1931, **159**, 202—212).—The administration of santonin to normal animals and men accelerates urinary flow. In rabbits, the liver or kidneys of which were damaged by administration of phosphorus or excess of ergosterol, santonin exerted a slightly favourable action on the urinary output, being itself excreted at approximately the normal rate. In patients suffering from diseases of the liver, kidneys, or circulation a slight increase was observed in the time taken for the completion of the urinary excretion of santonin (normally 24 hrs.), but the differences were not sufficiently well marked to be of use for diagnostic purposes.

W. O. KERMACK.

Hydroxypyruvaldehyde: its preparation and physiological behaviour. A. HYND (Biochem. J., 1931, **25**, 11—19).—The effect produced by monomeric and polymeric hydroxypyruvaldehyde when injected subcutaneously into mice is the same and is similar to that produced by glyoxal. It is quite distinct from that produced by glucosone. When hydrogen sulphide is used in the preparation of hydroxypyruvaldehyde (cf. Evans and Waring, A., 1926, 1227) the resulting product is contaminated with sulphur-containing by-products. Some of these are thermostable, others thermolabile. The latter produce toxic effects similar to those following the administration of cyanides. Similar toxic compounds are obtained when dihydroxyacetone or glyoxal, but not the sugars or glucosone, are treated with hydrogen

sulphide. The reported greater toxicity of "dimeric" hydroxypyruvaldehyde (cf. Kermack, Lambie, and Slater, A., 1929, 844) is due to the presence of an unstable toxic product. S. S. ZILVA.

Chemistry of anæsthesia. W. D. BANCROFT and G. H. RICHTER (J. Physical Chem., 1931, **35**, 215—268).—A review of the theories concerning anæsthesia. Bernard's theory that reversible coagulation of the colloids of the sensory nerves produces or accompanies anæsthesia is supported. L. S. THEOBALD.

Gaseous higher hydrocarbon narcotics. H. KILLIAN (Schmerz, Nark., Anæsth., 1930, **3**, 121—159; Chem. Zentr., 1930, ii, 2155).—In the series of unsaturated hydrocarbons the solubility increases; that of compounds possessing double and triple linkings is greater than that of homologous unsaturated simple substances, whilst branching of the chain has the opposite effect. For ethylene and narcylene the solubility in blood is greater than that in water. In the olefine series the narcotic power markedly rises, but the toxicity limit falls, with increase in the number of carbon atoms. The rise in narcotic power increases with the presence of double linkings and decreases with that of side chains, parallel with the changes in solubility in water, blood, and oil. Spectroscopic investigations did not indicate the formation of true compounds with hæmoglobin. A. A. ELDRIDGE.

Comparison of narcotic action on the intestine and on the whole animal. E. FREY (Arch. exp. Path. Pharm., 1931, **159**, 163—171).—The activities of various narcotics applied to the whole animal are not proportional to their activities on the isolated intestine, barbituric acid derivatives being relatively inactive on the intestine. The activities of barbituric acid derivatives on the isolated intestine is facilitated by an acid reaction and similarly luminal has greater activity on an animal receiving an acid diet than on one receiving an alkaline diet. W. O. KERMACK.

Toxicological investigation of chloral hydrate. L. W. RISING and E. V. LYNN (J. Amer. Pharm. Assoc., 1931, **20**, 9—11).—Periodic determinations of chloral hydrate which had been mixed with minced, fresh sheep's stomach with and without various preservatives and kept in sealed bottles showed that mercuric chloride was the best preservative, the maximum loss of poison in the treated sample being less than 9% after 7 months. Even in the unpreserved samples probably 18 months would elapse before the aldehyde was completely dissociated. Loss of chloral in the specimen treated with alcohol was very rapid and after 3 months was greater than in that unpreserved and subjected to the ordinary putrefactive changes. Arsenious acid, embalmer's fluid, and formaldehyde in that order were most efficient after mercuric chloride. E. H. SHARPLES.

Effect of lithium on the sea-urchin egg. J. RUNNSTROM (Acta Zool., 1928, **9**, 365—424; Chem. Zentr., 1930, ii, 3424).—Comparative plasmolysis experiments are described. A. A. ELDRIDGE.

Action of various salts on the first stage of the surface precipitation reaction in *Arbacia* egg protoplasm. L. V. HEILBRUNN (Protoplasma, 1930, **11**, 558—573).—The film formation on the extruded protoplasm of *Arbacia* eggs is examined. Salt solutions retard or inhibit the first stage of the reaction in the order $Mg>NH_4>Na>K>Li$. Although calcium is essential to the reaction, high concentrations of calcium salts have a similar retarding effect to other cations. The thiocyanate ion has a greater effect on the reaction than the chloride ion. The presence of a lipase as the active catalyst of the reaction is suggested. A. G. POLLARD.

Action of tincture of iodine and mustard oil on the gaseous metabolism and blood circulation in the skin. E. SAMETINGER (Arch. exp. Path. Pharm., 1931, **159**, 1—11).—Tincture of iodine applied to the ear of the dog increases the oxygen uptake and carbon dioxide production, but there is practically no change in the quantity of blood circulating through the ear. Mustard oil increases the rate of circulation and accelerates the carbon dioxide production, but inhibits the oxygen uptake during the first hour. During the next 2—5 hrs. the carbon dioxide production decreases, whilst the oxygen uptake increases above normal, the rate of circulation decreases, and œdema develops. W. O. KERMACK.

Determination of lead in fæces and urine and its significance in the diagnosis of lead poisoning. F. FRETWURST and A. HERTZ (Arch. Hyg., 1930, **104**, 215—225; Chem. Zentr., 1930, ii, 3446).—The fæces and urine of persons whose work did not bring them into contact with lead contained, respectively, 0—0·14 (in one case 0·6) mg. per 100 g. and 0·01—0·07 mg. per litre; values for persons working with lead but showing no toxic symptoms were 0—0·2 and 0—0·05, whilst for workers with lead who exhibited symptoms of poisoning they were 0·02—0·9 and 0—0·13. A tap-water after 12 hrs. in the pipes contained 0·03 mg., and another (Hamburg) contained 0·07 mg. of lead per litre. A. A. ELDRIDGE.

Absorption of finely-divided mercury. G. VITTE (Bull. Soc. Pharm. Bordeaux, 1930, **68**, 80—93; Chem. Zentr., 1930, ii, 2671; cf. B., 1931, 365). —Evaporation and dissolution of finely-divided mercury are much more marked than with compact mercury. Experiments on dissolution by artificial and natural gastric juice show that mercuric oxide is readily attacked; 0·1% hydrochloric acid dissolves it quickly and completely, but 0·8% sodium chloride solution has no action. Mercurous oxide is unattacked. A. A. ELDRIDGE.

Excretion of mercury after ingestion of Hydrargyrum cum Creta. G. VITTE (Bull. Soc. Pharm. Bordeaux, 1930, **68**, 93—102; Chem. Zentr., 1930, ii, 2671).—After daily ingestion of finely-divided mercury (0·03 g.), the urine after the fifth to the eighth day contains mercury. The liver and kidneys of dogs which have received 2 g. of finely-divided mercury in a month contain mercury. A. A. ELDRIDGE.

Effect of fluorine on the calcium metabolism of albino rats and the composition of the bones. F. J. MCCLURE and H. H. MITCHELL (J. Biol. Chem., 1931, **90**, 297—320).—The addition to the diet of

rats of either calcium fluoride or sodium fluoride in quantities equivalent to 0·03% F inhibits growth independently of any effect on food consumption. The calcium balance is not influenced by calcium fluoride or sodium fluoride at concentrations equivalent to 0·01% and 0·03% F, but at a concentration equivalent to 0·06% the percentage of calcium retained is below normal. With concentrations of sodium or calcium fluoride equivalent to 0·03% or 0·06% F the ash content of the bones is increased, the calcium content of the ash is decreased, but the phosphate content is approximately normal. It appears that the administration of fluoride especially in the form of the more soluble sodium fluoride results in the deposition in the bone of some non-calcium constituent, possibly fluoride. Abnormalities are also produced in the structure of the teeth, but in this respect calcium fluoride is as effective as sodium fluoride. W. O. KERMACK.

Hyperthermia. II. Acid–base equilibrium in hyperthermia induced by short radio waves. F. BISCHOFF, M. L. LONG, and E. HILL. **III. Phosphorus equilibrium.** F. BISCHOFF, L. C. MAXWELL, and E. HILL (J. Biol. Chem., 1931, **90**, 321—329, 331—339).—When the body temperature of a human subject is raised by the action of short radio waves the effect is the same as when the rise is brought about by external application of heat, except that a marked decrease in blood-volume occurs which is absent in the latter case. A loss of carbon dioxide and an increase in blood p_H were observed, but the urine was not markedly alkaline.

III. No phosphorus is eliminated in the perspiration during a hyperthermia induced by radio waves. The decrease in the excretion of phosphorus by the urine is due to the increase in metabolism associated with a change of inorganic to organic phosphate in the blood. Increased elimination of nitrogen occurs through the perspiration, and this accounts for the decrease in the nitrogen excretion in the urine.

W. O. KERMACK.

Permeability of human epidermis to ultra-violet radiation. N. S. LUCAS (Biochem. J., 1931, **25**, 57—70).—The apparent absorption of ultra-violet light by epidermis as determined by the usual methods of photometry is not entirely due to true absorption, but is in part due to scattering of the incident light by the epidermis. This scattering should, however, cause much less interference in transmission of the light to the underlying tissues when the skin is irradiated *in vivo*. For light of wave-length 300 mμ and less the effect of scattering is dwarfed by true absorption by the epidermis, since the shape of these absorption curves resembles those of many proteins and amino-acids. The percentage of ultra-violet light of physiologically active wave-lengths transmitted through the epidermis is higher than previously recorded by Hasselbalch (Skand. Arch. Physiol., 1911, **25**, 55) and is calculated to be about 1·5—30 times greater for wave-lengths from 404 to 289 mμ, respectively. S. S. ZILVA.

Active group of catalase. II. K. ZEILE (Z. physiol. Chem., 1931, **195**, 39—48).—After two adsorptions with tricalcium phosphate, liver-catalase gives a value for $k/[Fe_P]$ of 3430. The preparation of catalases from *Boletus scaber* and from pumpkin cotyledons is described. These catalases are spectroscopically identical with liver-catalase. After germination for 5 days between damp filter-paper, the cotyledons are ground in 5% disodium phosphate solution, kept on ice for an hour, and centrifuged. The middle layer has a k-value of about 250. The Fe_P of pumpkin-catalase has a value of about 0·0172. $k/[Fe_P]$ is about 8000. The activity of pumpkin-catalase, like that of liver-catalase (this vol., 123), can be suppressed by potassium cyanide. The dissociation constant of the enzyme–hydrogen cyanide complex is $2{\cdot}87\times10^{-7}$. A. RENFREW.

Ultra-violet irradiation and catalase. H. KOEPPE (Arch. Kinderheilk., 1930, **89**, 70 pp.; Chem. Zentr., 1930, ii, 3585).—The amount of hydrogen peroxide decomposed by a definite amount of catalase is constant. The extent of decomposition of hydrogen peroxide by irradiation with a quartz lamp is proportional to the surface illuminated. The function of blood-catalase is to render possible the combination of oxygen with the fat envelopes; hence oxyhæmoglobin is reduced. A. A. ELDRIDGE.

Determination of hydrogen peroxide and catalase in human blood. M. RIGONI (Atti Soc. med.-chir. Padova, 1928, 4 pp.; Chem. Zentr., 1930, ii, 3585).

Temperature coefficients and energy exchanges of the citric acid dehydrogenase of cucumber seeds. W. J. DANN (Biochem. J., 1931, **25**, 177—189).—At 25° the Michaelis constant of the citric acid dehydrogenase of cucumber seeds is $1{\cdot}65\times10^{-4}M$ and at 35° it is $8\times10^{-5}M$. Thus the temperature coefficient Q_{10} is 0·48 at 30° and the heat of formation of the citric dehydrogenase–citric acid compound is therefore 13,460 g.-cal. per mol. The temperature coefficient of the velocity of the reaction catalysed by the dehydrogenase has been measured; Q_{10} is 1·65 at 30°. The energy of activation of the citric dehydrogenase–citric acid compound is therefore 8790 g.-cal. per mol. S. S. ZILVA.

Protective substances of amylase. IV. Protective action of yeast, malt, and barley extracts. V, VI. Purification of the protective substances. VII. Protective action of the purified substances and their identification. H. NAKAMURA (J. Soc. Chem. Ind. Japan, 1931, **34**, 16B—22B; cf. this vol., 391).—The filtrate from yeast, plasmolysed with toluene and autolysed, and water extracts of malt and barley protect taka-diastase against destruction by heat, as has been shown for proteases and peptones (this vol., 391). No activating action is shown. The amount of toluene and duration of autolysis have an almost inappreciable effect on the protective action of yeast extract. By rendering dilute solutions of the protective materials alkaline (p_H 8·5—11·7), precipitates are obtained which contain the whole of the actual protective substance. The ash from this material, and the calcium separated from it, exert a protective action equivalent to that of the original material. The protective action of calcium salts is proportional to the amount of calcium

contained in them. The action of these protective substances is not due to colloid protection nor to change of p_H; it is considered that amylase is a compound of calcium, the activity of which is lost on removal of calcium, and protected by its introduction.

F. E. DAY.

Influence of cinchona alkaloids on the amylolytic enzyme. E. OHLSSON (Ar. Int. Pharm. Ther., 1930, **37**, 108—114; Chem. Zentr., 1930, ii, 2909).—Experiments were performed at constant p_H. Quinidine has no effect on taka-diastase or pancreatic amylase. Quinine, cinchonine, cinchonidine, and optoquin retard the enzymic hydrolysis of starch. Increased enzymic action in the presence of small concentrations of the alkaloids was not observed.

A. A. ELDRIDGE.

Influence of citrates on the enzymic hydrolysis of starch. E. OHLSSON (Ar. Int. Pharm. Ther., 1930, **37**, 98—107; Chem. Zentr., 1930, ii, 2909).—Citrates do not affect taka-diastase at the optimum p_H, but at other p_H values they retard its action. In the absence of sodium chloride they retard the action of pancreatic amylase even at the optimum p_H; they have no effect at the p_H of the intestine.

A. A. ELDRIDGE.

Mechanism of fermentation by invertases. E. AVTONOMOVA (Biochem. Z., 1931, **231**, 13—24).—A mathematical formula independent of any theory of the process of fermentation has been worked out for the hydrolysis of sucrose by invertase; it is very similar to that deduced by Maximovitsch and Avtonomova (A., 1928, 549). It seems that the differences in behaviour which the various enzymes exhibit are due more to experimental conditions than to individual peculiarities of the enzymes, and that general formulæ based on the law of mass action, and taking into account the order of the reactions, can be found for all fermentative processes.

W. MCCARTNEY.

Kinetics of esterase action compared with acid catalysis. E. A. SYM (Biochem. Z., 1931, **230**, 19—50).—The action of esterase (from pig-pancreas powder) in acetone–water mixtures shows a minimum at a concentration of 6—8*M* of water. Esterification of acetic acid by the homologous series of alcohols is more active the greater is the mol. wt. of the alcohol used; this is also true for homologous acids of the aliphatic series. In the former the gradation of the ease of reaction is fairly independent of the medium, but in the latter the reaction velocities in esterase action are different from those in hydrochloric acid catalysis or thermal reaction. With butyl alcohol the equilibrium point is displaced by change of alcohol concentration (cf. Dietz, A., 1907, ii, 677) and the reaction velocity is considerably altered. Esterase action increases with increasing concentration of butyric acid up to 0·6*M*, but further increase results in the action remaining constant or even decreasing. Water activates esterase action but inhibits hydrochloric acid catalysis.

F. O. HOWITT.

Enzymic production of mandelic esters. P. RONA, R. AMMON, and H. A. OELKERS (Biochem. Z., 1931, **231**, 59—66; cf. A., 1930, 373).—No stereochemical specificity in the production of esters can be observed when esterases (in the form of dried powders) from the pancreas, liver, or kidneys of the pig, from human liver, or from cat's liver are allowed to act on *n*-butyl alcohol and *d*-, *l*-, or *dl*-mandelic acid in equimolecular proportions.

W. MCCARTNEY.

Specificity of phosphatases. K. P. JACOBSOHN and J. TAPADINHAS (Biochem. Z., 1931, **230**, 304—311).—The preparation of menthylorthophosphoric, dimenthylorthophosphoric, and dimenthylpyrophosphoric acids is described and the action of animal and vegetable phosphatases on them investigated. Animal organ extracts (liver and kidney of sheep and rabbit), extracts of top yeast, or the juice of green leaves caused no hydrolysis of these substrates although the same samples of enzyme readily hydrolysed potassium diphenylpyrophosphate and bornylorthophosphate.

P. W. CLUTTERBUCK.

Esterification of phosphoric acid, production of lactic acid, and phosphatase action in muscle-pulp and -powder. J. BODNAR and B. TANKÓ (Biochem. Z., 1931, **230**, 228—232; cf. A., 1929, 1106).—Lactic acid formation by fresh pulp of pigeon breast-muscle decreases on keeping in proportion to the decrease in the ability of the pulp to bring about esterification of phosphoric acid. The agents responsible for the latter reaction together with the total activity are found in the powder prepared from the pulp by alcohol–ether or acetone–ether treatment. The powder, however, exhibits a decreased power of lactic acid formation due to a reduced phosphatase content.

F. O. HOWITT.

Refutation of Schutz' law and its analogous equations in the kinetics of enzyme action. K. NAKAJIMA (J. Fac. Agric. Hokkaido, 1930, **28**, 329—356).—The Schutz equation is considered to hold only for dilute solutions of pepsin.

CHEMICAL ABSTRACTS.

Nature of proteases. VIII. Refractometric studies on the activity of different pepsin preparations. J. A. SMORODINCEV, A. N. ADOVA, and S. S. DROSDOV (Z. physiol. Chem., 1931, **195**, 113—120).—The refractive indices of solutions of various pepsin preparations in hydrochloric acid are slightly higher for strong than for weak preparations; the values for 1% solutions of pepsin in varying concentrations (0·11—0·653%) of hydrochloric acid increase with rise in the concentration of the acid. The refractive indices of 1% solutions (p_H 1·26—1·50) of pepsin in hydrochloric acid do not alter during 72 hrs. at the ordinary temperature or during 24 hrs. at 38°; the values increase when the solutions are boiled. The activity of pepsin preparations can be determined by the alteration in the refractive index of a pepsin-hydrochloric acid digest of denatured fibrin; the enzyme solution is used as a control. There is generally a larger increase in the refractive index with strong than with weak preparations. Fibrin has no effect on the refractive index of hydrochloric acid.

H. BURTON.

Specificity of animal proteases. Mode of action of peptidases. A. K. BALLS and F. KOHLER (Ber., 1931, **64**, [*B*], 294—301; cf. this vol., 392).—The action of aminopolypeptidase of the intestine is

restricted by benzoyl-, bromo*iso*hexoyl-, and *p*-nitrobenzoyl-glycine, aceturic acid, phthalimide, and sarcosine, but not by allantoin, creatinine, or glycine anhydride. The action appears therefore to be due to the presence of an imino-group attached to an acid residue. The dependence of the reactivity of the imino-group on its acidic character is further illustrated by the behaviour of di- and amino-polypeptidase towards substituted di- and tri-peptides. Only the peptide group vicinal to the acid residue has a restricting action. Equivalent amounts of bromo*iso*hexoyl-glycine, -diglycine, and -triglycine exert the same action. Introduction of a second acidic group, for example tyrosine, increases this action, since more than one imino-group is enabled to react with the enzyme. In some cases it appears possible that the necessary activation of the imino-group is induced by the enzyme itself and that the union of the enzyme with the amino-group of the peptide molecule enables the imino-group to function as second point of attachment. The entry of the enzyme into the amino-group saturates its basic character to such an extent as is necessary for the activation of the imino-group. The tendency towards decomposition of the enzyme–substrate compound is considered to depend not on an increased instability to hydrogen-ion concentration, but on an enhanced reactivity of the imino-group.

H. WREN.

Proteolytic enzymes of green malt. II. Action of the proteinase on egg-albumin, caseinogen, edestin, and fibrin at different reactions. R. H. HOPKINS and H. E. KELLY (Biochem. J., 1931, **25**, 256—264).—The optimum p_H at 46° is as follows: crystalline egg-albumin 3·3—3·6, caseinogen 3·35—5·57, fibrin 3·8 (or less) and at 6·0, edestin at 37° 4·3. These values approximate in most cases very closely to those of the maximum buffering power of the protein measured at 18°. The enzyme appears to act on ionised protein on both sides of the isoelectric point. S. S. ZILVA.

End-point of tryptase action. J. T. GROLL (Pharm. Weekblad, 1931, **68**, 109—121).—The end-point of the action of tryptase on peptone can be regarded as reached when the Sørensen titration figure does not increase by more than 0·1 c.c. of 0·1*N*-sodium hydroxide solution in 24 hrs. This point is reached after a week, although only 20% of the peptone-nitrogen can be titrated; the value rises to about 30% after several weeks, but this occurs also in the absence of enzyme. S. I. LEVY.

Effect of heat on the activating efficiency of enterokinase. J. PACE (Biochem. J., 1931, **25**, 1—7).—The heat-inactivation of enterokinase, like that of purified trypsin, proceeds according to the unimolecular formula. The stability is influenced considerably by the p_H of the medium, but there is an optimum region between p_H 6 and 7. The critical increment of the process at p_H 6·5, 5·12, or 3·2 is of the order of 40,000 g.-cal. S. S. ZILVA.

Hitherto undescribed proteolytic action of intestinal extract. A. K. BALLS and F. KOHLER (Ber., 1931, **64**, [*B*], 383—387).—The enzyme is prepared from the glycerol extract of the intestine of the pig. After adsorption by aluminium hydroxide at p_H 4·5—5, it remains in the residual solution, from which it can be isolated by adsorption with aluminium hydroxide *C* at p_H 7·0, followed by elution with secondary phosphate. It can be freed from ereptic enzymes by treatment with hydrogen sulphide or hydrocyanic acid. It is stable towards the two last-named substances and formaldehyde, but is completely destroyed at 70° within 2—3 min. It exerts hydrolytic action on peptide-like substances which do not contain a free amino- or carboxyl group. With "aniline peptides" the increase in acidity is very slight, but the hydrolysis can be followed readily with the aid of the diazo-reaction. With chloroacet-*o*-nitroanilide the incidence of hydrolysis is shown by the yellow colour of the free *o*-nitroaniline, but increase of acidity is scarcely noticeable, since the base impedes the action of the enzyme; addition of formaldehyde, which combines with the base, causes a marked increase in hydrolysis. The activity of the enzyme preparation towards chloroacetyl-*dl*-alanine, chloroacetyl-*dl*-leucine, and benzoyltriglycine but not towards benzoyl-glycine or -diglycine has been established. H. WREN.

Proteolytic action of papain and cathepsin. H. A. KREBS (Naturwiss., 1931, **19**, 133).—A defence of the author's work against the criticisms of Waldschmidt-Leitz (A., 1930, 1217; this vol., 124).

A. J. MEE.

Structural conceptions of the action of enzymes in leather chemistry. M. BERGMANN (Collegium, 1930, 516—520).—Certain enzymes hydrolyse the hide proteins into amino-acids, others oxidise the amino-acids by removing two hydrogen atoms, and a third class produces the final products of putrefaction. A hydrogen acceptor is necessary for the functioning of the oxidising enzymes. Using chloroacetic acid as the acceptor, it has been combined with phenylalanine, and in presence of acetic anhydride as catalyst the acid $CHPh.C(CO_2H)\cdot NHAc$ has been obtained. The resemblance to the enzyme action is shown by the similarity of the end-products of the reaction and by the readiness with which the reaction proceeds in presence of a catalyst. Thus at the ordinary temperature an unsaturated dipeptide containing two hydrogen atoms less than glycyl-*l*-phenylalanine which could not be hydrolysed by any of the known pancreatic enzymes has been prepared, but was hydrolysed by commercial pancreatin, thus indicating the presence in the latter of a hitherto undescribed proteolytic enzyme. D. WOODROFFE.

Chemical nature of urease. E. WALDSCHMIDT-LEITZ and F. STEIGERWALDT (Z. physiol. Chem., 1931, **195**, 260—266).—Addition of varying amounts of amino-acids, peptides, and potassium cyanide to crude and purified urease preparations usually causes an alternation in their activity; pure amino-acids need not be used, since a tryptic digest of caseinogen has a greater activating power than either alanine or cystine. Contrary to the statement of Tauber (A., 1930, 1217), crystalline urease (Sumner, A., 1926, 1061, 1176) is not inactivated by trypsin or by other proteolytic enzymes; hydrolysis of the admixed globulin occurs, since no precipitate occurs with sulphosalicylic acid. H. BURTON.

Influence of neutral-red on the respiration of yeast. M. Geiger-Huber (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 1059—1068).—The respiration of baker's yeast at 20° and between p_H 5·0 and 8·1 is independent of the hydrogen-ion concentration. Addition of neutral-red (1 in 10) increases the respiration immediately by 20—30% in an acid medium and 10—20% in an alkaline medium, but a subsequent decrease occurs, and about 1 hr. after addition of the dye the value is the same for all p_H values and is only about 80% of that of the undyed cells. With increasing age of the cells the change in respiration on addition of the dye increases and a final steady value is attained only after a much longer period. Since changes are observed in the respiration of the yeast in the presence of insufficient dye to colour the cells. it is suggested that the neutral-red influences the protoplasmic boundary wall. J. W. Smith.

Selective fermentation. Alcoholic fermentation of mixtures of dextrose and lævulose by brewer's and Sauterne yeasts. R. H. Hopkins (Biochem. J., 1931, **25**, 245—255).—The factor $K_{G/F}$ (the relative degree of fermentation of the two sugars) for brewer's yeast is not appreciably influenced by the relative proportions of dextrose and lævulose in the original solution nor by modification of the invertase activity of the yeast. The invertase of Sauterne yeast resembles that of brewer's yeast in that it is inhibited more strongly by lævulose than by dextrose. The addition of invertase to a mixture of dextrose and lævulose undergoing fermentation by zymin from brewer's yeast does not affect the selectivity. $K_{G/F}$ for brewer's yeast decreases with rise in temperature of fermentation, whilst that for Sauterne yeast increases. Brewer's yeast ferments dextrose faster than lævulose in separate solutions when the concentration of sugar is less than 1%. Sauterne yeast ferments lævulose faster than dextrose in separate solutions at all concentrations up to 10%, but especially at low concentrations. The mutarotation of partly fermented solutions of the sugars is for dextrose by brewer's yeast in the positive direction, dextrose by Sauterne yeast in the negative, lævulose by brewer's yeast in the positive, and lævulose by Sauterne yeast in the negative direction. S. S. Zilva.

Biochemistry of zinc. Zinc and fermentation by yeast. A. Zlatarov, M. Andreitscheva, and D. Kaltscheva (Biochem. Z., 1931, **231**, 123—134).—At a dilution of 0·002*N* solutions of zinc sulphate or nitrate inhibit completely the fermentation of dextrose by yeast. More dilute solutions (0·002*N*—0·0011*N*) restrict the fermentation, which, however, is not affected by solutions of still greater dilution. The action of the zinc salts alone is quantitatively and qualitatively different from that of mixtures of these salts with salts of other metals (nitrates of calcium, potassium, manganese, and iron, and sodium succinate). Of the salts of the other metals potassium and calcium nitrates always stimulate fermentation, manganese and iron nitrates stimulate or restrict, according to the degree of dilution, and sodium succinate always restricts fermentation, dilute solutions (not more concentrated than 0·1*N*) being considered in all cases. Calcium nitrate is the salt which stimulates most strongly, sodium succinate that which restricts most strongly, the effects being proportional to the degree of dilution. Zinc sulphate at a dilution of 0·001*N* converts the stimulating action of other salts into a restricting action and increases the action of sodium succinate. In the presence of 0·001*N*-calcium nitrate solution or of 0·001*N*-sodium succinate solution fermentation is completely suppressed by 0·00139*N*-zinc nitrate solution. Similar effects are observed with other mixtures, but the inhibiting action of 0·002*N*-zinc nitrate solution is not affected by the presence of any of the other salts. W. McCartney.

Role of iron and copper in the growth and metabolism of yeast. C. A. Elvehjem (J. Biol. Chem., 1931, **90**, 111—132).—Baker's yeast has been grown on a medium containing sucrose 2·5%, magnesium sulphate 0·25%, potassium chloride 0·25%, ammonium chloride 0·25%, disodium hydrogen phosphate 0·25%, and calcium chloride 0·05%, but deficient in iron and copper, the content in these elements being less than 0·0025 mg. and 0·001 mg. per 100 c.c., respectively. The yeast grew at an abnormally slow rate, was pale in colour, possessed an abnormally low total iron content, was completely devoid of free inorganic iron, had a low cytochrome content, and showed a low oxygen consumption. The addition of a small amount of iron increases the rate of growth, the cytochrome content, and the oxygen consumption. When copper is added as well as iron a distinctly high rate of growth is obtained and the yeast produced is particularly rich in the cytochrome-*a* component. In old cultures the oxygen consumption decreases owing to the acidity of the medium. In 48 hrs.' old cultures at least 80% of the respiration is inhibited by potassium cyanide, but in 7 days' old cultures the oxygen uptake is completely unaffected by potassium cyanide. The potassium cyanide-stable system metabolises dextrose, is destroyed at 60°, and is inhibited to the extent of 70% by urethane. The respiration of yeast grown on beer wort, which prevents the development of high acidity, is largely inhibited by cyanide. In this medium the total respiration may be low, due to an insufficient supply of iron in the wort. The addition of bios to the synthetic media used in this work stimulated the rate of growth to a small extent, but had no effect on the respiratory activity of the yeast. The concentration of copper which gives maximum stimulation of cytochrome-*a* is 0·01 mg. per 100 c.c. Higher concentrations of copper inhibit growth during the first 48 hrs., but the toxic effect disappears as the concentration of cells in the medium increases. Yeast low in inorganic iron cannot assimilate iron from a phosphate buffer at p_H 7·0, but readily takes up iron at p_H 4·0. W. O. Kermack.

Staining of yeast-cells with methylene-blue and the permeability of the yeast-cell membrane. I. H. Fink (Z. physiol. Chem., 1931, **195**, 215—240; cf. von Euler and Florell, A., 1920, i, 267).—The influence of hydrogen-ion concentration, neutral salts, and various sugars on the adsorption of methylene-blue by yeast-cells has been studied. Little methylene-

blue is adsorbed by washed, dry bottom yeast from an acid solution, whilst at p_H 7·4—9·0 about 92% of the dye is adsorbed. Conversely, the dye is eluted from the stained cells much more readily by an acid than by an alkaline medium. The influence of small amounts of salts on the staining is particularly noticeable when yeast is suspended in distilled water, whereby the number of cells stained increases rapidly with time; in tap water, the number remains constant. There is a marked increase in the number of stained cells when salt-free solutions of dextrose, lævulose, sucrose, or galactose are used; maltose is somewhat less active, mannitol is inactive, whilst glycerol has only a slight action. It is suggested that the yeast-cell membrane is altered so as to allow the methylene-blue to permeate the cell. The above effect with sugars is not obtained if the sugar solution contains small amounts of salts. Yeast-cells, suspended in dextrose solution and then treated with methylene-blue, could not be grown on wort–gelatin plates; growth occurred in absence of the dye or when potassium chloride was added prior to the dye. Subsequent staining of the colonies with methylene-blue shows that those grown from the dextrose solution alone are mainly dead, whilst those from a suspension of cells in tap water are living to the extent of about 95%.

Fermentation of dextrose by yeast in salt-free solution occurs much less readily than in presence of salts; addition of methylene-blue causes a retardation in the evolution of carbon dioxide which is much more pronounced in the salt-free medium. This retardation is almost completely abolished by addition of salts; the effect for anions is acetate < citrate < tartrate < nitrate < sulphate and bromide < thiocyanate < iodide < chloride, and for cations lithium < sodium < potassium < ammonium. H. BURTON.

Activator-*Z*. H. VON EULER and T. PHILIPSON (Z. physiol. Chem., 1931, **195**, 81—100).—Using the autolysate of bottom yeast (this vol., 263) as the source of *Z*-activity, the acceleration of fermentation due to caffeine, theobromine, xanthine, tryptophan, adenosine, thymidine, or hæmin is found to be zero. The *Z*-activity of malt-germ extract is comparable with that of boiled yeast extract; the *Z*-activities of extracts of fresh barley cotyledons, rutabagas, moulds, tea, and coffee are weak.

The *Z*-factor is practically insoluble in 95% acetone, but dissolves in 90% acetone. Colloidal ferric hydroxide treatment does not alter the activity of activator-*Z*. "Fe-Extract" prepared by precipitating the dialysate with lead acetate and mercuric chloride, treating with hydrogen sulphide, neutralising, adding iron hydrosol, centrifuging, concentrating, suspending in 1% monopotassium phosphate solution, again centrifuging, is not, at any p_H, adsorbed by blood-charcoal. Phosphate in neutral and alkaline solutions adsorbs the active substance. By extracting the aluminium phosphate extract with acetic acid a solution having half the activity of "Fe-Extract" is obtained. Silicic acid does not adsorb the active substance.

The absorption capacity of top yeast for activator-*Z* is unaltered by, and independent of, the state of saturation. Bottom yeast is activated in exactly the same way by dialysate and "Fe-Filtrate," and is only influenced by that part of activator-*Z* which is not adsorbed by ferric hydroxide. A. RENFREW.

Hexosemonophosphoric esters. R. ROBISON and E. J. KING (Biochem. J., 1931, **25**, 323—338).—An aldosemonophosphoric ester, $[\alpha]^{20}_{5461}$ +41·4° (barium salt $[\alpha]^{20}_{5461}$ +21·2°), has been isolated from the hexosemonophosphoric ester produced by fermentation of hexoses with yeast juice. The reducing power of the ester measured by an iodometric method is equal to that of the equivalent amount of dextrose, or by the Hagedorn and Jensen method 80% of that of dextrose. The Selivanov reaction is not appreciably greater than that given by dextrose. The phenylhydrazine salt of the osazone of aldosemonophosphoric ester is identical in m. p. (154—154·5°) and rate of hydrolysis with the corresponding salt of the osazone of fructosemonophosphoric ester. The ester is very resistant to hydrolysis by acids at 100°. Hydrolysis proceeds more rapidly when the free aldosemonophosphoric acid is heated alone than in presence of sulphuric acid. The sugar product of acid hydrolysis has the character of *d*-dextrose. Hydrolysis by bone-phosphatase proceeds rapidly at the ordinary temperature and p_H 7·0, but the sugar product contains both dextrose and lævulose. Oxidation of the aldosemonophosphoric ester with bromine yields a phosphohexonic acid, from which gluconic acid has been obtained by hydrolysis with bone-phosphatase. The constitution of the ester is that of a dextrose-6-phosphate. The specific rotations of the free ester and of its barium salt differ considerably from those of the synthetic ester prepared by Levene and Raymond (this vol., 63). A ketosemonophosphoric ester similar in most respects to Neuberg's fructosemonophosphoric ester has also been isolated from the fermentation products, whilst evidence has been obtained of the presence of another ester as yet unidentified. S. S. ZILVA.

Easily cleavable phosphoric acid compound in yeast. H. VON EULER and R. NILSSON (Z. physiol. Chem., 1931, **195**, 273—276).—Yeast contains an easily cleavable phosphoric acid compound which is not completely precipitated by magnesia mixture and ammonia, and gradually gives a precipitate with Embden's reagent. H. BURTON.

Behaviour of yeasts and some *Hyphomycetes* towards quinic acid. W. W. PERWOZWANSKY (Zentr. Bakt. Par., 1930, II, **81**, 372—392).—All fungi examined developed normally when quinic acid was the sole source of carbon. Benzene derivatives were produced in all cases, protocatechuic acid being prominent. In the presence of sugars, organisms utilising quinic acid could not produce a typical alcoholic fermentation. Organisms utilising quinic acid produced organic acids (notably oxalic) when grown in sugar media containing calcium carbonate. Oxidation of dextrose to gluconic acid occurred in cultures of *Dermatium pullulans*. A. G. POLLARD.

New substances produced by action of moulds. N. WIJKMAN (Annalen, 1931, **485**, 61—73).—Two new acids are produced by growth of *Penicillium*

glaucum on sucrose media, and may be separated by fractional crystallisation from alcohol. *Glauconic acid* 1, $C_{18}H_{20}O_7$, m. p. 202°, titrates with alkali in the cold between a di- and tri-basic acid, and in the warm as a tetrabasic acid; it is considered, therefore, to contain one or more lactone rings. It is unaffected by methyl-alcoholic hydrogen chloride, and is converted by diazomethane into oily unidentified products. It gives *mono-acetyl*, m. p. 175°, and *-benzoyl*, m. p. 170°, derivatives, a *nitro*-derivative, m. p. 159°, by nitration in concentrated sulphuric acid, and a *dihydro*-derivative (a tribasic acid), m. p. 235°, by reduction with zinc and acetic acid. Thermal decomposition at 215° gives an unsaturated *ketone*, $C_7H_{12}O$, b. p. 146°/720 mm. (*dinitrophenylhydrazone*, m. p. 173°; *semicarbazone*, m. p. 183°), and a *substance*, m. p. 171°, which on titration with alkali behaves similarly to the original acid, is unaffected by bromine, methylating agents, or acetic anhydride, and is reduced to a tribasic acid by zinc and acetic acid. The ketone absorbs two atoms of bromine, but rather more than two atoms of hydrogen, and is oxidised by alkaline permanganate to propionic acid. *Glauconic acid* 2, $C_{18}H_{20}O_6$, behaves as a tetrabasic acid when titrated with alkali in the warm, can be distilled undecomposed in a high vacuum, and does not react with acetic anhydride and pyridine.

H. A. PIGGOTT.

Determination of enzyme yield in fungus cultures. Z. I. KERTESZ (J. Biol. Chem., 1931, **90**, 15—23).—A method is described for determining the amounts of invertase in the mycelium of a mould, and in the medium in which it is grown. Although with cultures of *Penicillium glaucum* grown under apparently identical conditions, the total dry matter in the mycelium varies greatly, the enzyme content of the whole mould is approximately constant. When the salt content of the medium is adequate, the enzyme content of the mould increases as the sucrose content of the medium is increased, but in the absence of either potassium, phosphorus, or magnesium the enzyme content remains approximately constant with variations of sucrose concentration. In the case of normal cultures of *P. glaucum* the total enzyme content of the culture reaches a maximum in the first few days.

W. O. KERMACK.

Biochemistry of micro-organisms. XIX. 6-Hydroxy-2-methylbenzoic acid, a product of the metabolism of dextrose by *Penicillium griseo-fulvum*, Dierkx. W. K. ANSLOW and H. RAISTRICK (Biochem. J., 1931, **25**, 39—44).—This compound was obtained by ether extraction of the medium. The medium on treatment with bromine water yields a precipitate consisting principally of 2 : 4 : 6-tribromo-*m*-cresol.

S. S. ZILVA.

Formation of citric acid by moulds. IV. Conversion of saccharic acid. K. BERNHAUER, H. SIEBENAUGER, and H. TSCHINKEL (Biochem. Z., 1931, **230**, 466—474).—The formation of saccharic acid as an intermediate in the conversion, during fermentation with *Aspergillus niger*, of dextrose and gluconic acid into citric acid (claimed by Challenger, Subramaniam, and Walker, A., 1927, 228) is investigated, using 21 strains of the mould, including the culture employed by these authors. In no case could either the formation of saccharic acid from dextrose or gluconic acid or the formation of citric from saccharic acid or its salts be detected. With some of the cultures, a precipitate was obtained with Deniges' reagent, but this was shown to be mercuric oxalate.

P. W. CLUTTERBUCK.

Characterisation of the group of *Aspergillus niger*. III. Comparison of different strains. K. BERNHAUER, F. DUDA, and H. SIEBENAUGER (Biochem. Z., 1931, **230**, 475—483).—The formation of citric and gluconic acids by a number of strains of *A. niger* is determined. Acid-forming power is increased by removing the ripe spores and storing dry or by subculturing on a natural acid medium (lemon juice). Good acid-forming strains spore relatively late, sporing being inhibited by the high acidity. The best yield of citric acid represents 76·3% on the original sugar or 96·8% on the sugar fermented and of gluconic acid 66·53% on the sugar used or 96·42% of theory (cf. A., 1929, 472).

P. W. CLUTTERBUCK.

Relationships between organic acids elaborated by *Aspergillus niger*. MOLLIARD (Compt. rend., 1931, **192**, 313—315).—When *A. niger* is cultivated on media containing sucrose and only small amounts of ammonium nitrate and other essential salts, gluconic acid formation is rapid during 10 days, does not alter appreciably during the next 50 days, and then diminishes; the amount of citric acid produced increases steadily during 90 days. At the end of the experiment, reducing sugar (formed by inversion of the sucrose) is present, but oxalic acid is not. The citric acid is not produced from the gluconic acid. The use of sodium gluconate or citrate in the media causes formation of oxalic acid, which is considered to be a definite excretion. Gluconic and citric acids are oxidation products of the sugar; these can be metabolised by the fungus.

H. BURTON.

Enzymic conversion of guanidine into urea. N. N. IVANOV and A. N. AVETISSOVA (Biochem. Z., 1931, **231**, 67—78).—In the presence of dextrose *Aspergillus niger* grown on peptone produces an enzyme *guanidase* which decomposes guanidine into urea and ammonia, the guanidine serving as a nitrogen source for the growth of the mould. The decomposition is quantitative if a dried preparation of the dead micro-organism containing guanidase (but no urease) is used. Guanidase is destroyed by boiling with water.

W. MCCARTNEY.

Production of kojic acid by *Aspergillus flavus*. O. E. MAY, A. J. MOYER, P. A. WELLS, and H. T. HERRICK (J. Amer. Chem. Soc., 1931, **53**, 774—782).—The effects of the amount and source of nutrient nitrogen, temperature, sugar concentration, and depth of the culture medium on the production of kojic acid from dextrose by *A. flavus* are investigated. Ammonium nitrate is the most satisfactory source of nitrogen and the best yields of acid are obtained at 30—35°. Maximum amounts of the acid are obtained most conveniently from 20% dextrose solutions after 12 days; the yield of acid is about 55% (on the sugar consumed).

H. BURTON.

Kojic acid: formation from trioses by *Aspergillus oryzæ*. F. CHALLENGER, L. KLEIN, and T. K. WALKER (J.C.S., 1931, 16—23).—The authors agree with Corbellini and Gregorini (A., 1930, 959) that the formation of kojic acid from pentoses and hexoses is best explained by assuming a preliminary breakdown to the triose followed directly by condensation to kojic acid, and not passing through dextrose. *A. oryzæ* grows on 5% dihydroxyacetone and 5% glycerol in the standard medium (A., 1929, 1042), producing kojic acid, in the case of dihydroxyacetone in 30% yield, and grows also on 2% calcium gluconate, 2% potassium hydrogen saccharate, 2% potassium citrate containing 0·5% citric acid, 1% glyceric acid, and 5% trimethylene glycol without producing kojic acid. On rhamnose it yields minute quantities of a substance, probably kojic acid.

A. niger grows on 5% glycerol, but the product of its action varies with the strain of mould, one strain producing glyceraldehyde, and another oxalic acid. No citric acid was identified in either case, and the second strain gave oxalic acid from arabinose.

G. DISCOMBE.

Allantoinase in fungi. A. BRUNEL (Compt. rend., 1931, **192**, 442—444).—The presence of allantoinase in a fungus extract is demonstrated by incubating at 40° with a 0·2% solution of allantoin containing 0·125% of ammonium hydrogen carbonate. The allantoic acid formed is hydrolysed by hydrochloric acid at 100° to glyoxylic acid and urea, the former being recognised by a colour reaction and the latter isolated as xanthylcarbamide. Alternatively, allantoic acid is isolated as its silver salt. A list of fungi containing allantoinase is given. P. G. MARSHALL.

Specific polysaccharides from fungi. H. D. KESTEN, D. H. COOK, E. MOTT, and J. W. JOBLING (J. Exp. Med., 1930, **52**, 813—822).—When tested by direct precipitation against the corresponding antisera the polysaccharides from the yeast-like fungi exhibit only partial specificity. Cross-precipitin reactions are frequent. A relatively high degree of specific precipitability can, however, be demonstrated by absorption of precipitin on the intact mycotic bodies. CHEMICAL ABSTRACTS.

Effects of carbon dioxide, hydrogen sulphide, methane, and of the absence of oxygen on water organisms. J. NIKITINSKY and F. K. MUDREZOWA-WYSS (Zentr. Bakt. Par., 1930, II, **81**, 167—198).—Carbon dioxide and hydrogen sulphide are toxic to the majority of water organisms. Methane and hydrogen are non-poisonous. Many organisms can withstand the absence of oxygen for periods up to 20—30 days. The resistance of organisms to carbon dioxide and hydrogen sulphide and (to a smaller extent) to the absence of oxygen is closely related to their saprophytic activities. Such resistance decreases with the complexity of the organism, *i.e.*, in the order crustaceæ < rotifers < protozoa.

A. G. POLLARD.

Wall structure and mineralisation in coralline L. G. M. BAASBECKING and E. W. GALLIHER (J. Physical Chem., 1931, **35**, 467—479).—The cell walls of *Corallina officinalis*, L., and *Amphirora dorbigniana*, Dec., are non-cellulosic but contain pectin-like substances. They are birefringent in longitudinal section and isotropic in cross-section. *X*-Ray examination [by O. L. SPONSLER] of decalcified and natural *Amphirora* showed that calcite is the only mineral deposited by the living coralline. The deposition of magnesium is a secondary phenomena.

L. S. THEOBALD.

Fermentation of cellulose at high temperatures. P. A. TETRAULT (Zentr. Bakt. Par., 1930, II, **81**, 28—45).—Organisms capable of fermenting cellulose at 60° are described and a new type of organism from pigmented cultures is separated. Dextrose is the principal product. A. G. POLLARD.

Biological oxidation of carbohydrate solutions. I. Oxidation of sucrose and ammonia in sectional percolating filters. S. H. JENKINS (Biochem. J., 1931, **25**, 147—160).—A mixture of 0·033% sucrose, 0·033% acetic acid, and 0·033% lactic acid, when fed at a suitable rate of flow, is readily oxidised by a mixed microbial population. A biological film is built up and the organic matter is oxidised even if the C : N ratio of the nutrient solution is 80—1. Acid and invert-sugar are formed if a 0·1% sucrose solution is allowed to trickle through a mature portion of the sectional filter. The maximum drop observed is from p_H 7·0 to 6·6. Oxidation of ammonia proceeds best in the lower sections where the concentration of sugar is least. It is not inhibited by concentrations of sugar up to 0·05—0·06%. Both nitrites and nitrates are produced by micro-organisms in the presence of 3—4 parts per 100,000 parts of nitrogen as ammonia. Each section rapidly shows nitrifying activity when placed in a suitable part of the filter. S. S. ZILVA.

Biological oxidations in the succinic acid series. J. H. QUASTEL and A. H. M. WHEATLEY (Biochem. J., 1931, **25**, 117—128).—The biological oxidation of fumaric acid proceeds largely if not entirely through *l*-malic acid. Fumarate and *l*-malate inhibit the oxidation of succinate in presence of various bacteria and of muscle- and brain-tissue. Strict aerobes, *B. alkaligenes*, *B. subtilis*, and *M. lysodeikticus*, and muscle-tissue attack *l*-aspartate in a different manner from the facultative anaerobes *B. coli*, *B. proteus*, and *B. acidi lactici*. The latter oxidise the acid through fumaric and *l*-malic acids. Malonate inhibits the oxidation of succinate not only by bacteria, but also by muscle- and brain-tissue, the degree of inhibition being greatest with these tissues. The wide variation with different cells in the degrees of inhibition by malonate is associated with difference between velocities of oxidation of fumarate and those of succinate. Neither malonate nor oxalate inhibits the velocity of oxidation of *p*-phenylenediamine by brain-tissue. S. S. ZILVA.

Hydrogenase: a bacterial enzyme activating molecular hydrogen. I. Properties. II. Reduction of sulphate to sulphide by molecular hydrogen. M. STEPHENSON and L. H. STICKLAND (Biochem. J., 1931, **25**, 205—214, 215—220).—I. The enzyme has been found in some strains isolated from a mixed culture from river mud as well as in *B. coli*, *B. acidi lactici*, etc. It is not present in baker's

yeast or in sheep's-heart muscle. At a hydrogen pressure of one atmosphere the enzyme is saturated. The maximum velocity of the action of the enzyme is at p_H 6·0. The shape of the p_H–velocity curve suggests the possibility of the existence of two hydrogenases. In its reactions to cyanide and urethane hydrogenase behaves as a typical dehydrogenase. By means of the enzyme hydrogen reduces molecular oxygen, methylene-blue, nitrate, and fumarate. *B. coli* in a buffer solution at p_H 6·5 does not take up molecular hydrogen.

II. An organism from river mud reduced sulphate quantitatively to sulphide by means of molecular hydrogen. It also reduced sulphite and thiosulphate to sulphide. The curve obtained by plotting the hydrogen-ion concentration against the velocity of reduction of methylene-blue is of the same character as that obtained with other organisms containing hydrogenase. The optimum reaction for the activation of hydrogen in this case is p_H 6·3.

S. S. ZILVA.

Mechanism of the degradation of citric acid by *B. pyocyaneus* (*Pseudomonas pyocyanea*). II. Action of *B. pyocyaneus* on succinic acid. T. K. WALKER, V. SUBRAMANIAM, H. B. STENT, and J. BUTTERWORTH (Biochem. J., 1931, **25**, 129—137; cf. Butterworth and Walker, A., 1929, 1493; Challenger, Subramaniam, and Walker, A., 1927, 228).—The addition of small quantities of acetone to cultures of *B. pyocyaneus* on calcium acetate media is followed by the formation of lactic acid. The action of this organism on succinates leads to the formation of *dl*-malic acid and *l*-malic acid. When the organism acts on *dl*-malic acid dextrorotatory activity is developed in the medium. *l*-Malic acid is therefore not formed by resolution, but by the action of *B. pyocyaneus* on ammonium succinate. *dl*-Malic acid most probably arises by direct hydroxylation of succinic acid and the *l*-malic acid by dehydrogenation of succinic acid to fumaric acid followed by asymmetric addition of water to the latter.

S. S. ZILVA.

Oxidation–reduction potentials of pneumococcus cultures. II. Effect of catalase. L. F. HEWITT (Biochem. J., 1931, **25**, 169—176).—Some of the characteristic differences in behaviour between pneumococci and catalase-forming bacteria disappear when catalase preparations are added to the former. The electrode potential of aerobic pneumococci cultures remains at a low level after the addition of the enzyme. In aerated cultures the potential falls to a much lower level and growth is much more luxuriant when it is added. Bacteria differ in oxidation–reduction behaviour in respects other than that of peroxide formation. Bacterial peroxide and hydrogen peroxide possess many properties in common. There are indications of an acceleration of reduction effect by killed aerobic bacteria (*M. lysodeikticus*) and of a poisoning effect by erythrocytes. S. S. ZILVA.

Dissociation of the diphtheria anatoxin–antitoxin complex and recovery of the anatoxin. G. RAMON, R. LEGROUX, and M. SCHOEN (Compt. rend., 1931, **192**, 512—514; cf. A., 1924, i, 1149).—A solution of anatoxin is obtained when the anatoxin–antitoxin flocculate, after washing in isotonic saline, is dissolved in slightly acidulated water at p_H 6—6·5.

C. C. N. VASS.

Purification and concentration of diphtheria toxin and anatoxin. S. SCHMIDT, A. HANSEN, and K. A. KJAER (Ann. Inst. Pasteur, 1931, **46**, 202—221).—The methods utilised include adsorption by alumina or charcoal and elution by sodium hydrogen phosphate solution, precipitation by alcohol or acetone, precipitation by acids, dialysis through cellophane membranes, and evaporation in a vacuum.

F. O. HOWITT.

Lipins of tubercle bacilli. XXII. Carbohydrates of the purified wax. E. G. ROBERTS and R. J. ANDERSON. **XXIII. Separation of the lipoid fractions from the timothy bacillus.** E. CHARGAFF, M. C. PANGBORN, and R. J. ANDERSON (J. Biol. Chem., 1931, **90**, 33—43, 45—55).—XXII. From the water-soluble fraction obtained by hydrolysis with alcoholic hydrochloric acid of the purified wax (cf. A., 1929, 1342) there have been isolated *d*-arabinose, and traces of glucosamine hydrochloride and inositol. When the wax is hydrolysed by alcoholic potassium hydroxide an amorphous alcohol-insoluble polysaccharide fraction is obtained which on acid hydrolysis yields mannose, *d*-arabinose, and galactose together with unidentified reducing sugars. A barium salt containing barium (27·88%) and phosphorus (5·06%) was also obtained.

XXIII. Timothy-grass bacilli (*Mycobacterium phlei*) grown on the Long's medium have been analysed, the methods previously adopted in the case of the tubercle bacillus being followed closely. The following results were found: phosphatide 0·59%, acetone-soluble fat 2·75%, chloroform-soluble wax 4·98%, total lipins 8·37%; polysaccharide 3·90%, dried bacterial residue 87·70%. The acetone-soluble fat had saponification value 231·8, acid value 62·7, iodine value 72·3. The timothy-grass bacillus contains less lipin than does the avian or bovine strain and much less than the human strain of the tubercle bacillus, whilst the polysaccharide content is considerably greater than that of the tubercle bacillus.

W. O. KERMACK.

Nucleic acid of the timothy bacillus. R. D. COGHILL (J. Biol. Chem., 1931, **90**, 57—63).—By extraction with 2% sodium hydroxide solution of the residue from timothy-grass bacilli after treatment with alcohol–ether and chloroform, an impure nucleic acid was obtained in a yield of about 2%, which on hydrolysis yields guanine, uracil, and cytosine, but no thymine. It contains at least 20% of pentose. It was therefore apparently a nucleic acid of the plant type, in contradistinction to the nucleic acid of the tubercle bacillus which is of the animal type.

W. O. KERMACK.

Tuberculosis. I. Reaction of the connective tissues of the normal rabbit to lipins from the tubercle bacillus, strain H 37. F. R. SABIN, C. A. DOAN, and C. E. FORKNER. **II. Reaction of the connective tissues of the normal rabbit to a water-soluble protein and a polysaccharide from the tubercle bacillus, strain H 37; spontaneous pseudo-tuberculosis aspergillina as a complication in fraction testing.** C. A. DOAN, F. R. SABIN,

and C. E. Forkner (J. Exp. Med., 1930, **52**, Suppl. 3, 3—72, 73—87). Chemical Abstracts.

Fermentation in a heterogeneous and discontinuous medium. A. Demolon and G. Barbier (Compt. rend., 1931, **192**, 514—515).—Comparison of the rates of fermentation due to motile and non-motile organisms shows that in sand containing 6—8% of water, diffusion and migration readily occur; in an argillaceous medium similar results are observed only when the medium contains 17·0—21·5% of water. C. C. N. Vass.

Gas-metal electrode potentials in sterile culture media for bacteria. E. M. Boyd and G. B. Reed (Canad. J. Res., 1931, **4**, 54—68).—A method is described for determining the gas-metal electrode potential of media and for the preparation of a standard buffered medium for the purpose. The passage of air through sterile media caused an increase in potential at platinum and gold electrodes. Hydrogen produced a decreased potential at a platinum electrode and little change at a gold electrode. Carbon dioxide and nitrogen produced little change in either case. The observed potentials were in agreement with those recorded for electrodes immersed in potassium chloride solutions. Mercury electrodes reacted with the media (cf. French and Kahlenberg, A., 1928, 1330). A. G. Pollard.

Conditions of antibacterial and antitoxic action of the bile. I. A. Clementi. **II.** A. Clementi and A. Castelli (Arch. Sci. biol., 1929, **13**, 211—220, 221—234; Chem. Zentr., 1930, ii, 3588).—Retardation of coagulation in lactic fermentation of milk in presence of bile salts is due to combination of the latter with the acid. Bile and sodium taurocholate retard the development of *Bacillus coli*. A. A. Eldridge.

Action of intestinal disinfectants. F. Eichholtz and R. Wigand (Arch. exp. Path. Pharm., 1931, **159**, 81—92).—Trichlorocresol and tetrachloro-derivatives of certain hydrocarbons were highly active as intestinal disinfectants in the sense of reducing the number of living bacteria and yeasts in the fæces of various animals. Creolin and guaiacol were less active, whilst a number of the accepted intestinal disinfectants appeared to be without effect. W. O. Kermack.

Bactericidal action of sodium salicylate. M. Garofeanu and E. Ioan (Compt. rend. Soc. Biol., 1930, **104**, 513—514; Chem. Zentr., 1930, ii, 2663). —The growth of *B. coli*, streptococci, and staphylococci is arrested or inhibited by sodium salicylate. A. A. Eldridge.

Influence of pituitrin on the ionic excretion. L. T. Poulsson (Z. ges. exp. Med., 1930, **72**, 232—243; Chem. Zentr., 1930, ii, 2910).—After intramuscular injection of pituitrin the reaction of human urine is displaced towards alkalinity; the ammonia content falls and the total fixed base rises relatively to the sodium content. A. A. Eldridge.

Effect of pituitary preparations on the blood-lipin. E. George (Z. ges. exp. Med., 1930, **72**, 303—1.; Chem. Zentr., 1930, ii, 2910).—Raab's observation (Z. ges. exp. Med., 1928, **62**, 366) of the fall in blood-lipins after injection of pituitrin was not confirmed. A. A. Eldridge.

Substance resembling anterior pituitary extract in human urine. Pregnancy reaction. M. Aron and M. Klein (Compt. rend. Soc. Biol., 1930, **103**, 702—704; Chem. Zentr., 1930, ii, 3165).—Injection of the urine of man, woman, or pregnant woman into rabbits caused thyroid changes qualitatively resembling, but less marked than, that of anterior pituitary extract. Zondek's anterior pituitary hormone differs from that which affects the thyroid. A. A. Eldridge.

Anterior pituitary hormone. W. Falta and F. Hogler (Klin. Woch., 1930, **9**, 1807—1812; Chem. Zentr., 1930, ii, 2794).—" Prahormon " caused reduced basal metabolism and frequently increased specific dynamic protein action. This hormone, but not " Prolan," greatly increased growth in infantilism, although both hormones had the usual effect on sexual development. A. A. Eldridge.

Anterior pituitary hormones. II. B. Zondek (Klin. Woch., 1930, **9**, 393—396; Chem. Zentr., 1930, ii, 3049).—Normal male or female urine contains less than 110 mouse units of prolan-A. In the climacteric three stages associated with different hormone production are distinguished. Ten days after operative castration prolan-*A* appears in the urine and may be detected during a year; after *X*-ray sterilisation, in spite of amenorrhœa, it is first observed after 1—1·5 years, and remains for 1·5 years. A. A. Eldridge.

Relation between the anterior pituitary body and the gonads. III. Fractionation and dilution of ovary-stimulating extract. M. Hill and A. S. Parkes (Proc. Roy. Soc., 1931, **B**, **107**, 455—463).—Saline suspensions of pituitary tissue, " alkaline " extracts of ox anterior lobes, and extracts of urine of pregnancy all give (*a*) follicular luteinisation and (*b*) follicular maturation and ovulation, in one or more of the species of animals used, viz., mice, rats, rabbits, and ferrets, the relative intensities of the two effects varying with different extracts and in different animals. Dilution experiments with urine extracts gave no evidence that the two reactions are due to the same hormone at different concentrations. By alcohol fractionation of urine extracts, partial separation of luteinising and maturating actions appears to be effected, the 50% alcohol-soluble material being predominantly luteinising, whilst the 30% alcohol-soluble fraction was mainly follicle-maturing. W. O. Kermack.

Separation of the male sexual hormone from the female hormone (menformone). E. Dingemanse, J. Freud, S. Kober, E. Laqueur, A. Luchs, and A. W. P. Munch (Biochem. Z., 1931, **231**, 1—5). —The male sexual hormone possesses basic properties and can be separated from the female hormone (menformone) by adding water to a concentrated benzene extract of male urine, the extract having first been mixed with alcoholic sodium hydroxide. The liquid separates into two layers, the male hormone passing into the benzene layer. Since the male hormone distils in a high vacuum at 90° separation by distillation is also possible. W. McCartney.

Male sexual hormone. J. Freud, S. E. de Jongh, E. Laqueur, and A. P. W. Münch (Klin. Woch., 1930, **9**, 772—774; Chem. Zentr., 1930, ii, 3048).—By means of methods corresponding with those for the preparation of menoformone, ox testicles and male human urine afforded extracts which were active towards the combs of castrated cocks and hens and the seminal vesicles of castrated or infantile rats. A. A. Eldridge.

Action of parathyroid hormone on the magnesium content of blood. H. G. Scholtz (Arch. exp. Path. Pharm., 1931, **159**, 233—235).—The administration of parathyroid extract to adult dogs results in a rise in the magnesium content of the serum, which reaches its maximum more quickly than does the rise in calcium content. W. O. Kermack.

Calcium metabolism and parathyroid hormone in various animal species. M. Thölldte (Krankheitsforsch., 1930, **6**, 397—430; Chem. Zentr., 1930, ii, 2666).—Injection of parathyroid hormone into the dog, cat, or rabbit leads to a rise in serum-calcium of about the same percentage. A. A. Eldridge.

Antagonism between adrenaline and insulin. R. Cario (Klin. Woch., 1930, **9**, 1623—1624; Chem. Zentr., 1930, ii, 2277).—Injection of 6% dextrose solution into the pancreatico-duodenal artery even after removal of the adrenals does not lead to rise in blood-sugar, presumably owing to increased secretion of insulin. A. A. Eldridge.

Effect of insulin on growth, nitrogen excretion, and respiratory metabolism. M. W. Goldblatt and R. W. B. Ellis (Biochem. J., 1931, **25**, 221—235).—The injection of 2—50 units of insulin did not influence the growth of rats on restricted and unrestricted amounts of food. Insulin has no effect on the urinary nitrogen excretion of rats consuming an exclusively fatty diet or during starvation. Insulin hypoglycæmia in a starving human subject is associated with a marked increase in the respiratory quotient. This effect ceases when the blood-sugar recovers. Progressive fall in blood-sugar and disappearance of glycosuria may be induced in a glycosuric patient without any change in the respiratory quotient or calorie output. Insulin can increase the liver-glycogen of young dogs during starvation without any change in muscle-glycogen. This may be accompanied by marked hypoglycæmia. The attainment of blood-sugar values of vanishing proportions may be accompanied by an acute fall in respiratory quotient. S. S. Zilva.

Influence of large doses of insulin on the lipins of blood and organs. I. H. Page, L. Pasternak, and M. L. Burt (Biochem. Z., 1931, **231**, 113—122).—Subcutaneous administration of large doses of insulin to rabbits causes a 30% decrease in the phosphate content of their blood-serum and less pronounced alterations in the cholesterol content of the blood and of some of the organs (kidneys, brain). The amount of fatty acids in the brain and blood and the degree of unsaturation of the fats of the brain, liver, and blood are also affected. The cholesterol content of the blood-serum of hares is increased by the administration of large doses of insulin. W. McCartney.

Action of insulin on the glycogen content of the perfused rabbit's liver. N. A. Nielsen (Biochem. Z., 1931, **230**, 259—268).—By perfusion of rabbit's liver with defibrinated blood without addition of insulin, a gradual decrease of dextrose in blood and a corresponding deposition of glycogen in the liver are observed, the glycogen being distributed very unevenly. Addition of insulin ($\frac{1}{3}$ to 20 international units) brings about an increase of dextrose in the perfusing blood and a decrease of glycogen in the liver. No action is detectable using less than one third of a unit of insulin. P. W. Clutterbuck.

Initial insulin hyperglycæmia. A. von Koranyi (Deut. med. Woch., 1930, **56**, 1683; Chem. Zentr., 1930, ii, 2911).—Extracts of the muscle of rabbits in hypoglycæmia (strychnine, phloridzin, or insulin) or of diabetic animals cause hyperglycæmia in rabbits. The cause of initial insulin hyperglycæmia is discussed. A. A. Eldridge.

"Insulin diabetes." P. Wichels and H. Lauber (Z. klin. Med., 1930, **114**, 20—26, 27—32; Chem. Zentr., 1930, ii, 2277).—When insulin (5 units) is administered intravenously to a rabbit at 10 min. intervals, marked hyperglycæmia continues for 1 hr., the liver being free from glycogen. The effect with dogs and man is similar, but less marked. It is not due to direct action of insulin on the liver. Although increased secretion of adrenaline may be partly responsible it is not the only cause, since the hyperglycæmia is observed after removal of the adrenals or thyroid gland. A. A. Eldridge.

Inhibition of the formation of insulin by excessive administration of carbohydrate. F. Verzar and A. von Kuthy (Pfluger's Archiv, 1930, **225**, 606—612; Chem. Zentr., 1930, ii, 2795).—Dogs received for a long period sufficient sucrose or dextrose to appear constantly in the urine. When the sugar diet was discontinued excretion of dextrose continued for several days, the blood-sugar being practically normal. With renewal of the sugar diet for a short time the hyperglycæmic curve was longer and flatter than normally, simulating that observed in diabetes. Hence exhaustion of the pancreas by excessive administration of sugar is possible; this may be a cause of diabetes. A. A. Eldridge.

Growth factors. W. J. Boyd, J. Latter, and W. Robson (Nature, 1931, **127**, 308).—A growth-inhibiting substance extracted from the flesh of vertebrates is thermo-stable, is not a sterol, and probably contains nitrogen. L. S. Theobald.

Plant colouring matters and vitamin-*A*. E. Burgi (Deut. med. Woch., 1930, **56**, 1650—1652; Chem. Zentr., 1930, ii, 3166).—Identity of, or close relation between, chlorophyll and vitamin-*A* is indicated by experiments with phæophytin, sodium chlorophyllin, and chlorophyll free from carotene. A. A. Eldridge.

Carotene and vitamin-*A*. Conversion of carotene into vitamin-*A* by fowl. N. S. Capper, I. M. W. McKibbin, and J. H. Prentice (Biochem. J., 1931, **25**, 265—274).—Chickens can be reared

successfully to maturity on a synthetic vitamin-*A*-free diet to which carotene or cod-liver oil concentrate is added. The carotene is not stored in the liver as such, but is converted into vitamin-*A* (cf. Moore, A., 1929, 1343; 1930, 962). The beaks and shanks of chickens which had become colourless through the absence of carotenoids from the diet did not become more yellow when carotene was added to it. The disease known as visceral gout is curable by the administration either of carotene or of cod-liver oil. The vitamin-*A* contents of hen-liver oils are very high and the vitamin-*A* requirements of the fowl are large.
S. S. ZILVA.

Vitamin-*A* and carotene. VII. Distribution of vitamin-*A* and carotene in the body of the rat. T. MOORE (Biochem. J., 1931, **25**, 275—286).—An excess of carotene was found throughout the alimentary tract in albino rats fed on large quantities of red palm oil or carrot-fat for prolonged periods. The pigmented fat derived from the fæces was biologically active proportionately to its carotene content. The liver oils gave higher colorimetric values for vitamin-*A* than those characteristic for cod-liver oil concentrates. Small amounts of carotene were also found in the liver oils of rats which received the pigment up to the time of killing. This was, however, almost absent after 68 days on the deficient diet. The concentration of vitamin in the "storage" fats of the body was only about 1/100,000 of the concentration of the liver oils. Other tissues gave very weak or no reactions for the vitamin. The conversion of carotene most probably takes place in the liver. S. S. ZILVA.

Spectrographic data concerning vitamin-*A* and liver oils. R. A. MORTON, I. M. HEILBRON, and A. THOMPSON (Biochem. J., 1931, **25**, 20—29).—The vitamin-*A* band at 328 mμ is free from fine structure. Nearly all cod-liver oils exhibit selective absorption in the region 260—295 mμ. The blue solutions obtained in cod-liver oils with antimony trichloride give a clear band at 328 mμ and a single sharp band at 604—608 mμ. In the case of crude cod-liver oils of high potency an additional selective absorption between 565 and 585 mμ is frequently observed in the blue solution. In the blue solutions obtained with concentrates the main band is at 620—624 mμ, but on dilution with an inactive oil to the approximate concentration of cod-liver oil it reverts to 604—608 mμ. In many cases the colour test with concentrates shows a less intense band at 582—593 mμ. Vitamin-*A* is decomposed on treatment with sodium ethoxide and concentrates yield in consequence acids characterised by a series of well-defined absorption bands with maxima near 394, 375, 350, 330, 316, 302, 282, 271, and 260 mμ. Similarly, absorbing acids which are not present as simple glycerides in the oil itself are produced by ordinary saponification.
S. S. ZILVA.

Spectrographic data of natural fats and their fatty acids in relation to vitamin-*A*. A. E. GILLAM, I. M. HEILBRON, T. P. HILDITCH, and R. A. MORTON (Biochem. J., 1931, **25**, 30—38).—Fatty acids (or esters prepared therefrom) produced in the ordinary hydrolysis of vitamin-*A*-containing liver oils or some other fatty oils from animals the liver of which contains vitamin-*A*, yield highly characteristic banded absorption spectra which are absent from the corresponding acids of vitamin-*A*-free oils.
S. S. ZILVA.

Colour reactions of substances containing vitamin-*A*. N. I. ORLOV (Z. Unters. Lebensm., 1930, **60**, 254—267).—The Bezssonoff reaction is unspecific and of little use. That with sulphuric acid appears to be related to the vitamin-*A* content, but it is not sufficiently sensitive and it is too evanescent for colorimetric purposes. The antimony trichloride reaction is the most useful, but it fails in the presence of pigments and other substances. The removal of these results in loss of vitamin-*A*. A solution prepared by mixing 1 c.c. of crystal-violet solution (0·040 g. in 100 c.c. of 95% alcohol), 0·6 c.c. of methylene-blue solution (0·040 g. in 100 c.c. of 95% alcohol), and 25 c.c. of 95% alcohol is used as standard. Numerous solutions of the oil of varying concentration are examined and the concentrations are plotted against the readings. A similar series of tests is carried out on the standard oil and the curves obtained are compared. The method is only approximate.
W. J. BOYD.

Colour reactions of sterols with nitric acid. O. ROSENHEIM and R. K. CALLOW (Biochem. J., 1931, **25**, 74—78).—Nitric acid or a solution of mercuric acetate in nitric acid ("mercury reagent") gives characteristic colour reactions with certain sterols. A red colour with the mercury reagent is characteristic of the $\Delta^{1:2}$ (or $\Delta^{1:13}$) linking in sterols. A greenish-blue colour is given by ergosterol in dilute solutions, whilst a yellow colour results when concentrated solutions of ergosterol are employed. The latter reaction can be used as an index of the purity of ergosterol, since oxidised or otherwise changed specimens give finally an intense green reaction. Certain liver oils and the unsaponifiable fraction from cod-liver oil which are sources of vitamin-*A* give a gentian-blue colour with the reagent. S. S. ZILVA.

Chemical nature of the antixerophthalmic vitamin-*A*. H. SEEL (Arch. exp. Path. Pharm., 1931, **159**, 93—110).—Highly-active preparations of vitamin-*A* have been obtained from the unsaponifiable fraction of shark-liver oil. The purified material, which is active when administered to rats in doses of 0·1—1·0 γ, is very unstable, being readily destroyed by exposure to atmospheric oxygen. This instability increases with purification. Oxidation of cholesterol with benzoyl peroxide yields oxycholesterol, possessing an apparent vitamin-*A* activity and giving a blue antimony trichloride reaction. The greater stability of the blue reaction in the case of oxycholesterol as compared with natural vitamin-*A* may be due to the presence of interfering substances associated with the natural vitamin. The ultra-violet absorption spectra of vitamin-*A* derived from a natural source and of suitably oxidised cholesterol have been determined and show distinct similarity, both possessing bands at 327 mμ and 293 mμ. W. O. KERMACK.

Destructive action of finely-divided solids on vitamin-*A*. J. K. MARCUS (J. Biol. Chem., 1931, **90**, 507—513).—Measurement of the antimony trichloride colour reaction shows that vitamin-*A* of

cod-liver oil concentrates undergoes considerable destruction when intimately mixed with several powders and stored for some days under air or carbon dioxide. Finely-divided vegetable charcoal ("nuchar") destroys 90% of the vitamin in 3 hrs. even if the charcoal is previously reduced. The destructive action of lactose is markedly inhibited by quinol and, to a smaller extent, by water.

A. COHEN.

Absorption and retention of vitamin-*A* in young children. J. I. ROWNTREE (J. Nutrition, 1930, **3**, 265—287).—The antimony chloride test is not specific; biological assay methods were employed. Vitamin-*A* is not excreted in the urine; the fæcal loss is 2—12% of the intake. The vitamin-*A* of cod-liver oil and egg-yolk was equally well utilised; inconclusive results were obtained with that from carrots.

CHEMICAL ABSTRACTS.

Antineuritic vitamin. II, III. A. G. VAN VEEN (Rec. trav. chim., 1931, **50**, 200—207, 208—220; cf. this vol., 270).—The extraction of this vitamin from rice-bran by Jansen and Donath's method (A., 1926, 644) has been investigated both by physiological effects (on birds) and by determination of the nitrogen content of the various fractions. Approximately 33% of the rice-bran (1·6% nitrogen) goes into solution on extraction, whilst acid clay absorbs most of the vitamin with only a relatively small proportion (25%) of the material precipitated with phosphotungstic acid (nitrogen, 1·6%). Only 25% of the adsorbed material is recovered by elutriation of the clay with barium hydroxide (p_H 12—13), and the remaining 75% cannot be removed even by treatment with hot concentrated alkali or with strong acids. If the alkaline extract is immediately acidified with sulphuric acid (to p_H 4) almost no destruction of the vitamin by the alkali occurs.

III. The fractions obtained by fractional precipitation of the acid clay extract with silver nitrate and barium hydroxide at various hydrogen-ion concentrations have been investigated. The fraction precipitated at p_H 4·5 affords xanthine, guanine, adenine, and hypoxanthine. Of the fraction precipitated at p_H 4·5—7, the portion not precipitated by silicotungstic acid contains histidine and uracil, and gives two unidentified picrolonates, m. p. 260° (decomp.) (nitrogen 31·7%), and m. p. 220—224° (decomp.) (nitrogen 20·4%). The third fraction precipitated at p_H 6·5—7, which is partly precipitated in fraction 2, contains guanidine and arginine, and gives a picrate, m. p. 247—250° (decomp.) (nitrogen 22·5%), a picrolonate, and an amorphous substance (nitrogen 16%). The portion not precipitated by silver nitrate and barium hydroxide contains a small quantity of monoamino-acids, betaine, choline, and an unidentified hydrochloride (nitrogen 16·3%).

J. W. BAKER.

Further fractionation of yeast nutrilites and their relationship to vitamin-*B* and Wildiers' "bios." R. J. WILLIAMS and E. M. BRADWAY (J. Amer. Chem. Soc., 1931, **53**, 783—789).—The "bios" of Wildiers is not adsorbed to any marked extent on fuller's earth and it is apparently identical with that previously described (A., 1925, i, 342; 1929, 1339). No evidence is available that this bios is other than a single substance. The growth of the yeast used by Miller (Science, 1924, **59**, 197) and Eastcott (A., 1928, 1056) is stimulated to a marked extent by inositol, whilst Wildiers' is not. Old process baker's yeast and yeast 578 (A., 1927, 592) require more complex growth-stimulants than Wildiers' yeast. Evidence is now brought forward to show the existence of a fourth nutrilite concerned in the growth-stimulation of yeast 578. Some of the nutrilites may be components of vitamin-*B* (cf. A., 1930, 1222).

H. BURTON.

Vitamin-B_1 and -B_2 contents of yeast. E. J. QUINN, F. B. WHALEN, and J. G. HARTLEY (J. Nutrition, 1930, **3**, 257—263).—The vitamin-*B* content of various American and Canadian yeasts varied considerably, whilst the vitamin-B_2 content was uniform. The antineuritic vitamin was the limiting factor in two samples of brewer's yeast.

CHEMICAL ABSTRACTS.

Complex nature of vitamin-*B*. II. Evidence that a third factor exists. C. H. HUNT and W. WILDER (J. Biol. Chem., 1931, **90**, 279—291).—For the normal growth of the rat and for the prevention and cure of pellagra in that animal a third fraction in the vitamin-*B* complex is required which is non-adsorbable on fuller's earth and thermolabile in an alkaline medium when autoclaved for 5 hrs. at 15 lb. pressure. It is distinguished from the antineuritic fraction B_1 (*B*), which is thermolabile both in an acid and in an alkaline medium, and from the pellagra-preventive factor B_2 (*G*), which is relatively thermostable at both acid and alkaline reactions. All three factors are necessary for the normal growth of the rat.

W. O. KERMACK.

Effect of nitrous acid on components of the vitamin-*B* complex. H. C. SHERMAN and M. L. WHITSITT (J. Biol. Chem., 1931, **90**, 153—160).—When either vitamin-B_1 (*B*) or -B_2 (*G*) is treated with nitrous acid by aspirating the gases generated by the action of hydrochloric acid on sodium nitrite through the solution the activity is not reduced, but when subjected to more drastic treatment by generating the nitrous acid directly in the solution, considerable reduction of potency takes place in the case of B_1 and a less marked reduction in the case of B_2. It is considered probable that B_2 itself is unaffected by nitrous oxide, but that some of the other more recently discovered but not yet completely differentiated factors may be destroyed by the treatment.

W. O. KERMACK.

Esterification of phosphoric acid and phosphatase action in avitaminosis-*B*. J. BODNAR and A. KARELL (Biochem. Z., 1931, **230**, 233—237).—The musculature and liver of pigeons suffering from avitaminosis-*B* exhibit a power to esterify phosphoric acid 77—146% greater than that of the organs from healthy birds. No such difference, however, exists between the respective phosphatase activities.

F. O. HOWITT.

New diet for the study of avitaminosis-*B*. L. RANDOIN and R. LECOQ (Compt. rend., 1931, **192**, 444—447).—The following avitaminous diet, resembling in composition dried cows' milk, has been found suitable for pigeons: purified caseinogen 8, purified fibrin 8, ovalbumin 8, purified butter-fat 8,

lard 18, purified carbohydrate 35, saline mixture (Osborne and Mendel) 5, agar-agar 8, and filter-paper 2%. Daily addition of 0·35—0·50 g. of dried brewer's yeast produces a complete diet. The above regime possesses the advantage that the rate of development of polyneuritis is not appreciably affected by the nature of the carbohydrate, whilst with those containing 66% of carbohydrate and only 4% of fat the rate of development of symptoms varies with the ease and rapidity of the intestinal absorption of the carbohydrate. P. G. MARSHALL.

Relation of a fat-free diet to the scaly tail condition in rats described by Burr and Burr. E. M. HUME and H. H. SMITH (Biochem. J., 1931, 25, 300—306).—The condition developed when the rats were kept on coarse wire grids with highly purified caseinogen and usually when extracts of yeast were used as a source of *B*-vitamins, and could be cured by whole dried, but not by autoclaved, yeast. The condition may be correlated with some deficiency in the yeast–vitamin complex.

S. S. ZILVA.

Antiscorbutic potency of apples. II. M. F. BRACEWELL, F. KIDD, C. WEST, and S. S. ZILVA. **III.** M. F. BRACEWELL, T. WALLACE, and S. S. ZILVA (Biochem. J., 1931, 25, 138—143, 144—146).—II. Newton Wonder apples possess a vitamin-*C* content of the order of that possessed by Cox's Orange Pippin, whilst Lane's Prince Albert occupies an intermediate position between the latter and the much more potent Bramley's Seedling. This last variety can be frozen at −20° and kept at this temperature for 4 months without losing appreciably in antiscorbutic activity. Immature small apples of this variety gathered in July are not more active per g. than the ripe apples gathered normally. Bramley's Seedling apples stored at 3° in air for 5 months do not lose any of their antiscorbutic activity. The concentration of vitamin-*C* in the tissue of the apple increases as the skin is approached from the core, and is more than six times as great in the peel as in the flesh near the core.

III. King Edwards containing about 0·0307% N were about 1·5 times as potent antiscorbutically as apples of this variety containing about 0·0387% N. No significant disparity in the vitamin-*C* content was found between Bramley's Seedlings containing high and low quantities of nitrogen. S. S. ZILVA.

Chemical nature of vitamin-*D*. E. TAKAMIYA (J. Dept. Agric. Kyushu, 1930, 3, 1—27).—Irradiation of various vegetable oils with ultra-violet light results in a decrease in the rates of hydrolysis by lipase, which increases with the time of exposure and with the degree of unsaturation of the oil as measured by its iodine value. The decrease in the rate of enzyme hydrolysis after irradiation is accompanied by a decrease in the iodine value, probably due to ozonide formation. Irradiation also produces an increase in the viscosity of the oils, but the non-irradiated oils which are the most viscous are also most rapidly hydrolysed by lipase. Ozonisation of the oils causes a decrease in iodine value, increase in viscosity, and a decrease in the rate of hydrolysis by lipase, and in general the effects of ozonisation and of irradiation by ultra-violet rays both of cholesterol and of unsaturated oils are strikingly similar. Ozone exerted some definite curative action on rachitic rats fed in an ozonised atmosphere and it also activated ergosterol. An excessive exposure of ergosterol to ozone diminished the activity and ultimately resulted in loss of activity. It is suggested that vitamin-*D* is the mono-ozonide of ergosterol.

W. O. KERMACK.

Sterol content and antirachitic activatibility of mould mycelia. L. M. PRUESS, W. H. PETERSON, H. STEENBOCK, and E. B. FRED (J. Biol. Chem., 1931, 90, 369—384).—Various moulds have been grown on a synthetic medium containing 4% of dextrose as the source of carbon. The yields of dry pad varied from 7·3 to 35·0% of the dextrose consumed. When the concentration of dextrose in the medium was increased to 10—20%, the yield of dry pad was more than doubled. The autoclaved, dried, and finely-ground pads of twelve moulds and also five types of mushrooms grown in the open were irradiated with ultra-violet light. When these products were tested on rats, those from eight moulds and three mushrooms showed distinct antirachitic activity in doses of 10 mg. of irradiated material per rat over a period of 7 days. The total alcohol-soluble sterol determined by the digitonin method in eleven moulds and four mushrooms varied from about 0·1 to 1·0% of the dry weight of the fungus. The amount of sterol unextracted by alcohol ranged from 0·01 to 0·40% of the dry pad. In most cases 90% or more of the alcohol-soluble sterol was present in the free state. The effect of various factors on the growth and sterol content of the moulds has been investigated.

W. O. KERMACK.

Vitamin-*D*. I. Action of ozone and ultra-violet light on cholesterol and oils. II. Rickets and ozone. E. TAKAMIYA (Bull. Agric. Chem. Soc. Japan, 1929, 5, 71, 72—73).—Ozone activates ergosterol. Rachitic rats are cured by ozonised air without treatment with vitamin-*D* or ultra-violet rays.

CHEMICAL ABSTRACTS.

Antirachitic vitamin unit. Standardisation of commercial vitamin-*D* preparations. O. K. SCHULTZ (Z. Vitamin-Kunde, 1930, 51—54, 81—83; Chem. Zentr., 1930, ii, 2799).—It is proposed that there should be produced a definite degree of rachitis which is eliminated by the preparation in a certain time. The unit is defined as the smallest quantity of an antirachitic material which within 21 days will convert ++++ rachitis in rats into − rachitis.

A. A. ELDRIDGE.

Evaluation of vitamin-*D* preparations. M. SCHIEBLICH (Biochem. Z., 1931, 230, 312—319).—Comparative investigation with rats of the antirachitic action of vitamin-*D* preparations shows that the curative dose is usually much greater than the protective dose (cf. A., 1929, 1111; B., 1929, 996).

P. W. CLUTTERBUCK.

Critique of the line test for vitamin-*D*. C. E. BILLS, E. M. HONEYWELL, A. M. WIRICK, and M. NUSSMEIER (J. Biol. Chem., 1931, 90, 619—636).—A review, in which it is claimed that certain graphic relations between the degree of healing and dosage may be applied to assays with greater accuracy than has hitherto been considered possible. A. COHEN.

Toxicology of the irradiation products of ergosterol. W. Heubner (Nachr. Ges. Wiss. Gottingen, 1930, 149—163; Chem. Zentr., 1930, ii, 2798).—Experiments on the effects of various preparations in high doses on rabbits, including the determination of blood-phosphate, indicate that several different active substances are present. Moreover the antirachitic potency can be diminished to a much greater extent than the toxicity by suitable treatment of a preparation. A. A. Eldridge.

Calcifying and toxic actions of large doses of irradiated ergosterol on animals. Separation of the two actions. H. Simonnet and G. Tanret (Compt. rend., 1931, **192**, 586—588; cf. A., 1930, 506, 1071).—Administration of irradiated ergosterol to rabbits in doses of 40 mg. per day causes death in 6—18 days and 8—12 days when the irradiation periods are 45 min. and 6 hrs., respectively. 20 Mg. per day of the former irradiation product are fatal in 15—25 days. The calcium content of the thoracic aorta reaches a maximum value of 23·6%. The active material is stable to oxidation and reduction. Resistance is observed in some animals which survive for many months. Survival may also be maintained by treatment on alternate days. Rabbits receiving potassium iodide at the same time as irradiated ergosterol survive much longer than controls, and show only slight calcification of the aorta. The toxic and calcifying actions may be separated by employing massive doses (0·1 and 0·2 g. per day) when death occurs in 6—8 days, whilst the calcium content of the aorta shows only a slight increase to 1—4%. A. Cohen.

Local calcification of tissue after subcutaneous injection of irradiated ergosterol. T. von Brand and F. Holtz (Z. physiol. Chem., 1931, **195**, 241—247).—Subcutaneous injection of large doses of irradiated ergosterol in soya-bean oil causes calcification at the site of injection. This is due to the specific action of a conversion product of ergosterol, namely, the " calcinosis factor " (A., 1930, 1481). H. Burton.

Calcification of the bones of rats on a diet low in ergosterol. E. M. Hume and H. H. Smith (Biochem. J., 1931, **25**, 292—299).—Rats subsisting on vitamin-*D*-free diet which were irradiated by exposure to a mercury quartz lamp, rats which were receiving ergosterol and irradiation, and rats which were receiving no irradiation but ergosterol in their diet showed about the same percentage of ash in their bones. Animals which received neither ergosterol in their diet nor irradiation had a lower ash content. All the rats used which received a fat-free diet developed the " scaly tail " condition (cf. Burr and Burr, A., 1929, 853). S. S. Zilva.

[Effect of] white phosphorus and " vitasterin " [on animals]. C. R. H. Rabil (Arch. exp. Path. Pharm., 1931, **159**, 47—53).—Experiments on mice give no support to the view that the administration of white phosphorus promotes calcification in presence of vitamin-*D*. W. O. Kermack.

Poisoning by metallic salts during vitamin-*D* feeding. H. Hoff (Med. Klin., 1930, **26**, 1560—1562; Chem. Zentr., 1930, ii, 3308—3309).—Guinea-pigs receiving much vitamin-*D* were less susceptible to poisoning by basic lead carbonate or mercury succinate than normal animals. Resistance was diminished by theophylline or alcohol. A. A. Eldridge.

Spierer lens and what it reveals in cellulose and protoplasm. W. Seifriz (J. Physical Chem., 1931, **35**, 118—129).—The Spierer lens, an oil-immersion objective carrying a mirror, smaller than the lens, which reflects all the direct light coming into the objective, is described, together with the structure which it reveals of certain tissues of *Sambucus*, *Allium*, and *Apium*. Cellulose and protoplasm are seen to consist of minute rods or super-micelles, 1—2 μ in length and 0·5—0·7 μ in thickness, arranged end to end to form long, parallel striæ. L. S. Theobald.

Carbon dioxide dissolved in plant sap and its effect on respiration measurements. J. J. Willaman and W. R. Brown (Plant. Physiol., 1930, 5, 535—542).—Dissolved carbon dioxide in plant sap is determined by immersing plant material in boiling 95% alcohol and removing the gas under reduced pressure. The importance of distinguishing between carbon dioxide formation and the release of dissolved carbon dioxide in plant tissue is emphasised. Apples having greatest winter hardiness have the lowest output of carbon dioxide. A. G. Pollard.

Respiration of apple twigs in relation to winter hardiness. W. A. de Long, J. H. Beaumont, and J. J. Willaman (Plant. Physiol., 1930, 5, 509—534).—Carbon dioxide production from excised apple twigs is conditioned by previous temperature environment. If the previous temperature was higher a constant rate of carbon dioxide production is assumed, whereas if the previous temperature was lower there is a peak of carbon dioxide production prior to reaching the constant rate. This is ascribed in part to the liberation of carbon dioxide formed during cold storage and dissolved in the cell-sap. Hardier varieties have a lower peak production than more tender ones. Low-temperature storage of twigs without aspiration results in a slight gain in sugar content, but with aspiration there is a small decrease in sugars and an increase in starch. A. G. Pollard.

Respiration of the seeds of oil-bearing plants. A. I. Ermakov and N. N. Ivanov (Biochem. Z., 1931, **231**, 79—91).—The respiration of oil-bearing seeds (linseed, castor, almond) does not differ from that of seeds in which carbohydrate is the reserve material, and in the early stages of germination of the oil-bearing seeds the respiratory coefficient is approximately 1. During the same period there is no increase in the dry weight of the seeds and both the quantity and quality of the oil remain unaltered. Since the iodine value of the oil does not change even in the later stages of germination when its amount decreases as a result of conversion into carbohydrate, it follows that the oil does not undergo direct atmospheric oxidation. In the early stages of the germination the amount of mono- and di-saccharides present in the seeds increases as a result of enzymic hydrolysis of the polysaccharides. W. McCartney.

Function of hexuronic acid in the respiration of the cabbage leaf. A. SZENT-GYORGYI (J. Biol. Chem., 1931, **90**, 385—393).—The oxygen uptake of finely-minced cabbage leaf decreases rapidly during the first 5 min. This decrease is correlated with the disappearance of reduced hexuronic acid (cf. A., 1929, 98) as the result of oxidation in the air. The fresh pulp reduces Folin's phenol reagent without addition of alkali, but after a short exposure to the air this reducing power, which depends on the presence of the reduced hexuronic acid, is lost. The mechanism which effects the reduction of hexuronic acid is damaged by the mincing to a greater extent than the mechanism effecting its oxidation. If the original concentration of reduced hexuronic acid is restored by addition of this substance a vigorous uptake of oxygen again takes place, which lasts until the theoretical quantity is taken up. The thermolabile catalyst is present to a large extent in the cell sap uncombined with the formed elements of the cell. By precipitation with barium acetate, which does not remove the hexoxidase from the juice, followed by salting out of the hexoxidase by ammonium sulphate, and repeated redissolution and reprecipitation, the enzyme may be obtained in a purified condition exhibiting no oxygen uptake until hexuronic acid is added to it. The enzyme in a phosphate buffer solution (p_H 5·9) is relatively stable, resisting the action of 1% acetic acid, sodium carbonate, or formalin for 5 min. and capable of being kept for 1 week in an ice-chest without loss of activity. It is, however, relatively sensitive to alcohol or acetone and to heat. Low concentrations of sodium cyanide (0·005% or less) have no effect on the oxidation; 0·01% slightly and 0·1% largely inhibits the activity. As small quantities of cyanide are not inhibitory, it appears that oxygen activation is not involved (cf. Dixon, A., 1927, 901; Szent-Gyorgyi, A., 1926, 867). The reduction of methylene-blue by hexuronic acid is not increased by the presence of hexoxidase nor is the action of this enzyme inhibited by 5% urethane or chloroform. These facts indicate that hydrogen activation is not involved. The kinetics of the oxidation of hexuronic acid in presence of hexoxidase also indicates that the mechanism involved is different from that of any other known enzyme. Hexoxidase appears to act on no substrate except hexuronic acid. Glutathione is oxidised in presence of both hexoxidase and hexuronic acid, although hexoxidase itself is without effect.

W. O. KERMACK.

The benzidine reaction in potatoes. F. YOSHIOKA (Biochem. Z., 1931, **231**, 233—238; cf. Boas, this vol., 122).—The enzyme from potatoes described by Boas is very stable towards changes in reaction, but is also very unstable towards heat. Although at 50° its activity is unaffected, at 60° it is reduced, and at 70° destroyed. It readily loses its solubility in water and is precipitated from solutions by alcohol or acetone, by half saturation with ammonium sulphate, or by complete saturation with magnesium sulphate. The precipitated insoluble material even when dried retains all the activity of the enzyme. Although it can be precipitated by kaolin it cannot recovered from this material by elution and it cannot be adsorbed by aluminium hydroxide. Potassium cyanide, mercuric chloride, and mercuric oxycyanide inhibit its action, but nickel powder has no effect on it.

W. MCCARTNEY.

Effect of various methods of storage on the chlorophyll content of leaves. P. A. HARRIMAN (Plant Physiol., 1930, **5**, 599—606).—Losses of chlorophyll during the drying of leaves of soya bean and nasturtium were least when temperatures of 45—60° were used. At 88° the loss approximated to 70% and at 18—24° to 20—30%. Low-temperature drying was ineffective in preventing chlorophyll losses unless the leaves were actually frozen. Leaves frozen in carbon dioxide "snow" retain all their chlorophyll.

A. G. POLLARD.

Effect of fertility on the carbohydrate : nitrogen relation in the soya bean. F. A. WELTON and V. H. MORRIS (Plant Physiol., 1930, **5**, 607—612).—Comparison of soya beans grown in sand cultures and soil showed that with increasing fertility the total dry matter and carbohydrate content of the stems decreased, the principal constituents affected being the easily hydrolysable carbohydrates, cellulose, and lignin. High carbohydrate contents were not associated with low proportions of nitrogen as in non-legumes. High nitrogen contents were associated with heavy nodulation of the roots. The stems of plants grown in poor soil or sand were tough and rigid and did not lodge.

A. G. POLLARD.

Transport in the cotton plant. I. Transport of phosphorus, potassium, and calcium. T. G. MASON and E. J. MASKELL (Ann. Bot., 1931, **45**, 125—173).—Analyses are made on samples from normal plants and from a group in which a ring of bark has been removed. Two regions (upper and lower) are distinguished, depending on their situation immediately above or below the first fruiting branch. A downward movement of phosphorus by way of the bark is definitely established, whilst a similar mechanism for the transport of ash and potassium seems probable. There is no evidence of a similar transport of calcium. Although the content of all constituents of the leaves is increased in the "ringed" group, there is no evidence as to what elements are responsible for the significant increase of ash, since the increases of phosphorus, potassium, and calcium are too slight to be significant. Upward movement of phosphorus and potassium to the leaves probably occurs normally by way of the wood, whilst no evidence of such a movement of calcium has been obtained. From data obtained with two groups of plants, in which the upper and lower regions, respectively, were deprived of leaves, it is shown that upward (as well as downward) transport of phosphorus and ash may occur by way of the bark. A significant increase in the phosphorus content of the wood and bark (about 20%) occurs, on removal of the growing bolls, in both the upper and lower regions, whilst the ash content shows a similar increase in the upper region only, and calcium no significant increase in either. The effect of fertilisation in increasing the uptake of phosphorus, ash, potassium, and, to a smaller extent, calcium by the ovules and carpels lends support to the view that phosphorus and

potassium travel to the boll by way of the phloem, whilst calcium does so by way of the xylem.

P. G. MARSHALL.

Effect of light on the migration of nutritive material at the opening of buds. E. MICHEL-DURAND (Compt. rend., 1931, **192**, 440—442).—Buds of *Æsculus hippocastanum* were investigated. In the dark, the total glucosides and protein-nitrogen increase during the first fortnight and diminish thereafter, whilst the soluble nitrogen increases in a regular manner. When exposed to light, the buds show a slower, but more regular, increase in both simple and complex glucosides, combined with a larger increase in protein-nitrogen particularly after the first fortnight; the increase in dry weight is also greater. Both synthetic and hydrolytic phenomena occur more rapidly in the presence of light and are related to the formation of chlorophyll. P. G. MARSHALL.

Diffusion of certain solutes through membranes of living plant cells and its bearing on certain problems of solute movement in the plant. F. C. STEWARD (Protoplasma, 1930, **11**, 521—557).—Apparatus for examination of the diffusion of fluids through cell membranes is described. Plasmolysis markedly affects the extent of diffusion through membranes. Rates of diffusion may be expressed mathematically in terms of membrane thickness. The coefficient of diffusion of dextrose through tissue is approximately 0·01 of that in water. The value for potassium phosphate is still lower. The general problem of solute movement in tissues is discussed. A. G. POLLARD.

Permeability of the cell wall. I. Membrane of the reed-grass (*Arundo phragmites* var. *pseudodonax*, Asch and Graeb); its use as osmometer and its permeability to sucrose. V. ULEHLA (Protoplasma, 1930, **11**, 574—600).—Manipulative details are recorded. The membrane is less permeable to water, sucrose, and salt solutions than is collodion. Theoretical values were obtained for sucrose solutions, but with salt solutions some anomalous osmosis occurs.

A. G. POLLARD.

Penetration of α-naphthol-2-sulphonate-indophenol, *o*-chlorophenol-indophenol, and *o*-cresol-indophenol into *Valonia*. M. M. BROOKS (Proc. Nat. Acad. Sci., 1931, **17**, 1—3).—The penetration of 0·000048—0·000384*M* solutions of the dyes in sea-water into the sap of *Valonia* at 25° has been studied. The results indicate that the sulphonic acid group inhibits penetration. The non-sulphonated dyes are absorbed in a colourless form, and although penetration is more rapid from acid than from alkaline solutions, the equilibrium concentration is independent of the external p_H, and varies with the nature of the buffer salts used; borates appear to interfere with the process. H. F. GILLBE.

Thermodynamics of ion concentration by living cells. F. P. ZSCHEILE (Protoplasma, 1930, **11**, 481—496).—Free energy changes during the accumulation of ions by plant-cells are calculated from published data and values for different plants compared. The radioactive energy of potassium is inadequate to supply the energy necessary for its accumulation in plants. A. G. POLLARD.

Effect of nitrate fertiliser on stomatal behaviour. A. L. PLEASANTS (J. Elisha Mitchell Sci. Soc., 1930, **46**, 95—116).—Nitrates made the stomata of bean plants more responsive to light; the rate of loss of water was diminished.

CHEMICAL ABSTRACTS.

Negative correlation between nitrate-nitrogen in the juice of beet leaves and the weight of the leaves. D. E. FREAR (J. Agric. Res., 1931, **42**, 53—56).—A negative correlation exists between the nitrate content of the leaf-juice and the weight of the leaves of beet. Juice from the midrib contains more nitrate than that from other parts of the leaf. Leaves for examination should be of approximately the same size, since the proportional weight of midrib to whole leaf decreases with increasing leaf size.

A. G. POLLARD.

Nature of drought-resistance in crop plants. R. NEWTON and W. M. MARTIN (Canad. J. Res., 1930, **3**, 336—427).—The bound water in a solution of a hydrophilic colloid, such as plant press-juice, is determined by cryoscopic observation of the apparent sucrose content when sufficient of the sugar has been added to give a molar solution in the total water. This value is not independent of the concentration of sucrose employed, and is, in the case of gum-arabic, considerably greater with molar solutions of sucrose than with similar solutions of dextrose. The bound water in sols of gelatin, agar, albumin, blood-fibrin, dextrin, and gum-arabic increases with the concentration of the solute, but in all cases except the last the rate of increase diminishes with increasing concentration.

By fine grinding and pressing at a pressure not exceeding 3—4 atm. at 0° a fluid is obtained which is substantially identical with the original tissue fluids. The concentration of solute in this juice is conveniently determined in a sugar refractometer by the application of a suitable factor; in the cereal group this factor is 0·83. Hydrolysis of added sucrose by the enzymes of the press-juice increases with rise of temperature and time of storage, but is insufficient in amount to vitiate bound water determinations.

Dialysis of the press-juice in a collodion sac leads, with the progressive removal of the salts, to a partial coagulation of the colloids. This coagulation is not entirely prevented by dialysing against 1% sodium chloride solution. During the course of the dialysis the gold number tends to rise, whilst changes in the bound water correspond generally with changes in p_H. In both fresh and dialysed juice, the reaction of which has been modified by the addition of lactic acid or sodium carbonate, the bound water shows a minimum value at p_H 7—8.

The concentration, osmotic pressure, bound water, and properties of the colloidal constituents of the leaf press-juice of various crop plants have been determined. It is considered, in the case of the wheats and grasses, that the bound water content gives a satisfactory indication of adaptation to drought-resistance.

The loss of moisture from cactus segments is in extreme cases but 5% in 148 days. The rate of loss is not widely different at 0, 25, and 50% R.H., but is greater than in an atmosphere of 75 or 100% humidity.

The leaves of the grasses, *Phleum pratense* and *Agropyron tenerum*, lose water rapidly at zero humidity, almost complete desiccation occurring in 4 days. The course of the dehydration is similar notwithstanding great differences of the two plants in resistance to drought. T. H. MORTON.

Selective cultivation of beetroot and the fixity of the composition of the vegetation as postulated by Liebig. E. SAILLARD (Compt. rend., 1931, **192**, 504—507).—An examination of the analytical data obtained over a period of 30 years discloses no constant ratio between the sugar content and the basic oxides or phosphorus content. The amounts of the bases combined with the organic acids decrease as the sugar concentrations increase. Selective cultivation has produced varieties which require a decreased mineral content to elaborate the same amount of sugar. C. C. N. VASS.

Maintenance of moisture equilibrium and nutrition of plants at and below the wilting percentage. J. F. BREAZEALE (Arizona Agric. Exp. Sta. Tech. Bull., 1930, No. 29, 137—177).—There is a continuous film of moisture between the soil and the growing plant at all moisture contents above the wilting point; this is the point of equilibrium between the suction force of the plant and the adhesive forces of the soil. The available moisture of a soil is that held by the soil with a force less than the suction force of the plant (approximately 5 atmospheres). Water may pass from soil to plant-root or *vice versa*, according to the relative magnitude of the forces involved. Plants take up nutrient ions as a result of their electrical charges, and the actual passage of water into the plant-root is not essential to the process. The intake of nutrients by plants may continue at the wilting point. Plants may absorb moisture from a particular soil area, and transport and exude this in drier areas in which nutrients may be dissolved and absorbed by the plant.

A. G. POLLARD.

Formation of oil in plants. S. IVANOV (Chem. Rund. Mitteleuropa Balkan, 1930, 7, No. 1, 115—117, No. 2, 9—11; Chem. Zentr., 1930, ii, 2662—2663).—Similarity of the oils produced indicates that the process of formation is similar in a genus of plants. Plants of northern habitat always contain a larger proportion of unsaturated glycerides than those of southern habitat; oils containing oleic acid, however, are unaffected by climate. A. A. ELDRIDGE.

Glyceride structure of laurel fats. G. COLLIN (Biochem. J., 1931, **25**, 95—100).—Laurel-kernel fat contains 43·1% of lauric, 6·2% of palmitic, 32·3% of oleic, and 18·4% of linoleic acid. There is, however, present in it 36% of saturated glycerides, of which trilaurin is the predominant constituent. Apparently the unsaturated unlike the saturated acids do not link up with each other, but distribute themselves among the residual palmitic and lauric acids. The laurel-kernel fat, therefore, does not resemble other kernel fats. Laurel-pulp fat, on the other hand, resembles analogous specimens of other origin.

S. S. ZILVA.

Starch in plant seeds. A MÜHLDORF (Bot. Arch., 1930, **30**, 167—194; Chem. Zentr., 1930, ii, 2791).—The starch grain of sphagnum seed consists of two components; one, deposited chiefly in the outer layer, may probably be regarded as analogous to amylopectin, and the other, present within the grain, to amylose. A. A. ELDRIDGE.

Iodometric determination of reducing sugars in the apple. H. K. ARCHBOLD and E. M. WIDDOWSON (Biochem. J., 1931, **25**, 101—116).—Dextrose is quantitatively oxidised to gluconic acid by alkaline iodine in 2 hrs. at 1° and some oxidation of lævulose also occurs. In mixtures of dextrose and lævulose the amount of iodine reduced per g. of lævulose increases from 0·013 to 0·017 g. as the latter to the former increases from 1/1 to 5/1, and then decreases slowly as this ratio is further increased. The value 0·017 can be used for determination of lævulose and dextrose in apples by combination of the iodometric and copper reduction methods. The treatment of extracts of mature apples with basic lead acetate and subsequent deleading with disodium phosphate or potassium oxalate removes oxidisable material other than sugar under certain conditions.

S. S. ZILVA.

Gums. II. Tragacanthin—the soluble constituent of gum-tragacanth. A. G. NORMAN (Biochem. J., 1931, **25**, 200—204).—Tragacanthin may be separated by ordinary filtration in extreme dilution. Uronic acid units constitute about one half of the molecule. Arabinose was the only sugar found. A portion of the arabinose is possibly united to the uronic acid to form a resistant nucleus and the residue is attached by a glucosidic linking and is therefore easily removable. S. S. ZILVA.

Catechin of the cacao bean. W. B. ADAM, F. HARDY, and M. NIERENSTEIN (J. Amer. Chem. Soc., 1931, **53**, 727—728).—*l*-Acacatechin is present in cacao beans from various sources to the extent of about 0·8%. H. BURTON.

Algin from *Laminaria*. H. COLIN and P. RICARD (Bull. Soc. Chim. biol., 1930, **12**, 1392—1400).—The solution obtained by the hydrolysis of algin with water under pressure or sulphuric acid does not contain any appreciable amount of reducing sugars. From this liquid, a barium salt having approximately the composition indicated by the formula $(C_6H_9O_7)_2Ba$ was isolated. The authors conclude that algin is a glucoside containing glycuronic acid as part of the molecule, and that the reducing action of the hydrolysis product is due to the formation of this acid. B. LEVIN.

Rye-mucilage. E. BERLINER and R. RUTER (Z. ges. Mühlenwesen, 1930, 7, 52—57; Chem. Zentr., 1930, ii, 1790).—A 10% aqueous suspension of the flour at 27° is shaken at 5 min. intervals for 30 min.; 3 c.c. of 15% sodium tungstate solution are added, and concentrated sulphuric acid until thymol-blue is reddened. Enzymic activity may be inhibited by addition of these substances at first. The filtrate is treated with 6 vols. of methyl alcohol; the precipitate of mucilage still contains $N\times5·7=6·7\%$, traces of reducing sugar, α_D before inversion $-77°$ or $-90°$, after inversion $+77°$, η^{20} 7 in 0·2% solution. It is non-fermentable; hydrolysis affords non-fermentable

reducing sugars (11% of dry weight). Various strains of rye were examined. The viscosity of the clarified aqueous extract affords the best indication of the mucilage content, and may serve for evaluation of the quality of rye flour. A. A. ELDRIDGE.

Chemical composition of pollen. E. ELSER and J. GANZMÜLLER (Z. physiol. Chem., 1931, **194**, 21—32).—Methods are described for the determination of moisture, sugar, fat, protein, total ash and its constituents, and enzymes in pollen. Analytical data are presented for the alder, pine, and hazel, and the results are discussed in relation to the nutritional value of the pollen to the honey-bee. A. COHEN.

Membranes of spores and pollen. II. *Lycopodium clavatum*, L. III. *Picea orientalis*, *Pinus sylvestris*, L., and *Corylus avellana*, L. F. ZETZSCHE and H. VICARI. **IV. Fossil sporopollens from Tasmanite and Moscow lignite.** F. ZETZSCHE, H. VICARI, and G. SCHARER (Helv. Chim. Acta, 1931, **14**, 58—62, 62—67, 67—78).—II. Digestion of the spore membrane of *L. clavatum* with 75% sulphuric acid at the ordinary temperature gives a cellulose-free sporonin (cf. A., 1928, 524) which has, however, undergone some change. Prolonged treatment of the membrane with 85% phosphoric acid at about 30° removes the cellulose completely; subsequent treatment of the residue with hydrofluoric acid affords sporonin, probably $C_{90}H_{142}O_{27}$ (cf. *loc. cit.*), which is nearly ash-free. Boiling acetic anhydride converts this into an *acetylsporonin*, $C_{90}H_{127}O_{12}(OAc)_{15}$, hydrolysed by 0·1*N*-alcoholic potassium hydroxide to the original substance. Acetylation of the acetylsporonin in presence of zinc chloride at 70—80° causes degradation of part of the substance to resinous material; the insoluble residue contains 35·4% Ac.

III. Successive treatment of the pollens from *P. orientalis*, *P. sylvestris*, and *C. avellana* with potassium hydroxide, 85% phosphoric acid, and hydrofluoric acid affords *substances* of the probable formulæ $C_{90}H_{146}O_{25}$, $C_{90}H_{131}O_{11}(OH)_{13}$, and $C_{90}H_{138}O_{22}$, respectively, resembling sporonin.

IV. Details are given for the extraction of *tasmanin*, $C_{90}H_{134}O_{15}(OH)_{x}$, and *bothrodendrin*, $C_{90}H_{111}O_{13}(OH)_9$, from Tasmanite and Moscow lignite, respectively. H. BURTON.

Phytochemical studies of Oregon plants. I. H. M. BURLAGE (J. Amer. Pharm. Assoc., 1931, **20**, 33—40).—*Artemisia heterophylla*, Nutt. ("Golden-rod sage"): the leaves and tops of this herb (7 samples) on steam-distillation gave 0·77—1·72% of oil having d^{20} 0·9187—0·9639, $[\alpha]_D^{20}$ −0·91° to +39·95°, n_D^{20} 1·4196—1·4994, acid value 2·75—12·63, saponif. value 23·36—51·97, acetyl value 40·44—201·43, ester value 20·34—39·34, free acids 4·0—21·0%, phenols 4·0—8·0%, aldehydes and ketones 0—4·0%. *Heracleum lanatum*: distillation of the fruits (3 samples) yielded 0·26%—0·57% of oil having d^{20} 0·8640—0·8698, $[\alpha]_D^{20}$ −0·07° to +0·93°, n_D^{20} 1·4268—1·4290, soluble in 1·2 vols. of 80% alcohol, acid value 2·40—5·30, saponif. value 249·70—266·90, acetyl value 33·20—48·00, ester value 244·40—263·50, free acids 1·0—5·0%, phenols 1·0—2·0%, aldehydes and ketones 1·0—2·0%. Constants of oils of the same genus are given for comparison. *Melissa officinalis*, L. (Lemon mint): steam-distillation yielded 0·13% of oil having d^{20} 0·9632, $[\alpha]_D^{20}$ −10° 6′, n_D^{20} 1·4999, acid value 9·20, saponif. value 34·41, acetyl value 43·30, ester value 25·13, free acids 2·0%, phenols 4·0%, aldehydes and ketones 17·0%; it was insoluble in 20 parts of 80% alcohol. *Micromeria douglasii*, Benth. (Tea vine): distillation of the fresh herb gave 0·25% of oil having 0·9217, $[\alpha]_D$ −21° 3′, n_D^{20} 1·4572, acid value 6·06, saponif. value 27·01, acetyl value 55·54, ester value 20·95, solubility in 80% alcohol 1 : 10. Chemical investigations of the whole plants of the above species are also recorded. E. H. SHARPLES.

Anthocyans in [grape] hybrids. E. PARISI and I. COSMO (Ital. Agric., 1930, No. 5, 10 pp.; Chem. Zentr., 1930, ii, 2971—2972).—The anthocyans of European and American grapes and their hybrids, when isolated by Willstatter's method, give similar red solutions, but differentiation may be accomplished by means of ferric chloride. The aqueous hydrochloric acid extract is shaken with amyl alcohol, and the red alcoholic solution is shaken with water containing a trace of ferric chloride. American grapes give a dark blue precipitate at the interface, the violet colour of the amyl alcohol vanishing after a few hours. German grapes give no precipitate, and the solution long remains coloured. With hybrids the amyl alcohol remains reddish-violet and the characteristic precipitate appears. A. A. ELDRIDGE.

Anthocyanins in the etiolated shoots of buckwheat and wheat. S. JONESCO (Compt. rend., 1931, **192**, 438—440).—The chromogen obtained from etiolated shoots of buckwheat is a yellow powder which yields galactose on hydrolysis. When boiled in alcoholic solution for 5—10 min. with 20% hydrochloric acid, it gives rise to the red anthocyanin. The chromogen from etiolated wheat shoots reduces ammoniacal silver nitrate and Fehling's solution and yields arabinose on hydrolysis. It can be transformed into the pigment by oxidation with a mixture of barium peroxide and manganese dioxide, but not by boiling with alcoholic hydrochloric acid. P. G. MARSHALL.

Biochemistry of the colouring matter of tomatoes. H. VON EULER, P. KARRER, E. VON KRAUSS, and O. WALKER (Helv. Chim. Acta, 1931, **14**, 154—162).—When green tomatoes are allowed to ripen at 20—21°, the normal ripening process (formation of red colouring matter) occurs. At 30°, ripening is accompanied by an orange-yellow pigmentation, and the colouring matter consists mainly of flavones or flavonols together with small amounts of carotene and xanthophyll. Lycopene formation is probably an enzymic process taking place at an optimum temperature below 30° (the enzyme is thermolabile at this temperature). The colouring matter of "Golden Queen" tomatoes does not contain lycopene. Light appears to have no function in the formation of lycopene. H. BURTON.

***Leonurus sibericus*, L. I. Leonurine.** S. KUBOTA and S. NAKASHIMA (Folia Pharmacol. Japon., 1930, **11**, No. 2, 153—158).—The plant contains about 0·05% of the alkaloid *leonurine*, $C_{13}H_{19}O_4N_4$, m.p. 238°, soluble in amyl alcohol. CHEMICAL ABSTRACTS.

Source of error in determination of amide-nitrogen in plant extracts. H. B. VICKERY and G. W. PUCHER (J. Biol. Chem., 1931, **90**, 179—188).—When the amide-nitrogen in extracts of fresh tobacco leaf which contains a large amount of nitrate-nitrogen is determined by hydrolysis in presence of excess of hydrochloric acid and measurement of the ammonia formed, a result is obtained which is too large on account of the reduction of nitrate to ammonia by some unknown substance present in the leaf. This substance largely disappears during curing of the leaf. Octyl alcohol is found to have the same effect. A second error in the determination of amide-nitrogen occurs as the result of the oxidation of the ammonia by the mixture of hydrochloric acid and nitric acids. Under the conditions proposed by Sachsse (J. pr. Chem., 1873, **6**, 118) these two actions almost exactly counterbalance and approximately accurate results may be obtained. When no hydrochloric acid and only sulphuric acid is used in the hydrolysis, more latitude is allowable both in the concentration of acid and in the time of boiling. It is suggested that $2N$-sulphuric acid should be employed and that hydrolysis should be continued for 6 hrs.

W. O. KERMACK.

Proteins of Indian foodstuffs. III. Globulins of Bengal Gram (*Cicer arietinum*, Linn.) and Horse Gram (*Dolichos biflorus*). N. NARAYANA (J. Indian Inst. Sci., 1930, **13A**, 153—158; cf. Sundaram and others, A., 1930, 260).—The arginine content of Bengal Gram protein was considerably higher than that of other Indian pulses. The two proteins examined contained sufficient proportions of arginine, tyrosine, and lysine, but were deficient in cystine and tryptophan. A. G. POLLARD.

Hydrogen cyanide in the *Leguminosæ*. P. GUÉRIN (Bull. Soc. Chim. biol., 1930, **12**, 1338—1354). A review. B. LEVIN.

Enzymes of tobacco. C. NEUBERG and M. KOBEL (Biochem. Z., 1930, **229**, 455—463).—Neither the enzymes (amylase, invertase, phosphatase, pectase, glycolase, keto-aldehyde mutase) nor the carbohydrates (pectin) of tobacco leaves are damaged or otherwise appreciably affected when these are rapidly dried in a current of air heated at temperatures not exceeding 100°. W. MCCARTNEY.

Lignin as a possible factor in lodging of cereals. J. DAVIDSON and M. PHILLIPS (Science, 1930, **72**, 401—402).—Wheat grown on a plot heavily fertilised with sodium nitrate showed characteristic lodging close to the " milk " stage of the grain. The silica and ash contents of the straw were lower than those of the control, but, contrary to expectations, the lignin content was markedly higher. A high lignin content thus appears to favour lodging by making the straw brittle. L. S. THEOBALD.

Magnesium content of certain foods. JOACHIMOGLU and G. PANOPOULOS (Med. Welt, 1929, **3**, ; Chem. Zentr., 1930, ii, 1789).—Olives and raisins are particularly rich in magnesium. The following magnesium contents ($MgCl_2$%) are recorded: milk 0·0428, wholemeal flour 0·1248, mutton 0·0129, olive 0·1132, currants 0·0764—0·2145, white wine 0·0037. The magnesium resides chiefly in the skin of the grape. A. A. ELDRIDGE.

Toxic action. I. Swelling and shrinkage of plant tissue in solutions of toxic substances. W. STILES (Protoplasma, 1930, **11**, 349—381).—The rate of swelling of tissues of potato tuber in toxic solutions is best examined by direct weighing of the liquid intake. Two types of toxic action may occur, viz., that characterised from the commencement of the test by a continuous reduction in the rate of swelling as compared with that in distilled water, and that in which there occurs an initial increase in the rate of swelling, followed by a decline. Mercury cyanide, copper sulphate, quinine hydrochloride, and chloroform have the former effect, whilst the latter is produced by sulphuric and osmic acids, mercuric chloride, and primary aliphatic alcohols. No acceleration of the rate of intake of water was observed in red-beet tissue immersed in mercuric chloride. The order of toxicity of the substances named was quinine hydrochloride > mercuric chloride > chloroform > copper sulphate > ethyl alcohol. A. G. POLLARD.

Toxic effects of iodine and nickel on buckwheat grown in solution cultures. M. COTTON (Bull. Torrey Bot. Club, 1930, **57**, 127—140).—Iodine (1·27 in 10^6) caused depression of growth; 40 parts in 10^6 killed the plants. Nickel was highly toxic at concentrations of 5·87 in 10^6.

CHEMICAL ABSTRACTS.

Microscopy and microchemistry of common indigenous fruits. A. NIETHAMMER (Planta [Z. wiss. Biol.], 1930, **12**, 399—413).—Calcium oxalate crystals are commonly found in unripe fruits. These gradually dissolve as the fruit ripens. The acetaldehyde content of the fruit increases during the ripening process. The nature and distribution of organic acids in the fruits are examined. A. G. POLLARD.

Increased permeability of barley due to acetylene. F. F. NORD and J. WEICHHERZ (Protoplasma, 1930, **11**, 440—446).—The permeability of barley grain to methylene-blue is increased by the presence of acetylene. A. G. POLLARD.

Spike disease of *Dodonæa viscosa*. B. N. SASTRI and N. NARAYANA (J. Indian Inst. Sci., 1930, **13A**, 147—152).—The nitrate, nitrite, ammonia, and amide contents of diseased tissues of *D. viscosa* were higher than those of corresponding healthy tissue. The diseased tissues were characterised by a tendency to accumulate sugars and starch and by a deficiency of calcium (cf. Rao and Sreenivasaya, A., 1929, 1204). A. G. POLLARD.

Association of biochemical products with cellulose esters. J. LOISELEUR and L. VELLUZ (Compt. rend., 1931, **192**, 159—160; cf. this vol., 167).—Membranes containing a protein and a cellulose derivative can be prepared by mixing a solution of the protein in a suitable amount of anhydrous formic acid with one of cellulose acetate in a mixture (10 : 7) of acetone and methyl alcohol, the methyl alcohol preferably containing 10—40% of formaldehyde. C. A. SILBERRAD.

Determination of oxygen consumption of a single cell. R. B. HOWLAND and A. BERNSTEIN

(J. Gen. Physiol., 1931, **14**, 339—348).—An improved apparatus which gives consistent results under constant conditions is described. The oxygen consumption of a single *Actinosphærium eichhornii* is 0·00113 mm.^{3} per hr., and that of a single *Paramecium caudatum* 0·00049 mm.^{3} P. G. MARSHALL.

Determination of oxygen in sea-water and fresh water. M. NICLOUX (Bull. Soc. Chim. biol., 1930, **12**, 1326—1337).—The method previously described for sea-water (A., 1930, 1143) has also been applied to fresh water. B. LEVIN.

Determination of carbon dioxide by Van Slyke's method. F. MAINZER (Biochem. Z., 1930, **229**, 311—314).—In Van Slyke and Neill's method (A., 1924, ii, 872) for the determination of carbon dioxide in urine loss of the gas by dissolution in the paraffin and by diffusion is avoided if the paraffin is first saturated with carbon dioxide at the same pressure as that maintained over the urine during the measurement and if the temperature is reduced to 5°. If the measuring vessel of Van Slyke's apparatus is replaced by one of a type described by the author, volumes up to 6·0 c.c. can be measured, although the accuracy of measurements in excess of 2·0 c.c. decreases in proportion to the volume measured. W. McCARTNEY.

Determination of dextrose by electrometric titration: application to blood-sugar. L. MARICQ (Bull. Soc. Chim. biol., 1930, **12**, 1366—1381).—Dextrose may be determined by utilising the method for the electrometric titration of iodomercurates (cf. A., 1929, 1259) under the following optimum conditions. To 5 c.c. of a dextrose solution containing 0·2 g. per litre are added water (10 c.c.), 1 c.c. of *N*-sodium hydroxide, and 5 c.c. of a reagent prepared by adding about 6 g. of mercuric iodide to a solution of 4·150 g. of potassium iodide in 100 c.c. of water. The mixture is heated on the water-bath for 5 min., cooled, diluted with 30 c.c. of water, and then acidified with 2 c.c. of *N*-nitric acid. It is then titrated electrometrically with mercuric chloride. Blood-sugar may be determined as follows. To 1 c.c. of blood in 7 c.c. of water are added 1 c.c. of 10% sodium tungstate solution and 1 c.c. of 0·66*N*-sulphuric acid. The mixture is shaken, filtered, and 2 c.c. of the filtrate are added to 13 c.c. of water, 1 c.c. of *N*-sodium hydroxide solution, and 5 c.c. of the reagent prepared as before, but diluted five times. The mixture is shaken, heated for 5 min. on the water-bath, cooled, acidified with 2 c.c. of *N*-nitric acid, and titrated as before. B. LEVIN.

Volumetric determination of sugars by the mercurimetric method. A. IONESCO-MATIU and M. VITNER (Bull. Soc. Chim. biol., 1930, **12**, 1414—1422).—The authors have applied the method of determination of mercury to the volumetric determination of sugars (cf. A., 1928, 1230; B., 1929, 698). The method is based on the reduction of mercuric iodide to mercury by the sugar in alkaline solution, separation of the mercury by centrifuging, dissolving in a mixture of nitric and sulphuric acids, and determining the mercury as in the method previously described. The method is satisfactory for the determination of dextrose, lactose, maltose, and for sugar in urine and blood. B. LEVIN.

Fate of lævulose in the animal organism. I. Determination of lævulose by the diphenylamine method. W. W. OPPEL (Biochem. Z., 1930, **229**, 85—99).—Lævulose, in amounts from 0·085 to 0·438 mg., can be determined by heating at 100° for 20 min. 1 c.c. of a solution mixed with 0·1 c.c. of a 20% alcoholic solution of diphenylamine and 1 c.c. of 25% hydrochloric acid, extracting the cooled liquid with 2—2·5 c.c. of *iso*amyl alcohol, diluting the extract to 30 c.c. with ethyl alcohol, and comparing the colour of the liquid so obtained with that produced by a simultaneously prepared and approximately equally concentrated solution containing a known weight of lævulose. The error of the method varies from 3 to 10%. W. McCARTNEY.

[Analysis.] XII. [A. Extraction apparatus for liquids. B. Determination of bromine in urine. C. Micro-determination of ammonia and urea by the urease method.] L. PINCUSSEN (Biochem. Z., 1930, **229**, 233—237). A. A description is given of an apparatus for the continuous ether extraction of liquids. B. Filtered urine (5—10 c.c.) is treated with 6—12 drops of concentrated sodium hydroxide solution and evaporated to dryness at 100°. The residue is ignited at red heat in a nickel crucible, cooled, and dissolved in water. After filtration into a distilling flask the solution is made strongly acid with concentrated sulphuric acid, potassium hydrogen sulphate (20 c.c. of 10% solution) is added, potassium permanganate solution (2%) is run in drop by drop until a permanent red colour appears, and, for 1·5 hrs., air is then drawn through the flask into two bottles containing potassium iodide (10—20 c.c. of 2% solution). The contents of the bottles are titrated with 0·01*N*-sodium thiosulphate solution, starch (1% solution) being used as indicator. C. The substances are determined by the method described in the author's "Mikromethodik," 5th Ed., 1929, except that the removal of the ammonia from the solution is facilitated by increasing to saturation its sodium chloride content. This saturation has no effect on the determination of urea. W. McCARTNEY.

Micro-determination of iodine in organic materials [blood and urine.] T. VON FELLENBERG [with C. BURCKHARDT] (Mitt. Lebensm. Hyg., 1930, **21**, 183—188; Chem. Zentr., 1930, ii, 1893).—Oxalated blood (10 c.c.) is evaporated with saturated potassium carbonate solution (1 c.c.) and the residue is carbonised in a muffle furnace just below red heat or in a closed tube; after extraction with water it is again ignited. Potassium nitrate is not employed to facilitate ashing. On addition of 50 γ of iodine to slaughterhouse blood containing 1·50—1·37 γ, 41·2—44 γ was found; on addition of a like amount to urine containing 2·45—2·37 γ of iodine 44·6—46·6 γ was found. A. A. ELDRIDGE.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

MAY, 1931.

General, Physical, and Inorganic Chemistry.

New bands in the secondary spectrum of hydrogen. D. S. Jog (Phil. Mag., 1931, [vii], **11**, 761—786; cf. Richardson, A., 1930, 387).—The known electronic levels of hydrogen are summarised, and are interpreted on Hund's theory of axial quantisation; the method is applied to the calculation of the electronic terms of the hydrogen molecule.
N. M. Bligh.

Fine structure in hydrogen band lines. O. W. Richardson and W. E. Williams (Nature, 1931, **127**, 481).—An examination of the spectrum of hydrogen in a large Hilger quartz spectrograph crossed by a reflexion echelon establishes the correlation between the spectrum of molecular hydrogen and atomic helium. L. S. Theobald.

Gaseous discharges. I. Characteristics of the discharges in hydrogen and nitrogen at reduced pressures with an incandescent cathode. II. Influence of the thermal treatment of the electrode on the glow discharge. III. Influence of gas-loading of the cathode on the ignition potential of the glow discharge in hydrogen. E. Badareu (Bull. Fac. Stiinte Cernauti, 1929, **3**, 221—236, 304—306, 1—8; Chem. Zentr., 1930, ii, 1043). L. S. Theobald.

Cold emission from unconditioned surfaces. W. H. Bennett (Physical Rev., 1931, [ii], **37**, 582—590).—Emission from unconditioned metals in high electric fields and the effect on the emitting surfaces of discharges through hydrogen were investigated. Loose fine particles have a greater influence on the quantity of emission than nature and conditioning of cathode. N. M. Bligh.

Clean-up phenomenon in hydrogen. E. Hiedemann (Ann. Physik, 1931, **8**, [v], 456—474).—The clean-up phenomenon in hydrogen follows a normal (in essentials similar to that described by Johnson) or an abnormal (observed by Mierdel) course depending on the treatment to which the discharge tube has been previously subjected. The normal clean-up is characterised by adsorption of hydrogen, whilst the abnormal appears to be the result of condensation of a mixture of silicon hydrides. W. Good.

Visible spectrum of helium. J. S. Townsend and F. L. Jones (Phil. Mag., 1931, [vii], **11**, 679—685; cf. A., 1930, 973).—The relation between the light emitted by a discharge in a gas and the energy of the electrons causing ionisation by collision with the gas molecules was investigated by observations on the change in intensity of the light due to changes of pressure in helium over the range 20—2 mm., and electron energies 3—4 volts. Bohr's model of the helium atom, requiring a minimum of 20 volts for radiation emission, is not supported.
N. M. Bligh.

Hyperfine structure of Li⁺. II. P. Güttinger and W. Pauli (Z. Physik, 1931, **67**, 743—765).—Theoretical (cf. A., 1930, 1487). Hyperfine separations in the Li^+ lines, $^3P_{0,1,2}-{}^3S_1$, are comparable with fine structure separations.
A. B. D. Cassie.

Vacuum spark spectra to 40 Å.: spectra of Be III, Be IV, B IV, B V, and C V. B. Edlén (Nature, 1931, **127**, 405—406).—The hydrogen- and helium-like spectra previously traced to Be IV (A., 1930, 263) have been completed with B IV B V, and C V, and the limit of optical spectra has been brought down to 40·28 Å. Wave-lengths of the series $1^2S-n\text{-}P$ and 1^2S-3^2P, and 1^1S-n^1P are tabulated. The calculated quantum defect from the series of Be III is $n-n^*=-0{\cdot}013\pm0{\cdot}001$. L. S. Theobald.

Intensity measurements in the atmospheric oxygen band at 7600 Å. W. H. J. Childs and R. Mecke (Z. Physik, 1931, **68**, 344—361).—The intensity of absorption due to the A-group of oxygen near 7600 Å. was determined by Frerichs' method (*ibid.*, 1925, **31**, 305), using a dispersion of 2·6 Å. per mm., and columns of air 14, 33, and 62 metres long. Deviations from Lambert's law were investigated and allowed for, and the statistical weights of the rotational levels were determined.
A. B. D. Cassie.

Starting potentials of the corona discharge in neon. F. M. Penning (Phil. Mag., 1931, [vii], **11**, 961—980).—Contrary to the results of Huxley (cf. A., 1928, 567), the starting potential of a positive discharge in pure neon was found to be higher than that of a negative discharge. The former could, however, be decreased below the latter by the addition of traces of argon. N. M. Bligh.

Photometry of the neon lamp. M. J. Druyvesteyn and N. Warmoltz (Z. Physik, 1931, **68**, 378—394).—Light emitted normally to the cathode of a neon lamp was investigated visually by means of a rotating sector photometer. Fifteen international candles are emitted per amp. passing through the lamp; this intensity is proportional to the current and independent of cathode fall and gas pressure. A study of the influence of helium and argon suggests

that excitation is due to slow electrons of 25 volts energy. A. B. D. CASSIE.

New resonance series of sulphur vapour. III. J. GENARD (Bull. Acad. roy. Belg., 1931, [v], **17**, 184—190).—The extent of the excitation region of the resonance spectrum of S_2 was investigated. Conditions used were other than those giving the optimum fluorescence; excitation was by means of magnesium spark. The lower limit of the excitation spectrum is between 2890 and 2850 Å. A. J. MEE.

Rotational analysis of the S_2 bands. S. M. NAUDÉ and A. CHRISTY (Physical Rev., 1931, [ii], **37**, 490—506; cf. Rosen, A., 1927, 608).—The emission spectrum of S_2 was obtained by means of a Geissler tube, and the bands 9—1 (λ 2857·36), 7—0 (λ 2860·13), 8—1 (λ 2887·84), 9—1 (λ 2917·38), and 7—1 (λ 2920·28) were investigated. Each band consists of three *R* and three *P* branches; the structure is similar to that of the Schumann–Runge bands of oxygen. Wave numbers and intervals for the lines of each band are tabulated, and the rotational analysis is obtained. N. M. BLIGH.

Spark spectra of chlorine. K MURAKAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, **15**, 105—109; cf. this vol., 276).—The spectrum of Cl III was excited by increasing the spark gap and current in a Geissler tube with tungsten electrodes, one containing a little sodium chloride. Intensities, wave-lengths, and term combinations are tabulated for 29 newly-classified lines. The classification of Cl II lines is extended. N. M. BLIGH.

Band spectra of scandium, yttrium, and lanthanum monoxides. W. F. MEGGERS and J. A. WHEELER (Bur. Stand. J. Res., 1931, **6**, 239—275).—The band spectrum of scandium oxide contains 139 band heads, all degraded towards the red. They are divided into five systems, the 0–0 transitions having heads at 4857·79 and 4858·09, 6017·07, 6036·17, 6064·31, 6079·30 Å. Yttrium oxide gives 120 band heads degraded towards the red, the five 0–0 transitions being 4817·38 and 4818·20, 5939·08, 5972·04, 6096·78, 6132·06 Å. Lanthanum monoxide gives 300 band heads, divided into nine systems, seven of which include all bands shaded towards the red, and the other two of groups of weaker bands shaded away from the red. C. W. GIBBY.

Intensity measurements in the spectrum of manganese. R. S. SEWARD (Physical Rev., 1931, [ii], **37**, 344—361; cf. McLennan, A., 1926, 766; Duffendack, A., 1929, 966).—Relative intensity measurements were made, and full data tabulated for 150 lines of 23 multiplets of Mn I, and 3 of Mn II. N. M. BLIGH.

Fluorescence of zinc vapour. W. KAPUŚCIŃSKI (Bull. Acad. Polonaise, 1930, **A**, 453—459).—The fluorescence spectrum of zinc vapour extends from 2130 to 4900 Å., and consists of lines and bands. The triplets originate in levels not directly excited from the ground level. A. B. D. CASSIE.

Optical excitation functions of cadmium and zinc lines. K. LARCHÉ (Physikal. Z., 1931, **32**, 180—181).—A lecture. W. GOOD.

Critical potentials of the spark spectrum of cadmium. D. COLSON (Proc. Iowa Acad. Sci., 1929, **36**, 307).—Excitation by electron impact (8·8—200 volts) was employed. CHEMICAL ABSTRACTS.

Second spectrum of xenon. C. J. HUMPHREYS, T. L. DE BRUIN, and W. F. MEGGERS (Bur. Stand. J. Res., 1931, **6**. 287—293).—A partial list of identified terms and their combinations is given. C. W. GIBBY.

Probabilities of recombination into the 1^2S state of cæsium. C. BOECKNER (Bur. Stand. J. Res., 1931, **6**, 277—285).—The intensity distribution in the 1^2S series of cæsium has been measured between 3184 and 2750 Å. From this and the velocity distribution of the discharge electrons the relative probability of recombination of free electrons into the 1^2S state is shown to fall nearly as the inverse fourth power of the velocity for energies greater than 0·15 volt. C. W. GIBBY.

Measurements in the arc spectrum of rhenium. W. MEIDINGER (Z. Physik, 1931, **68**, 331—343).—A number of lines between 2600 and 3500 Å. and between 4040 and 5300 Å. were measured with an accuracy of ±0·1 Å. in the arc spectrum of rhenium. A. B. D. CASSIE.

Absorption spectrum of dissolved mercury. H. REICHARDT and K. F. BONHOEFFER (Z. Physik, 1931, **67**, 780—789).—A furnace containing a quartz absorption vessel which could contain liquids at 200 atm. and 250° is described. A double mercury 2537 Å. line, displaced towards the red, appeared at 120° when the mercury was dissolved in water, at 50° when in methyl alcohol, and at 15° when in hexane. Doubling is a Stark effect due to the electric field within the solution. The doublet separation diminishes with rise of temperature or decreasing density of the solvent. An absorption edge at 2200 Å. is ascribed to ionisation of dissolved mercury atoms. A. B. D. CASSIE.

Fluorescence of mercury vapour under atomic and molecular absorption. H. NIEWODNICZAŃSKI (Nature, 1931, **127**, 406).—The view that the fluorescence of mercury vapour is due mainly to atomic absorption is supported by the author's work on the influence of a magnetic field on fluorescence (A., 1929, 979; cf. Rayleigh, this vol., 137). L. S. THEOBALD.

Spark spectra of mercury. B. RICARD (Compt. rend., 1931, **192**, 618—620).—With the electrodeless discharge new lines have been measured belonging to the Hg II, Hg III, and Hg IV spectra from 4000 to 2700 Å. C. A. SILBERRAD.

Fine structure in the mercury singlet terms. S. TOLANSKY (Proc. Roy. Soc., 1931, **A**, **130**, 558—578).—By the use of a low-pressure high-frequency electrodeless discharge in pure mercury vapour, which increases the relative and intrinsic intensities of the singlet and inter-combination lines involving upper singlet levels, numerous structure have been examined. An explanation, based on the conception of nuclear spin, is suggested for the origin of the fine structures. This accounts for most of the difficulties and explains the apparent multiplicity of the 7^1S_0 level. L. L. BIRCUMSHAW.

Resonance line of mercury on addition of rare gases. P. KUNZE (Ann. Physik, 1931, **8**, [v], 500—520).—The effect of helium, neon, and argon on the emission and absorption of the resonance line of mercury (2537) has been experimentally investigated. A quantitative discussion of the results is given. W. GOOD.

Hyperfine structure of the mercury resonance line 2537 A. I. S. MROZOWSKI (Bull. Acad. Polonaise, 1930, **A**, 464—503).—The Zeeman effect in absorption was studied for the mercury 2537 Å. line with fields up to 8 kilogauss. Anomalies observed by McNair (A., 1928, 807) between 1 and 3·5 kilogauss in emission appear in absorption. This hyperfine structure and Zeeman effect cannot be explained by ordinary hypotheses.
A. B. D. CASSIE.

Hyperfine structure of certain mercury lines. B. VENKATESACHAR and L. SIBAIYA (Mysore Univ. J., 1930, **4**, 145—148).—Analyses of the mercury lines 6716, 6123, 6072, and of 4916 Å. are given.
C. W. GIBBY.

Intensity of mercury lines excited by positive ions. D. FRISCHE (Proc. Iowa Acad. Sci., 1929, **36**, 307—308).—The results were compared with those of investigation of the electron spectrum.
CHEMICAL ABSTRACTS.

Life of the excited state and the fine structure of the mercury arc spectrum. S. MROZOWSKI (Z. Physik, 1931, **68**, 278—283).—It is shown that the times of life of different levels which take part in the production of a multiplet are nearly equal to each other so far as transitions to other levels belonging to the same term system are concerned.
A. J. MEE.

Thallium–inert gas bands. H. KREFFT and R. ROMPE (Naturwiss., 1931, **19**, 269).—Mixtures of thallium vapour with inert gases give absorption bands in the neighbourhood of the strongest thallium lines (5350 and 3776 Å.). Probably these arise from a thallium–inert gas molecule. The separation of the band heads varies with the inert gas.
W. R. ANGUS.

Influence of ion density on the arc spectrum of thallium. H. KREFFT (Naturwiss., 1931, **19**, 269—270).—Spectrograms are given showing the influence of different current strengths on the absorption spectrum obtained from a discharge in mixtures of thallium with inert gases. The observed phenomena are discussed. W. R. ANGUS.

Determination of energy of dissociation from predissociation spectra. L. A. TURNER (Z. Physik, 1931, **68**, 178—183).—An explanation of the existence of two types of predissociation spectrum is given. In the one the disappearance of fine structure is sharp, in the other gradual. A. J. MEE.

Reduction of intensity of spectral lines in strong electric fields. C. LANCZOS (Z. Physik, 1931, **68**, 204—232).—The reduction of the intensity of the emission lines of the hydrogen atom is discussed quantitatively on the basis of wave mechanics, and ascribed to " pre-ionisation." The electric field sets the atom in a state of spontaneous ionisation, so that radioactive disintegration can take place. In the higher excited states this disintegration takes place in a time which is less than the life of the excited atom, and as radiation transition cannot take place the emission line disappears.
A. J. MEE.

Zeeman effect of forced radiation transitions produced by inner electric fields. G. P. ITTMANN and H. C. BRINKMAN (Naturwiss., 1931, **19**, 292).—The occurrence of a forbidden line in absorption or emission spectra may be due to two causes, which can be distinguished by a study of the Zeeman effect. The Zeeman effect for transitions which are forced by electric fields by no means agrees with that produced for permitted transitions. A. J. MEE.

After-glow and its life in discharge tubes. D. B. DEODHAR (Nature, 1931, **127**, 485).—A strong after-glow persisting for 45 min. has been observed in silica tubes filled with gases at low pressures and excited for 2 min. by induction coils giving an output of 400 volts. The rate of decay is extremely slow. The flash phenomenon recorded by Braddick (this vol., 1) is seen in these after-glows. L. S. THEOBALD.

Sensitivity of photographic plates in the region between ultra-soft *X*-rays and the ultra-violet. M. SODERMAN (Z. Physik, 1931, **67**, 790—793).—Schumann plates are best suited to photographing spectra between 50 and 500 Å.
A. B. D. CASSIE.

Sources of illumination for ultra-violet microscopy. B. K. JOHNSON (Proc. Physical Soc., 1931, **43**, 127—137).—Quantitative measurements have been made of the relative intrinsic brightness of spectrum lines given by various sources of radiation. Spark discharge between cadmium electrodes is the most suitable source of radiation for quartz monochromat microscope objectives computed for a wavelength in the neighbourhood of 0·275 μ. A special transformer and condenser is described.
W. E. DOWNEY.

Influence of the crystal-orientation of the cathode on that of an electrodeposited layer. W. A. WOOD (Proc. Physical Soc., 1931, **43**, 138—141).—*X*-Ray examination shows that the orientation of a copper deposit for small currents is the same as that of the cathode. Nickel at low current densities assumes a distinct orientation. As the current is increased there is a region of no orientation, but at still higher currents the orientation is the same as that of the cathode surface. W. E. DOWNEY.

Intensity of *X*-rays reflected from platinum, silver, and glass. H. W. EDWARDS (Physical Rev., 1931, [ii], **37**, 339—343).—The intensity of a monochromatic beam of *X*-rays of wave-length 0·69 Å., obtained by reflexion from calcite, was measured on reflexion from platinum, silver, and glass mirrors for angles of incidence varying from 0·75 to 1·25 times the critical angle. N. M. BLIGH.

Frequencies of characteristic *X*-radiation for the elements 11 Na to 17 Cl, calculated more accurately than at present with hypotheses extending the classical theory. S. BJORCK (Z. Physik, 1931, **68**, 133—144).—Theoretical.
A. B. D. CASSIE.

Mass absorption coefficient of the *K* shell according to the Dirac relativistic theory of the electron. L. C. ROESS (Physical Rev., 1931, [ii], **37**, 532—555).—Mathematical. With a model atom containing two non-interacting electrons and a fixed nucleus the mass absorption coefficient is calculated with the help of the Dirac relativistic equation. Results for lead, tin, zinc, and aluminium are tabulated and graphed for comparison with experimental data, and with values calculated on a non-relativistic basis (cf. Stobbe, this vol., 138). N. M. BLIGH.

Distribution of electricity in the lithium atom. B. ARAKATZU and P. SCHERRER (Helv. phys. Acta, 1930, **3**, 428—435; Chem. Zentr., 1931, i, 13—14). —The scattering of *X*-rays by lithium has been examined by the powder method, and the electronic distribution is discussed. A. A. ELDRIDGE.

The ionisation formula and the new statistics. W. ANDERSON (Phil. Mag., 1931, [vii], **11**, 685—686). —Remarks on a paper by Chandrasekhar (A., 1930, 833). N. M. BLIGH.

Ionisation of argon, neon, and helium by various alkali ions. R. M. SUTTON and J. C. MOUZON (Physical Rev., 1931, [ii], **37**, 379—382; cf. A., 1930, 656).—Cæsium, rubidium, potassium, and sodium positive ions from Kunsman catalyst sources and lithium ions from spodumene were used to produce ionisation in helium, neon, and argon. Maximum ionisation was produced in each gas by the alkali ion nearest to it in atomic number (cf. Beeck, A., 1930, 1494). N. M. BLIGH.

Theory of the photo-electric effect in metals. I. TAMM and S. SCHUBIN (Z. Physik, 1931, **68**, 97—113).—Theoretical. Photo-emission is related to the potential barrier at the metal surface (surface effect) and to the energy of binding of conduction electrons (volume effect). The influence of surface layers is discussed. A. B. D. CASSIE.

Photo-electric effect and reflexion of electrons at hydrogenised potassium surfaces. W. KLUGE and E. RUPP (Physikal. Z., 1931, **32**, 163—172).—An experimental arrangement is described with which parallel investigations of the structure and photo-electric emission of potassium surfaces were carried out. The results support the view that the selective photo-electric effect exhibited by the potassium surface after a glow discharge in hydrogen at low pressure is due to interspersion of potassium in potassium hydride. The investigations of surface structure by electron reflexion lead to the values 7·3 volts for the mean inner potential of potassium and 5·4 Å.±0·1 for the lattice constant of potassium hydride (cubic lattice). W. GOOD.

Quantum dynamics of the electron. E. SCHRÖDINGER (Sitzungsber. Preuss. Akad. Wiss., Berlin, 1931, 12 pp.).—Mathematical.

Directions of emission of photo-electrons. P. AUGER and (MLLE.) T. MEYER (Compt. rend., 1931, **192**, 672—673).

Elastic scattering of slow electrons in argon. E. C. BULLARD and H. S. W. MASSEY (Proc. Roy. Soc., 1931, **A**, **130**, 579—590; cf. Ramsauer and Kollath, A., 1930, 269, 1495).—With the object of obtaining further insight into the Ramsauer effect, experiments have been carried out in which the angular distribution of slow electrons (velocities from 4 to 40 volts) scattered elastically in argon have been measured over the angular range 15—125°. Scattering curves are obtained showing pronounced maxima and minima. L. L. BIRCUMSHAW.

Diffraction of electrons in mercury vapour. F. L. ARNOT (Proc. Roy. Soc., 1931, **A**, **130**, 655—667; cf. preceding abstract).—By means of the apparatus previously described (A., 1930, 6), the angular distributions of electrons of 15 different velocities (8·6—800 volts) scattered in mercury vapour have been measured over an angular range of 18—126°. L. L. BIRCUMSHAW.

Scattering of high-velocity electrons in hydrogen as a test of the interaction energy of two electrons. H. C. WOLFE (Physical Rev., 1931, [ii], **37**, 591—601).—Mathematical. N. M. BLIGH.

Absorption coefficient for slow electrons in thallium vapour. R. B. BRODE (Physical Rev., 1931, [ii], **37**, 570—573; cf. A., 1930, 657).—The absorption coefficient was obtained by sending a beam of electrons through thallium vapour and measuring the decrease in intensity of the beam as a function of the vapour pressure; plotted against the velocity of the electrons there is a minimum at 1·4 and a maximum at 4·5 volts. N. M. BLIGH.

Liberation of electrons by collision with positive ions at low gas pressures. II. Silver, aluminium, potassium, sodium, and mercury in hydrogen, nitrogen, mercury vapour, and rare gases. A. GÜNTHER-SCHULZE and F. KELLER (Z. Physik, 1931, **68**, 162—173).—The yield of electrons due to collision in hydrogen and nitrogen increases with the amount of gas, but in the rare gases is independent of this factor. It increases with the energy of collision, but above 1000 volts the increase is small. In general the number of electrons set free is greater the smaller is the mass of the ion colliding. A. J. MEE.

Pyrometry and the radiation properties of heated metals. R. HASE (Proc. Physical Soc., 1931, **43**, 212—216).—It is experimentally shown that the maximum of the energy emitted by a radiating metal is proportional to the square root of the specific resistance at zero and to the sixth power of the absolute temperature, instead of to the fifth power as in the case of a black body. The results are in good agreement with theoretical predictions, based on Maxwell's theory. W. E. DOWNEY.

Direct measurement of molecular velocities. I. F. ZARTMAN (Physical Rev., 1931, [ii], **37**, 383—391; cf. Eldridge, A., 1928, 108; Lammert, A., 1929, 970).—A method is described in which molecules condense on a glass plate fastened to a rapidly revolving cylinder. A stream of bismuth molecules having velocities of 168—673 m. per sec. was spread over a band 3 cm. wide; the vapour was found to consist of 40% Bi and 60% Bi_2 at 851°. N. M. BLIGH.

Positive ion emission from thin platinum films on glass. R. A. NELSON (Rev. Sci. Instr.,

1931, [ii], **2**, 173—179; cf. this vol., 26).—An apparatus for the production of Na^+ or K^+ ions from an equipotential surface of controlled thermionic activity is described. The positive ion current from platinised glass was greater than that from unplatinised glass at the same temperature. A new effect, the existence of a maximum and minimum in the positive thermionic current–electrolysis potential curves, was more pronounced with the equipotential emitter. N. M. BLIGH.

Interchange of translational, rotational, and vibrational energy in molecular collisions. C. ZENER (Physical Rev., 1931, [ii], **37**, 556—569).—Mathematical. The change in internal energy of molecules on collisions is investigated. The interchange of vibrational and translational energy for a collision in line of an atom and diatomic molecule, and the interchange of rotational and translational energy for the collision in a plane of an atom and a rigid symmetrical molecule are examined. N. M. BLIGH.

At. wt. of oxygen. Relative amounts of the three isotopes. R. MECKE and W. H. J. CHILDS (Z. Physik, 1931, **68**, 362—377).—The intensities of absorption of the $AO^{16}O^{16}$ band due to a few metres of air and of the $A'O^{16}O^{18}$ band due to the earth's atmosphere were compared, and the isotope ratio $O^{16}:O^{17}:O^{18}$ was found to be $630\pm20:0·2:1$. The at. wt. of oxygen is accordingly $16·0035\pm0·0003$, and the mass spectrographic wt. of an element is 1·00022 times its chemical at. wt. A. B. D. CASSIE.

At. wt. of iodine. Analysis of iodine pentoxide. G. P. BAXTER and A. Q. BUTLER (J. Amer. Chem. Soc., 1931, **53**, 968—977).—Thermal decomposition of iodine pentoxide produced by dehydration of iodic acid affords the iodine : oxygen ratio 3·17262, compared with 3·17330 deduced from accepted at. wt. The discrepancy is attributed to abnormal composition of the pentoxide. J. G. A. GRIFFITHS.

Chlorine isotope of nuclear mass 39. G. HETTNER and J. BÖHME (Naturwiss., 1931, **19**, 252). —An examination of the rotation–vibration lines of hydrogen chloride in the vicinity of 1·7 μ has demonstrated the existence of a chlorine isotope with the nuclear mass 39 (cf. Becker, A., 1930, 393). R. CUTHILL.

Connexion between relative proportions of isotopes and core moments of certain elements. H. SCHÜLER and J. E. KEYSTON (Z. Physik, 1931, **68**, 174—177).—A quantitative relation between the relative proportions of the isotopes of certain elements can be found if the isotopes are considered as even and odd. This classification is related to the nuclear moment for a given atom, and in consequence the relative proportions of isotopes are also related to this quantity. A. J. MEE.

Radioactive decomposition appearances in fluorite. L. GOEBEL (Z. Krist., 1931, **76**, 457—458; cf. Leitmeier, A., 1926, 367).—The coloration of fluorite is due to radioactive action liberating fluorine which escapes, leaving free calcium in colloidal form. When the particles of calcium are smallest, a green colour results; blue, violet, or colourless material arises from progressively larger particles. Changes in size of the particles, and consequently in colour, can be effected by heat, pressure, or radiation, and the changes can be followed by the ultramicroscope. This change may, however, be due to the liberated calcium atoms forming a definite lattice, a view supported by the detection in an X-ray photograph of faint indications of a line corresponding with the calcium lattice. C. A. SILBERRAD.

Absorption of β-rays by matter. G. FOURNIER and M. GUILLOT (Compt. rend., 1931, **192**, 555—557).—By a slight modification of the method previously described (cf. A., 1926, 880) the following mass absorption coefficients (μ/ρ) for β-rays from radium-$D+E$ have been determined: boron 16·4; phosphorus, white (solid or liquid) 20·9, red 20·2; vanadium 19·7; arsenic 20·9; bromine 23·0; sodium 16·8. C. A. SILBERRAD.

Number and internal absorption of γ-rays from radium-*D*. E. STAHEL (Z. Physik, 1931, **68**, 1—11; cf. this vol., 281).—The number of β-rays emitted by internal conversion of the 263 X units γ-radiation from disintegration of 100 radium-*D* nuclei was determined by means of a Geiger counter. Assuming an internal conversion coefficient corresponding with 97% absorption, this gives an emission of one γ-quantum by each disintegrating nucleus. A. B. D. CASSIE.

Initial charge of the recoil atoms produced during the disintegration of radon. W. MUND, P. CAPRON, and J. JODOGNE (Bull. Soc. chim. Belg., 1931, **40**, 35—74).—The initial charge on the recoil atoms of radon is positive and approximates to $2e$, corresponding with the loss of two electrons. The charge originates in the primary disintegration, and is not a result of subsequent collisions with other particles. H. F. GILLBE.

Electronic energy levels of the elements: sizes and electronic states of atoms in metallic crystals. W. HUME-ROTHERY (Phil. Mag., 1931, [vii], **11**, 649—678; cf. A., 1930, 1233).—Theoretical. If Z is the atomic number the interatomic distances in the crystals vary as $1/Z$, $1/Z^2$, $1/Z^3$, and $1/Z^5$ for elements at the beginning of the first, second, third, and fourth periods, respectively, whilst the electronic energy levels vary linearly as Z^2, Z^4, Z^6, and Z^{10} for the N_1 electrons of the outermost group of electrons of the atomic core or ion. This correspondence is examined in detail and plotted for the groups concerned, and is applied to a discussion of the interatomic distances in the crystals of the transitional elements of the long periods, and a method is suggested for determining the electronic states of the atoms in the solid crystals. It is concluded that the transition process begins in the solid crystals at group VI, and in the free atoms at group III. For the valency electrons it is shown that in groups 0, IA, and IIA a linear relation exists between $n\sqrt{V}$ and $Z^{2·3}$ for the members of any one group, where V is the ionisation potential and n the electron quantum number. In group 0 the interatomic distances agree with the law of the sub-groups $d/n=(1/aZ)^x$, previously deduced. N. M. BLIGH.

Statistics of nuclei. P. Ehrenfest and J. R. Oppenheimer (Physical Rev., 1931, [ii], **37**, 333—338).—Mathematical. N. M. Bligh.

Statistics of complex systems according to the new quantum mechanics. J. Wigner (Math. Naturwiss. Anz. Ungar. Akad. Wiss., 1929, **46**, 576—582: Chem. Zentr., 1930, ii, 3502—3503).

Arrangement of protons and electrons in the atomic nucleus. W. M. Latimer (J. Amer. Chem. Soc., 1931, **53**, 981—990).—Theoretical. From a consideration of the relative abundance of elements and of the number of protons and electrons in atomic species the at. wts. of which are approximately integral multiples of 4, an arrangement of electrons and protons in a geometrical space lattice in the atomic nuclei consistent with the numbers of "extra" electrons in the heavier elements is suggested. Each α-particle is situated at the corner of a tetrahedron, and combination of such tetrahedra leads to a face-centred cubic lattice of α-particles. Since an α-particle is represented as a tetrahedral arrangement of 4 protons about an electron pair, the insertion of an electron pair at each point about which four spin vectors converge, as in the α-particle, leads to a diamond-type lattice of electron pairs. J. G. A. Griffiths.

Band spectrum of tin oxide. I. Analysis of the vibration systems of the bluish-violet bands. P. C. Mahanti (Z. Physik, 1931, **68**, 114—125).—The wave-lengths of the heads of bands due to tin oxide between 3200 and 4600 Å. were determined by a concave grating, 6—18 Å. per mm. Most of the bands were fitted to three systems. The heat of dissociation for the ground state is $3{\cdot}66\pm0{\cdot}1$ volts. A. B. D. Cassie.

Simple relations between molecular spectra and structure. H. Deslandres (Compt. rend., 1931, **192**, 521—525; cf. this vol., 283).—Further examples of relations between the frequencies of certain lines or bands, the "fundamental frequency" (1062·5), and atomic number are given in conformity with the formula previously deduced. C. A. Silberrad.

Absorption spectra of aqueous solutions of the coloured ions Cu, Cr, and Co. M. Kahanowicz and P. Orecchioni (Z. Physik, 1931, **68**, 126—132).—The extinction coefficients for infinitely dilute electrolytic solutions containing nickel, copper, chromium, and cobalt were determined throughout the visible spectrum. The photometric curves show three phases of absorption which can be ascribed to molecules, free ions, and complex ions, respectively. A. B. D. Cassie.

Absorption of light and constitution. II. Heteropolar organic compounds. A. Burawoy (Ber., 1931, **64**, [B], 462—492; cf. this vol., 144).—The absorption of light by onium salts depends on conjugated systems. These, like those of homopolar compounds (*loc. cit.*), have polar construction and their absorption of light increases with their length and degree of polarity. Positively-charged atoms function as negative terminal atoms of the conjugated systems in cations. In harmony, the bathochromic action increases in the sequence $NR_2<O{\cdot}R<S{\cdot}R$, hence not with the positive, but with the negative character. In homopolar compounds and in cations, and in contrast to the positively-charged groups, further uncharged groups have increased bathochromic action in the sequence $O{\cdot}R<S{\cdot}R<NR_2$ when they are in conjunction with the conjugated system causing absorption, that is, when they are terminal members of the chromophore group and consequently increase the polarity. If they are not terminal members of the chromophore group, their hypsochromic effect is strong in case of direct substitution but weak in union to aromatic substituents. The complete spectrum of a compound is regarded as the resultant of the absorption bands of different chromophoric groups and isolated bands as a consequence of particularly favoured chromophors. These different chromophors are not formed in the same molecule, but in different "electron-isomeric" molecules. Small persistence is not a specific property of *R* bands, but is to be attributed to the presence of only a very small amount of radical-like molecules in a compound.

Addition of acid causes principally a change in the degree of polarity of the conjugated system in so far as it alters only the negative terminal group. The groups $C{:}NH_2$, $C{:}OH$, $C{:}SH$ arise from the groups $C{:}NH$, $C{:}O$, $C{:}S$. Positively-charged atoms have a more strongly bathochromic action and are therefore more negative than the corresponding uncharged atoms. In the conjugated system of a cation, the most positive atom invariably gives the electron to the anion, and is therefore the negative terminal atom. Addition of an acid molecule to an *R* chromophor annihilates the corresponding bands; consequently *R* bands do not occur in the spectra of cations.

The absorption of light of *aci*-salts or their anions is attributed to conjugated systems and subsidiarily to *R* chromophors. In this connexion, negatively-charged atoms behave as positive groups (atoms); in particular, the negatively-charged oxygen atom comports itself as the nitrogen of an amino-group. It is bathochromic only when it is the terminal atom of a chromophor. In anions in branchings of a conjugated system, the positive groups $O{\cdot}R$, $S{\cdot}R$, NR_2 have a hypsochromic effect.

A chromophor is an atom or a group which is necessary for the occurrence of an absorption band, independently of possible substituents which merely cause displacement of the bands. The absorption of light by organic compounds is attributable (1) to unsaturated individual atoms characteristic for the free radicals (*R* chromophors) and (2) to conjugated systems, therefore groups of atoms (*K* chromophors).

It is proposed to replace the conception of "auxochromic groups" by "auxochromic atoms." The latter are the terminal atoms of the chromophoric groups. The atoms O, S, N of the groups $O{\cdot}R$, $S{\cdot}R$, NR_2 and all negatively-charged atoms in anions are positive auxochromic atoms; the atoms N, O, S of the groups $C{:}N$, $C{:}O$, $C{:}S$, $N{:}N$, $N{:}O$, together with all positively-charged atoms in cations, are negatively auxochromic atoms, whereas the uncharged carbon atom is amphoteric. H. Wren.

Absorption of synthetic spinels coloured by manganese and chromium. K. SCHLOSSMACHER (Z. Krist., 1930, **75**, 399—409; Chem. Zentr., 1931, i, 438).

Colours of inorganic salts. M. N. SAHA and S. C. DEB (Nature, 1931, **127**, 485; cf. A., 1930, 272).—Absorption spectra of chromic and ferrous chlorides obtained in a vacuum furnace at 1000—1400° show bands at 4100 and 4350 Å., respectively. These bands are ascribed to Cr^{+++} and Fe^{++} and are due to magnetic transitions in the d^3 and d^6 shells. Continuous absorption from 3000 to 2200 Å., the limit of the apparatus used, is also observed and is ascribed to the Cl′ ion. L. S. THEOBALD.

Optical connexion between the phosphorescence of alkali halides and solutions of complex halides of lead and thallium. H. FROMHERZ (Z. Physik, 1931, **68**, 233—243).—An extension to the heavy metals of earlier work on the complex halides of copper and silver (cf. A., 1929, 626).

A. J. MEE.

Colouring and luminescence by Becquerel radiation. III. K. PRZIBRAM (Z. Physik, 1931, **68**, 403—422; cf. A., 1924, ii, 85; 1927, 393).—Work on the colouring of rock salt is summarised. Colouring is due to two large classes of centres: neutralised cations, and neutral atoms in irregular surroundings. Many different centres are distinguished, and come under one of these two classes. Pressure favours disturbance of the crystal lattice, and so increases the rate of colouring of a crystal. Radioluminescence and the action of Becquerel radiation were studied; many natural minerals owe their colour to Becquerel radiation.

A. B. D. CASSIE.

Exact solution of the Harries–Hertz collision problem, and its application to experimental arrangement in Raman effect experiments. H. BARTELS and C. H. NORDSTROM (Z. Physik, 1931, **68**, 42—63).—Theoretical. The number of collisions suffered by an electron in traversing a given thickness of gas is redetermined by Bartels' method (A., 1930, 1336) instead of the original diffusion method. The earlier method fails at low densities of scattering material, when the number of collisions depends on the direction of incidence of the electrons. The results are applied to scattering of light by turbid media, and it is concluded that turbid media give no greater intensity of Raman radiation than do clear media. A. B. D. CASSIE.

Transition probability in the Raman effect. L. S. ORNSTEIN and J. REKVELD (Z. Physik, 1931, **68**, 257—259).—A formula is developed for the relation between the intensities of Stokes and anti-Stokes lines. There is some ground for a general formula for the probability of a transition.

A. J. MEE.

Raman spectrum of hydrogen peroxide. S. VENKATESWARAN (Nature, 1931, **127**, 406).—A Raman frequency of 875 accompanied by a weak component at 903 $cm.^{-1}$ has been observed in the Raman spectrum of an aqueous solution of Merck's perhydrol. Other diffuse bands have been obtained.

L. S. THEOBALD.

Modified scattering by hydrogen halides. E. O. SALANT and A. SANDOW (Physical Rev., 1931, [ii], **37**, 373—378; cf. Wood, A., 1930, 978).—Raman lines of gaseous hydrogen chloride, bromide, and iodide, and liquid hydrogen chloride and bromide were measured. The shifts of the first two gases agree with the infra-red bands; that of hydrogen iodide does not agree, and is considered the more accurate determination of the (0,1) HI vibrational transition. Intensities of scattering are in the reverse order of those of absorption, in agreement with the Hill–Kemble theory of scattering by diatomic gas molecules (cf. A., 1929, 865). The lines scattered by the liquids differ in appearance from, and show smaller shifts than, those of the gases; the differences in the shifts are too large to be attributed to a Lorentz–Lorenz force, and are evidence of quantum-mechanical molecular interactions (cf. Breit and Salant, A., 1930, 1496). N. M. BLIGH.

Raman effect in water and in some solutions. R. BRUNETTI and Z. OLLANS (Atti R. Accad. Lincei, 1930, [vi], **12**, 522—529).—The effect was studied with water, with solutions of nitric acid, of nitrates of sodium, ammonium, potassium, barium, aluminium, lanthanum, cerium, and thorium, of hydrochloric acid, and cerium chloride. The effect of the nitrate ion is to cause depolymerisation of the water, which, however, does not become homogeneous.

F. G. TRYHORN.

Raman effect and problems of constitution. II. Cyano-compounds. A. DADIEU (Ber., 1931, **64**, [*B*], 358—361; cf. A., 1930, 1162).—Measurements of the Raman spectra of the following compounds are recorded: acetonitrile, *o*-toluonitrile, hydrogen and potassium cyanide, methyl- and ethyl-carbylamine, phenyl- and α-naphthyl-carbimide, ethyl thiocyanate, ethyl-, *iso*butyl-, phenyl-, and *p*-tolyl-thiocarbimide. The presence of a treble linking is established in the thiocarbimides, to which the constitution $\mathrm{R{\cdot}N}\lll^{\mathrm{C}}_{\mathrm{S}}$ is therefore ascribed, thus indicating a structural difference from the carbimides, R·N:C:O. The data for the carbylamines do not accord with either of the classical structures, but are interpreted by the formula R·N=C; an analogous constitution appears appropriate to carbon monoxide, fulminic acid, and all other compounds containing "bivalent" carbon. In hydrocyanic acid the *iso*-form is calculated to be present to the extent of about 0·5%. H. WREN.

Raman spectra of some organic halides. C. E. CLEETON and R. T. DUFFORD (Physical Rev., 1931, [ii], **37**, 362—372).—Raman spectra obtained by helium excitation (cf. Wood, A., 1929, 741) were photographed, and results tabulated and discussed for 19 simple organic halides not previously reported, including magnesium methyl bromide and iodide and ethylidene chloride and iodide. It is shown that in many cases the observed frequencies can be expressed in terms of four assumed fundamentals (five in the cyclic compounds), two of which are not observed. The application of available theory is discussed.

N. M. BLIGH.

Raman lines of *cyclo*propane and valency properties of some organic compounds. R. C. YATES

(Physical Rev., 1931, [ii], **37**, 616—618; cf. A., 1930, 1349).—Mathematical. Three fundamental wave-numbers for *cyclo*propane are calculated from the equations of motion of a system of three particles vibrating in a plane. The character of a single linking acting adjacent to a double linking in acetaldehyde and to a triple linking in acetonitrile is studied. N. M. BLIGH.

Mass spectra of glasses, salts, and metals and construction of a circular mass-spectrograph. H. MURAWKIN (Ann. Physik, 1931, **8**, [v], 353—432; cf. this vol., 407).—The method of investigating mass spectra is described. A strong emission of sodium, potassium, magnesium, calcium, a considerable emission of silicon and oxygen, and an irregular weak emission of heavy metals from Lindemann, Jena, Thüringen, lead, uranium, and silver glass, alundum cement, and combustion glass have been investigated mass-spectrographically in the temperature range 900—1600° Abs. The mechanism of the emission appears to be due both to electrolysis and to ionisation by impact. Mass spectrograms of aluminium phosphate, Kunsman's mixture, tungsten, platinum, and copper were also studied. W. GOOD.

Transparency of glasses to ultra-violet rays. P. GILARD, P. SWINGS, and A. HAUTOT (Bull. Acad. roy. Belg., 1931, [v], **17**, 235—248).—The effect of differing concentrations of constituents of glasses on their ultra-violet transmission is examined. Transparency increases with silica content, but there is an optimum concentration, depending on the other substances present. The concentration of lime has little effect on the transparency. Increase in barium oxide or alumina is favourable; increase in potassium is more favourable than a corresponding increase in sodium concentration. The addition of boron trioxide extends the transparency. A. J. MEE.

Electrolytic valve action. I. Tantalum oxide layer. A. GÜNTHER-SCHULZE and H. BETZ (Z. Physik, 1931, **68**, 145—161).—Experiment shows that the layer responsible for valve action in the case of tantalum consists of a compact non-porous layer of Ta_2O_5. The active layer has the same dielectric constant when in the electrolyte as when in the dry state, and this value is known. This fact may be utilised to determine the thickness of the layer, and it is found that this amounts to 82 mμ when the layer is produced by a voltage of 100.

A. J. MEE.

Electric conductivity of liquid hydrocarbons in thin layers. L. BRÜNINGHAUS (J. Phys. Radium. 1931, [vii], **2**, 69—85).—A more detailed account of work already noted (this vol., 285).

Mechanism of the "electric" discharge in solid insulators. I. II. A. VON HIPPEL (Z. Physik, 1931, **67**, 707—724; **68**, 309—324).—The paths of electrons in crystals during electrical discharges were studied. Results suggest that the potential variations giving mechanical strength to a crystal also determine its electrical resistance.

A. B. D. CASSIE.

Reciprocal relations in irreversible processes. I. L. ONSAGER (Physical Rev., 1931, [ii], **37**, 405—426).—Mathematical. Thermoelectric phenomena, transference phenomena in electrolytes, and heat conduction in an anisotropic medium are considered as examples of coupled irreversible processes, and a general class of reciprocal relations is deduced by a new theoretical treatment from the principle of microscopic reversibility. N. M. BLIGH.

***E.M.F.* of dielectrics.** K. LARK-HOROVITZ (Nature, 1931, **127**, 440).—Previous work by the author is discussed. L. S. THEOBALD.

Dielectric constant and electric moment of some amines. P. N. GHOSH and T. P. CHATTERJEE (Physical Rev., 1931, [ii], **37**, 427—429).—Using a heterodyne null-beat method (cf. Mahanti, A., 1930, 841) the dipole moment $\times 10^{18}$ for methyl-, dimethyl-, trimethyl-, ethyl-, diethyl-, and triethyl-amines gave the values 0·99, 0·90, 0·82, 0·99, 0·90, and 0·82 e.s.u., respectively. Values of the dielectric constant are also given, and, except in the case of methylamine, increase with the b. p. of the compound. The polar groups NH_2, NH, and N in the respective amines are mainly responsible for the development of the dipole moment of the molecule. N. M. BLIGH.

Dielectric constant of water as determined by a resonance method. E. P. LINTON and O. MAASS (J. Amer. Chem. Soc., 1931, **53**, 957—964).—Sources of error in the method of Cuthbertson and Maass (A., 1930, 523) have been investigated. With liquids of high dielectric constant, results are best obtained with a high-power oscillating circuit permitting the determination of the resonance point by means of the harmonic instead of the fundamental. Provided the conductivity of the medium is less than a certain value (4×10^{-6} ohm^{-1} in the case of water), the resonance point is independent of the conductivity. The dielectric constants at 25° are: ether 4·255, ethylene dichloride 10·38, water 79·2, and hydrogen peroxide at 0° 93·5 (cf. *loc. cit.*).

J. G. A. GRIFFITHS.

Dependence of the molecular polarisation of gaseous αβ-dichloroethane on temperature. R. SÄNGER (Helv. phys. Acta, 1930, **3**, 461—463; Chem. Zentr., 1931, i, 229).—A lecture (cf. this vol., 147).

A. A. ELDRIDGE.

Variations with temperature and frequency of dielectric loss in a viscous mineral insulating oil. H. H. RACE (Physical Rev., 1931, [ii], **37**, 430—446).—From measurements of dielectric loss using an open quartz insulated cell over a wide range of frequency and temperature, Debye's theory of polar molecules has been extended to give simple expressions for conditions of maximum loss per cycle.

N. M. BLIGH.

Theory of dielectrics. J. H. J. POOLE (Phil. Mag., 1931, [vii], **11**, 995—996).

Mol. volume and density at the absolute zero. G. L. CHABORSKI (Bul. Chim. pura appl., Bukarest, 1929, **31**, 53—66; Chem. Zentr., 1930, ii, 1046).—By the use of Longinescu and Chaborski's "molar concentration" $Cm-1000d/M$ equations are derived for evaluating the mol. volume and density at 0° Abs.: $V_0=1000/Cm_0$; $d_0=MCm_0/1000$; $Cm_0=Cm+1000(v-b)/b^-$, where $v-b$ is the covolume and b is

van der Waals' correction. Values for 47 organic compounds have been computed. Traube's (A., 1902, ii, 551) values for b at 0° for *iso*pentane, water, and methyl alcohol are criticised, and new values computed. A. A. ELDRIDGE.

Refractive indices of mixed crystals of magnesium and zinc sulphates. M. W. PORTER (Z. Krist., 1930, **75**, 288—300; Chem. Zentr., 1930, ii, 3500).—The pure salts, $XSO_4,7H_2O$, have n_α 1·4321, 1·4567; n_β 1·4551, 1·4800; n_γ 1·4605, 1·4840; d 1·679, 1·968, respectively. Values for nine mixed crystals are recorded. A. A. ELDRIDGE.

Production of residual double refraction by pressure in certain glasses at atmospheric temperature. F. C. HARRIS (Phil. Mag., 1931, [vii], **11**, 745—748).—The residual double refraction produced in specimens of glass by cooling under pressure having been found to decrease after keeping for 4 years, specimens of different composition were subjected to high pressures for long periods at atmospheric temperature, and observations were made in sodium light by a Babinet compensator.

N. M. BLIGH.

Magnetic rotatory power of some higher fatty acids. C. SALCEANU (Compt. rend., 1931, **192**, 675—677).—The specific magnetic rotatory powers, ρ/d (d density), for $\lambda=578$ mμ, of decoic, lauric, myristic, palmitic, and stearic acids are respectively 1·509, 1·545, 1·577, 1·596, and $1{\cdot}612\times10^{-2}$. Perkin's law regarding the molecular magnetic rotatory power of members of a homologous series is only approximately followed. C. A. SILBERRAD.

Molecular association. G. G. LONGINESCU (Bul. Chim. Soc. Romane Stiin., 1930, **31**, 21—76).—A review.

Application of space-energy to the calculation of chemical, electrical, and gas-kinetic transformations of energy, matter, and form. R. VON DALLWITZ-WEGENER (Z. Elektrochem., 1931, **37**, 25—33).—A summary and an extension of previous publications (cf. A., 1929, 885). The calculation of the energy changes involved in chemical reactions and galvanic cells from cohesion pressures is described. The modifications necessitated in the second law of thermodynamics by the introduction of the concept of space-energy are discussed; it is asserted that the possibility of a perpetual motion of the second kind must be conceded. R. CUTHILL.

Variable valency, especially in compounds of sulphur and tellurium. T. M. LOWRY (Bull. Soc. chim. Belg., 1931, **40**, 91—104).—A survey.

H. F. GILLBE.

Co-ordination. III. Energy of co-ordination. F. J. GARRICK (Phil. Mag., 1931, [vii], **11**, 741—744; cf. A., 1930, 1096).—The consistency of the electrostatic theory of co-ordination and values of the energy of co-ordination with general theories and established energy quantities is examined. From the lattice energy and heat of formation of some of the group of hexammine chlorides isomorphous with $[Ni(NH_3)_6]Cl_2$ the cycle lattice energy of the chloride of the central cation (zinc, iron, and manganese)—lattice energy of the ammine+heat of formation of ammine, gives the energy of co-ordination in good agreement with the theoretical value. A possible extension of the method to the energies of co-ordination of hydrates is considered. N. M. BLIGH.

Quantum theory of chemical binding in polyatomic molecules. W. HEITLER and G. RUMER (Z. Physik, 1931, **68**, 12—41).—Heitler and London's theory of chemical binding in diatomic molecules (Physikal. Z., 1930, **31**, 185) is extended to polyatomic molecules. A formula is deduced for the exchange energy due to interaction of pairs of atoms in the molecule, assuming only one atom not in an S state. In general, molecular states of least multiplicity give binding and greatest multiplicity repulsion of the component atoms. Examples discussed are hydrogen cyanide, which theory predicts as H·C·N, cyanic acid, O:C:N·H, molecules of the type $(H{\cdot}A)_2$, which are stable provided A has a valency greater than two, hydrazine, and dicyanogen. $NH_2{\cdot}NH_2$ and CN·CN are unstable for large separations of the components NH_2 and CN, respectively, but activation may overcome this potential barrier, and binding result for smaller separations. A. B. D. CASSIE.

Magnetism and molecular structure. II. Influence of position isomerism on diamagnetic susceptibilities. S. S. BHATNAGAR and R. N. MATHUR (Phil. Mag., 1931, [vii], **11**, 914—926).—Using the apparatus previously described (cf. A., 1930, 1096), magnetic susceptibility determinations were extended to *n*- and *iso*-propyl and *n*- and *tert*.-butyl alcohols at temperatures up to 50°; *o*-, *m*-, and *p*-tolyl methyl ether, *o*- and *m*-toluidine, *o*- and *p*-phenetidine, and *n*- and *iso*-butyric acid at 40°, and *n*- and *iso*-butyl bromide at 20°. For the benzene derivatives the influence of the size of the substituent groups on the difference between the susceptibilities was studied. Results for the alcohols cannot be explained by differences in the degrees of molecular association. An explanation on the basis of the electronic significance of valency linkings is given. N. M. BLIGH.

Significance of magnetic measurements for chemical problems. W. KLEMM (Z. angew. Chem., 1931, **44**, 250—259).—A survey of the theory of magnetism in its chemical aspects, with details of some particular cases and an account of methods of measurement. H. F. GILLBE.

Change in the relative concentration of paramagnetic $^2\Pi_{3/2}$ and diamagnetic $^2\Pi_{1/2}$ molecules in nitric oxide. E. BRODY, T. MILLNER, and R. SCHMID (Z. Physik, 1931, **68**, 395—402).—The ground state of nitric oxide is a $^2\Pi$ term, the levels being separated by 343 g.-cal. per mol. At the ordinary temperature the two forms are present in almost equal numbers, but at lower temperatures the diamagnetic $^2\Pi_{1/2}$ predominates. This was shown by diminution in the intensity of absorption bands arising in the $^2\Pi_{3/2}$ level relative to those arising in the $^2\Pi_{1/2}$ level. At the temperature of liquid air the paramagnetic form almost disappeared.

A. B. D. CASSIE.

Suggestions for rational symbolisation of organic and inorganic compounds and their

applicability to the discussion of the properties of compounds. W. MADELUNG (Z. Elektrochem., 1931, 37, 197—218).—Old and new methods of representing molecular structure are described and discussed in the light of modern electronic conceptions. It is suggested that electronic formulæ could be simplified by indicating whether an atom has its complete octet or is 1 or 2 electrons short by the use of symbols in different type or by the use of an index number. E. S. HEDGES.

Directed valency in polyatomic molecules. J. C. SLATER (Physical Rev., 1931, [ii], 37, 481—489: cf. A., 1930, 675).—Theoretical. The interactions of atoms in polyatomic molecules and the directional effects of valencies are described and discussed qualitatively; illustrations from the structure of metals and of organic and inorganic compounds are given. N. M. BLIGH.

Orbital valency. J. H. BARTLETT, jun. (Physical Rev., 1931, [ii], 37, 507—531).—Mathematical. The interaction of two atoms, each with one $2p$ electron, is studied with the help of an atomic wave function (cf. Kemble and Zener, A., 1929, 623). The views of Heitler on orbital valency and of Slater on directed valency are supported. N. M. BLIGH.

X-Ray spectrograph for wave-length determinations in air. S. ZEIDENFELD (Rev. Sci. Instr., 1931, [ii], 2, 153—163).—A Bragg type spectrograph with a rotating crystal was designed for the accurate recording and measurement of wave-lengths which could be investigated in air. The approximate range is 0·5—2·0 Å. A special type of double crystal holder is described. N. M. BLIGH.

New methods of interpreting photographs with convergent X-rays. C. KRATKY (Z. Krist., 1931, 76, 517—524; cf. this vol., 413).
C. A. SILBERRAD.

X-Ray determination of the form and boundary surfaces of submicroscopic crystals. R. BRILL (Z. Krist., 1930, 75, 217—227; Chem. Zentr., 1930, ii, 3699).—A discussion. The method has been applied to the examination of highly disperse electrolytic nickel. A. A. ELDRIDGE.

Hydrochloric acid as an etching agent for galena. E. STOICOVIC (Z. Krist., 1931, 76, 310—314).—Aqueous hydrochloric acid containing about 17% HCl is satisfactory. C. A. SILBERRAD.

Lattice energy of wurtzite. B. GROSS (Z. Krist., 1931, 76, 562—568).—The molecular lattice energy is $-10{\cdot}71e^2/d$, where e is the electronic charge and d, the shorter side of the unit cell, is 3·84 Å. This gives as the molar lattice energy -919 kg.-cal.
C. A. SILBERRAD.

Dependence of lattice dimensions on crystal size. J. E. LENNARD-JONES (Z. Krist., 1930, 75, 215—216; Chem. Zentr., 1930, ii, 3505).—Mathematical. A. A. ELDRIDGE.

Structure of films. I. Transformations of the lattice of cellulose nitrate film. II. Structure of nitrated and acetylated cotton. J. J. TRILLAT (J. Phys. Radium, 1931, [vii], 2, 65—68).—I. A dried film of cellulose trinitrate from acetone was compared by X-ray examination with that of the original product. New lines were observed in the spectrogram of the film and it seems that whilst some of the trinitrate in the film is in its original form a portion of it is in a new crystalline form. The dried film retains tenaciously about 1% of acetone. Nitrated cotton containing less than 12% N gives rise to films which are almost entirely amorphous.

II. The "amorphous" films of cellulose nitrate and acetate consist partly of truly amorphous material and partly of crystallites having no definite orientation. The greater is the degree of nitration of cotton, the more complete is the orientation of the crystallites. E. S. HEDGES.

Crystal structure of sputtered deposits. (MISS) Z. DĘBIŃSKA (Bull. Acad. Polonaise, 1930, A, 460—463).—Deposits several mμ thick show no crystal structure until heated beyond a critical temperature: platinum 250—300°, gold 150—200°.
A. B. D. CASSIE.

Nomenclature of space-groups. C. MAUGUIN (Z. Krist., 1931, 76, 542—558).—A complete system of nomenclature for space-groups is given based on that used by the author and that of Hermann (cf. A., 1930, 21). C. A. SILBERRAD.

Mauguin's nomenclature. C. HERMANN (Z. Krist., 1931, 76, 559—561; cf. preceding abstract).—A criticism. C. A. SILBERRAD.

Tabular synopsis of the distribution of crystal types of the elements arranged according to long periods. H. PERLITZ (Z. Krist., 1931, 76, 473—474).—The elements are arranged in long periods with graphs of types of crystal structure exhibited by each. Various relations between such structures and the position in the table are brought out.
C. A. SILBERRAD.

Structure of plastic sulphur. J. J. TRILLAT and J. FORESTIER (Compt. rend., 1931, 192, 559—561).—A thread of plastic sulphur, drawn out rapidly immediately after formation, can be extended to eight or ten times its initial length. Such a thread is flexible at first, but after a few days becomes brittle. X-Ray examination shows that the sulphur is not amorphous, but possesses a structure analogous to that of metal wire or cellulose thread with a 9·35 Å. The change of ordinary plastic sulphur to rhombic is greatly accelerated by exposure to X-rays.
C. A. SILBERRAD.

Structure of solid N_2O_4 at the temperature of liquid air. L. VEGARD (Z. Physik, 1931, 68, 184—203).—A new apparatus for determining the structure of a solidified gas is described. In the case of nitrogen peroxide the elementary cube contains twelve NO_2 molecules. Each of these is symmetrical, and they form three mutually perpendicular chains.
A. J. MEE.

Dimensions of the ClO_4 group in perchlorates. C. A. SCHUSTERIUS (Z. Krist., 1931, 76, 455).—The irregularity of the tetrahedra defined by the oxygen atoms in the ClO_4 group is confirmed by ionisation measurements on ammonium and potassium perchlorates (cf. Zachariasen, A., 1930, 1351).
C. A. SILBERRAD.

Cubic high-temperature structure of perchlorates. H. Braekken and L. Harang (Z. Krist., 1930, **75**, 538—549; Chem. Zentr., 1931, i, 214).—The temperature, lattice constant (Å.), and $d_{calc.}$ (assuming 4 mols. per unit cell) are, respectively: sodium perchlorate 314°, 7·08±0·02, 2·26; potassium perchlorate 310°, 7·50±0·02, 2·15; rubidium perchlorate 300°, 7·70±0·01, 2·66; cæsium perchlorate 230°, 7·98±0·02, 3·00; ammonium perchlorate 243°, 7·67±0·02, 1·71; silver perchlorate 160°, 7·00±0·01, 3·96; thallium perchlorate 280°, 7·70±0·01, 4·37. The lattice is face-centred; space-group T^2 or T_d.

A. A. Eldridge.

Structure of salts of the type $R'PF_6$. H. Seifert (Z. Krist., 1931, **76**, 455—456).—Potassium, ammonium, and cæsium hexafluorophosphates crystallise in the cubic system with face-centred lattice. The unit cells contain 4 mols., and have respectively *a* 7·76, 7·92, and 8·19 Å. The great similarity in chemical behaviour exhibited by hexafluorophosphoric and similar acids with perchloric acid indicates tetrahedra of fluorine around each phosphorus atom, with the remaining fluorine atoms elsewhere, and not a PF_6' complex.

C. A. Silberrad.

Symmetry of crystals of potassium dichromate. A. Schubnikow (Z. Krist., 1931, **76**, 469—472).—Photographs support the conclusion (cf. A., 1912, ii, 155) that potassium dichromate crystallises in the asymmetric class of the triclinic system (cf. Terpstra, etc., A., 1929, 18; this vol., 27).

C. A. Silberrad.

Crystal structure of some fluorides of the eighth group. F. Ebert (Z. anorg. Chem., 1931, **196**, 395—402; cf. A., 1929, 1254).—The crystal structure of iron, cobalt, rhodium, and palladium trifluorides is of trigonal rhombohedric symmetry, with 1 mol. in the unit cell; 3·56, 3·89, 5·64, and 5·15 Å., respectively, and distances between the anions and cations 2·05, 2·02, 1·98, and 2·06 Å., respectively. Palladium difluoride possesses a tetragonal structure, with 2 mols. in the unit cell; *a* 4·93, *c* 3·38 Å., $d_{calc.}$ 5·8, and distance between cations and anions 2·15 Å.

H. F. Gillbe.

Precision measurements of the lattice constant of cuprous oxide. M. C. Neuburger (Z. Physik, 1931, **67**, 845—850).—This constant redetermined by the powder crystal method is 4·252 ± 0·002 Å.

A. B. D. Cassie.

Crystal form of nickel oxides. O. G. Bennett, R. W. Cairns, and E. Ott (J. Amer. Chem. Soc., 1931, **53**, 1179—1180).—Nickelous oxide, subjected to temperatures not greater than 110°, compared with the oxide outgassed at 285°, is a better adsorbent of carbon dioxide at 56°. *X*-Ray data show that the low-temperature oxide is a new cubic modification of which the edge of unit cube is 4·64 Å., *d* is 4·8, and unit cell contains 4 mols. The crystal is not of the face-centred cubic type.

J. G. A. Griffiths.

Crystal structure of dihydrodecaborane, $B_{10}H_{14}$. H. Moller (Z. Krist., 1931, **76**, 500—516).—The substance has a unit cell with *a* 14·46, *b* 20·85, *c* 5·69 Å. containing $8B_{10}H_{14}$; space-group V_h^{21}, with rhombic lattice Γ_0'. The 8 mols. are arranged in four pairs. If the boron atoms are in a chain this must be much folded or bent, but a double-ring, naphthalene-like structure is equally probable.

C. A. Silberrad.

Space-group of arsenic tri-iodide. D. Heyworth (Z. Krist., 1930, **75**, 574; Chem. Zentr., 1931, i, 214). H. Braekken (Z. Krist., 1930, **75**, 574; Chem. Zentr., 1931, i, 214).

Crystal structure of the tri-iodides of arsenic, antimony, and bismuth. H. Braekken (Z. Krist., 1930, **74**, 67—72; Chem. Zentr., 1930, ii, 1033).—Bismuth iodide shows di-trigonal symmetry, but arsenic and antimony iodides are only trigonal. For arsenic tri-iodide, antimony tri-iodide, and bismuth tri-iodide the values for *a* and *c* are 7·187 and 21·39, 7·466 and 20·892, and 7·498 and 20·676 Å., respectively; 6 mols. per unit cell.

L. S. Theobald.

Gradual transition of crystalline sodium nitrate. F. C. Kracek and E. Posnjak (J. Amer. Chem. Soc., 1931, **53**, 1183—1184).—The properties change over a range of temperatures rather than suddenly at a definite transition point. The coefficient of expansion above 150° increases to a maximum at 275° and then decreases rapidly to a normal value beyond 280°; the absorption of heat during rise of temperature is maximal at 275·5°, and with fall of temperature evolution of heat commences at 278°. The crystals are uniaxial to the m. p.; small changes occur in *X*-ray patterns and in the solubility curve in the transition region.

J. G. A. Griffiths.

Crystal structure of cubic carborundum. H. Braekken (Z. Krist., 1930, **75**, 572—573; Chem. Zentr., 1931, i, 213—214).—The face-centred cube has *a* 4·348 ± 0·005 Å.

A. A. Eldridge.

Crystal structure of iron silicide, FeSi. F. Wever and H. Möller (Z. Krist., 1930, **75**, 362—365; Chem. Zentr., 1930, ii, 3505).—The substance has *a* 4·467 ± 0·001 Å., with 4 mols. in the unit cell; space-group T^4.

A. A. Eldridge.

Crystal structure of magnesium nitride. G. Hägg (Z. Krist., 1930, **74**, 95—99; Chem. Zentr., 1930, ii, 1033).—Powder photographs indicate a cubic structure with *a* 9·93 Å. The translation group is space-centred with 12 mols. in the unit cell. All 36 magnesium atoms cannot be equivalent.

L. S. Theobald.

Crystal structure of hambergite, $Be_2BO_3(OH)$. W. H. Zachariasen (Z. Krist., 1931, **76**, 289—302).—The unit cell contains 8 mols., and has *a* 9·73, *b* 121·8, *c* 4·42 Å.; space-group V_h^5. Each beryllium atom is at the centre of a nearly regular tetrahedron of three oxygens and one hydroxyl, average distances Be–O (or OH) 1·74 Å., O–O (or OH) 2·80 Å. Each boron is at the centre of a nearly equilateral triangle of oxygens, B–O (average) 1·35 Å., O–O 2·35 Å. The tetrahedra and triangles share corners only. Each oxygen is linked to two berylliums and one boron, each hydroxyl to two berylliums only.

C. A. Silberrad.

Crystal structure of koppite. E. Brandenberger (Z. Krist., 1931, **76**, 322—334).—Analysis of koppite gave: CaO 15·88, MnO 0·01, MgO 0·27,

Fe_2O_3 9·73, Ce_2O_3 8·15, La_2O_3 1·68, TiO_2 0·75, ZrO_2 0·61, Nb_2O_5 56·43, Ta_2O_5 0·15, Na_2O 2·89, K_2O 1·64 H_2O^- 1·09, H_2O^- 0·00, F_2 1·53; total 100·81%, less O for F 0·65; *d* 4·56. It crystallises in the cubic system; the unit cell contains 32 metallic and 56 anionic atoms, and has *a* 10·37 Å. C. A. SILBERRAD.

Crystal structure of eulytite. G. MENZER (Z. Krist., 1931, 76, 454).—Eulytite, $Bi_4(SiO)_3$, space-group T_d^6, has a body-centred lattice; the unit cell contains 4 mols., *a* 10·272 Å. The silicon is situated at the centres of tetrahedra of oxygen atoms, O–O 2·65 Å., each oxygen belonging to two tetrahedra. Each silicon is equidistant from 8 bismuths, Si–Bi 3·55 Å., Bi–Bi 3·80 Å.; each bismuth is equidistant from 6 silicons. C. A. SILBERRAD.

Formula of tourmaline. F. MACHATSKI (Z. Krist., 1931, 76, 475—476).—Niggli's formula for tourmaline (cf. *ibid.*, 1930, 75, 502) is criticised and $Mg_3Al_5[Si_6O_{27}B_3],CaMg(OH,F)_4$, or more generally $Y_8[Si_6O_{27}B_3],XY(OH,F)_4$, suggested.
C. A. SILBERRAD.

Molecular unit of pyrosmalite. B. GOSSNER and F. MUSSGNUG (Z. Krist., 1931, 76, 525—528).—The formula $(MnFe)Si_2O_5,3(MnFe)(OH,Cl)_2$ is deduced for pyrosmalite. It has a unit cell with *a* 13·44, *c* 7·20 Å., containing 4 such mols. Space-group D_{3d}^3, *a* : *c*—1 : 0·536. C. A. SILBERRAD.

Structure of hardystonite, $Ca_2ZnSi_2O_7$. B. E. WARREN and O. R. TRAUTZ (Z. Krist., 1930, 75, 525—528; Chem. Zentr., 1931, i, 248).—Hardystonite has *a* 7·83, *c* 4·99 Å.; space-group D_{2d}^3. The arrangement of the atoms is similar to that in melilite.
A. A. ELDRIDGE.

Structure of apatite, $(CaF)Ca_4(PO_4)_3$. S. NÁRAY-SZABÓ (Z. Krist., 1930, 75, 387—398; Chem. Zentr., 1931, i, 247).—Apatite has *a* 9·37 ±0·01, *c* 6·88±0·01 Å., space-group C_{6h}^2, with 2 mols. in the unit cell. A. A. ELDRIDGE.

Structure of apatite. I. M. MEHMEL (Z. Krist., 1930, 75, 323—331; Chem. Zentr., 1930, ii, 3530).—Jumilla apatite has *a* 9·36, *b* 6·85, *c* 6·85 (±0·02) Å., with 2 mols. of $CaFCa_4(PO_4)_3$ in the unit cell; space-group C_6^2. A. A. ELDRIDGE.

Structure of anthophyllite, $H_2Mg_7(SiO_3)_8$. B. E. WARREN and D. I. MODELL (Z. Krist., 1930, 75, 161—178; Chem. Zentr., 1930, ii, 3730—3731).—*X*-Ray investigation supports the formula $H_2Mg_7(SiO_3)_8$ instead of $MgSiO_3$. Anthophyllite has *a* 18·5, *b* 17·9, *c* 5·27 Å., with 4 mols. in the unit cell; space-group *V* . A. A. ELDRIDGE.

Structure of analcime, $NaAlSi_2O_6,H_2O$. W. H. TAYLOR (Z. Krist., 1930, 74, 1—19; Chem. Zentr., 1930, ii, 1054—1055).—No indications of a symmetry lower than pseudo-cubic have been obtained; space-group O_h^{10}. It is hence assumed that the basis of structure is a linking of oxygen tetrahedra; the atoms of silicon and aluminium, which are here assumed to be equivalent, are in the centre of the tetrahedron, the water mols. occupy the [$\frac{1}{8}$, $\frac{1}{8}$, $\frac{1}{8}$] positions, whilst the 16 sodium atoms are distributed over [0, $\frac{1}{8}$]. In agreement with optical properties, this arrangement permits a tetragonal symmetry for the unit cell.
L. S. THEOBALD.

Space lattice of natrolite. F. HALLA and E. MEHL (Z. Krist., 1930, 75, 421—429; Chem. Zentr., 1931, i, 438).—Natrolite has *a* 18·384±0·004, *b* 18·715±0·027, *c* 6·632±0·008 Å. The face-centred unit cell contains 8 mols. of $Na_2Al_2Si_3O_{10},2H_2O$; space-group V_h^{23} (holohedral), C_{2v}^{19} or V^7 (hemihedral).
A. A. ELDRIDGE.

Crystallographic relationships of crocoite, lautarite, and dietzite. B. GOSSNER and F. MUSSGNUG (Z. Krist., 1930, 75, 410—420; Chem. Zentr., 1931, i, 437—438).—Crocoite has *a* 6·28, *b* 7·48, *c* 7·16 Å.; β 102° 33′. The unit cell contains 4 mols. of $PbCrO_4$: $d_{calc.}$ 6·0, space-group C_{2h}^5. Lautarite has *a* 7·18, *b* 11·38, *c* 7·34 Å., β 106° 22′. The unit cell contains 4 mols. of CaI_2O_6; $d_{calc.}$ 4·59, space-group C_{2h}^5. Dietzite has *a* 10·16, *b* 7·30, *c* 14·03 Å., β 106° 32′; since it has *d* 3·617 the formula $7CaI_2O_6,CaCrO_4$ cannot be correct. The formula is $CaI_2O_6,CaCrO_4$ with a limited possibility of mutual replacement. A. A. ELDRIDGE.

Scattering of *X*-rays and the structure of vitreous solids. J. T. RANDALL, H. P. ROOKSBY, and B. S. COOPER (Z. Krist., 1930, 75, 196—214; Chem. Zentr., 1930, ii, 3506).—*X*-Ray investigation of quartz, wollastonite, borax, potassium and sodium felspars, a borosilicate glass, sodium silicate, boron trioxide, potassium borate, and dextrose indicates that glasses are composed of small crystallites (10^{-6} to 10^{-7} cm.). The connexion between crystal size and lattice dimensions is discussed. A. A. ELDRIDGE.

[Crystal] structure of carbamide. R. W. G. WYCKOFF (Z. Krist., 1930, 75, 529—537; Chem. Zentr., 1931, i, 214—215).—Carbamide has *a* 5·670, *c* 4·726 Å. (powder method). A. A. ELDRIDGE.

Crystal structure of guanidonium chloride. W. THEILACKER (Z. Krist., 1931, 76, 303—309).—Contrary to previous statements (cf. Delitsch, A., 1874, 576) guanidonium chloride is very hygroscopic and crystallises in the rhombic system, *a* : *b* : *c*= 0·842 : 1 : 1·416. The unit cell contains 8 mols., *a* 7·76, *b* 9·22, *c* 13·06 Å.; space-group V_h^{15}. The lattice is ionic $[C(NH_2)_3]^+Cl^-$, and the guanidonium ion exhibits no symmetry. C. A. SILBERRAD.

Crystal structure of *p*-nitrostilbene. E. HERTEL and G. H. ROEMER (Z. Krist., 1931, 76, 467—469).—*p*-Nitrostilbene, *d* 1·293, crystallises in the rhombic system. The unit cell contains 8 mols., *a* 7·94, *b* 28·3, *c* 10·22 Å. Space-group C_{2v}^5 or V_h^1. The length of 2 mols. is 28·3 Å. (for stilbene 24·84 Å.). C. A. SILBERRAD.

Translations in some artificial crystals. O. MÜGGE (Z. Krist., 1931, 76, 359—369).—Pinol glycol, $C_{10}H_{16}O(OH)_2$, monoclinic, *a* : *b* : *c*=0·8400 : 1 : 0·7692, β 89° 03′, 2*E*=40° 40′; pinocamphoroxime, $C_{10}H_{16}$:NOH, monoclinic, *a* : *b* : *c*—1·5042 : 1 : 1·2326, β 87° 54′; pinonic acid oxime, $C_{10}H_{16}O_2$:NOH, rhombic holohedral, *a* : *b* : *c*=0·900 : 1 : 1·063; *r*-propionylmenthylamine, monoclinic halohedral, *a* : *b* : 1·0492 : 1 : 0·5766, β 89° 24′. Other data on optical and cohesion properties, cleavage, translations, etc. are given for the foregoing and for hexagonal silver iodide, borneol, acet-2 : 4-dichloro-

anilide, *p*-xylylene dichloride, 2 : 4 : 6-tribromotoluene, *iso*benzil, *i*-sobrerol, and methylarsonic acid.
C. A. SILBERRAD.

Polymerisation in the crystal lattice. Crystal structure of trinitroresorcinol and trinitrophloroglucinol. E. HERTEL and K. SCHNEIDER (Z. physikal. Chem., 1931, **B**, **12**, 139—150).—The principal periods of identity of the crystals of 2 : 4 : 6-trinitro-resorcinol and -phoroglucinol are practically identical, and the space-groups are almost certainly the same, probably C_{3v}^{2}. In each case the lattice is built up of groups of molecules in threes, with the symmetry C_3. Nevertheless, the equilibrium diagram for the binary system shows the absence of complete miscibility in the solid state. R. CUTHILL.

Amino-acids. IV. G. TAKAHASI, T. TAGINUMA, and K. HAYAKAWA (Proc. Imp. Acad. Tokyo, 1931, **7**, 57—60).—Optical and crystallographic measurements have given the following results: *l*-leucine, $[\alpha]_D^{20}$ +15·51°, *d*-leucine, $[\alpha]_D^{20}$ −11·16°, rhombic, $a:b:c=1·5139:1:1·0025$, negative double refraction, n_α 1·5331, n_β 1·5361, n_γ 1·5514; *l*-norleucine, $[\alpha]_D^{26·5}$ −21·5°, *d*-norleucine, $[\alpha]^{26·5}$ +18·3°, rhombic, $a:b:c=1·3929:1:2·8662$, positive double refraction, n_α 1·5074, n_β 1·5104, n_γ 1·5400; histamine picrate, m. p. 232—233°, monoclinic, $a:b:c=1·2216:1:1·2266$, positive double refraction, n_α 1·6922, n_β 1·7135, n_γ 1·7535. E. S. HEDGES.

***d*- and *l*-Rhamnitol trihydrates.** R. NOVAČEK (Z. Krist., 1931, **76**, 569—571; cf. Valentin, this vol., 62).—*d*- and *l*-Rhamnitol trihydrates are rhombic bisphenoidal, $a:b:c=0·9947:1:1·1759$; 2 52° 30′, n_D^{a} 1·442, 1·492, γ—α 0 06. C. A. SILBERRAD.

Crystallography of some α-hydroxyiminosulphonates and α-hydroxyamides. J. THOREAU and J. VERHULST (Bull. Soc. chim. Belg., 1931, **40**, 18—34).—The crystallographic constants of a number of the compounds have been determined.
H. F. GILLBE.

Crystal structure of diphenylpolyenes. J. HENGSTENBERG and R. KUHN (Z. Krist., 1930, **75**, 301—310; Chem. Zentr., 1930, ii, 3505—3506).—CHPh:CH·CH:CHPh, *a* 7·71, *b* 11·70 Å., β 97°; number of mols. in unit cell (*z*) 4; space-group C_{2h}^{2}. Ph·[CH:CH·]$_3$Ph, *a* 6·33, *b* 7·43, *c* 14·43 Å.; *z* 2; C_{2h}^{5}. Ph·[CH:CH·]$_4$Ph, *a* 6·25, *b* 7·44, *c* 16·03 Å.; *z* 2; C_{2h}^{5}. The molecules of hexatriene and octatetraene are thus constructed very similarly. Ph·[CH:CH·]$_5$Ph, *a* 10·25, *b* 7·66, *c* 21·2 Å.; *z* 4; probably V_h^{15}. Ph·[CH:CH·]$_6$Ph, *a* 10·20, *b* 7·60, *c* 23·58 Å.; *z* 4. Ph·[CH:CH·]$_7$Ph, *a* 10·2, *b* 7·57, *c* 25·95 Å.; *z* 4. A. A. ELDRIDGE.

Crystalline form of a new modification of 2:4-dinitroanisole. M. H. WERTHER and J. A. BAAK (Z. Krist., 1930, **73**, 572; Chem. Zentr., 1930, ii, 1070—1071).—The monoclinic, prismatic crystals, m. p. 94·55°, of the modification described by Alphen (A., 1930, 337) have $a:b:c=0·6920:1:1·3158$, β 113° 14′, d^{15} 1·546. L. S. THEOBALD.

Crystal structure of pentaerythrityl tetraformate. M. A. BREDIG (Z. Krist., 1930, **74**, 49—55; Chem. Zentr., 1930, ii, 1034).—The compound crystallises differently from the tetra-acetate and nitrate; it has *a* 19·80, *b* 9·90, and *c* 11·70 Å.; space-group V_h^{18}. The crystal structure shows racemate bimolecules of $C_9H_{12}O_8$ as micro-units in agreement with Weiszenberg's hypothesis. L. S. THEOBALD.

Crystal structure of *n*-amylammonium chloride. S. B. HENDRICKS (Z. Krist., 1930, **74**, 29—40; Chem. Zentr., 1930, ii, 1033).—The carbon atoms in the hydrocarbon chain are arranged rectilinearly.
L. S. THEOBALD.

Röntgen data of monoalkylammonium iodides. R. W. G. WYCKOFF (Z. Krist., 1930, **74**, 25—28; Chem. Zentr., 1930, ii, 1033—1034; cf. preceding abstract).—Photographs of crystals of members with C_4 to C_{12} give for the tetragonal unit cell the constant value *a* 5·18 Å. The height of the cell is about 2·10 Å. larger for each carbon atom. The determination of atomic positions is not yet possible, since the arrangement of adjacent carbon atoms about a vertical axis is not in agreement with that of other compounds. L. S. THEOBALD.

***X*-Ray diagram of collagen (fibre-period).** R. O. HERZOG and W. JANCKE (Z. physikal. Chem., 1931, **B**, **12**, 228—229; cf. A., 1927, 69).—The reasons for believing in the existence of a period of identity of about 20 Å. along the fibre-axis of collagen are detailed (cf. Herrmann, Gerngross, and Abitz, this vol., 27). R. CUTHILL.

Theory of the magnetisation curve of sugar crystals. N. S. AKULOV (Z. Physik, 1931, **67**, 794—807).—Mainly theoretical. The measurements of the magnetisation curves for the symmetrical axes of single iron crystals are in formal agreement with those of Honda, Masumoto, and Kaya (A., 1928, 823).
J. FARQUHARSON.

Ferromagnetism. N. TUNAZIMA (Z. Physik, 1931, **67**, 817—825).—Theoretical. The connexion of the theories of Weiss and Heisenberg and of Ewing, Honda, and Okubo is demonstrated. The formula of Steinhaus and Gumlich is derived as a special case.
J. FARQUHARSON.

Diamagnetism, field strength, and crystal structure. W. J. DE HAAS (Nature, 1931, **127**, 335—336).—The diamagnetic susceptibility of pure crystals of bismuth has been measured as a function of field strength at 14° and 20° Abs.
L. S. THEOBALD.

Charge distribution and diamagnetic susceptibility of atoms and ions. G. W. BRINDLEY (Phil. Mag., 1931, [vii], **11**, 786—792).—Slater's method of calculating charge distributions (cf. A., 1930, 1234) leads to susceptibility values in closer agreement with experiment than those calculated by Pauling (cf. A., 1927, 394). N. M. BLIGH.

Magnetic properties of thin, electrolytically deposited cobalt films. E. P. T. TYNDALL and W. W. WERTZBAUGHER (Proc. Iowa Acad. Sci., 1929, **36**, 297).—In general the films behave like iron films, but the specific properties depend largely on the acidity of the electrolyte. CHEMICAL ABSTRACTS.

Strain and diamagnetic susceptibility. H. E. BANTA (Physical Rev., 1931, [iii], **37**, 634—637).—The magnetic susceptibility of copper and silver, measured by the Gouy method, was found to be increased up to 20% and 3%, respectively, by anneal-

ing at red heat for 15 min. in carbon dioxide; the increase is probably due to release of occluded gases or to oxidation or recombination of impurities. The effect reported by Bitter (cf. A., 1930, 1505) due to straining beyond the elastic limit was not found.

N. M. Bligh.

Alteration in the electrical resistance of purest electrolytic iron in transverse magnetic fields. O. Stierstadt (Z. Physik, 1931, **67**, 725—742).—The change in resistance of electrolyte iron is considerably less than that of other samples of iron containing impurity. J. Farquharson.

Dependence of the resistance of ferromagnetic metals on temperature. G. Borelius (Ann. Physik, 1931, [v], **8**, 261—266).—It is shown that the electrical resistance of ferromagnetic metals can be regarded as the sum of a resistance which is dependent on temperature in the normal way, and a resistance the magnitude of which depends on the demagnetisation. W. Good.

Change of resistance in magnetic fields. H. Bethe (Nature, 1931, **127**, 336—337).—Theoretical.

L. S. Theobald.

Change of resistance in a magnetic field of single crystals of bismuth. R. A. Nelson and G. R. Watson (Proc. Iowa Acad. Sci., 1929, **36**, 304).

Chemical Abstracts.

Resistance of bismuth in alternating magnetic fields. W. W. Macalpine (Physical Rev., 1931, [ii], **37**, 624—633).—The production with a 50-watt tube of a field of 100 gauss at 10^6 cycles, and a potentiometer method of measuring the behaviour in it of a bismuth wire at liquid air temperature are described. The resistance of the bismuth was found to follow the instantaneous values of the field.

N. M. Bligh.

Strength of wetted salt crystals. A. Smekal (Physikal. Z., 1931, **32**, 187—192).—Experiments are described which show that by dissolving away the surface of loaded salt crystals it is impossible in the statical sense to realise ideal lattice tenacity.

W. Good.

Crystallographic investigation of some mechanical properties of metals. III. Damping of lateral vibration of aluminium crystal plates. IV. Internal slip of metals. Y. Kidani (J. Fac. Eng. Tokyo, 1931, **19**, 107—113, 115—129; cf. A., 1930, 1101).—The logarithmic decrement of lateral vibration of aluminium crystals depends on the crystallographic orientation.

IV. Mechanical properties of metals are discussed from the point of view that as the individual grains are variously oriented, they will slip by different amounts under the influence of an external load.

C. W. Gibby.

Nature of solidity. M. Pólanyi (Metallwirt., 1930, **9**, 553—558; Chem. Zentr., 1930, ii, 1031).—Starting from the different distribution of atoms in liquids and solids, the different plastic behaviour of amorphous and crystalline substances is discussed.

L. S. Theobald.

Peculiarity of sylvite. X. Johnsen (Z. Krist., 1931, **76**, 456—457).—When sodium chlorate crystallises on a cleavage face of sylvite a preponderance of lævorotatory crystals is obtained, supporting the view that sylvite displays enantiomorphous hemihedry (*O*). C. A. Silberrad.

Physico-chemical studies of organo-metallic compounds. H. Gilman, L. L. Heck, and J. A. Leermakers (Proc. Iowa Acad. Sci., 1929, **36**, 270).—A study of mol. wt., conductivity, absorption spectra, and reaction towards oxygen, nitrous oxide, and hydrogen (in presence of platinum).

Chemical Abstracts.

Peltier effect in single crystals of bismuth. H. E. Fagan (Proc. Iowa Acad. Sci., 1929, **36**, 300—301). Chemical Abstracts.

Thermo-electric properties of Monel metal. E. Meschter (Science, 1931, **73**, 132—133).—The curves dE/dt against t show maxima at 100° and 87° for two rods of Monel metal. L. S. Theobald.

Electrical resistance of titanium, zirconium, and their mixed crystals. J. H. de Boer and P. Clausing (Physica, 1930, **10**, 267—269; Chem. Zentr., 1931, i, 28).—The specific resistance of titanium at 0° is about 0·475; the temperature coefficient is approx. 0·00425. A. A. Eldridge.

Extension of Ramsay and Young's b.-p. rule. T. S. Wheeler (Phil. Mag., 1931, [vii], **11**, 441—449).—For any system in equilibrium there is a linear relation between the reciprocals of the temperatures (Abs.) at which two given powers of a variable or pair of variables are in a constant ratio corresponding with the equation $\log(\text{variable})=a+b/T$, where T is the temperature and a and b are constants. It is found empirically that the following rule, of which Dühring's rule is a special case, holds fairly accurately over temperature ranges of about 100°: the temperatures (Abs.) for which the vapour pressures of a liquid or of a pair of liquids are in a constant ratio satisfy a linear equation. R. Cuthill.

Heat capacities at low temperatures of manganese sulphide, ferrous sulphide, and calcium sulphide. C. T. Anderson (J. Amer. Chem. Soc., 1931, **53**, 476—483).—The heat capacities have been determined between 58° and 297° Abs. The heat capacity curve of manganese sulphide exhibits a double cusped maximum between 135° and 150° Abs. Extrapolation of the heat capacity curves to 0° Abs. is effected by means of Debye and Einstein functions and the entropy, S_{298}, of manganese, ferrous, and calcium sulphides is computed to be 18·7, 16·1, and 13·5 entropy units, respectively. These values, in conjunction with existing data, yield the corresponding free energies, Δ —64,000, —23,600, and —109,800 g.-cal., respectively.

J. G. A. Griffiths.

Additive calculation of molecular heats of gases. M. Trautz (Ann. Physik, 1931, [v], **8**, 267—285)—It is shown how for a compound of which the mol. wt., approximate critical temperature, and approximate constitution are known, C_v may be calculated empirically. W. Good.

M.-p. curves of monobasic fatty acids. A. M. King and W. E. Garner (J.C.S., 1931, 578—580).—Theoretical. The minimum in the m.-p. curves of the monobasic fatty acids can be accounted for on the

basis of the probability of attachment of the molecule to the crystal surface. This factor also enters into the relationship between heat of crystallisation and temperature. The entropy change on crystallisation can be represented by the relationship $Q/T-0{\cdot}002698n-0{\cdot}0061+0{\cdot}00475\ \Sigma_{3}^{n}\log_{10}[n/(n-2)]$.

A. J. MEE.

Entropy, elastic strain, and the second law of thermodynamics: the principles of least work and of maximum probability. W. S. KIMBALL (J. Physical Chem., 1931, **35**, 611—623).—Theoretical. A new mechanical aspect of entropy is presented.

L. S. THEOBALD.

Specific heat of electricity in ferromagnetics. E. C. STONER (Proc. Leeds Phil. Soc., 1931, **2**, 149—158; cf. A., 1930, 1101).—In calculating the specific heat of electricity from thermoelectric data for metals it is not in general possible to obtain agreement with the experimental data if the free electrons alone are considered; it is necessary to treat a metal as an equilibrium distribution of neutral atoms, positive ions, and free electrons. The assumption that in a ferromagnetic metal the carriers are ions or atoms with fewer electrons than are required for a completed configuration leads to the relationship $f\Delta\sigma_e=-\Delta S_a$, where $\Delta\sigma_e$ is the change in the specific heat of electricity per electron at the Curie point, ΔS_a the change in the atomic heat, and f the number of electrons missing per atom. This equation is in agreement with existing experimental data.

R. CUTHILL.

Physical properties of compressed gases. I. Nitrogen. W. E. DEMING and (MISS) L. E. SHUPE (Physical Rev., 1931, [ii], **37**, 638—654).—Theoretical. A graphical process is applied to the compressibility data obtained by Bartlett and others (cf. A., 1930, 678, 679) and from the accurate $p-v-T$ data obtained values of the specific volume, density, fugacity, C_p, C_v, C_p-C_v, μ, and the coefficients $(-p/v)(dv/dp)_T$ and $(T/v)(dv/dT)_p$ are calculated, tabulated, and illustrated graphically for 14 pressures and 12 temperatures in the ranges 20—1200 atm., and $-70°$ to 600°.

N. M. BLIGH.

Physical constants of silicon tetrafluoride and tungsten and molybdenum hexafluorides. O. RUFF and E. ASCHER (Z. anorg. Chem., 1931, **196**, 413—420).—The m. p., b. p., heat of sublimation in kg.-cal., latent heat of evaporation in kg.-cal., Trouton constant, $d_{\text{m.p.}}$, and mol. vol. at m. p. of tungsten hexafluoride are 2·3° (420 mm.), 17·5°, 8·72, 6·25, 21·5, 3·515, and 84·9, respectively, and of molybdenum hexafluoride 17·5° (406·5 mm.), 35°, 8·30, 6·36, 20·6, 2·551, 82·4. Silicon tetrafluoride has b. p. $-95{\cdot}0°$, and heat of sublimation 6·19 kg.-cal. Equations for the sublimation pressure and vapour-pressure curves of silicon tetrachloride, tungsten hexafluoride, and molybdenum hexafluoride are given. (See also Patnode and Papish, A., 1930, 1104.)

H. F. GILLBE.

Heat of formation of nitrogen trifluoride. O. RUFF and H. WALLAUER (Z. anorg. Chem., 1931, **196**, 421—428).—The heat of formation of nitrogen trifluoride, determined from the reaction with hydrogen at 6 atm., is 26±2 kg.-cal.

H. F. GILLBE.

Optical determination of the heat of dissociation of salt vapours. A. TERENIN (Physica, 1929, **9**, 283—286; Chem. Zentr., 1931, i, 238).—Polemical. G. H. VISSER (*ibid.*).—A reply.

A. A. ELDRIDGE.

Absolute temperature scale. D. D. JACOBUS (Abs. Theses Mass. Inst. Tech., 1931, **7**, 54—56).—An apparatus is described for the direct comparison of the platinum resistance and gas scales of temperature between 0° and 500° with an error of 0·001%, and for the determination of the thermodynamic temperature of the m. p. of ice by measurements with helium and hydrogen. The helium data yield $273{\cdot}15_8°$ Abs., and the hydrogen data $273{\cdot}19_7°$ Abs., and the true value is regarded as $273{\cdot}16°\pm0{\cdot}02°$ Abs.

H. F. GILLBE.

Determination of heat of vaporisation of aliphatic alcohols using an adiabatic microcalorimeter. E. BARTOSZEWICZÓWNA (Rocz. Chem., 1931, **11**, 90—94).—The recorded heats of vaporisation at 20° are: methyl 287·0, ethyl 224·3, propyl 180·1, *iso*propyl 175·8, butyl 149·5, and *iso*butyl alcohol 147·2 g.-cal.

R. TRUSZKOWSKI.

Calculation of the volume correction in van der Waals' equation. G. L. CHABORSKI (Bul. Chim. pura appl., Bukarest, 1929, **31**, 119—132; Chem. Zentr., 1930, ii, 1047).—The value of b for any temperature may be calculated from d_t and V_0. Values of $b_{\text{b.p.}}$ are computed for 92 substances. To a first approximation b is a linear function of temperature.

A. A. ELDRIDGE.

Velocity of sound in carbon dioxide. H. O. KUESER (Physikal. Z., 1931, **32**, 179).—The velocity of sound in gaseous carbon dioxide increases with increasing frequency between 0·5 and 3×10^5 sec.$^{-1}$, thereafter attaining the constant value 268·2±0·3 metres per sec. Assuming the increase in velocity is due to a change in γ, a value for the latter equal to 1·40 is obtained.

W. GOOD.

Calculations of velocity of sound in nitrogen tetroxide. F. VERHOEK and F. DANIELS (J. Amer. Chem. Soc., 1931, **53**, 1186—1187).—Unpublished data for the dissociation of nitrogen tetroxide afford values for the velocity of sound, calculated by means of Einstein's equation, 1·5—3·0 metre sec.$^{-1}$ less than those observed by Kistiakowsky and Richards (this vol., 314), suggesting a constant error in theory or experiment. The heat of dissociation of the oxide is 13,960 g.-cal. per mol. at constant volume.

J. G. A. GRIFFITHS.

Classical thermodynamics and the chemical constant. A. AKOPIAN (Z. Physik, 1931, **67**, 851—859).—From classical thermodynamics, general expressions are derived for the constant $J^a{}_i=J_i$ in the formula for $\log p^a{}_i$ and for the constant J found in the formula for $\log K_p$, and the relationship between J, n_i, and $J^a{}_i$ is deduced. This does not lead to the Nernst relation $J=\Sigma n_iJ_i$, but the latter follows on introduction of the Nernst heat theorem.

J. W. SMITH.

Vapour-pressure diagram. G. CALINGAERT (Chim. et Ind., 1931, **25**, 307—308).—If the logarithm of the vapour pressure of a liquid is plotted against a modification of $1/T$ a straight line is obtained. The lines for similarly constituted organic liquids, *e.g.*, alkyl bromides, converge to a point.

D. K. MOORE.

Equation of state of propellant gases. A. D. CROW and W. E. GRIMSHAW (Phil. Trans., 1931, **A**, **230**, 39—73).—A method has been developed for measuring the pressure of the gases resulting from the explosion of a propellant, and an expression has been established for the energy losses due to cooling of the gases by the walls of the explosion vessel. From the experimental results the equation of state of the gaseous mixture is found to be $p_0=84{\cdot}80\{(\Sigma\text{ g.-mols.})/\text{g.}\}T_0/(1/\Delta-\eta)$, where Δ is the density and η the co-volume; η may be evaluated from the hard-kernel values of the mol. radii, increased by 2·5%, of the constituent gases, according to the equation $\eta=1{\cdot}092\times10^{25}\times\Sigma[(0{\cdot}5\sigma_x)^3\,.\,g]$, where $0{\cdot}5\sigma_\infty$ is the hard-kernel molecular radius and g the number of g.-mol. per g. for each component gas. Under the conditions of the experiment Δ is of the order of 0·25—0 025, and the pressure and temperature attain values of 3800 kg. per cm.^{2} and 4000° Abs., respectively. The mean mol. heats of carbon dioxide, hydrogen, water, and carbon monoxide plus nitrogen at temperatures between 2000° and 4000° have been calculated from the equation $\bar{c}_v=6+(7/15)(T/1000)+(16/45)(T/1000)^2+\ldots$, where c_v is the mean mol. heat between 0 and T° Abs.; this equation is more satisfactory than that of Bjerrum at temperatures above 3000° Abs. The equilibrium constant of the reaction $CO-H_2O \rightleftharpoons CO_2+H_2$ has been calculated at temperatures between 1000° and 4200° Abs. by various formulæ.

H. F. GILLBE.

Molecular heats and critical data. M. TRAUTZ (Ann. Physik, 1931, **8**, [v], 433—455; cf. this vol., 417).—By examination of the variation of $(C_v-3R/2)-M^{-3}$ with temperature simple whole-number relationships connecting the values of C_v for different gases are found. The values of M^a/T_c^2 are also found to bear simple ratios to each other, a being a simple whole number or a fraction composed of small integers.

W. GOOD.

Pressure–volume–temperature values for ammonia to 1000 atm. from 30° to 200°. F. G. KEYES (J. Amer. Chem. Soc., 1931, **53**, 965—967).—Data are tabulated. J. G. A. GRIFFITHS.

Constants of the Beattie–Bridgeman equation of state with Bartlett's *P–V–T* data on hydrogen. W. E. DEMING and (MISS) L. E. SHUPE (J. Amer. Chem. Soc., 1931, **53**, 843—849; cf. A., 1930, 679; Bartlett and others, *ibid.*, 678; A., 1928, 698).—Pressures as high as 1000 atm., within the range −70° to 300°, are reproduced with a maximum root mean square deviation of 0·4% at densities less than 0·024 mol. per c.c., and with a maximum deviation of 2·1% at $d=0{\cdot}027$ and −70°, by inserting the values $R=82{\cdot}0489$, $a=56{\cdot}18$, $A_0=124{,}040$, $c=20\times10^6$ (units: atm., c.c., g.-mol.) in the Beattie–Bridgeman equation of state (A., 1927, 819): below the critical density, 0·0154, $b=-7{\cdot}22$ and $B_0-20{\cdot}22$, whilst above the critical density, $b-\,-19{\cdot}68$ and $B_0-17{\cdot}50$. The calculated pressures become markedly too low at very high densities. Evidence for the predominance of repulsive forces between the molecules at $d>0\ 018$ is adduced. J. G. A. GRIFFITHS.

Equations for vapour pressure and latent heat, including approximate equations for solid compounds containing a gaseous component. L. J. GILLESPIE (Proc. Amer. Acad. Arts Sci., 1930, **66**, 153—165).—Mathematical. Methods for applying the equations to experimental data are described.

CHEMICAL ABSTRACTS.

Anomalous velocity distribution in thin layers of lubricant. H. UMSTATTER (Kolloid-Z., 1931, **54**, 220—226).—A mathematical discussion of the validity of the Hagen–Poiseuille law and relations between viscosity, mol. wt., temperature, and the form of the molecules. E. S. HEDGES.

Characteristic equation for mixtures of ethylene and argon. P. GLANSDORFF (Bull. Acad. roy. Belg., 1931, [v], **17**, 203—216).—The equation $V=N_1V_1+N_2V_2+N_1N_2\phi_{12}$, where V_1 and V_2 are the molecular volumes of the constituents and ϕ_{12} is a function of temperature and pressure only, is suggested as a characteristic equation for binary mixtures. It is applied to mixtures of ethylene and argon.

A. J. MEE.

Beattie–Bridgeman equation of state and Bartlett's *P–V–T* data for a 3 : 1 hydrogen–nitrogen mixture. W. E. DEMING and (MISS) L. E. SHUPE (J. Amer. Chem. Soc., 1931, **53**, 860—869: cf. Bartlett and others, A., 1930, 678; 1928, 698).—Between −70° and 300°, pressures are reproduced with deviations of less than 0·3% at densities less than 0·0245 mol. per c.c., whilst at $d=0{\cdot}027$ the calculated pressure is 2·5% too low at −70°. At high densities, repulsive forces between the molecules predominate. Constants for the mixture derived by combination of the constants of the constituents afford calculated pressures with a root mean square error of less than 1·17% at densities smaller than 0·007. J. G. A. GRIFFITHS.

Influence of low temperatures on the thermal diffusion effect. T. L. IBBS and K. E. GREW (Proc. Physical Soc., 1931, **43**, 142—156).—Measurements of thermal diffusion at temperatures between 15° and −190° have been made on mixtures of neon with helium, hydrogen, and argon and of helium with argon and nitrogen. The ratio k_t of the coefficient of thermal diffusion to the coefficient of ordinary diffusion generally decreases at low temperatures. For helium–neon and hydrogen–neon mixtures with low liquefying points, the change in k_t between 15° and −190° is small. The bearing on theory is discussed. W. E. DOWNEY.

Refractivity of a binary mixture and its relation to the molecular size of the components. T. ISHIKAWA (Chikashige Anniv. Vol., 1930, 275—294).—Formulæ relating the refractive index to the composition are critically reviewed and a theoretical equation is derived. The refractive indices of binary mixtures of alcohols and of alcohols with benzene have been determined, and by application of the equation consistent values for the molecular diameters σ of the alcohols are obtained. When applied to known optical data the equation yields for non-polar substances values of σ which are concordant with the values derived from viscosity measurements and from the relation between van der Waals' b and the volume of the molecule; for polar molecules the agreement is less satisfactory. Contrary to the

Lorentz–Lorenz formula, the new equation indicates that the molecular dimensions of *n*-propyl and butyl alcohols are greater than those of the *iso*-compounds, and that the dimensions of a single molecule in a liquid, whether associated or not, are the same as in the gaseous state and may be calculated from optical data for a mixture of the liquid with another, chemically indifferent, liquid of known molecular diameter. H. F. GILLBE.

Molar refraction of methyl alcohol. I. Influence of the concentration in a non-polar solvent. II. Influence of temperature on solutions in a non-polar solvent. M. VELASCO (Anal. Fis. Quim., 1931, **29**, 15—20, 171—176).—I. The molecular refractivity of solutions of methyl alcohol in benzene is a linear function of z, where z is the molar fraction of the alcohol. The concentration is therefore without influence on the polarisation of the polar component, and the linking involved in the association of the dipoles of the alcohol does not influence the forces acting on the peripheral electrons.

II. The influence of temperature on the molar refraction of benzene solutions of methyl alcohol has been investigated. The refractive indices of the components and of the solutions are given by $n=a+bT$, where a and b are 1·5142 and −0·00068 for benzene and 1·3386 and −0·00043 for methyl alcohol. The molar refraction of the solutions increases slightly with rise of temperature, and the increase is greatest in the more concentrated solutions. The effect is due to an increase of electronic polarisation of the alcohol, caused probably by an increase in the number of the molecules for which the velocity is sufficiently large to disturb the peripheral electrons of other molecules with which they collide. H. F. GILLBE.

Electrochemical examination of the system aluminium chloride–sodium chloride. V. A. PLOTNIKOV and P. T. KALITA (J. Russ. Phys. Chem. Soc., 1930, **62**, 2195—2202).—Maximal conductivity of fused mixtures containing 19·2—49 mol.-% NaCl is found at the eutectic, whilst for solid mixtures the conductivity rises with sodium chloride content. The conductivity of solidified melts is increased 200-fold by the addition of 1·7% of sodium sulphate. Aluminium is deposited on the cathode and the current is conveyed chiefly by sodium ions.

R. TRUSZKOWSKI.

Physical properties of the ternary system phenol–benzene–water. S. H. WEIDMAN and L. E. SWEARINGEN (J. Physical Chem., 1931, **35**, 836—843).—The densities, viscosities, surface tensions, and refractive indices have been measured at 25° for homogeneous mixtures over a wide range.

L. S. THEOBALD.

Influence of temperature on the dielectric constants of some glasses in the softening interval. G. TAMMANN and W. BOEHME (Z. anorg. Chem., 1931, **197**, 1—17).—The dielectric constants of salicin, brucine, selenium, phenolphthalein, and colophony increase linearly with rise of temperature until the sp. vol. and refractive index curves exhibit breaks; this temperature corresponds with that at which the brittleness characteristic of the vitreous state appears. At higher temperatures the increase of the dielectric constant is linear, but is more rapid since the fraction of the dielectric constant due to molecular polarisation is zero for a material in the vitreous form, but becomes evident when the material passes into the condition of a highly viscous liquid. The magnitude of the change of the principal physical properties as the glass passes through the softening interval is proportional to the appropriate temperature coefficient for the vitreous condition. Neither the Maxwell nor the Clausius–Mosotti relation applies to salicin and brucine. The temperature–log conductivity curves for selenium, salicin, and phenolphthalein are linear, but a break occurs at the temperature at which threads may be drawn from the glass. The dielectric constants of some boron, lead, and barium glasses have been measured up to 700°; the increase with rise of temperature is at first small and linear, but at 200—300° the dielectric constant commences to increase rapidly and more than doubles by 600°. The form of the various curves bears no simple relation to the composition of the glass, but the asymptotic temperature approximates closely to the cohesion temperature in several cases; when plotted logarithmically, breaks occur in the neighbourhood of the temperature at which brittleness appears. H. F. GILLBE.

Segregation in continuous series of mixed crystals. G. TAMMANN and A. RUPPELT (Z. anorg. Chem., 1931, **197**, 65—89).—The mean temperature of segregation in mixed crystals of potassium and sodium bromides and potassium and sodium iodides has been determined by observation of the temperatures at which opalescence appears and disappears. Moisture accelerates the process of segregation. In mixed crystals of lithium and sodium bromides segregation occurs between 20 and 60 mol.-% of sodium bromide, the maximum effect being at 200°. The temperatures obtained for the system potassium chloride–sodium chloride lie rather below those derived from the cooling curves. Measurements have been made also with mixed crystals of potassium chloride and iodide, bromide and iodide, and chloride and bromide; segregation does not appear to take place in the last-named system. Microscopical investigation of sodium nitrate–potassium nitrate melts indicates that a continuous series of mixed crystals is formed, since no eutectic is visible and the crystallites increase in size on heating to 200°. On cooling, the large crystallites break down into numerous small crystals, as a result of segregation; this process is reversible, and is catalysed by water at the ordinary temperature, although not at 100°. The system sodium metaphosphate–potassium metaphosphate has been examined; the salts have only limited mutual solubility, and segregation of the mixed crystals has been observed with mixtures containing 90 mol.-% of the potassium salt, at about 370°. The opalescence shown by mixed crystals is discussed; at high temperatures it may result from the aggregation of molecules of the same kind, whereas at low temperatures, when caused by the action of water, it is due to the appearance of a new, finely-dispersed phase. The formation and breakdown of mixed crystals has been correlated with the differences

Δa of the lattice parameters of the component salts; for values of Δa less than 0·115 Å. continuous series of mixed crystals are formed; for Δa 0·135—0·144 Å. a break occurs in the series, and at higher values the miscibility in the solid state is very limited. Segregation occurs only when Δa exceeds about 0·05 Å.

H. F. GILLBE.

The δ and β transformations of brasses. D. IITSUKA (Chikashige Anniv. Vol., 1930, 305—309).—Observations on zinc–copper alloys containing 45—60% Cu confirm the view that double transformations take place in the β and γ+β alloys, and also, contrary to the report of Ruer and Kremers (A., 1930, 161), in the α alloys. H. F. GILLBE.

Solid solutions of the copper–silver system. D. STOCKDALE (Inst. Metals, Mar., 1931, Advance copy, 14 pp.).—The mutual solubilities of copper and silver have been determined by means of microscopic examination of quenched specimens and at low temperatures by measurement of the electrical resistance of quenched wires. For the latter purpose a differential method, which shows up small abrupt changes in the resistance of alloys, is described. The copper-rich solidus near the triple point is lowered very suddenly by the addition of a few tenths of 1% Ag. The solubility of silver in copper at the eutectic temperature is 8·2% by weight, 4·7% at 700°, 0·7% at 400°, and at the ordinary temperature silver is almost insoluble in copper. The silver-rich solidus is nearly a straight line joining the m. p. of silver with the point 8·8% Cu and 778·5°. The solubility of copper in silver at the eutectic is 8·8%, 5·8% at 700°, 1·1% at 400°, and about 1% at the ordinary temperature. "Standard silver" containing 7·5% Cu is a uniform solid solution only between 750° and 810°.

O. J. WALKER.

X-Ray study of the copper end of the copper–silver system. R. W. DRIER (Ind. Eng. Chem., 1931, 23, 404—405).—X-Ray spectrographic examination of samples of copper containing 0·003—1·0% Ag shows that at the ordinary temperature silver is not soluble in copper. There is evidence, however, that copper is soluble in silver. E. S. HEDGES.

Constitution of the cadmium-rich alloys of the system cadmium–silver. P. J. DURRANT (Inst. Metals, Mar., 1931, Advance copy, 15 pp.).—The constitution of the alloys containing from 0 to 40 wt.-% Ag has been reinvestigated by thermal and micrographic methods. The liquidus consists of four smooth curves intersecting with three peritectic horizontals at 343°, 592°, and 640°. The following solid solutions exist: I 0—6%, II 18—33·5%, and III 36·2—39% Ag. In phase II, which includes the solid solutions ε and δ described by Petrenko and Federov (A., 1911, ii, 281, 800), the solidus and liquidus are roughly parallel and do not intersect, as was previously thought, at 25 at.-% Ag. No transformations below the solidus have been detected in any of the solid solutions, but III has not been examined below 400°.

O. J. WALKER.

The silver-rich aluminium–silver alloys above 600°. T. P. HOAR and R. K. ROWNTREE (Inst. Metals, Mar., 1931, Advance copy, 6 pp.).—Using aluminium of high purity the system aluminium–silver has been investigated above 600° up to 15 wt.-% Al, and Petrenko's diagram (A., 1905, ii, 635) has been modified. The α/β and β/γ peritectics are found to be at 779° and 729°, respectively, instead of at 770° and 723°, and the α/α+β and α+β/β boundaries slope towards the axis with rise of temperature and are not vertical. The β-phase possibly consists of Ag_4Al and not Ag_3Al. The resemblance between this system and the aluminium–copper system is pointed out. O. J. WALKER.

Eutectic point in the system silicon–aluminium. H. KOTO (Chikashige Anniv. Vol., 1930, 303—304).—The eutectic corresponds with 11·7% Si and 578°. H. F. GILLBE.

Electrical conductivity of alloys at low temperatures. J. C. MCLENNAN, J. F. ALLEN, and J. O. WILHELM (Trans. Roy. Soc. Canada, 1930, [iii], 24, III, 25—32).—The resistances of lead–bismuth, lead–antimony, and bismuth–thallium alloys have been measured down to temperatures of about 4·2° Abs. Bismuth tends to increase the superconductivity transition temperature, whilst the presence of antimony in some cases causes a lowering and in others a raising of the superconducting point. The lead–bismuth alloy shows a superconducting point 1·6° higher than any previously obtained. W. GOOD.

Superconductivity of alloys. J. C. MCLENNAN, J. F. ALLEN, and J. O. WILHELM (Trans. Roy. Soc. Canada, 1930, [iii], 24, III, 53—64; cf. preceding abstract).—Alloys of members of the bismuth group with lead, tin, thallium, and gold show, with the exception of lead–antimony, a pronounced elevation of the superconducting point, whilst silver–thallium alone shows a transition temperature higher than that of the pure conductor alone. W. GOOD.

Ternary silver alloys. III. System Ag–Cu–Al. IV. Mechanical properties of some ternary silver alloys. S. UENO (Chikashige Anniv. Vol., 1930, 57—75, 77—83).—III. The system has been studied by thermal analysis and photomicrography. The α solid solution of the system Ag–Al dissolves copper to form a ternary solid solution, and the β solid solution, composed of $AlAg_3$ and $AlAg_2$, dissolves copper and $CuAl_2$. The temperature of the Cu–Ag eutectic is first raised from 776° to 796° and then lowered to 525° as a result of the incidence of a reaction involving the production of $CuAl_2$. The complex reactions in copper-rich Al–Cu systems disappear on addition of 5% Ag, a series of homogeneous solid solutions being formed. The temperature of the $CuAl_2$+ε eutectic in the Al–Cu system is lowered from 545° to 502° on addition of silver, and that of the $AlAg_2$+ε eutectic from 565° to 502° on addition of copper, on account of the occurrence of an invariant reaction at the latter temperature.

IV. The Brinell hardness, malleability, and corrosion-resistance of the ternary alloys Ag–Cu–Zn, Ag–Al–Zn, and Ag–Cu–Al have been investigated. The maximum hardness of the 10% Zn alloys in the Ag–Al–Zn system occurs at 10% Al, *i.e.*, in the ternary β alloy, and of the 20% Zn alloys at 3% Al (α—β). The hardness of the 30% Zn alloys in the Ag–Cu–Zn system increases to a maximum on increase

of the silver content up to 50%, whilst in presence of 10% Zn the maximum is at 30% Ag, *i.e.*, in the binary silver–copper eutectic. Two maxima occur in the 5% Al alloys in the system Ag–Cu–Al, viz., at 10% and 70% Ag. The corrosion-resistance towards hydrochloric acid of Ag–Cu–Zn alloys containing 30% Zn diminishes on addition of silver to a minimum at the composition corresponding with the binary silver–copper eutectic; increase of the silver content greatly reduces the rate of corrosion of the alloys by 0·5*N*-ammonia solution. Increase of the aluminium content beyond 10% very greatly increases the rate of corrosion of Ag–Al–Zn alloys by acid or ammoniacal solutions. The malleability of Ag–Cu–Zn alloys containing 10% Zn is a minimum at 20—30% Ag, whilst that of Ag–Al–Zn alloys containing 20% Zn falls rapidly as the aluminium content increases up to 3%.

H. F. GILLBE.

Metallographic investigation of the iron–silicon–carbon alloys. I. Transformations of silicon steels. T. SATÔ (Tech. Rep. Tôhoku, 1931, 9, 53—103).—The equilibria in the system iron–carbon–silicon have been determined by micrographical examination and by magnetic and dilatometric analysis and the results are shown by sectional diagrams for alloys containing 0·5—8% Si and 0—0·8% C. With increasing silicon content the magnitude of the A1 and A3 transformations decreases and the temperature of the magnetic change point decreases almost linearly, reaching 660° with 8% Si; the carbon content has no influence on the magnetic transformation. The austenite field in the stable system, iron–silicon–graphite, extends to about 7% Si, but in the metastable system iron–silicon–Fe_3C it extends to more than 8% Si. The solubility of carbon in the α and δ phases increases at temperatures above the A1 point with increasing silicon content and the separation of carbide from these solid solutions on cooling becomes more difficult to suppress so that, even on quenching, carbide readily separates along the crystal boundaries. The peritecto-eutectic reaction, δ + liquid $\rightleftharpoons \gamma$ + graphite, in the stable system takes place at 1195° in the alloy with 0·37% C and 6·5% Si.

A. R. POWELL.

Metallographic investigation of the ternary alloys of the iron–tungsten–carbon system. I. Carbides in tungsten steels. II. Transformation and constitution of tungsten steels. S. TAKEDA (Tech. Rep. Tôhoku, 1931, 9, 21—52, 165—202).—I. The system tungsten–carbon–iron contains three carbide phases, namely, WC, a ternary solid solution (η) with a composition approximating to Fe_xW_3C, and a solid solution (θ) of tungsten and iron in Fe_3C. The θ-phase is ferromagnetic and the other two are non-magnetic. The η-phase is coloured by etching with an alkaline solution of potassium ferrocyanide and is unstable in alloys with a high carbon content, decomposing into iron and WC when the alloy is cooled slowly or annealed. The compound WC is a hard grey constituent formed in high-carbon steels by decomposition of the η-phase or by reaction between liquid and austenite. The magnetic changes in alloys containing θ usually take place in two steps at temperatures between 0° and 400°, depending on the composition and previous heat treatment of the alloy; an excess of tungsten lowers the critical point below 200° and an excess of iron raises it towards 400°.

II. The constitution of steels with up to 15% W and 1·5% C has been determined by dilatometric, magnetic, and microscopic analyses; the system contains a metastable equilibrium between iron, θ, and η, and a stable equilibrium between iron, carbon, and WC. Immediately after solidification the alloys consist entirely of metastable phases, but after annealing the metastable state persists only in steels with a low carbon content. The field of existence of the γ-phase decreases with increasing tungsten content and finally disappears with 12% W; addition of carbon enlarges the γ-field up to 0·33% C, then diminishes it again. The $(\gamma+\delta)$ field disappears with 0·33% and reaches its maximum at 0·2% C; with increasing tungsten content it gradually becomes smaller and finally ceases to exist in the alloy with 14·5% W; the homogeneous δ-field exists only in alloys with less than 0·2% C. At 735° the peritecto-eutectoid reaction $\gamma+\eta \rightleftharpoons \alpha+\theta$ takes place; the univariant point of this reaction corresponds with the composition 1% W, 0·9% C, 98·1% Fe. The binary eutectoid temperature for the reaction $\gamma \rightleftharpoons \alpha+\eta$ rises with increasing tungsten content to 1335°, at which point the peritecto-eutectic reaction, liquid $+\delta \rightleftharpoons \gamma+\eta$, occurs; similarly, the temperature of the binary eutectoid reaction $\gamma \rightleftharpoons \theta+\eta$ rises to 1085°, at which point a ternary eutectic reaction, melt $\rightleftharpoons \gamma+\theta+\eta$, takes place. In low-carbon alloys a binary eutectoid reaction $\alpha \rightleftharpoons \eta+\varepsilon$ (Fe_3W_2) occurs.

A. R. POWELL.

Solubility of calcium carbonate in water containing an alkali chloride. R. DUBRISAY and R. FRANÇOIS (Compt. rend., 1931, 192, 741—743).—That the reaction $CaCO_3+2KCl \rightleftharpoons K_2CO_3+CaCl_2$ is responsible for the fixation of potassium in agricultural soils is made probable by the fact that solutions which are saturated with calcium carbonate show increasing alkalinity and increasing content of calcium with increasing concentration of potassium chloride.

C. A. SILBERRAD.

Solubility of nitrogen in water at high pressures and temperatures. J. B. GOODMAN and N. W. KRASE (Ind. Eng. Chem., 1931, 23, 401—404).—A method for determining the solubility of gases in liquids at ordinary and higher temperatures and at pressures from 100 to 1000 atm. is described. The solubility of nitrogen in water has been measured between 0° and 170° and at pressures of 100, 125, 200, and 300 atm. and curves are given showing the deviations from Henry's law. The departures are attributed to the solvent rather than to a peculiarity of nitrogen. These results and the existence of a minimum solubility at constant pressure are discussed in relation to solvent density, viscosity, internal pressure, surface tension, association, compressibility, and thermal expansion, but no definite conclusion is reached.

E. S. HEDGES.

Solubility of U.S.P. chemicals. W. SCHNELLBACH and J. ROSIN (J. Amer. Pharm. Assoc., 1931, 20, 227—233).—The following solubilities (g. in 100 g. of solvent) at 25° are recorded: (*a*) in water: sodium dihydrogen phosphate (anhydrous), 48·69 g.; methylene-

blue, 2·3 g.; emetine hydrochloride, 16·53 g.; (*b*) in ethyl alcohol: ferric chloride, 51·45 g.; methylene-blue, 1·47 g.; sodium diethylbarbiturate, 0·313 g.; sulphonal, 13·9 g.; vanillin, 48·42 g.; (*c*) in glycerol: potassium chlorate, 1·055 g.; potassium citrate, 28·20 g. H. E. F. NOTTON.

Solubilities of salts in ethylene glycol and its mixtures with water. H. M. TRIMBLE (Ind. Eng. Chem., 1931, **23**, 165—167).—Metallic salts in general are less soluble in ethylene glycol than in water, but the sequence of the salts is the same. Halides with a marked tendency to form hydrates are very soluble, and hydrated salts are more soluble than the corresponding anhydrous salts. The effect of temperature is not marked except in the case of magnesium ammonium chloride, but unstable solutions are temporarily formed in the boiling solvent, from which the salt is soon precipitated in an amorphous form. The ternary systems formed by glycol and water in combination with potassium iodide, bromide, chloride, and sulphate, sodium chloride, and copper sulphate pentahydrate have been examined at 30°. H. A. PIGGOTT.

Theory of solubility. P. A. BOND (Proc. Iowa Acad. Sci., 1929, **36**, 262—263).—The theory postulates two forces, (*a*) tending to arrange substances in the lattice forms of the solid state, and (*b*), thermal, tending to break up such forms. CHEMICAL ABSTRACTS.

Langmuir's adsorption isotherm. R. S. BRADLEY (Phil. Mag., 1931, [vii], **11**, 690—696).—Mathematical. The temperature variation of the constants in Langmuir's equation is derived theoretically for the adsorption of gases on charcoal, and the results are found to be in accord with those of Zeise (cf. A., 1928, 1182). N. M. BLIGH.

Adsorption of di-substituted benzene derivatives. B. TAMAMUSHI (Bull. Chem. Soc. Japan, 1931, **6**, 74—79).—The adsorption by charcoal of *o*-, *m*-, and *p*-nitrophenols, -nitroanilines, and -dinitrobenzenes in benzene solution has been measured. The nitrophenols and nitroanilines are adsorbed in the order $p>m>o$, which is the inverse order of their solubilities in benzene. Similarly, *m*-dinitrobenzene is less adsorbed and more soluble than the *o*- and *p*-compounds, but *o*-dinitrobenzene is both more soluble and more adsorbed than *p*-dinitrobenzene. It is suggested that the dipole moment, which is much greater for *o*- than for *p*-dinitrobenzene, may affect the adsorption through electrostatic forces. The order of the m. p. and of the molecular association appears to support this view. A. A. LEVI.

Discontinuous nature of the process of sorption of gases and vapours by porous solids. A. J. ALLMAND and L. J. BURRAGE (Proc. Roy. Soc., 1931, **A**, **130**, 610—632).—Adsorption isothermals for carbon dioxide, carbon tetrachloride, benzene, water, and amyl alcohol have been determined at 25° by a static method (Allmand and Puttick, this vol., 160), using four different de-gassed charcoals, the pressure range being 0·13—19·2 mm. Measurements were also made with silica gel and benzene, water, and carbon tetrachloride, respectively. All these isothermals afford evidence of discontinuity, in some cases very marked and in others barely exceeding the limits of experimental error. These and previous results are discussed. The authors' views agree largely with those of Goldmann and Polanyi (A., 1928, 579) and of Semenov (A., 1930, 851). L. L. BIRCUMSHAW.

Heat of adsorption of certain organic vapours by charcoal at 25° and 50°. J. N. PEARCE and G. H. REED (J. Physical Chem., 1931, **35**, 905—914).—The heats of adsorption of methyl and methylene chlorides, chloroform, and carbon tetrachloride by a steam-activated, acid-washed coconut charcoal of 0·28% ash content have been determined at 25° and 50° by the method previously described (A., 1928, 481). The heats of adsorption can be represented by the equation $h{-}aX^b$, where a and b are specific constants, and X is the number of c.c. adsorbed per g. of charcoal. The mol. heat of adsorption increases with the number of chlorine atoms in the molecule. The temperature coefficient is very small. L. S. THEOBALD.

Adsorption of gases by glass walls. VIII. Hydrogen chloride. M. CRESPI and E. MOLES (Anal. Fís. Quím., 1931, **29**, 146—157).—With hydrogen chloride, as with other gases, there is a slow absorption and a rapid adsorption which occur simultaneously. The former predominates, and the result of the whole process accords with the Freundlich equation. The results of previous workers are reviewed and Scheuer's values (A., 1909, ii, 991) shown to involve a considerable error. H. F. GILLBE.

Desorption of gases from molecularly plane glass surfaces. J. R. CURRY (J. Physical Chem., 1931, **35**, 859—873).—The desorption of air, carbon monoxide and dioxide, hydrogen, ammonia, ethylene, and toluene from molecularly plane surfaces at −78° and 25° has been determined. Except in the case of carbon dioxide, desorption is complete at fairly low temperatures (150—250°). Contact with water vapour causes a change in the surface of the glass and subsequent adsorption of toluene and hydrogen is increased and desorption is retarded, but the glass surface tends to become molecularly plane after repeated desorption experiments. Water vapour itself is strongly adsorbed and is expelled continuously as the temperature is raised. The surface of a fresh, unwashed tube of soft glass is rendered molecularly plane by continued heating at a temperature slightly below the m. p. L. S. THEOBALD.

Direct measurement of the adsorption of soluble substances by the bubble method. D. M. GANS and W. D. HARKINS (J. Physical Chem., 1931 **35**, 722—739).—The adsorption of *p*-toluidine and of *iso*amyl alcohol in the air–solution interface has been directly measured by the bubble method. The results agree with those of McBain and Davies (A., 1927, 1022) in that adsorption increases with concentration until it reaches a constant value greater than that which corresponds with a unimolecular film. In general, however, the adsorption now measured is less than that obtained by McBain and Davies (*loc. cit.*). The adsorption appears to decrease as the adsorbing bubbles decrease in size and may approach the value for each solute which is given by

the usual adsorption equation and by experiments with insoluble films. L. S. THEOBALD.

Adsorption of ions and sols by freshly-prepared precipitates and its influence on the formation of Liesegang rings. II. A. C. CHATTERJI and S. C. VARMA (Z. anorg. Chem., 1931, **196**, 247—256).—During the formation of lead chromate by the interaction of lead acetate and potassium chromate no chromate ions are adsorbed by the precipitate, but a part of the lead chromate goes into the aqueous phase as a result of the peptising action of the chromate ions. Freshly-precipitated and washed lead chromate does not adsorb more than 5% of chromate ions, and the amount adsorbed decreases with increase in the concentration of the potassium chromate. The freshly-prepared precipitate adsorbs a considerably greater amount of lead chromate sol. The adsorption of a sol of lead chromate stabilised by gelatin decreases as the concentration of gelatin increases and at sufficiently high concentrations of gelatin the adsorption is reduced to zero. This fact is believed to explain the difficulty of obtaining periodic structures of lead chromate in concentrated gelatin gels. The cause of the spaces between the bands of precipitate is traced to adsorption of the peptised sol by each band of precipitate and not to adsorption of the reacting electrolyte as assumed by Bradford. E. S. HEDGES.

Adsorption compounds. E. NEGRI (Arch. Farm. sperim., 1931, **51**, 193—215).—The precipitation of tricalcium phosphate in an aqueous cod-liver oil emulsion by successive addition of phosphoric acid, calcium chloride, and ammonia results in the formation of a stable compound which liberates fat when treated with hydrochloric acid. The proportion of fat thus adsorbed gradually increases if the quantity of fat is kept constant while the adsorbing surface is increased. If, however, this surface remains unchanged while the amount of oil is increased, the adsorbed fat increases in absolute amount but diminishes relatively to the total amount of oil present. These results are considered to indicate the formation of adsorption compounds. T. H. POPE.

Heats of wetting and of adsorption on zinc oxide. W. W. EWING (Ind. Eng. Chem., 1931, **23**, 427—429).—The heats of adsorption of gaseous carbon dioxide, sulphur dioxide, ammonia, water, benzene, xylene, and pyridine, and the heats of wetting of liquid water, benzene, xylene, pyridine, "nujol," linseed oil, and solutions of zinc oleate in benzene and in pyridine by zinc oxide have been measured. The effect of particle size of the pigment has also been studied, using water vapour as the adsorbed vapour. The heats of wetting or of adsorption vary with the nature of the liquid or gas, and the tenacity with which the adsorbed material is held, as measured by the speed of outgassing, also varies with the nature of the gas, but there seems to be no direct relation between the two. Carbon dioxide and pyridine have about the same heats of adsorption, but the former is readily released and the latter is not. The heat of adsorption of water is greater than its heat of wetting, perhaps indicating that the heat of adsorption is made up of the heat of wetting and the heat of condensation. The heat of adsorption is directly proportional to the surface of the adsorbent and is independent of the size of the particles. E. S. HEDGES.

Surface tensions of aqueous solutions of *p*-toluidine. R. C. BROWN (Phil. Mag., 1931, [vii], **11**, 686—690).—Values obtained by different methods are in fair agreement with those of Gans and Harkins (cf. A., 1930, 991). N. M. BLIGH.

Thermodynamic study of surface tension, affinity, and rate of adsorption. IX. Change of variables. R. DEFAY (Bull. Acad. roy. Belg., 1931, [v], **16**, 1425—1441).—Mathematical (cf. A., 1930, 686). C. W. GIBBY.

Thermodynamic study of surface tension, affinity, and rate of adsorption. X. R. DEFAY (Bull. Acad. roy. Belg., 1931, **17**, 73—89; cf. A., 1930, 1109).—Mathematical. Equations similar to that of Duhem and Margules are derived for processes of adsorption. J. R. I. HEPBURN.

Thermodynamic study of surface tension, affinity, and rate of adsorption. XI. R. DEFAY (Bull. Acad. roy. Belg., 1931, [v], **17**, 217—234).—Theoretical. A. J. MEE.

Molecular theory of surface energy: the surface energy of the liquefied inert gases. R. S. BRADLEY (Phil. Mag., 1931, [vii], **11**, 846—849).—Mathematical. The calculated surface energy for argon and helium is in satisfactory agreement with observed values. N. M. BLIGH.

Problems of the boundary state. (SIR) W. HARDY (Phil. Trans., 1931, **A**, **230**, 1—37).—Films are considered as a fourth state of matter characterised by the sharing of the energy with the adjacent phases. The most promising view of the boundary state in liquids is that it is due to the formation of chains of highly-polarised molecules stretching through the lubricant from one enclosing solid to the other. Each chain has little strength in shear, great strength in tension, and in both the strength decreases as the chain lengthens. The intensity of polarisation at any level in a chain is the sum of two terms of the same sign contributed independently by the fields of attraction at the ends. The influence of each field diminishes as the distance from the solid face increases, and the least value of the sum of the two terms is at a mean value surface or surfaces. In the only instance in which the position is known with certainty the mean value surfaces for slip and for break coincide, but this is after the joint has been frozen. The Leslie pressure is considered as the osmotic pressure of the lubricant. If the molecular chains help to support the loading by their resistance in compression, in which case the expression for the Leslie pressure would include two terms, one representing the rigidity of the structure, the other representing the defect in mobility, the Leslie pressure becomes strictly analogous to the swelling pressure of a gel. Difficulties in the acceptance of a Leslie pressure in air and the presence of a complete air-gap are discussed. The total strength of all the chains of molecules in tension increases as the length of the molecules of which they are built increases, whilst the total strength of all the chains in shear decreases and, when allowance is made for perturbation due to

the end groups of atoms, the relation in both instances is always linear. When the length of the molecules is great enough strength in shear vanishes. The strength in tension must be due to the lateral fields of attraction of the molecules, at least as much as to the fields at the ends. The decrease in the strength in shear may be due merely to the increase in the moment of the applied force. E. S. Hedges.

Optical investigation of thin metallic films, especially of silver. W. Reinders and L. Hamburger (Rec. trav. chim., 1931, **50**, 351—376).—The light absorption and ultramicroscopic structure of thin silver films formed in a vacuum have been investigated. Their structure depends on their thickness, the temperature of their formation, and on the nature of the under-surface. Silver films formed in a high vacuum at the ordinary temperature and of average thickness of less than two atoms are invisible in the ultramicroscope, but slightly thicker films show a mosaic pattern of ultramicrons. The invisible films of subatomic thickness were developed in various ways, but no method of carrying out this process gave a trustworthy record of the structure of the primary deposit. Using a solution of a silver salt as developer films as thin as 10^{-10} to 10^{-11} cm. or 0·001 atom average thickness could be developed, but development with metal vapours required considerably thicker films. The developed structure of these thin primary films shows no linked mosaic form, but only individual nuclei. This indicates that only a few of the larger aggregates formed are capable of development. Aggregates of three atoms can be developed, but single atoms or two-atom aggregates cannot. The particle size of these thin sublimates shows a frequency distribution according to a probability law. The mean nuclear size decreases with decreasing mobility of the atoms in the under-surface. J. W. Smith.

Anomalous flow of a strong solution of lithium chloride through narrow glass tubes. G. W. S. Blair and R. K. Schofield (Phil. Mag., 1931, [vii], **11**, 890—896).—Flow-pressure curves for nearly saturated solutions of lithium chloride were obtained and compared with those for glycerol–water mixtures of the same viscosity. The Poiseuille law is not obeyed. The curves are linear, but give a small intercept on the pressure axis, indicating that small strains are not dissipated immediately during flow, probably due to the tendency of the ions to maintain a non-random distribution. Using tubes of different radius and length, it was found that the simple r^4 law (where r is the radius) is not exactly obeyed, indicating anomalous flow close to the wall of the tube. N. M. Bligh.

Equilibria in osmotic systems in which forces act. II. Osmotic systems in which there is an active membrane permeable for more than one substance. F. A. H. Schreinemakers (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 1133—1139; cf. this vol., 163).—The previous theoretical treatment is extended to the case of an active membrane permeable for more than one substance. O. J. Walker.

Highly-polymerised compounds. L. Molecular complexity of compounds of high mol. wt. H. Staudinger (Z. physikal. Chem., 1931, **153**, 391—424; cf. this vol., 465).—A summary of previous work on the determination of the mol. wts. of highly-polymerised compounds. Viscosity data, in particular, show that in dilute solutions of such compounds the dispersed particles are not micelles but single molecules of very high mol. wt., and there is good reason for believing that these large molecules persist in the solid state. It is considered that X-ray analysis in itself is of little value for the determination of molecular complexity. R. Cuthill.

Temperature of maximum density of aqueous solutions. Deviations from the law of Despretz. N. Gregg-Wilson and R. Wright (J. Physical Chem., 1931, **35**, 624—628).—The lowering of the temperature of maximum density of amine solutions shows that the law of Despretz does not hold for the more concentrated solutions. The relative densities at 5° and the coefficients of expansion between 12·5° and 15° are tabulated. L. S. Theobald.

Fictive volumes of sodium sulphate in aqueous solutions of sulphuric acid and of iodine in an aqueous solution of potassium iodide. R. E. Gibson (J. Physical Chem., 1931, **35**, 690—699; cf. A., 1927, 508).—The specific volumes of solutions of sodium sulphate in approximately 5% and in 10% sulphuric acid at 25° are used to calculate the fictive volume of sodium sulphate in these solutions. The curves connecting this with concentration show peculiarities which are correlated with the formation of sodium hydrogen sulphate in solution. The specific volumes of iodine in a 49% solution of potassium iodide at 25° show that the fictive volume of the iodine for solutions containing 10—50% I is 0·2396 c.c. per g. A large amount of interaction between iodine and potassium iodide is thus precluded. L. S. Theobald.

Volume of electrolyte solutions. O. Redlich (Naturwiss., 1931, **19**, 251).—From the Debye–Huckel theory it is deduced that the partial molar volume of an electrolyte in dilute solution is a linear function of the square root of the concentration. This relation agrees with the experimental data and is of value for the determination of the partial molar volume at infinite dilution. R. Cuthill.

Viscosity of electrolytes. H. Falkenhagen (Nature, 1931, **127**, 439–440).—A discussion. L. S. Theobald.

Dielectric constants of solutions of electrolytes. R. Furth (Physikal. Z., 1931, **32**, 184—187).—The dielectric constant decreases rapidly with increasing concentation, passes through a minimum, and then increases continuously. The significance of this general observation is discussed. W. Good.

Colloids prepared by molecular stream condensation methods. I. Organosols of alkali metals. A. J. Rabinovitsch, V. A. Kargin, and E. B. Fodiman (Kolloid-Z., 1931, **54**, 288—295).—An improvement on the method of Roginsky and Schalnikov (A., 1927, 1137) for preparing organosols of the alkali metals by the simultaneous condensation of the vapours of the metal and the organic liquid is described and a method developed for measuring the

electrical conductivity and cataphoretic migration velocity of these sols in a vacuum. All the organosols obtained were negatively charged. Sols of sodium in ethyl ether and ethylamine, and sols of potassium in ethyl ether, ethylamine, and propylamine prepared by this means are fairly stable; they coagulate slowly in the dark and rapidly in the light. Attempts to prepare pure potassium sols in benzene, toluene, and tripropylamine were unsuccessful, the solvent undergoing decomposition. The sols may be purified by a second condensation and they are then more stable and have a higher cataphoretic migration velocity. After repeated purification sols of sodium and potassium in ethyl ether and sols of potassium in propylamine and ethylamine precipitate to form the compact metal. The electrical evidence leads to the view that the surface of the particles is the seat of ionogenic groups, the alkali metal cation being directed towards the dispersion medium. Both potassium and sodium sols in ethylamine contain the metal partly in a molecularly dispersed form. The molecular solutions are left when the colloidally dispersed particles coagulate.

E. S. HEDGES.

Colloidal synthesis of readily crystallisable organic substances. N. VON WEIMARN (Kolloid-Z., 1931, **54**, 296—306).—Colloidal solutions of naphthalene, papaverine, camphor, salol, and benzophenone are not stable for more than a few seconds at the ordinary temperature, but may be kept stable indefinitely at $-80°$ in the form of a glass, the dispersion medium being 68% sucrose solution. A very stable sol of anthracene may be prepared by pouring a 0·025% alcoholic solution of anthracene into a large volume of water, with vigorous stirring. Phenanthrene sols can be prepared similarly, but are less stable in virtue of the greater solubility; they are fairly stable at 0° when the dispersion medium contains sucrose. Anthraquinone sols prepared in this way are more stable. Anthracene and phenanthrene sols are described as unidimensional colloids, the crystalline particles being of microscopic size in two directions and of colloidal thickness. Anthraquinone forms a two-dimensional colloid, the length of the particles exceeding colloidal size. E. S. HEDGES.

[Relations of] gum arabic to colloidal silver and gold. J. VOIGT (Kolloid-Z., 1931, **54**, 307–310).—Pure gum arabic has no reducing action on silver oxide or chloroauric acid solutions either with or without the aid of ultra-violet radiation. The rotective effect of gum arabic, however, is reduced y irradiation with ultra-violet light and simultaneously the viscosity of the sol decreases. Arabic acid has a different absorption spectrum after the irradiation. The use of gum arabic sols as a vehicle for the injection of colloidal silver is discussed.

E. S. HEDGES.

Physico-chemical properties of gum arabic–water systems and their interpretation. R. TAFT and L. E. MALM (J. Physical Chem., 1931, 35, 874—892).—The viscosities, densities, f. p., p_H values, and conductivities of gum arabic–water systems have been determined. In agreement with Thomas and Murray (A., 1928, 706), most of the properties are best explained by the assumption that purified gum arabic is a strong organic electrolyte of high equivalent weight and not a distinct colloidal phase.

L. S. THEOBALD.

Diffusion of colloid particles. I. Abnormally high diffusion velocities in hydrophilic sols. II. New ion effect in hydrophilic sols. H. R. BRUINS (Kolloid-Z., 1931, **54**, 265—272, 272—278.—I. An apparatus previously described (this vol., 302) has been used to determine the diffusion velocities of the particles of two kinds of soluble starch and of gum arabic. In each case exceptionally high values were obtained and the diffusion constants were higher the more readily soluble were the colloids and the more stable the sols. From the diffusion constants the values 1·9 and 1·4 mμ were calculated for the radii of the particles of two different soluble starch sols, and 0·85 mμ for gum arabic particles. The values are thus not far removed from those obtained for true molecular solutions and are scarcely consistent with viscosimetric and dialysis data. The anomalies cannot be explained by the presence of an equilibrium portion of the colloid in the molecular state of solution, nor by the presence of electrolytes.

II. The diffusion constants of sols of soluble starch and of gum arabic are lowered very considerably by adding small quantities of electrolytes. The effect is relatively greatest at low concentrations (1 milliequiv. per litre), and further additions produce little more change. The magnitude of the decrease in diffusion velocity increases with the valency of the ion with an opposite charge to that of the colloid; on the other hand, the effect produced by the ion of similar charge to the colloid decreases with increasing valency of the ion and is in general less marked.

E. S. HEDGES.

Dispersoidological study of silver salts in aqueous alcohol, acetone, and diethyl ketone solutions. I. S. ISHII (Bull. Chem. Soc. Japan, 1931, **6**, 53—60).—The solubility of highly purified silver iodide in solutions of potassium iodide in aqueous ethyl alcohol and aqueous acetone of varying composition has been measured and the results are expressed graphically. The decrease in solubility when acetone is diluted with water corresponds with the increase of dielectric constant of the mixture.

E. S. HEDGES.

Polyatomic hydroxy-compounds in the synthesis of electronegative sols. VII. Formation of ferric hydroxide sols in the presence of polymeric carbohydrates. A. DUMANSKI and V. S. PUTSCHKOVSKI (J. Russ. Phys. Chem. Soc., 1930, **62**, 2249—2259).—The systems ferric chloride–sodium hydroxide or ammonia–polysaccharide are represented graphically, using triangular co-ordinates. The diagrams obtained with inulin and dextrin are the most similar to those previously obtained for monoses. The peptising action of the various carbohydrates studied increases in the order: inulin > dextrin > soluble starch > gum arabic. The protective action of gum arabic is, however, greater than that of starch. The peptising action diminishes after a certain point with increasing alkalinity, and is greater at the same alkalinity using sodium hydroxide than ammonia. The peptising action of polysaccharides is on the whole feebler than that of monoses. R. TRUSZKOWSKI.

Specific inductive capacity and mol. wt. of colloids. N. MARINESCO (Compt. rend., 1931, **192**, 625—628).—The mol. wt. of a colloid can be determined from the equation $M=\lambda RT/3c\eta v$, where λ is the wave-length of anomalous dispersion of the dissolved colloid, R the gas constant, T the absolute temperature, c the velocity of light, η the viscosity, and v the specific volume of the colloid in solution. Calculated in this way the mol. wt. of gelatin is 11,300.

C. A. SILBERRAD.

Dielectric constant of protein solutions. I. Zein. J. WYMAN, jun. (J. Biol. Chem., 1931, **90**, 443—476).—Two methods, based on resonance, are described for measuring the dielectric constant of solutions of zein in 70% *n*-propyl alcohol. Anomalous dispersion is present, and the zein molecule is highly polar; a value of 60×10^{-18} e.s.u. is deduced for the permanent electric moment. Gelation of zein solutions on keeping is not accompanied by a change in dielectric constant.

A. COHEN.

Graphical method for calculation of partial specific volumes of proteins. T. KATSURAI (Suppl. Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, **15**, 7—8).—In the determination of the mol. wt. of proteins by the ultracentrifugal method the partial specific volume of the protein is calculated from pyknometric measurements. A graphic method which enables the specific volume to be read directly from the density of the solution is described.

E. S. HEDGES.

Dielectric constant and structure of thixotropic sols. S. S. KISTLER (J. Physical Chem., 1931, **35**, 815—829).—The degree of hydration derived from the dielectric constants increases with the oscillation frequency. With a wave-length of 32·7 cm. dialysed sols of aluminium and ferric oxides show little hydration until an electrolyte is added. The first small addition of electrolyte produces the largest depression of the dielectric constant, which is very near to that of water. No change of the dielectric constant of the thixotropic sols before and after gelation could be detected. The viscosity of the intermicellar solution is practically the same in the gel and in the sol before gelation. Thixotropy is best explained by the assumption that some form of oriented anisotropy of the water, probably chains of water molecules, extends from the surface of each colloidal particle and tends to link it with those surrounding it.

L. S. THEOBALD.

Colloidal ferric oxide and various factors which influence its ability to catalyse the decomposition of hydrogen peroxide. R. J. KEFFER and J. H. WALTON (J. Physical Chem., 1931, **35**, 557—577).—The decomposition of aqueous solutions of hydrogen peroxide by colloidal ferric oxide, prepared by the method of Sorum (A., 1928, 703), has been investigated in the dark at 30—60°. The reaction is approximately unimolecular, but the values of k increase as the reaction progresses. Between 30° and 60°, k_{t+10}/k_t is approximately 2·33, indicating that the decomposition is a true chemical reaction independent of a process of diffusion. Doubling the concentration of catalyst between the limits 0·286 and 2·281 g. per litre increases the rate of decomposition 2·2 times. The effect of additions of sodium or barium chloride, potassium sulphate, sodium dihydrogen phosphate, disodium hydrogen phosphate, hydrochloric acid, sodium hydroxide, and copper sulphate has also been determined. For the first three electrolytes, the curves show (i) a marked decrease in catalytic activity followed by a gradual decrease, both of which are due to adsorption of chloride ions by the sol, (ii) a second marked decrease due to coagulation of the sol, and (iii) a region of little change corresponding with further adsorption of electrolyte by the coagulated sol. For the other electrolytes modified curves are obtained and these are explained by changes in the stability of the solutions of hydrogen peroxide. A mechanism involving the formation of ferric acid or a higher oxide of iron as an intermediate compound is suggested.

L. S. THEOBALD.

Liquid ammonia as a lyophilic dispersion medium. II. Ammono-gels of cellulose acetate. R. TAFT and J. E. STARECK (J. Physical Chem., 1931, **35**, 578—587; cf. this vol., 164).—Cellulose acetate is readily dispersible in liquid ammonia, and sols containing 60 g. or more of the acetate in 100 c.c. of the medium have been obtained. Two types of gels, one heat-reversible and the other heat-irreversible, have been obtained; the former results when a sol of 10 g. of acetate in 100 c.c. of liquid ammonia is kept in a bath of boiling ammonia for several days, and the latter when a sol is allowed to warm to the ordinary temperature. The setting points of the reversible gels are lower than their m. p. The time required for gelation of the irreversible gels depends on concentration, temperature, and water content of the dispersion medium. The effect of water on dispersion in liquid ammonia has also been determined. Small quantities of cellulose acetate can be dispersed in the presence of large amounts of water, and as little as 0·05 g. of acetate in 100 c.c. of liquid ammonia may give rise to a gel. The gels form more rapidly and are firmer in structure at an optimum concentration of water, but in the absence of water precipitation takes place.

L. S. THEOBALD.

Determination of the hydrogen-ion concentration in gold sols. T. R. BOLAM and J. CROWE (J. Physical Chem., 1931, **35**, 602—610).—The conditions affecting the determination of hydrogen-ion concentration in gold sols by means of the hydrogen electrode have been investigated. This electrode gives satisfactory results with Nordenson sols or with sols prepared by Zsigmondy's method and buffered with alkaline phosphate, or with Zsigmondy's sols in which potassium carbonate is replaced by sodium citrate. In the unbuffered Zsigmondy sols the displaced *E.M.F.* is attributed to the removal of carbon dioxide by the hydrogen used. Curves showing the change in p_H of the gold sol with increasing concentration of sodium (as hydroxide, phosphate, or citrate) are given. The unsatisfactory behaviour of the electrode reported by previous investigators is discussed.

L. S. THEOBALD.

Optimum conditions for the formation of silica gel from alkali silicate solutions. II. R. C. RAY and P. B. GANGULY (J. Physical Chem.,

1931, **35**, 596—601; cf. A., 1930, 413).—Previous work has been extended to solutions of sodium silicate in which the ratio $Na_2O : SiO_2$ is 1 : 3·3 and 1 : 4·0. The curves enclosing the area of gel formation are similar to that obtained (*loc. cit.*) for the ratio 1 : 2·25. The presence of silica in the higher ratio solutions either as colloidal aggregates or as definite complex silicate ions does not affect the conditions of gel formation to any extent. Provided that dilution is sufficient to prevent gel formation, solutions of sodium silicate can be titrated against ferric chloride with potassium ferrocyanide as indicator. The heats of reaction for ferric chloride and sodium silicate decrease as the ratio $SiO_2 : Na_2O$ increases; this is taken to indicate that different ferric silicates are formed in solution. L. S. Theobald.

Influence of heating on formation of ultra-microscopic particles in salt crystals. R. Matthäi (Z. Physik, 1931, **68**, 85—96).—Determinations of the number of ultramicroscopic particles in transparent crystals show the influence of impurities in quantities too small for detection chemically. The number of ultramicroscopic particles in natural and artificial rock salt reaches a definite value when the crystal is raised to a definite temperature; it reaches a maximum at 400°, and vanishes just below the m. p. The increase may be attributed to coagulation, and the diminution to dissolution in the crystal. The impurity, therefore, is least dispersed at 400°. This agrees with the minimum light absorption at this temperature, assuming the impurity to be the absorbing medium. A. B. D. Cassie.

Temperature and stability of colloidal solutions. S. I. Dijatschkovski (Kolloid-Z., 1931, **54**, 278—284).—The effect of low temperatures on the stability of a large number of colloidal solutions has been studied in some cases by observation of the coagulation process and in others by measuring the electrical conductivity of the sol before and after freezing. The general results show that typical hydrophilic colloids, such as albumin, hæmoglobin, tungstic acid, etc., do not coagulate at low temperatures; semi-colloids of the type of soaps and starch coagulate incompletely and reversibly, the coagulum going into solution again on warming. Protected sols do not coagulate. Non-dialysed silicic acid coagulates and hydrophobic sols in general coagulate. Well-dialysed sols of ferric hydroxide give a "schlieren" effect after freezing due to the production of an ultramicrocystalline suspension. Non-dialysed sols of ferric hydroxide are not coagulated by freezing, indicating that the presence of electrolytes has a protective effect. The addition of alcohol also protects most colloids from coagulation by freezing. Whether the colloid is coagulated or not, a certain amount of it always remains in the form of a sol. By a step-wise lowering of temperature or by freezing sols for different intervals of time fractional coagulation of the sol may be effected, the coarser particles suffering coagulation first. E. S. Hedges.

Effect of stirring on the rate of coagulation of gold sol. E. Jones (Trans. Faraday Soc., 1931, **27**, 51—58).—The coagulation of a gold sol by electrolytes under controllable conditions of stirring has been investigated. Stirring produces a marked acceleration in coagulation when the concentration of electrolyte is sufficiently great to cause rapid coagulation. The formation of air bubbles in the sol is partly effective in causing this acceleration. Coagulation is retarded or inhibited by stirring when the electrolyte concentration is such as to give rise to slow coagulation. This may be accounted for by a disruption of the incomplete outer layer of the double layer on the particles, causing a temporary increase of charge, and, in consequence, a decrease in coagulation velocity. F. G. Tryhorn.

Mechanism of the mutual coagulation process. H. B. Weiser and T. S. Chapman (J. Physical Chem., 1931, **35**, 543—556).—The mutual coagulation of standard sols of varied types has been studied. Complete mutual coagulation of two sols of opposite sign may take place over a range of concentrations which may be either narrow or wide. Further, for a given series of positive sols, the order of optimum concentration for mutual coagulation may vary widely with the nature of the negative sols. These facts are explained on the view that the precipitating power of positive for negative sols is not determined solely by the charge on the particles. Mutual adsorption of colloidal particles independent of charge, the presence of precipitating ions as impurities in the sols, and interaction between stabilising ions are all factors which affect the mutual coagulation process. Complete mutual coagulation is not, in general, due to interaction and removal of the stabilising electrolytes of the oppositely charged sols, although this factor may play an important part in some cases. L. S. Theobald.

Action of electrolytes on substantive dyes. L. Meunier and M. Lesbre (Compt. rend., 1931, **192**, 840—842).—The colour of a solution of Congo-red in pure water changes to blue on the gradual addition of an electrolyte, and coagulates with precipitation of blue particles consisting of larger blue and smaller red particles. In small concentration an electrolyte (*e.g.*, 0·005*N*-sodium chloride) has a protective effect on a 0·005% solution of the dye, although the subsequent addition of a large amount of electrolyte (*e.g.*, 0·2*N* in sodium chloride) produces coagulation. A solution which exhibits protective action shows a maximum transmission for light of 6100 Å., and consequently maximum dispersion, which explains the protective effect (cf. Boutaric, A., 1925, ii, 863). The concentrations at which different electrolytes cause the colour change in a 0·001% solution of the dye are in agreement with the Schulze–Hardy law. C. A. Silberrad.

Kinetic study of Liesegang rings. L. Bull and (Mlle.) S. Veil (Compt. rend., 1931, **192**, 682—683; cf. this vol., 301).—A further graphic study of the formation of Liesegang rings, an image of the drop of silver nitrate on the dichromated gelatin being passed through a slit on to a moving photographic film. The velocity of diffusion varies inversely as the square root of the time, and the production of a principal ring causes a temporary retardation of the diffusion. C. A. Silberrad.

Periodicity and its basis. M. Copisarov (Kolloid-Z., 1931, **54**, 257—265).—A review is made of

the conditions for the formation of different types of periodic structures involving the operation of mechanical, physical, and chemical factors. An attempt is made to embrace the most diverse forms of periodic structures and chemical reactions from the point of view that they are forms of expression of a periodic principle. Some experiments on the formation of periodic structures by the condensation of vapours are also described. When carbon dioxide is released rapidly from a cylinder and led through a long glass tube cooled in ether, solid carbon dioxide appears in the form of bands along the sides of the tube. A similar periodic structure appears in the sublimate produced when ammonium carbonate is heated in a long glass tube closed at one end; carbamide gives a less marked effect. When magnesium is ignited near the closed end of the tube, bands of magnesium oxide are formed along the tube. In some cases a spiral structure is obtained instead of discontinuous bands, and an analogy with the helical course of the explosion wave in gaseous mixtures described by Campbell and Finch (A., 1928, 1099) is suggested. Bands of ammonium carbamate have been obtained in the diffusion of dry ammonia and carbon dioxide towards each other in a glass tube (cf. Hedges, A., 1929, 1154). E. S. HEDGES.

Influence of light on the osmotic pressure of certain colloidal solutions. I. S. HORIBA and H. BABA (Chikashige Anniv. Vol., 1930, 245—260).—The osmotic pressure of colloidal solutions of carbon, silver, gold, ferric hydroxide, arsenious sulphide, Prussian-blue, Congo-red, and hæmoglobin is increased by exposure to visible radiation; no effect is observed with a gelatin sol. In many cases the conductivity undergoes a parallel change. Possible causes of the phenomena are discussed. H. F. GILLBE.

Pectography. Study of solutions by progressive desiccation. P. BARY (J. Chim. phys., 1931, 28, 1—13).—A microscopical study has been made of the washed dry deposit formed on a slide placed in an inclined position in a small beaker containing the solution to be investigated, which is then allowed to evaporate slowly (*e.g.*, at 60° for aqueous solutions). The nature of the deposit is dependent on the temperature, the vapour pressure of the solvent, the rate of removal of the vapour, and on the nature of the solvent and solute, and always falls into one of three classes, viz., crystalline, amorphous (points or small filaments), or continuous without visible structure. The addition of hydrophilic colloids to aqueous solutions of crystallisable substances modifies or suppresses the crystalline form, whilst such colloids alone give scaly films. With simple suspensions a striped pattern results owing to progressive coagulation on concentration. Pectographs of typical crystalloid and colloidal solutions, including those of metallic oxides and sulphides, gums, tannins, colouring matters, etc., are illustrated and discussed. Pectographs of colouring matters are dependent on the rate of evaporation and on the chemical constitution, and in their stablest forms the deposits are usually composed of gels or lyophobic granules. The bearing of the results on the production of periodic formations is discussed and it is shown that simple colloidal solutions may be differentiated from suspensions in that (1) they tend to form gels, (2) the Tyndall effect is absent, (3) they show the Schwedov rigidity effect, (4) they obey an exponential viscosity–concentration law instead of Einstein's linear law. J. GRANT.

Hydroxide systems in ferric oxide colours. H. WAGNER (Kolloid-Z., 1931, 54, 310—314).—A microscopical and X-ray spectrographic examination of technically important ferric oxide products has been carried out. The accepted views of the course of ageing of ferric hydroxide and aluminium silicate systems are applicable to these substances. Mars-yellow has an amorphous structure, whilst ferric oxide-yellow and ferrite-yellow have a goethite space lattice. Mars-yellow usually gives a calcium carbonate X-ray diagram and sienna generally gives lines due to hydrated silica in addition to those of goethite. A method for the characterisation of ochre by selective adsorption of dyes has been worked out and affords a distinction between the German material rich in amorphous hydrates and the French product which is aged and contains kaolin. E. S. HEDGES.

Electrophoretic velocities of gelatin and ovalbumin in different concentrations of their mixtures and the effect of ultra-violet irradiation. E. B. R. PRIDEAUX and F. O. HOWITT (Biochem. J., 1931, 25, 391—402).—The mean velocities of albumin are higher than those of gelatin both in acid and in alkaline solutions. Neither the curve of gelatin nor that of albumin is symmetrical on the acid and alkaline side of the isoelectric point. On the acid side the velocities increase rapidly with diminishing p_H to a maximum and then fall. On the alkaline side the velocities increase up to p_H 6—7, then fall, and reach a constant or nearly constant value which is lower and more nearly constant in the case of gelatin. Mixtures of gelatin and albumin behave anomalously. S. S. ZILVA.

Mechanism of plastic flow. G. E. CUNNINGHAM (J. Physical Chem., 1931, 35, 796—814).—The water retained by clay suspensions centrifuged at different speeds varies with the centrifugal force. The effect of external pressure on the mobility of clay pastes has been quantitatively determined. With thick pastes, mobility decreases at low pressures, increases beyond its original value at intermediate pressures, and decreases again at higher pressures. Plasticity is due to the ability of the plastic material to experience a change in mobility under the influence of an applied pressure which may be independent of the shearing force. L. S. THEOBALD.

Thermodynamic equilibrium in a static Einstein universe. R. C. TOLMAN (Proc. Nat. Acad. Sci., 1931, 17, 153-160).

Graphic method of calculating equilibrium in the water gas reaction. P. MONTAGNE (Compt. rend., 1931, 192, 677—679).—An application of the graphic method previously described (cf. A., 1929, 138).

Vapour pressure of liquids. II. Vapour pressure, Henry's constant, and osmotic pressure of concentrated solutions. K. WATANABE (Sci. Rep. Tokyo Bunrika Daigaku, 1931, A, 1, 67—84; cf.

A., 1930, 1357).—Theoretical. A general equation is derived for the vapour pressure of a solution. This agrees with van Laar's equation for substances which satisfy the van der Waals relation. Further equations are derived for Henry's constant and for the osmotic pressure. H. F. GILLBE.

Spectroscopic investigation of the dissociation relations in aqueous solutions of lead and thallous halides. H. FROMHERZ and K. H. LIH (Z. physikal. Chem., 1931, **153**, 321—375; cf. A., 1930, 1234).—The extinction curves for aqueous solutions of lead perchlorate, chloride, bromide, and iodide, of the corresponding thallous salts, and for solutions containing the halides of these metals and lithium or potassium halides have been determined over a range of concentration extending from near saturation to high dilutions. The absorption curves of the lead and thallous salts in dilute pure solution represent solely the absorption of the halogen ion and the simple hydrated metal ion; contrary to the assumption of Koch (A., 1929, 1364), there is no evidence of the presence of undissociated molecules in any appreciable quantity. In solutions of lead halides of higher concentrations, however, complex ions of the type $PbX^{\cdot}$ are present. The dissociation constants of the complex chloride, bromide, and iodide ions have been found to be in the ratios 2·225 : 2·066 : 1, respectively. In the case of thallous halides, ionic association is detectable only in nearly saturated solutions. In presence of alkali halides at concentrations exceeding about $4N$, lead and thallous halides are almost completely transformed into complex ions, possibly PbX_4'' and TlX_3'', respectively. As the alkali halide concentration falls, however, there is a continuous transition from these complex ions through indefinite mixtures of ions of various compositions to the ions $Pb^{\cdot\cdot}$, $PbX^{\cdot}$, and X' in the case of lead halides, and to the simple metal and halogen ions with the thallous halides. None of the solutions affords evidence of undissociated molecules of lead or thallous salt. R. CUTHILL.

Behaviour of phosphate buffer mixtures with different cations. S. M. NEUSCHLOSZ and R. P. IBÁNEZ (Biochem. Z., 1931, **232**, 106—122).—The equations of Sørensen are modified. In mixtures of primary and secondary ammonium phosphate, the p_H is always smaller than for the corresponding potassium phosphate mixtures, due partly to a decrease in the activity of HPO_4 ions in presence of NH_4 ions and partly to the hydrolysis of the secondary ammonium phosphate. A buffer equation for ammonium phosphate mixtures is developed, and agrees closely with the values obtained. The difference in acidity of potassium and ammonium phosphate mixtures increases as the total phosphate increases and also when sodium chloride is added to the mixture. The osmotic and conductivity factors of diammonium hydrogen phosphate are smaller than for dipotassium hydrogen phosphate of the same concentration. The primary phosphates of the two bases do not show these differences. P. W. CLUTTERBUCK.

Apparent dissociation constants of phenylalanine and of dihydroxyphenylalanine and the apparent free energy and entropy changes of certain amino-acids due to ionisation. S. MIYAMOTO and C. L. A. SCHMIDT (J. Biol. Chem., 1931, **90**, 165—178).—The titration curves of phenylalanine and dihydroxyphenylalanine have been examined and the apparent dissociation constants of a number of amino-acids in water at 25° derived. The free energy changes and the entropy changes of a large number of naturally occurring amino-acids have been calculated from the apparent dissociation constants. It is shown that no appreciable error results when concentration is used instead of activity in calculating the primary dissociation constant of aspartic acid and of glutamic acid. The values of K_a of aspartic and of glutamic acid derived from f.-p. data are compared with those calculated from a combination of electrometric and f.-p. data. W. O. KERMACK.

Hydrolysis measurements in beryllium halide solutions. M. PRYTZ (Z. anorg. Chem., 1931, **197**, 103—112).—The p_H curves for 0·005—0·1M-beryllium bromide and iodide when titrated with M-sodium hydroxide have been determined, and the mechanism previously suggested for the hydrolysis of the chloride and sulphate (A., 1929, 883) has been confirmed. The hydrolytic constant K_0 is for the bromide $5·9\times10^{-7}$ and for the iodide $4·4\times10^{-7}$. As with the sulphate and chloride, a precipitate is formed only when more than one equivalent of sodium hydroxide has been added, and the precipitate has the composition $Be_2O_3H_2$. The solubility product $[Be_2O^{\cdot\cdot}][OH']^2$, calculated from measurements with the bromide, is $2·7\times10^{-19}$, and from the iodide measurements is $3·3\times10^{-19}$. The final point of inflexion on the titration curve coincides exactly with the addition of two equivalents of sodium hydroxide. H. F. GILLBE.

Hydrolysis of zinc sulphate solutions, solubility product of hydrous zinc oxide, and composition of the latter precipitated from zinc sulphate solutions. I. M. KOLTHOFF and T. KAMEDA (J. Amer. Chem. Soc., 1931, **53**, 832—842; cf. this vol., 585).—Identical values of p_H are obtained for 0·01—0·1M-zinc sulphate solutions at 25° by the use of the hydrogen electrode and methyl-red. The hydrolysis constant, $[aZnOH^{\cdot}][aH^{\cdot}]/[aZn^{\cdot\cdot}]$, is $2·2\times10^{-10}$ and thus zinc hydroxide is a strong monoacid base. The second ionisation constant is $4·4\pm0·4\times10^{-5}$ at 25°. The p_H (6·13—6·22) of 0·05M-zinc sulphate at 25° saturated with zinc oxide or hydroxide is independent of the origin of the latter. Titration of 0·05M-zinc sulphate with sodium hydroxide results in the precipitation of hydrous zinc oxide at p_H 6·17; the solubility at 25° is thus about $10^{-6}M$. The composition of the hydrous oxide is approximately constant during the entire precipitation and corresponds with a basic salt, $3ZnO,ZnSO_4,xH_2O$. This substance is stable at the ordinary temperature, but at 80° it gradually becomes more basic and the p_H of the supernatant solution decreases. J. G. A. GRIFFITHS.

Dynamic azeotropism. II. (MLLE.) G. SCHOULS (Bull. Acad. roy. Belg., 1931, [v], **16**, 1412–1424; cf. A., 1930, 292).—Mathematical. C. W. GIBBY.

Dynamic azeotropism. III. (MLLE.) G. SCHOULS (Bull. Acad. roy. Belg., 1931, [v], **17**, 47—59; cf.

A., 1930, 1106).—Theoretical. The Gibbs–Konowalow and Duhem–Margules theorems, previously derived for ternary systems, are extended to systems with any number of components. A new form of the law of displacement of equilibrium is derived.

J. R. I. HEPBURN.

Dynamic azeotropism. IV. (MLLE.) G. SCHOULS (Bull. Acad. roy. Belg., 1931, [v], 17, 191—202).—Theoretical. The generalised Duhem-Margules equation is applied first to binary systems, and then to the more general case of systems with several constituents.

A. J. MEE.

Vapour-pressure depressions of aqueous solutions of phosphate buffer mixtures at 20·3°. A. GROLLMAN (Biochem. J., 1931, 25, 166—168).—Data are given for $M/15$ aqueous solutions of monopotassium and of disodium phosphate, and for mixtures of these salts.

S. S. ZILVA.

Lowering of vapour pressure of water by dissolved electrolytes. J. J. VAN LAAR (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 1140—1160).—The relative lowering of the vapour pressure of water has been derived from the thermodynamic potentials of the two components of a binary system without introducing the conceptions of fugacity or activity: $(p_0-p)/p_0x=i-\psi x^{1/2}+\rho x-\sigma x^{3/2}+\ldots$ For binary electrolytes $i=2$ and ψ is approximately 5 at 20°, and neither of these terms is affected by the state of association of the water. The coefficients ρ, σ, etc. depend on the mutual physical influence of the two components. The equation has been tested by means of the data available in the literature for solutions of the alkali halides and of potassium nitrate for values of x (mol. fraction of solute) between 0·001 and 0·14, *i.e.*, up to the saturation concentration in some cases, and in general good agreement is found between the experimental and calculated values.

O. J. WALKER.

Activity coefficient of a non-electrolyte in aqueous salt solutions from solubility measurements. J. W. BELTON (Proc. Leeds Phil. Soc., 1931, 2, 178—182).—From measurements of the solubility of *N*-chloroacetanilide in solutions of sodium chloride, barium chloride, and magnesium sulphate at 25° its activity coefficient, f, has been calculated. For each salt solution $\log f=\text{constant}\times\mu$, provided that μ, the ionic strength, does not exceed 4. At low salt concentrations slight deviations from this equation are, however, observed.

R. CUTHILL.

Solubility of acids in solutions of salts. V. Temperature coefficient of activity coefficients of benzoic acid molecule in solutions of sodium chloride, potassium chloride, and sodium benzoate. E. LARSSON (Z. physikal. Chem., 1931, 153, 466—470; cf. this vol., 431).—From measurements of the solubility of benzoic acid in solutions of the chlorides at 0·2° and 25° and in solutions of the benzoate at 0·2° the activity coefficients of the benzoic acid molecule in the various solutions have been calculated. The activity coefficient in sodium chloride solutions does not vary with the temperature, and that in potassium chloride solutions increases only slightly as the temperature rises. The activity coefficients in sodium benzoate solutions are, however, considerably greater at 0·2° than at 18°.

R. CUTHILL.

Solubility and activity of silver benzoate and silver nitrate in concentrated salt solutions. E. LARSSON and B. ADELL (Z. anorg. Chem., 1931, 196, 354—363).—The solubilities at 18° of silver benzoate and acetate in solutions of sodium, potassium, and barium nitrates, and sodium acetate have been measured. The relation between the calculated activity coefficients and the ionic strengths of the solutions is in good agreement with the Debye–Hückel theory if suitable values are chosen in each case for the constants. The activity coefficients of the two silver salts in sodium and potassium nitrate solutions of the same ionic concentration are almost identical; in sodium acetate solutions the activity coefficients of both salts are strongly depressed.

H. F. GILLBE.

Vapour pressure and heat of dilution. VII. Vapour pressures of aqueous solutions of sodium hydroxide and of alcoholic solutions of calcium chloride. (MISS) A. M. HAYWARD and E. P. PERMAN (Trans. Faraday Soc., 1931, 27, 59—69).—The air-bubbling method has been used to determine, over wide ranges of concentration, the vapour pressures of aqueous solutions of sodium hydroxide at 30°, 45°, 60°, 70°, and 80°, and of alcoholic solutions of calcium chloride at 20°, 30°, 40°, 50°, and 60°. From these data the respective heats of dilution have been computed by means of the Kirchhoff equation, and of the Porter modification of this equation. The respective osmotic pressures were computed by the use of the perfect gas law.

F. G. TRYHORN.

Activity coefficients and adsorption of organic solutes. I. *n*-Butyl alcohol in aqueous solution by the f.-p. method. W. D. HARKINS and R. W. WAMPLER (J. Amer. Chem. Soc., 1931, 53, 850—859).—The depression of the f. p. of water by *n*-butyl alcohol at concentrations between 0·001 and 1·0M has been determined to within 0·00001°. The activity coefficients of the alcohol at 1·0, 0·5, and 0·1 molal concentrations are 0·8227, 0·8681, and 0·9433, respectively. The application of the adsorption equation to existing surface tension data indicates that the film of the alcohol on its aqueous solutions is unimolecular, each molecule occupying an area of 23·7 sq. Å.

J. G. A. GRIFFITHS.

Activity coefficients of the lead halides and the normal electrode potential of lead. H. FROMHERZ (Z. physikal. Chem., 1931, 153, 376—390).—The activity coefficients of lead chloride in aqueous solution obtained from solubility and *E.M.F.* data by assuming complete ionisation have been corrected for the presence in the solutions of the $PbCl^{\cdot}$ ion (cf. this vol., 565); at concentrations up to 0·04M, the new values are identical with those for barium chloride at corresponding concentrations. These new data have been used to correct the solubility product, and by combining this with the potential of the electrode $Pb|PbCl_2$(solid),KCl the value of 0·1274 volt is deduced for the normal electrode potential of lead at 25° referred to the hydrogen electrode. The same value is also derived from solubility and *E.M.F.*

data for lead bromide and iodide by assuming that the activity coefficients of these salts are equal to that of barium chloride in a solution of the same ionic strength. The equilibrium constants and affinities of the reactions $PbCl^{\cdot} \rightleftharpoons Pb^{\cdot\cdot}+Cl'$, $PbBr^{\cdot} \rightleftharpoons Pb^{\cdot\cdot}+Br'$, and $PbI^{\cdot} \rightleftharpoons Pb^{\cdot\cdot}+I'$ have been calculated. R. CUTHILL.

Free energy of some copper compounds. M. RANDALL, R. F. NIELSEN, and G. H. WEST (Ind. Eng. Chem., 1931, **23**, 388—400).—A review of the available data relating to copper, and the oxides, sulphates, and sulphides of copper leads to the following values for the free energies of substances which are important in the thermodynamical study of the metallurgy of copper. Copper (vapour) +78,944, copper (liquid) +2282, copper (solid) 0, copper (in saturated amalgam) 0, copper (diatomic vapour) +82,565, cupric oxide (liquid) −19,469, cupric oxide (solid) −30,300, cupric hydroxide (solid) −113,766, cupric sulphide (solid) −11,755, cupric sulphate (anhydrous) −156,200, cupric sulphate monohydrate −216,962, cupric sulphate trihydrate −331,876, cupric sulphate pentahydrate −446,310, cuprous oxide (liquid) −20,230, cuprous oxide (solid) −34,990, α-cuprous sulphide −19,155, α'-cuprous sulphide −19,693, β-cuprous sulphide −19,243, cuprous sulphate (solid) −186,570. E. S. HEDGES.

Free energy of formation of thallium amalgams. C. E. TEETER, jun. (J. Amer. Chem. Soc., 1931, **53**, 1180—1181).—At 20°, the free energy attains a minimum at the composition Tl_2Hg_5, indicating the existence of this compound in solution.

J. G. A. GRIFFITHS.

Hydrogen cyanide. III. F. p. of hydrogen cyanide–water mixtures. J. E. COATES and N. H. HARTSHORNE (J.C.S., 1931, 657—665).—The f.-p. diagram is of the simple eutectic type, with a eutectic point at −23·4° and 74·5 mols.% HCN. Solutions of hydrogen cyanide in water are ideal up to concentrations of 9·1 mols.% HCN and of water in hydrogen cyanide up to 1 mol.% H_2O. The mol. wts. of the solutes are within 2% of the normal values. The water branch of the curve has a marked inflexion at −16·0° and about 35·5 mols.% HCN; corresponding with this inflexion a metastable system characterised by two liquid phases has been discovered. The critical solution temperature corresponds with −24·0°±0·5° and about 35·5 mols.% HCN. Two metastable solid phases have been recognised, one of which is thought to be hydrogen cyanide and the other a compound of hydrogen cyanide and water. The limited miscibility of hydrogen cyanide and water agrees with the large positive deviation from ideality shown by the partial vapour pressures. F. J. WILKINS.

Oxide hydrates. XXXVII. System barium oxide–water. G. F. HÜTTIG and A. ARBES [with Z. HERRMANN and C. SLONIM] (Z. anorg. Chem., 1931, **196**, 403—412).—Dehydration of moist barium hydroxide at constant (10 mm.) pressure takes place with decreasing velocity as the water content falls. The Debye diagrams indicate that the mono- and octo-hydrates of barium hydroxide possess characteristic structures, and that no hydrates of intermediate composition exist. The decomposition temperatures of the octo- and mono-hydrates at 10 mm. pressure are 30° and 82—92°, respectively. The method of preparation has but little influence on the form of the dehydration curve, except when the hydroxide is formed in absence of liquid water, *e.g.*, by the action of water vapour on anhydrous barium oxide; the decomposition temperature of the product is then about 60°. When prepared by precipitation of a barium nitrate solution with potassium hydroxide solution at 0°, barium hydroxide contains only about 0·3 mol. of water. H. F. GILLBE.

Fusion diagrams of highly-refractory oxides. III. H. VON WARTENBERG and W. GURR (Z. anorg. Chem., 1931, **196**, 374—383; cf. A., 1930, 847).—Ferric oxide, contaminated with the lower oxide, melts at about 1570°; the resulting mixture of oxides vaporises rapidly at 1800° and forms a eutectic with zirconium dioxide at 1520°. Manganomanganic oxide has m. p. 1705°, and the m. p. of the eutectic mixture with zirconium dioxide is 1620°. Zinc oxide and zirconium dioxide form a eutectic at 1810°, but the former volatilises completely within a few minutes. The m. p. of cerium dioxide is above 2600°, although it vaporises markedly at 2400°, but at 2300° it becomes black and evolves oxygen; at 2500° about 33—50% of the dioxide is reduced to sesquioxide, which is soluble in zirconium dioxide, forming a eutectic at 2400°. Nickelous and cobaltous oxides have m. p. 2090° and 1935°, respectively, and do not volatilise appreciably; the eutectics with zirconium dioxide lie at 2050° and 1850°. Above 1800° titanium dioxide evolves oxygen and becomes bluish-black; the resulting mixture of oxides has m. p. 1850°, is only slightly volatile, and forms a eutectic with zirconium dioxide at 1750°. Stannic oxide commences to volatilise at 1700°, its sublimation temperature being 1800—1900°, but its m. p. could not be determined. Zirconium metasilicate begins to lose silica at 1800°, and the process is rapid at 2000°; the compound is not appreciably soluble in zirconium dioxide.

H. F. GILLBE.

Systems carbamide–resorcinol and carbamide–pyrocatechol. J. P. VAN DER HAMMEN (Rec. trav. chim., 1931, **50**, 347—350; cf. Puschin and König, Sitzungsber. Akad. Wiss. Wien, 1928, **137**, IIB, 75).—In the first system the 1 : 1 compound melts at 104·4° and appears to be dissociated in the liquid state. The eutectic on the resorcinol side melts at 84·2° and that on the carbamide side at 91·1°. The second system also shows a 1 : 1 compound, m. p. 71·3°. The eutectic on the pyrocatechol side melts at 65·9°, whilst the other melts at 67°. Part of the metastable melt line could be followed at concentrations between 35 and 45% of carbamide.

J. W. SMITH.

Equilibrium in the iron–oxygen–hydrogen system at temperatures above 1000°. W. E. JOMINY and D. W. MURPHY (Ind. Eng. Chem., 1931, **23**, 384—387).—Mixtures of hydrogen and water vapour were passed over electrolytic iron at high temperatures for 30 min., after which the iron was quenched in water to stop the reaction and the sample was examined to see whether oxidation had occurred. By suitably controlling the ratio of hydrogen to water

vapour, this method provides a means of determining the equilibrium in the system iron–iron oxide–hydrogen–water vapour. The tests were made between 1097° and 1427°. The equilibrium data when plotted show a break in the curves at 1357°, which may be taken as the m. p. of ferrous oxide. The heat of fusion of ferrous oxide determined from these data is $+29,000\pm5000$ g.-cal. per g.-mol. E. S. Hedges.

Reduction of manganese oxides by carbon monoxide. E. Nishibori (Chikashige Anniv. Vol., 1930, 295—298).—The equilibria between carbon monoxide and manganese oxides at 780° have been determined. The gas phase contains 100% CO_2 until the composition of the solid approaches that of the monoxide, when the carbon monoxide content increases rapidly. Reduction beyond this stage proceeds very slowly, with about 7% CO_2 in the gas phase, and a substance is produced which on dissolution in sulphuric acid partly reduces the acid to hydrogen sulphide. The reaction in the reverse direction proceeds with extreme slowness. H. F. Gillbe.

Ternary systems. IX. Sodium iodate, sodium nitrate, and water. A. E. Hill and J. E. Donovan. **X. Magnesium iodate, magnesium nitrate, and water.** A. E. Hill and S. Moskowitz (J. Amer. Chem. Soc., 1931, **53**, 934—941, 941—946). —IX. Isotherms have been determined at 5°, 25°, and 50°. The double salt $2NaIO_3,3NaNO_3,15H_2O$ exists below 9·8°.

X. The transition temperatures corresponding with $Mg(IO_3)_2,10H_2O \longrightarrow Mg(IO_3)_2,4H_2O$ and $Mg(IO_3)_2,4H_2O \longrightarrow Mg(IO_3)_2$ are 13·3° and 57·5°, respectively. The metastability of the tetrahydrate permits of measurements of solubility beyond the transition temperatures. Isotherms for the ternary system have been determined at 5°, 25°, and 50°.

J. G. A. Griffiths.

Double decomposition in the absence of a solvent. XIV. The irreversible mutual system $Ag_2SO_4+Tl_2Cl_2 \longrightarrow Tl_2SO_4+Ag_2Cl_2$. S. I. Sokolov (J. Russ. Phys. Chem. Soc., 1930, **62**, 2329—2335).—The m.-p. diagram for the system Ag_2SO_4–Ag_2Cl_2 is of the simple eutectic type, but shows a break at the transition point of silver sulphate; solid solution and compound formation are similarly absent in the system Tl_2SO_4–Tl_2Cl_2. The fusion diagram for Tl_2SO_4–Ag_2SO_4 shows the formation of a compound, Tl_2SO_4,Ag_2SO_4, and of solid solutions. The system $Ag_2SO_4+Tl_2Cl_2 \longrightarrow Ag_2Cl_2+Tl_2SO_4$, constructed on the basis of the above, is an irreversibly mutual one, with complete solubility of the components, and without singularity on the chief diagonal section. R. Truszkowski.

Lowering of the ideal eutectic temperature in n-component systems. K. Iwasé and N. Nasu (Chikashige Anniv. Vol., 1930, 223—227).—The eutectic temperature of an n-component system is lower than that of any of the possible $(n-1)$-component systems. H. F. Gillbe.

Graphical representation of multi-component systems in phase-rule investigations. E. Janecke (Z. anorg. Chem., 1931, **196**, 337—353).—The usual graphical methods for the representation of multicomponent systems are summarised, and new methods, which employ the equivalents of the components as the units, are described. A tetrahedral C–H–O–N diagram, showing the relationships between the principal types of organic compounds, is reproduced; compounds of similar type, such as the amines, nitriles, or amides, appear on straight lines. In systems of five elements in which simple compounds are formed between all the components there are two distinct series of four-component systems derived from the ten binary compounds; one series may be represented by five different tetrahedra and the other by ten triangular prisms. The complete representation of all possible five-component systems would require an infinite series of tetrahedra, vanishing to a point, or an infinite series of triangular prisms, which in the limit become an equilateral triangle or a straight line. The prism method is illustrated by reference to such systems as C–H–S–O–N, H–O–Br–Cl–Na, and SiO_2–MgO–Al_2O_3–Na_2O–B_2O_3.

H. F. Gillbe.

Heats of combustion of some heterocyclic compounds. M. Milone and S. Allavena (Gazzetta, 1931, **61**, 75—90).—A micro-bomb has been used to determine the heats of combustion of 18 heterocyclic compounds of the furazan, azoxime, and oxadiazole types. The heats of combustion are shown to be constitutive, the moduli assigned to the furazan, azoxime, and oxadiazole rings being respectively 187, 158, and 146 kg.-cal. F. G. Tryhorn.

Electrical conductivity at high temperatures of solutions of common salt and of concentrated sulphuric acid. F. J. Symon (J. Roy. Tech. Coll. Glasgow, 1931, **2**, 395—401).—Apparatus is described for measurements up to 230° and pressures rising to 400 lb./in.^{2} The temperature coefficient of the conductivity is similar for all the solutions studied, *e.g.*, $\kappa_{100^\circ}/\kappa_{20^\circ}$ 3·0—3·04, and $\kappa_{200^\circ}/\kappa_{20^\circ}$ 4·92—5·14. The values in the Smithsonian Tables (No. 422, 1920) appear to be in error by about 4% at 100° and 17% at 218°. Values for sulphuric acid (94—99%) at 15—50° are also recorded. For the 99% acid the mean temperature coefficient for the range 18—50° is 0·0347, the coefficients for all solutions over the range 18—26° being slightly higher (0·0289—0·0297) than those of Kohlrausch. J. Grant.

Organic acids and bases in non-aqueous solutions. V. Ethyl salicylate and amines. F. Holzl (Monatsh., 1931, **57**, 375—382; cf. A., 1929, 59).—The electrical conductivity of mixtures of ethyl salicylate with ammonia, diethylamine, trimethylamine, ethylenediamine, benzylamine, and p-phenylenediamine in absolute ethyl-alcoholic solution passes through a maximum in each case at a mol. ratio of 1 : 1, indicating the formation of a compound. Aniline and o- and m-phenylenediamine do not combine with ethyl salicylate under these conditions. The results are discussed in relation to the compounds produced between phenol, pyrocatechol, and salicylic acid and the amino-compounds investigated.

E. S. Hedges.

Aqueous solutions of sodium aluminate. I. Electrical conductivity. M. Prasad, S. M. Mehta, and N. G. Joshi (J. Indian Chem. Soc., 1931, **7**, 973—

980).—The equivalent conductivity of solutions of aluminium hydroxide in sodium hydroxide of concentration greater than $0{\cdot}25N$ is at a minimum when the mol. ratio Na_2O/Al_2O_3 is 3, whence the existence of the compound Na_3AlO_3 is inferred. When the sodium hydroxide used is more dilute the minimum is masked in consequence of hydrolysis.

F. L. USHER.

Electrolysis of sodium amalgams and calculation of transport numbers of sodium, potassium, lithium, barium, and bismuth in their amalgams. R. KREMANN (Monatsh., 1931, **57**, 323—374).—The amalgam was placed in a long glass capillary tube, at the ends of which the electrodes were inserted. After electrolysis different portions of the amalgam were titrated with acid in order to determine the distribution of the sodium. The effect of the length and diameter of the tube and the concentration of amalgam was investigated. From measurements of the change in composition of the anode and cathode regions transport numbers for sodium, potassium, lithium, barium, and bismuth in mercury have been calculated. E. S. HEDGES.

Electrolysis of ternary alloys. R. KREMANN (Monatsh., 1931, **57**, 241—252).—The electrolysis of copper–tin alloys containing different amounts of bismuth proceeds readily at 1000° using a c. d. of 5—6 amp./mm.² Cooled specimens after electrolysis showed an increased copper content in the cathode portion, whilst the anode portion was richer in bismuth. Changes in the metallographic structure of the alloys are illustrated by means of photomicrographs. Ternary alloys consisting of sodium amalgam containing 0·52—4·79% of tin were electrolysed in glass capillary tubes at 240° for 20 hrs., using a c. d. of 6 amp./mm.² Both tin and sodium accumulate at the cathode. E. S. HEDGES.

Potential of the cadmium electrode. F. H. GETMAN (J. Physical Chem., 1931, **35**, 588—595).—The *E.M.F.* of the cell $Cd|CdCl_2|Hg_2Cl_2,Hg$ has been measured at 25° with single crystals or massive crystalline aggregates of cadmium. Single crystals of cadmium give constant and reproducible values which are always greater than those given by the aggregates. The normal electrode potential of cadmium calculated from the *E.M.F.* of cells with electrodes of single crystals is 0·395 volt. The activity coefficients of cadmium chloride solutions now calculated are slightly less than those deduced by Lewis and Randall from the experimental data of Horsch. L. S. THEOBALD.

Effect of pressures up to 16,000 atm. on the *E.M.F.* of the Weston standard cell. T. C. POULTER, C. RICHEY, R. WILSON, and J. FULTON (Proc. Iowa Acad. Sci., 1929, **36**, 304).—The shape of the curve showing increase of *E.M.F.* with pressure is affected by the material of the cell case.

CHEMICAL ABSTRACTS.

Liquid junction of dilute electrolytes. M. PLANCK (Sitzungsber. Preuss. Akad. Wiss., 1931, **7**, 10 pp.).—Further mathematical treatment yields an equation which, although giving a value for the *P.D.* at the junction of a $0{\cdot}1N$-potassium chloride solution with a $0{\cdot}1N$-hydrochloric acid solution which accords with the experimental value, nevertheless leads to paradoxical conclusions relating to the change of *P.D.* with time. Henderson's assumption cannot be upheld. It is shown that a linear relationship holds only when $U_n/U \quad V_2/V_1$; this condition obtains for two solutions of a single electrolyte which differ only in concentration. When U_2-U_1 and $V_2=V_1$ the relation becomes logarithmic. With the aid of this relation it becomes possible to calculate the variation of the *P.D.* with time as the boundary passes into the stationary condition. For this purpose an equation has been derived which appears to be satisfactory, but it is not possible to decide whether the correct sign is obtained for the difference between the *P.D.* in the initial and the stationary states. H. F. GILLBE.

Reduction potentials of some higher benzologues of the quinones. L. F. FIESER and E. M. DIETZ. See this vol., 623.

Reaction of hydrogen peroxide with some metallic ions. I. Potential of hydrogen peroxide. II. Alleged "reduction coefficient" of a reversible hydrogen peroxide electrode. III. Effects upon the potential and the photographic action of hydrogen peroxide exerted by the presence of several metallic acids and its stabiliser as well as by changes in its concentration. S. HAKOMORI (Tech. Rep. Tohoku, 1931, **9**, 106—120, 121—144, 145—164).—I. The normal oxidation and reduction potentials, referred to the normal hydrogen electrode, of hydrogen peroxide have been calculated theoretically as 1·7693 volts and 0·6819 volt, respectively. Palladium electrodes give better reversible values in hydrogen peroxide solution than do platinum or gold electrodes.

II. The term "reduction coefficient" is applied to the relation C/C_0, where C is the concentration of the peroxide solution in which the electrode is immersed and C_0 that of the part of the solution in direct contact with the electrode. It is shown that, if C/C_0-G, then $\log G=(\varepsilon F+\frac{1}{2}\Delta F_T)/1{\cdot}15RT+\log m$, where ε is the potential of the reversible electrode at 1 atm. pressure with reference to the normal hydrogen electrode, ΔF_T^1 is the free energy of the reaction $H_2+O_2=H_2O_2$(aq.) after time T, and m is the molar concentration of the peroxide.

III. The potential of hydrogen peroxide solutions against a normal hydrogen electrode is increased by the addition of various acidic oxides of metals; for a 1 : 1 ratio of metal oxide to peroxide this increase is 0·0047 volt for uranium trioxide, 0·0195 volt for titania, 0·1080 volt for molybdenum trioxide, 0·3107 volt for vanadium pentoxide, and 0·4802 volt for chromium trioxide. A. R. POWELL.

Oxidation–reduction potentials of sugar solutions. R. WURMSER and J. GELOSO (Compt. rend., 1931, **192**, 680—682; cf. A., 1929, 1393; 1930, 42).—To ascertain the system determining the limiting potential of a solution of dextrose, operations were carried out very slowly (*e.g.*, with p_H 7 at 20° 48 hrs. was allowed to elapse after each addition of either oxidiser or reducer). In this way a second system of normal potential $-0{\cdot}040$ volt (p_H 7, at 20°) designated as $G_1 \rightleftharpoons B+nH_2$, is found to exist in considerable quantity The amount of dye reduced by solutions

of dextrose etc. can be deduced from the titration curves, given the normal potential of the dye.

C. A. Silberrad.

Electro-capillary curve of mercury. K. Bennewitz and K. Kuchler (Z. physikal. Chem., 1931, **153**, 443—450).—As asserted by Frumkin and Obrutscheva (A., 1929, 145), the potential of mercury dropping from a capillary beneath the surface of a liquid is not the same as that of mercury at rest in contact with the same liquid, and the determination of the electro-capillary curve of mercury previously reported (A., 1927, 316) has therefore been repeated with a suitably modified technique. The maximum on the curve in the neighbourhood of 0·5 volt observed when dropping into pure very dilute mercurous nitrate solution is still present. Such additions as potassium nitrate, and probably also potassium hydroxide, cause considerable displacement of the curve. It seems fairly certain that there is a change in direction of the current at the maximum point, but in the absence of further evidence the maximum point cannot safely be regarded as corresponding with zero potential.

R. Cuthill.

Phase-boundary potential between quartz and solutions of electrolytes. B. von Lengyel (Z. physikal. Chem., 1931, **153**, 425—442).—The phase-boundary potential between quartz glass and aqueous solutions of sodium hydroxide, alkali halides, and various acids has been measured. The potential set up apparently depends solely on the adsorption of ions from the solution; no appreciable amount of ions can come from the quartz itself, and there is no evidence that a swollen surface layer on the quartz plays a part. It must be supposed that the quartz with its adsorbed ions behaves electrically like an ordinary electrode, the electrolytic solution tension depending on the concentration of adsorbed ions. As a result of the acid character of the adsorbent, the tendency is to take up positive ions, and the potential in solutions of acids is independent of the anion. In very dilute solutions of alkali salts the salt ions have little effect on the potential, but as the salt concentration increases the metal ions are adsorbed in greater and greater amount until ultimately the electrode becomes an alkali metal electrode instead of a hydrogen electrode; here also the anion has little influence on the potential. The potential in 0·01—0·1N-sodium hydroxide solutions seems to be determined by the sodium ions and not by the hydrogen ions. The potential in an acid solution rises as sodium hydroxide is added, passes through a maximum, and falls again, this behaviour probably being a consequence of the progressive replacement of adsorbed hydrogen ions by sodium ions.

R. Cuthill.

Electrokinetic potentials. VIII. Ion antagonism. H. B. Bull and R. A. Gortner (J. Physical Chem., 1931, **35**, 700—721; cf. this vol., 435).—The surface potential at a cellulose–solution interface has been determined for aqueous solutions of the chlorides of sodium, potassium, calcium, and magnesium alone and mixed in pairs with a total cation normality equal to 8×10^{-4}. Except in the case of calcium and magnesium chlorides which shows a suggestion of ion antagonism, the results for the mixtures are approximately an average of those obtained with the individual salts. Magnesium and calcium chlorides show no ion antagonism in a diluted physiological salt solution which is $2\times10^{-4}N$, and there is no antagonism which affects the electrokinetic potential between potassium chloride and sodium chloride (20 : 1) or between sodium chloride and calcium chloride (100 : 1).

L. S. Theobald.

Becquerel's "electro-capillary phenomenon." J. J. Bikerman (Z. physikal. Chem., 1931, **153**, 451—465).—It has been shown experimentally that the theories advanced by Ostwald (A., 1890, 1354) and by Girard and Platard (A., 1924, ii, 396) to account for the effects observed when a solution of a copper salt is separated from a sodium sulphide solution by a glass membrane containing a crack are untenable, neither can the effects be attributed to diffusion or Donnan potentials. A satisfactory explanation is, however, obtained by supposing that the two solutions form, in conjunction with the copper sulphide deposited in the crack, a cell. The circuit is completed through the pores of the sulphide by the solution of the sodium salt formed by the reaction and a continuous current therefore circulates, as a result of which copper is deposited on one side of the sulphide membrane, and sulphide ions undergo the reaction $S''+Na_2S=Na_2S_2+2\ominus$ at the other. Indirect determinations of the *P.D.* across the membrane show this explanation to be quantitative. If the membrane in the crack or the solutions are of such a nature that a current cannot circulate, no metal is deposited.

R. Cuthill.

Electrolytic dissolution and deposition of metals. J. Hoekstra (Rec. trav. chim., 1931, **50**, 339—342).—The current density–voltage curve for electrolytes generally shows a logarithmic form, the change in current with change of potential being almost zero at zero voltage. When the electrodes are scraped continuously, however, a straight line is obtained. Metallic deposition during electrolysis has also been studied photomicrographically. For most metals deposition appears to occur in films of approximately 1000 atoms thick. "Active lines" are seen on the surface of the crystals and these spread over the crystal face as deposition continues. The form and number of these active lines are modified by the applied voltage and by interruption of the current. Iron, nickel, and cobalt form exceptions to this rule, as they normally deposit in relatively thick films in nodule-like form. The results obtained are interpreted as due to adsorption phenomena.

J. W. Smith.

Relation between the hydrogen overvoltage and composition of brass. M. de K. Thompson (Trans. Amer. Electrochem. Soc., 1931, **59**, 65—69).—Hydrogen overvoltages for alloys ranging from pure zinc to pure copper have been determined at various current densities in N-potassium hydroxide. The overvoltage varies linearly with the composition, except in the ε-brass region, where there is a marked depression in the curve. There is no apparent relation between this curve and the f.-p. curve for the alloys.

H. J. T. Ellingham.

Reductivity of hydrogen at certain metal surfaces in relation to the overvoltage. G. R. Hood and F. C. Krauskopf (J. Physical Chem., 1931, **35**,

786—795).—The measurement of cathodic potentials during electrolytic reduction without contamination of the electrolyte is described. The electrolytic reduction of an aqueous solution of potassium chlorate ($0{\cdot}493M$) using cathodes of iron, copper, silver, nickel, platinum, cadmium, tin, or zinc has been studied. When the cathodic potential exceeds 1·5 volts electrolytic reduction is negligible, but it increases rapidly as the potential falls below this value. The results obtained by electrolytic reduction, catalytic reduction by hydrogen in the presence of platinum-black, and decomposition potential measurements are discussed in connexion with the mechanism of overvoltage.

L. S. Theobald.

New abnormality in the properties of aqueous solutions of cadmium salts. E. Tesche and P. J. van Rysselberghe (Trans. Amer. Electrochem. Soc., 1931, **59**, 71—75).—Apparent current efficiencies notably greater than 100% in the electrodeposition of cadmium from its aqueous iodide solutions are shown to be due to the adsorption of cadmium iodide on the metal during deposition. Electrodeposited or even cast cadmium adsorbs notable amounts of cadmium iodide when merely dipped into solutions of the salt, and desorption occurs when the metal is transferred to water. This effect is ascribed to neutral molecules of the salt and not to complex ions, because the amount of adsorption is somewhat increased when the metal is being deposited from a methyl-alcoholic solution of cadmium iodide, but becomes practically zero when it is deposited from aqueous solutions of the complex salts K_2CdI_4 and $KCdI_3$. Adsorption also occurs, but to a smaller extent, in the electrodeposition of cadmium from bromide solutions, and abnormally heavy deposits are obtained from nitrate solutions. From the chloride and sulphate solutions, however, pure cadmium is deposited. A tentative explanation of the difference in behaviour of the three halides is put forward. H. J. T. Ellingham.

Passivity of chromium. II. E. Müller and K. Schwabe (Z. Elektrochem., 1931, **37**, 185—197; cf. this vol., 173).—Experiments on the activation of chromium by cathodic polarisation in acid solutions show that each acid requires a definite activation potential. The negative potential at which activation occurs in normal acid solutions increases in the order hydrochloric<hydrofluoric<hydrobromic<sulphuric<perchloric<orthophosphoric; thus, activation is more easily effected the smaller is the anion. The potentials for electrolytic and thermite chromium are slightly different. When the activation is effected by grinding with an emery wheel there is again a definite activation potential, which depends on the anion of the acid, and the order is the same as that given above. The experiments lead to the following deductions concerning the nature of passivity. Chromium in the passive state is covered by a net-work of chromic oxide molecules, which are anchored to the units of the chromium space lattice. Acids cannot dissolve the oxide film except by penetrating between the molecules, and the size of the anion is therefore all-important. As the cathodic polarisation is increased the small hydrogen ion is drawn through the oxide net-work and the electrostatically bound anion can follow it and dissolve the oxide film, if the anion is not too large. At the corners and edges of the metal the oxide net-work is looser and anions can readily penetrate at such points, which therefore become active. A short-circuited cell is then set up, and if the potential reaches a higher negative value than the activation potential for the particular acid the whole metal will become active and dissolve. In the case of chromium at 20° this state of affairs is realised in hydrochloric acid only. The degree of polarisation may be increased also by mechanical grinding and by raising the temperature, whereupon the whole metal becomes active. E. S. Hedges.

Cathodic behaviour of pyrites and chalcopyrite. A. Matsubara and J. Takubo (Chikashige Anniv. Vol., 1930, 311—339).—Cathodic polarisation of iron pyrites in dilute sulphuric acid causes the ionisation of one or both atoms of sulphur, which then combine with the hydrogen ions present to form hydrogen sulphide. If the material is first made the anode, subsequent cathodic polarisation gives rise to an abnormal amount of hydrogen and certain natural specimens behave similarly without previous treatment. The current yield is, in general, smaller when much hydrogen is evolved. Copper pyrites in dilute sulphuric acid is decomposed cathodically into hydrogen sulphide, cuprous sulphide, and ferrous sulphate, and, ultimately, into metallic copper; preliminary anodic polarisation produces the reverse effect of that observed with iron pyrites. Copper pyrites which yields but little hydrogen gives abnormal quantities of decomposition products. It is suggested that the fraction of the mineral which is dissolved directly by the acid exists in the solid in an ionised condition, the degree of ionisation in various specimens of copper pyrites being 0·035—0·305.

H. F. Gillbe.

Statistical treatment of reaction velocity data. I. Critical review of current methods of computation. L. J. Reed and E. J. Theriault (J. Physical Chem., 1931, **35**, 673—689).—The possibility of obtaining a consistent series for the values of k should be discarded as a test for the unimolecular nature of a reaction. Procedures involving least squares are inapplicable to unimolecular data and the proposed systems for the weighting of unimolecular constants cannot be used in the presence of constant errors. L. S. Theobald.

Interpretation of the thermal decomposition of nitrous oxide. H. C. Ramsperger and G. Waddington (Proc. Nat. Acad. Sci., 1931, **17**, 103—105).—The theories of Rice and Ramsperger (A., 1927, 833) and of Kassel (A., 1928, 372) have been applied to the data obtained for the thermal decomposition of nitrous oxide at 665°. Only two squared terms (one classical oscillator) are required to fit the data. The minimum value obtained for the critical energy for breaking the nitrogen–oxygen linking is 42,000 g.-cal. E. S. Hedges.

Combustion of inflammable gases by electric sparks. J. D. Morgan (Phil. Mag., 1931, [vii], **11**, 158—163).—The amount of combination produced in the flameless combustion of very dilute coal gas–air mixtures by a succession of high-tension sparks is

closely proportional to the heat energy of the discharge when the gap between the electrodes is kept constant. When the heat energy of the discharge is maintained constant the amount of combustion is proportional over a wide range to the gap. The results are consistent with the hypothesis that combustion depends on the heating of the gas by conduction.

F. G. TRYHORN.

Flame temperatures of hydrocarbon gases. G. W. JONES, B. LEWIS, J. B. FRIAUF, and G. ST. J. PERROTT (J. Amer. Chem. Soc., 1931, **53**, 869—883; cf. Loomis and Perrott, B., 1928, 881).—The spectral line reversal method (Griffiths and Awbery, A., 1929, 534) has been applied to moist hydrocarbon–air mixtures. In qualitative agreement with calculations based on the dissociation of the products at the temperatures of the flames, mixtures containing hydrocarbon slightly in excess of that necessary to consume all of the oxygen afford the observed maximum temperatures: ethylene 1975°, propylene 1935°, butylene 1930°, propane 1925°, *iso*butane 1900°, butane and ethane 1895°, Pittsburgh natural gas (87% CH_4) 1890°, and methane 1880°. These values are about 100° and 40—70° lower than those calculated for the unsaturated and saturated hydrocarbons, respectively, and this discrepancy may be attributed to radiation losses. Mixtures affording maximum flame temperatures contain less hydrocarbon than those affording maximum speeds of uniform movement of flame (cf. Wheeler, Coward, Payman, and others).

J. G. A. GRIFFITHS.

Oxidation of gaseous acetaldehyde by oxygen as a typical example of the [slow] combustion of hydrocarbons. M. BODENSTEIN (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1931, III, 18 pp.; cf. Backstrom, A., 1927, 737, 1151).—Acetaldehyde vapour reacts slowly with oxygen at 55—90° and 70 mm. pressure, and the reaction can be followed, except in the later stages, by measuring the diminution of pressure. The primary product is peracetic acid, which towards the end of the reaction decomposes in an irregular manner, causing an increase of pressure. With a deficit of oxygen the pressure decreases linearly with time, and the reaction stops abruptly when all the oxygen has been used; with oxygen in excess the velocity of reaction decreases with time. In both cases a period of induction is generally, but not invariably, found. The course of the main reaction is expressed by the formula $d[P]/dt$—$k[A]^2/([O_2]+b)$, in which P denotes peracetic acid and A acetaldehyde. The sequence of changes, which is considered to occur generally in the oxidation of hydrocarbons, consists essentially in the activation of an aldehyde molecule, which combines with oxygen to form an activated molecule of peracetic acid. Normally, the energy of the latter is transferred to another aldehyde molecule, but in the presence of certain substances (*e.g.*, diphenylamine) which act as negative catalysts, the latter absorb the energy instead, and the reaction " chain " is then interrupted. There is evidence that the acetaldehyde reacts in a tautomeric form other than vinyl alcohol.

F. L. USHER.

Mechanism of oxidation of acetaldehyde and hydrocarbons. M. BODENSTEIN (Z. physikal. Chem., 1931, **B**, **12**, 151—164).—A mechanism is proposed for the slow reaction of gaseous acetaldehyde with oxygen, and shown to be applicable without essential modification to the slow combustion of hydrocarbons, the results of Spence and Kistiakowsky for the oxidation of acetylene (this vol., 313) being in particularly good agreement with the theory. In the explosive oxidation of hydrocarbons the series of reactions involved in slow oxidation appears to be initiated by reaction chains in which free atoms and radicals take part.

R. CUTHILL.

Inflammation limits of fuels containing alcohol. YANNAQUIS (Ann. Office Nat. Combust. liq., 1930, **5**, 175—178; Chem. Zentr., 1930, ii, 3878).—The dependence of the limits of inflammation of benzene–ethyl alcohol–methyl alcohol, benzene–ethyl alcohol–petrol, and ethyl alcohol–methyl alcohol mixtures on the temperature has been studied. Partial substitution of alcohol by benzene limits the inflammability region of the ethyl alcohol–methyl alcohol mixture without affecting the temperature coefficient. Substitution of methyl alcohol by petrol has the opposite effect in both cases.

A. A. ELDRIDGE.

Rates of intramolecular change between ammonium thiocyanate and thiocarbamide. W. URE and T. B. EDWARDS (Trans. Roy. Soc. Canada, 1930, [iii], **24**, III, 153—159).—The velocity of the opposing reactions in the system NH_4CNS $CS(NH_2)$, has been investigated in solution over a range of concentrations and temperatures. Although the presence of side reactions is indicated, the results seem to show that the main process consists of two opposing unimolecular reactions. The reaction coefficients are evaluated for two temperatures.

W. GOOD.

Kinetics of chlorine bleaching. J. J. WEISS (Z. angew. Chem., 1931, **44**, 102—104).—Polemical against Kauffmann (cf. B., 1930, 1062).

R. CUTHILL.

Kinetics of chlorine bleaching and of [decomposition of] hypochlorite solutions. J. J. WEISS (Z. Elektrochem., 1931, **37**, 20—25).—The velocity data of both Foerster (A., 1917, ii, 367) and Kauffmann (B., 1930, 1062) for the decomposition of hypochlorite in alkaline solution can be accounted for by the theory that the decomposition consists of two concurrent composite reactions, viz., $2ClO' \longrightarrow ClO_2' + Cl'$ followed by $ClO_2' + ClO' \longrightarrow ClO_3' + Cl'$, and $2HClO \longrightarrow 2H^{\cdot} + 2Cl' + 2O$ followed by $2ClO' + 2H^{\cdot} \rightleftharpoons 2HClO$, the first stage in each reaction determining the rate of the reaction as a whole (cf. A., 1930, 1379). In hypochlorite bleaching the active agent is not the complex ion $HClO,ClO'$ postulated by Kauffmann, but chlorine monoxide or undissociated hypochlorous acid. If it is assumed that in the bleaching of cellulose fibres the attack on the fibre itself runs parallel with the degree of swelling and that the latter is proportional to the concentration of adsorbed hydroxyl ions, it appears that the rate of attack is maximal for a certain p_H and falls rapidly with either increase or decrease of p_H. The predicted relationship between rate of attack on the fibre and p_H is, in fact, in satisfactory agreement with existing experimental data. It thus appears possible that by

suitable adjustment of the p_H the colouring matter may be rapidly destroyed without the fibre being appreciably attacked. R. CUTHILL.

Kinetics of chlorine bleaching. H. KAUFFMANN (Z. angew. Chem., 1931, **44**, 104–105).—A reply to Weiss (cf. preceding abstract). R. CUTHILL.

Reactions involving hydrogen peroxide, iodine, and iodate ion. III. Reduction of iodate ion by hydrogen peroxide. H. A. LIEBHAFSKY (J. Amer. Chem. Soc., 1931, **53**, 896—911; cf. this vol., 324).—The rate of the reaction at 50° in the system potassium iodate 0·0019—0·23M, hydrogen peroxide 0·002—2·5M, and perchloric acid 0·007—0·14M is given by the relation $-d[IO_3]/dt=$(i) $2{\cdot}6\times10^{-4}[H_2O_2][IO_3']+$(ii) $129\times10^{-4}[H_2O_2][IO_3'][H^{\cdot}]$ (units: min., mol., litre), which is no longer valid when $[H^{\cdot}]$ exceeds 0·14M. The first stages in the reduction may be $IO_3'+H_2O_2\longrightarrow IO_2'+H_2O+O_2$ and $IO_3'+H_2O_2+H^{\cdot}\longrightarrow HIO_2+H_2O+O_2$. The catalytic decomposition of hydrogen peroxide is minimised by removal of iodine by means of carbon tetrachloride. The induction period is approximately independent of the concentration of hydrogen and iodate ions and inversely proportional to the concentration of hydrogen peroxide. The relation between the induction period, the slow initial reaction, and the succeeding rapid reactions is discussed. From the temperature coefficient between 30° and 60°, the energies of activation of (i) and (ii) are computed to be 27,500 and 23,500 g.-cal., respectively, and the diameter 10^{-6} to 10^{-7} cm. is deduced for the entities H_2O_2 and IO_3'. It is concluded that the number of ternary collisions (ii) is insufficient to afford the observed reaction velocity and hence some complex must be present. The relation between this reaction and the decomposition of hydrogen peroxide catalysed by the iodide–iodate couple is discussed. J. G. A. GRIFFITHS.

Chemical kinetics of ionic reactions. II. Mechanism of the reaction between ferric and iodine ions. A. KISS (Magyar Chem. Fol., 1930, **36**, 49—59; Chem. Zentr., 1930, ii, 1030; cf. A., 1930, 1256).—The reaction between ferric and iodine ions is termolecular, being bimolecular with respect to iodine and unimolecular with respect to ferric ions. Hydrolysed ferric ions do not react with iodine ions. In dilute solution, the primary salt effect follows Bronsted's law of neutral salt action. The retarding effect of ferrous and sulphate ions must be regarded as a secondary salt effect. L. S. THEOBALD.

Period of induction of the reaction between ammonium sulphide and formaldehyde solutions. R. J. W. LE FEVRE and (MISS) M. MACLEOD (J.C.S., 1931, 474—478).—A mixture of aqueous solutions of ammonium sulphide and formaldehyde deposits after a period of induction a white precipitate. The induction period diminishes with rise of temperature, vanishing at about 60°. F. J. WILKINS.

Relationship of structure of hydrocarbon radical to velocity and position of equilibrium in organic reactions. W. HEROLD and K. L. WOLF (Z. physikal. Chem., 1931, **B**, **12**, 194—205).—It is suggested that in reactions between organic dipole molecules the effect of the radicals attached to the polar groups may be twofold: one radical may be of such dimensions as to prevent the close approach of the other molecule to the attached polar group ("steric hindrance"), and further the probability that the polar groups will come in contact in a collision will be diminished if either group is not readily accessible from all sides ("steric screening"). The degree to which the polar group is screened may, in the case of a group with absorbent power, be determined from the amount of displacement of its absorption bands under the influence of other dipole molecules; the less is the screening the greater will be the displacement. The relationships of the velocity and position of equilibrium of reactions occurring in solution to the nature of the reactants and solvent are, in general, in satisfactory agreement with the theory. R. CUTHILL.

Optical investigations in the system aldehyde–alcohol. W. HEROLD and K. L. WOLF (Z. physikal. Chem., 1931, **B**, **12**, 165—193).—Optical absorption measurements have been made with solutions of aliphatic aldehydes in water, heptane, and various alcohols. From the results the rate of formation of alcoholates and acetals from aldehydes in alcoholic solution and the position of equilibrium have been determined, the presence of free mineral acid being found not to be necessary for this reaction. In dilute alcoholic solution a large proportion of the aldehyde is converted into the semiacetal at equilibrium, but no detectable amount of the acetal is formed. As the screening of the reacting polar groups increases, the rate of reaction and the proportion of semiacetal formed at equilibrium diminish (cf. preceding abstract). The formation of a hydrate when propaldehyde is dissolved in water apparently takes place instantaneously. The optical data show that the hydrates and alcoholates of the simple aliphatic aldehydes are true valency compounds and not merely loose molecular compounds. R. CUTHILL.

Salt and medium effects on the temperature coefficient of velocity of decomposition of diacetone alcohol. G. M. MURPHY (J. Amer. Chem. Soc., 1931, **53**, 977—981; cf. Åkerlof, A., 1928, 716, 485, 137).—The velocity of the decomposition in 0·01—0·1M-sodium hydroxide, 0·05M-sodium hydroxide + 0—1·0M-sodium chloride, and 0·1M-sodium hydroxide in 0—60% aqueous methyl alcohol has been determined at 20°, 25°, 30°, and 35°. The temperature coefficient is independent of the concentration of sodium hydroxide alone and of that of the hydroxide–chloride mixtures. The energy of activation is computed to be 18,000 g.-cal. The temperature coefficient increases with increasing concentration of methyl alcohol. J. G. A. GRIFFITHS.

Influence of solvent on the decomposition of trichloroacetic acid. J. N. PEARCE and A. C. NELSON (Proc. Iowa Acad. Sci., 1929, **36**, 251—260).—The decomposition of trichloroacetic acid to chloroform and carbon dioxide is unimolecular in water, aniline, and mixtures of aniline with chloroform or toluene. Measurable decomposition does not occur in methyl alcohol, ethyl alcohol, chloroform, toluene, or pyridine. The reaction is accelerated by light. Only in aniline or in aniline (87·5 mol.-%) + chloro-

form is the effect of light considered to be photocatalytic. The velocity coefficients calculated from the heats of activation by the equations of Dushman and of Lewis are not in accord with those determined.

CHEMICAL ABSTRACTS.

Kinetic analysis of α-bromobutyric acid. R. AHLBERG (Svensk Kem. Tidskr., 1931, **43**, 69—74).—A repetition of the work of Senter and others on the hydrolysis of α-bromobutyric acid (cf. J.C.S., 1909, **95**, 1831; A., 1918, i, 250). The rate of hydrolysis of an aqueous solution of the barium salt at 25·2° has been studied. The results indicate that two different unimolecular reactions are involved, one of which proceeds 500 times as rapidly as the other; in two series of experiments 5% and 9%, respectively, of the acid was used in the faster reaction. The acid employed was prepared from the ordinary butyric acid of fermentation, and it is pointed out that in contradistinction to Fischer's statement such an acid is not suitable for the preparation of α-bromobutyric acid where a perfectly pure product is required.

H. F. HARWOOD.

Non-enzymic reduction of methylene-blue. F. LIEBEN and E. MOLNAR (Biochem. Z., 1931, **232**, 209—217).—Glycine does not reduce methylene-blue, but, like alanine, inhibits the deepening of the colour of the methylene-blue by dilute sodium hydroxide. The effect can be reproduced by use of an inorganic buffer. The anaerobic reducing powers of a number of carbamide and guanidine derivatives are examined. The reducing power is often increased by a CO and inhibited by a CH_2 group; cyclic substances reduce more quickly than the corresponding open-chain substances, and guanidine derivatives more quickly than the corresponding carbamide compounds.

P. W. CLUTTERBUCK.

Furfuraldehyde; properties, preparation, and industrial applications. B. GROTH (Svensk Kem. Tidskr., 1931, **43**, 23—42).—A description is given of the chemical and physical properties of furfuraldehyde, and of its technical production and uses. In the production of furfuraldehyde by heating acid solutions of pentoses, the yield obtained increases with the dilution of the original solution, and at infinite dilution would coincide with the value calculated theoretically on the assumption that the reaction is unimolecular. The maximum yield is nearly independent of the temperature and p_H value of the liquid, but depends largely on the concentration of the pentose. The production of by-products appears to be a bimolecular reaction, a fairly satisfactory coefficient being obtained in this case for pentose solutions of widely different concentrations. The decomposition of furfuraldehyde was investigated by heating it in an autoclave at 150—170° with buffered solutions. The rate of decomposition increases with the hydrogen-ion concentration in solutions of $p_H<2$, and with the hydroxyl-ion concentration where $p_H>6$; for the intermediate values a maximum is attained at about p_H 3·5. In solutions of $p_H<1{\cdot}5$ the reaction is unimolecular, provided that the solution does not contain large quantities of neutral salts, sugar, etc., as these considerably accelerate the rate of decomposition; in alkaline solution the reaction is possibly bimolecular.

H. F. HARWOOD.

Instability of colloidal powders. H. MURAOUR (Bull. Soc. chim., 1931, [iv], **49**, 276—279).—A discussion between the author and de Bruin.

F. J. WILKINS.

Influence of moisture on the rate of combustion of colloidal powders. H. MURAOUR (Bull. Soc. chim., 1931, [iv], **49**, 268—274).—The presence of moisture decreases the rate of combustion of colloidal powders, such as cellulose nitrate. It is suggested that this effect is to be attributed to the comparatively large amount of heat required to vaporise the moisture. This theory provides a satisfactory quantitative explanation of the phenomenon.

F. J. WILKINS.

Kinetics of a type of heterogeneous reactions. Mechanism of combustion of pulverised fuel. S. P. BURKE and T. E. W. SCHUMANN (Ind. Eng. Chem., 1931, **23**, 406—413).—A mathematical treatment is given of a highly exothermic reaction between a finely-divided reacting solid suspended in a reacting fluid medium, the products of reaction being totally fluid. The theory is applied to the combustion of pulverised solid fuel, employing only fundamental physical constants, such as coefficients of thermal conduction and diffusion, and the results are in agreement with published experimental data. The theory involves the hypothesis of a stagnant film of gas surrounding the burning particle, leading to the conclusion that combustion takes place by diffusion only. The effects of pressure, temperature, density, and size of the particle, ash content, formation of carbon monoxide, reactivity of carbon, content of volatile matter, and motion of fuel particles during combustion are discussed in the light of the theory and the conclusions reached are shown to be in agreement with experimental results. The peculiar motions of the particles predicted by the theory are confirmed by photographic records.

E. S. HEDGES.

Theory of corrosion [of metals]. E. MAASS and E. LIEBREICH.—See B., 1931, 298.

Principles of corrosion. G. MASING.—See B., 1931, 298.

Corrosion of metals. T. KUCZYŃSKI and M. SMIAŁOWSKI (Przemysł Chem., 1931, **15**, 52—61, 99—104).—Duffek's method (Korrosion u. Metallsch. Beih., 1929, 32) whereby the resistance to corrosion of a metal is measured as a function of the *P.D.* between the metal and a mercury electrode immersed in the same solution, does not yield good results. Tödt's method (Korrosion u. Metallsch., 1929, **5**, 169), depending on the measurement of the current flowing between the metal and a platinum electrode, gives better results, which are not, however, entirely trustworthy in every case. The most important factors in the corrosion of metals immersed in alkali chloride solution are the velocity of diffusion of oxygen to the cathodic parts of the metal surface, and the catalytic properties of these surfaces, depending on their ability to activate oxygen; platinum surfaces activated oxygen to a smaller extent than other metals examined, with the exception of tin. The quantity of current flowing between the metal and the platinum electrode was unaffected by the presence of quinoline, brucine, mannitol, and sodium arsenite in the solution, whilst 0·5% potassium cyanide considerably reduced

the current, acting probably as an anticatalyst. Measurements of the current flowing between a carbon cathode and a metal anode in alkali chloride solution under various conditions show that the deviations found from Ohm's law diminish with increasing density of current, and are ascribed to the resistance due to the formation of deposits on the anode. The velocity of dissolution of metals connected with a non-polarising cathode is expressed by $I=\chi(E'_a-E_a)/C+X_\chi$, where I represents density of current in amp., χ is the conductivity of the electrolyte, E'_a and E_a are the $P.D.$ at the anode during the passage of the current and with the circuit open, X is the additional resistance due to the deposit on the anode, and C is the resistance capacity of the cell.

R. TRUSZKOWSKI.

Mechanism of retardation of corrosion [of iron] by colloids. W. BECK and F. VON HESSERT (Z. Elektrochem., 1931, **37**, 11—20).—Friend's observation (J.C.S., 1921, **119**, 932; 1922, **121**, 466) that the rusting and corrosion of iron in water and aqueous solutions of acids are retarded by hydrophilic colloids has been confirmed, and it has been found that the protective action is a function of both the concentration and nature of the colloid. The retardation cannot, however, be explained by simple adsorption of the colloid on the metal, but seems rather to be the result of the deposition of a film of colloid on the metal by local coagulation brought about by iron ions. This view receives support from the observation that if the metal is vigorously shaken in contact with the acid solution the protective action is small or even absent.

R. CUTHILL.

Action of oxygen on the corrosion of iron and steel in aqueous solution. H. ENDO and S. KANAGAWA.—See B., 1931, 351

Resistance to corrosion of chromium–nickel–iron alloys [with reference to Tammann's theory of limits of resistance]. E. WELLMANN (Z. Elektrochem., 1931, **37**, 142—156; cf. Guertler and Ackermann, B., 1928, 753).—The corrodibility of alloys of chromium, nickel, and iron has been studied in relation to composition and temperature, the attacking substances being sulphur dioxide, hydrogen sulphide, sodium hypochlorite, phenol, tartaric acid, and citric acid. Sulphur dioxide causes oxidation with liberation of sulphur, the effect being noticeable between 350° and 400° and increasing rapidly with rise of temperature in all except nickel-free alloys with 22% Cr, which are resistant below 600°. Admixture of air or steam increases the corrosion. All alloys are corroded by hydrogen sulphide above 300°, the presence of chromium affording some degree of protection at temperatures below 500°. Hypochlorite with 1% of active chlorine is without action, whilst that with 4% attacks binary alloys of iron and chromium, the chromium going into solution and the iron forming rust. Ternary alloys of the type of "V_2A" steels are completely unattacked even when the hypochlorite contains iron. Aqueous phenol corrodes only binary chromium-free alloys. Chromium acts as a protective against attack by tartaric or citric acid when present in greater proportion than 12·5 at.-%.

F. L. USHER.

Kinetics of the combination of hydrogen and oxygen; influence of iodine. W. L. GARSTANG and C. N. HINSHELWOOD (Proc. Roy. Soc., 1931, **A**, **130**, 640—654).—The surface reaction between hydrogen and oxygen in porcelain and silica vessels was accelerated by iodine, the gas reaction was retarded at relatively high temperatures and pressures, whilst the explosion which normally occurs between certain limits of pressure was inhibited. The quantities of iodine necessary are small. Water vapour lowers the upper critical limit of the low pressure explosion region, and, if present in sufficient amount, inhibits the explosion altogether. The results of an investigation of the effect of pre-treatment of the vessel with hydrogen or oxygen agree, so far as the direction of the effect is concerned, with the experiments of Alyea and Haber (A., 1930, 1255), but the magnitude of the effect is much smaller. In the region of high temperature and pressure where the inhibiting action of iodine is observed it is calculated that the efficiency of collisions with iodine in breaking chains is less than about 10^{-4}. Commercial hydrogen contains no inhibiting substances.

L. L. BIRCUMSHAW.

Catalytic action of hydrogen on the carbon monoxide flame. W. E. GARNER, D. A. HALL, and F. E. HARVEY (J.C.S., 1931, 641—653).—The influence of dimensions of the explosion vessel, the addition of inert gases, etc. has been studied on the position and magnitude of the step on the curves showing the relation between the radiation from the flame and the percentage of hydrogen. The position of the step is unaffected by the length or the diameter of the vessel or the direction in which the radiation is measured, which suggests that it is due to changes in the chemical phenomena occurring in the flame and not to wave phenomena set up by it. The addition of carbon monoxide or oxygen in excess to the hydrogen-free flame does not affect the position of the step and, therefore, the hypothesis put forward previously that the position of the step is determined by the relation, $k=p_{H_2}.p_{CO}$ is amended to $k=p_{H_2}.p_{CO_2}$ (cf. A., 1930, 1379).

F. J. WILKINS.

Determination of catalytic coefficients from isocatalytic data. H. M. DAWSON and E. SPIVEY (Proc. Leeds Phil. Soc., 1931, **2**, 174—177).—The catalytic activity of a mixture of a moderately strong acid with one of its salts is, for a given acid concentration, minimal for a certain salt concentration, and from the composition of this "isocatalytic" mixture and the corresponding velocity the catalytic coefficients of the undissociated acid and its anion may be calculated. Calculations of this kind have been made with data for the iodine–acetone reaction in presence of sodium acetate and acetic acid at 25°.

R. CUTHILL.

Mechanism of iron catalysis in certain oxidations. C. V. SMYTHE (J. Biol. Chem., 1931, **90**, 251—265).—The results of determinations of the rate of oxidation of ferrous sulphate in presence of pyrophosphate and of metaphosphate at different hydrogen-ion concentrations confirm the view that the ferrous iron is oxidised in the form of a non-ionised complex, the effect of p_H on the oxidation being exerted only indirectly through its effect on the stability of the

complex. The catalytic effect of ferrous iron on the oxidation of organic acids such as citric acid or tartaric acid has been investigated and a detailed mechanism for the reaction is proposed.

W. O. KERMACK.

Catalytic decomposition of sodium hypochlorite solutions. III. Promoter action of hydrated magnesium oxide in the hydrated copper oxide catalysis of sodium hypochlorite. J. R. LEWIS (J. Physical Chem., 1931, **35**, 915—919; cf. A., 1928, 376).—Data showing the promoter action of hydrated magnesium oxide on the hydrated copper oxide catalysis of the decomposition of sodium hypochlorite are recorded. The maximum promoter action occurs when the ratio copper : magnesium is 1 : 3 or 4, but the effect disappears when this ratio is 1 : 8. The promoter preserves the activity of the catalyst by preventing agglomeration of the particles; this view is supported by the fact that in the catalyst most effectively promoted the colour of the hydrated copper oxide remains unchanged, which is not the case when the promoter is absent. L. S. THEOBALD.

Autoxidation of phosphorus dissolved in carbon tetrachloride. B. BLASER (Ber., 1931, **64**, [*B*], 614—619).—Finely-divided phosphorus suspended in carbon tetrachloride rapidly absorbs oxygen with strong phosphorescence and separation of a voluminous pale yellow precipitate. The rate of reaction depends greatly on the temperature and, apparently, on uncontrollable catalytic influences. Independently of the use of an excess of phosphorus or oxygen, the ratio P : O is very nearly 2 : 3 and, since the product differs completely from phosphorous oxide, the structure $(P_2O_3)_x$ must be ascribed to it. The compound inflames immediately when brought into contact with water, but cautious decomposition of it suspended in carbon tetrachloride yields a strongly-reducing aqueous solution which has an odour of phosphine and slowly deposits a yellow precipitate of phosphorus suboxide. It is relatively stable in a vacuum at 100° and does not appear to be affected by light.

H. WREN.

Quantum mechanics of adsorption catalysis. M. BORN and V. WEISSKOPF (Z. physikal. Chem., 1931, **B**, **12**, 206—227).—From the point of view of quantum mechanics the function of a catalysing surface is to keep the reactants in contact long enough for the probability of their surmounting the energy hill lying between the initial and final states to reach a maximum. If the surface itself takes part chemically in the reaction, it may be supposed that there is an energy hill between the adsorbed molecule and the atom of adsorbent, which is surmounted in the course of the sojourn of the molecule on the surface, a secondary reaction thus becoming possible. Whilst it is admitted that these two processes may not be essential in every case of adsorption catalysis, and that such factors as the resolution of primary linkings under the influence of adsorption forces may often be of prime importance, quantum mechanical theory has been used to deduce the reaction velocity in an adsorbed system as a function of its mechanical properties and the properties of the adsorbent (cf. this vol., 318). R. CUTHILL.

Combination of carbon monoxide with oxygen at mixed oxide catalysts. B. NEUMANN, C. KRÖGER, and R. IVANOVSKI (Z. Elektrochem., 1931, **37**, 121—128).—The effect of varying the composition of mixtures of manganese dioxide with cobalt oxide, nickel oxide, and silver oxide, and of silver permanganate with nickel oxide, on their catalytic activity in promoting the combination of carbon monoxide with oxygen has been studied at different temperatures. The relation between activity and composition depends on the temperature; *e.g.*, addition of 33% of cobalt oxide (Co_3O_4) to manganese dioxide depresses the activity of the latter at 50°, but increases it at 60°. At a given temperature the activities of the individual oxides are in the same order as their dissociation pressures. The function of the oxides is chemical, and their relative activities are not determined by the total amount of the reacting gases adsorbed. F. L. USHER.

Reactions at the surface of hot metallic filaments. V. Reaction $H_2+CO_2\longrightarrow CO+H_2O$ at the surface of platinum, platinum coated with barium oxide, and thoriated tungsten. B. S. SRIKANTAN (Indian J. Physics, 1930, **5**, 685—698; cf. A., 1930, 1531).—An apparatus for the investigation of electron emission from prepared filaments is described; the minimum temperature of perceptible emission obtained by extrapolation is that required to start the interaction of carbon dioxide and hydrogen on these surfaces, and for the activation of hydrogen. The effect of varying the proportions of the gases is considered. Carbon dioxide, on a barium oxide-coated platinum filament as more conducive to adsorption, is activated at a lower temperature. The temperature of oxidation of methane at the platinum surface was that of minimum electron emission. It is concluded that the activation of gases at a catalytic surface depends largely on the ability of the surface to emit electrons at that temperature.

N. M. BLIGH.

Catalytic conversion of gases containing methane into carbon monoxide and hydrogen. K. KELLER and W. KLEMPT.—See B., 1931, 325.

Conversion of carbon monoxide by means of steam or air into hydrogen or nitrogen–hydrogen mixtures. K. KELLER and W. KLEMPT.—See B., 1931, 326.

Catalytic decomposition of carbon disulphide by steam. B. NEUMANN and E. ALTMANN (Z. Elektrochem., 1931, **37**, 173—185).—The reaction between carbon disulphide and steam is catalysed by many substances. Copper, gold, and platinum catalysts, chromic oxide, and a mixture of the oxides of copper, lead, and chromium in molecular proportions are most effective at about 600° and the maximum yield of hydrogen sulphide is about 65%. Oxides of barium, calcium, magnesium, and aluminium are most effective at about 450° and the maximum yield of hydrogen sulphide is 77%. Thorium dioxide and cerium dioxide are most active at about 300° and the yields obtained are 81 and 87%, respectively. A mixture of magnesium oxide with 10% of thorium dioxide is a very active catalyst, having an optimal temperature of about 350° and giving a 98% yield.

Active carbon gives a 78% yield at 600° and the addition of oxides of magnesium, uranium, or iron does not increase the yield, but the addition of thorium dioxide increases the yield to 87% at 425°. The reaction probably takes the course (1) $CS_2+H_2O=COS+H_2S$, (2) $COS+H_2O=CO_2+H_2S$, and over the range 170—500° the products are as represented by (2). Below 170° the rate of decomposition of the intermediate carbon oxysulphide is greater than its rate of hydrolysis and carbon monoxide and free sulphur appear among the products. The action of the catalyst is probably to form a sulphide with the carbon disulphide vapour, which is then hydrolysed by the steam. The formation of sulphide occurs rapidly, but the subsequent hydrolysis is slow in the case of the heavy metals and more rapid in the case of the alkaline earths, particularly with the mixture of magnesium oxide and 10% of thorium dioxide.

E. S. HEDGES.

Behaviour of the catalyst in carbon monoxide filters. G. STAMPE and F. BANGERT.—See B., 1931, 368.

Catalytic formation of hydrogen cyanide. V. Cerium dioxide as catalyst. G. BREDIG and E. ELOD [with W. KONIG] (Z. Elektrochem., 1931, **37**, 2—11; cf. this vol., 176).—In the formation of hydrogen cyanide from carbon monoxide and ammonia in presence of cerium dioxide as catalyst it is not possible to detect the presence of cerium nitride, hydride, or carbide as an intermediate product, nor does any change occur in the crystal structure or lattice dimensions of the catalyst as a result of the reaction. Contrary to the observations of Lipski (A., 1909, ii, 478), no ammonia is produced by the reaction of metallic cerium with nitrogen and hydrogen unless oxygen is present, and even then reaction ceases when all the cerium has combined to form cerium dioxide. The activity of cerium dioxide in catalysing the formation of hydrogen cyanide runs approximately parallel with its adsorptive power for ammonia, carbon dioxide, and carbon monoxide, the adsorption of which on a given catalyst decreases in this order. It is therefore suggested that the adsorbed ammonia is highly active, perhaps even partly broken up into hydrogen and the NH group, and that similarly the adsorbed carbon monoxide is readily resolved into carbon and carbon dioxide, the formation of hydrogen cyanide occurring by reaction between this free carbon and the NH group.

R. CUTHILL.

Catalytic addition of hydrogen chloride to unsaturated hydrocarbons. W. J. PIOTROWSKI and J. WINKLER.—See B., 1931, 328.

Catalytic reactions of sulphur compounds present in petroleum. J. C. ELGIN and others.—See B., 1931, 327.

Catalytic synthesis of methyl alcohol under pressure. M. FLEURY.—See B., 1931, 385.

Thermal behaviour of phenols. III. Influence of the time of heating and the nature of the accompanying gas. A. HAGEMANN (Z. angew. Chem., 1931, **44**, 221—224).—When phenol vapour is passed over a heated filament about 92% is decomposed; the condensible fraction of the product (63%) contains about 34% of *cyclo*pentadiene and 27% of naphthalene and polymerised *cyclo*pentadienes, and the non-condensible fraction contains carbon monoxide 70·3% and methane 5·9%. In presence of nitrogen or hydrogen the quantity of phenol decomposed is reduced, but the yield of *cyclo*pentadiene is increased, and in the case of hydrogen a considerable quantity of benzene is formed. *m*-Cresol yields *cyclo*pentadiene 2·1%, benzene 14·2%, and toluene 12·8%, calculated on the cresol decomposed. A study of the influence of the rate of flow of the vapour shows that the shorter is the period of heating the higher lies the temperature of initial decomposition. At high filament temperatures the reactions involved are of a photochemical rather than a thermal type. Water vapour and, to a smaller extent, carbon dioxide favour the cracking of the primary decomposition products of pyrocatechol to a greater extent than do nitrogen and hydrogen. In presence of water vapour a 67·5% yield of butadiene has been obtained from pyrocatechol, whereas in presence of hydrogen or nitrogen the yield is only 30—33%.

H. F. GILLBE.

Effect of adding colloids to electrolytic solutions for preparing the anodic film on aluminium. S. SETOH and A. MIYATA.—See B., 1931, 352.

Electrochemical preparation of sodium and lead arsenates. W. A. PLOTNIKOV and M. IVANENKO (Z. Elektrochem., 1931, **37**, 88—91).—By the use of an anolyte containing 150 g. per litre of arsenious oxide as sodium arsenite and a catholyte containing 150 g. per litre of sodium hydroxide, sodium arsenate may be prepared by electrolysis with a current density of 3 amp. per $dm.^2$; the current efficiency is 100%. The process may be rendered continuous by circulating the anolyte and removing the precipitated arsenate. Iron or nickel electrodes are satisfactory, and the diaphragm should be of asbestos cement; although nickel electrodes yield a purer product, iron has the advantage of hindering the formation of arsine. Pure lead arsenate cannot be obtained by simultaneous oxidation of sodium arsenite and anodic dissolution of lead, as the oxidation potential of arsenious oxide and the solution potential of lead differ only slightly. By using an anolyte containing 20 g. of sodium arsenite and 70 g. of sodium nitrate per litre and sufficient acetic acid for neutralisation, and as the catholyte a 30% solution of sodium nitrate, an almost theoretical yield of lead arsenate may be obtained. The anode should be of lead and the cathode of iron, and the current density 5·5—6 amp. per $dm.^2$

H. F. GILLBE.

Electrolytic oxidation of solutions of manganous salts in hydrofluoric acid. L. VON PUTNOKY and B. VON BOBEST (Z. Elektrochem., 1931, **37**, 156—163).—Solutions of manganous sulphate in hydrofluoric acid (4—8%), electrolysed at an anode current density of 0·01—0·04 amp. per $cm.^2$, become at first dark brown owing to the formation of manganic fluoride, and are finally converted into permanganic acid, the yield of the latter reaching 80%. No permanganic acid is detectable in the anode liquid until all manganous ions have disappeared. Quadrivalent manganese cannot be detected at any stage of the

oxidation. Microscopic observation shows that in the initial stage the primary product at the anode is permanganic acid, which diffuses into the solution and immediately reacts with any manganous salt present to give manganic fluoride. The latter is finally directly oxidised to permanganic acid.

F. L. USHER.

Action of electrical discharge on gaseous hydrocarbons. S. C. LIND, B. M. MARKS, and G. GLOCKLER (Trans. Amer. Electrochem. Soc., 1931, **59**, 33—40).—Determinations have been made of the amounts of hydrogen produced by the decomposition of methane, ethane, propane, and butane under the influence of high-speed electrons (125—130 kilovolts) emitted from a Slack–Lenard cathode-ray tube. The number of hydrogen molecules liberated was always about ten times the number of electrons corresponding with the filament current. Assuming that only 1% of these electrons actually enter the reaction vessel, it is estimated that the number of ion pairs produced in the gas is of the same order of magnitude as the number of molecules reacting.

H. J. T. ELLINGHAM.

Electrolytic reduction of dicarboxylic acids. H. NAKATA (Chikashige Anniv. Vol., 1930, 49—55).—By electrolysis of a 10% solution of oxalic acid in $2N$-sulphuric acid with a lead anode and mercury cathode, and a current density of 8·3 amp. per dm.^{2}, at 5—7°, an 88·3% yield of glyoxylic acid is obtained after 6 hrs. The current efficiency is about 88% during the first 2 hrs., but falls to about 37% in the later stages of the reduction. Formaldehyde does not appear among the reduction products, but dihydroxytartaric acid is probably formed. At higher temperatures (60°) the current efficiency diminishes, but the yield of glycollic acid, which is formed directly from the oxalic acid, is increased; the glyoxylic acid produced undergoes immediate reduction. In $6N$-sulphuric acid solution at 60° the glycollic acid yield is further increased. Experiments with various electrodes show that a mercury cathode gives the best yield of glyoxylic acid and a mercury cathode the best yield of glycollic acid. The progress of the reduction in hydrochloric acid solution is almost identical with that in sulphuric acid. The current and material yield may both be raised to nearly 100% by employing a current density of 4·15 amp. per dm.^{2} Malonic and succinic acids are not cathodically reduced in sulphuric acid solution.

H. F. GILLBE.

Study of chemical reactions from potential energy diagrams. A. R. OLSON (Trans. Faraday Soc., 1931, **27**, 69—76).—Potential energy diagrams have been employed to discuss the molecular rearrangement of dichloroethylene. On this basis the effects of temperature, pressure, solvents, and light frequency are considered.

F. G. TRYHORN.

Function of Br_3' and I_3' ions and influence of chlorine ions in oxidation reactions in light. R. M. PURKAYASTHA (J. Indian Chem. Soc., 1931, **7**, 991—996; cf. A., 1930, 718).—The velocity coefficients of the rates of photochemical reaction of mandelic acid and of lactic acid with bromine in the presence of potassium bromide at 30°, are zero-molecular. Whilst the oxidation of hydroxy-acids by bromine is accelerated by chlorine ions in the dark, it is retarded in the light. The light reactions are zero-molecular, but the oxidation of phenyl-lactic acid appears unimolecular on account of the preponderance of the dark reaction. The function of I_3' ions in photochemical oxidations by iodine is discussed.

F. L. USHER.

Photochemical reaction between iodine and hydrogen. N. SASAKI and K. NAKAMURA (Chikashige Anniv. Vol., 1930, 299—302).—No hydrogen iodide is produced when an equimolecular mixture of hydrogen and iodine at 1 atm. pressure and 270° is irradiated by mercury arc light from which radiation of wave-length shorter than 3500 Å. has been removed. Under the action of ultra-violet radiation, using a streaming method, atomic hydrogen is produced in the mixture, probably by the action of excited iodine molecules on the hydrogen molecules, and hydrogen iodide is then formed by combination of atomic hydrogen with molecular iodine.

H. F. GILLBE.

Photo-reaction between hydrogen and iodine monochloride. G. K. ROLLEFSON and F. E. LINDQUIST (J. Amer. Chem. Soc., 1931, **53**, 1184—1185).—The results of Mellor and Iredale (this vol., 180) are not inconsistent with those of the authors (A., 1930, 1135).

J. G. A. GRIFFITHS.

Photosensitised decomposition of nitrogen trichloride. I. T. G. A. GRIFFITHS and R. G. W. NORRISH (Proc. Roy. Soc., 1931, **A**, **130**, 591—609; cf. this vol., 179).—The decomposition of nitrogen trichloride (up to 3 mm.) in chlorine is photosensitised by chlorine, and is a zero-molecular order reaction until decomposition is almost complete, when a semi-explosive reaction occurs. The velocity of the reaction is directly proportional to the light flux absorbed by the chlorine. The quantum efficiency (γ) in homogeneous blue (436 mμ) and ultra-violet (365 mμ) is less than 2° at low pressures of chlorine and decreases with increase of chlorine pressure to the limiting value 2·0 (approx.). The equation $\gamma=1/0{\cdot}0038P_{Cl_2}+2{\cdot}5$ expresses the results quantitatively. No decomposition is produced by the wave-lengths 579 or 546 mμ.

L. L. BIRCUMSHAW.

Photochemical decomposition of nitrous acid. K. S. MURTY and N. R. DHAR (J. Indian Chem. Soc., 1931, **7**, 985—990; cf. A., 1925, ii, 691).—The unimolecular velocity coefficients of the decomposition of nitrous acid by light of wave-lengths 4725, 5650, 7304, and 8500 Å. decrease in the order given. The temperature coefficient of the dark reaction increases from 1·58 (20—30°) to 2·21 (30—40°), whilst that of the light reaction falls below unity in the range 30—50°. Both these effects are explained by the reversibility of the decomposition. The velocity coefficient is proportional to the cube root of the intensity of the incident light. The reaction does not obey the law of photochemical equivalence. Quantum yields for different temperatures and wave-lengths are given.

F. L. USHER.

Photochemical decomposition of carbonyl chloride vapour by ultra-violet radiation of different wave-lengths. F. ALMASY and T. WAGNER-JAUREGG (Naturwiss., 1931, **19**, 270).—Under similar conditions, at 20° the amount of photochemical

decomposition of highly purified carbonyl chloride at 300 mm. produced by light of 2750—3041 Å. was 1/4·2—1/8·7 that produced by the full radiation of the mercury arc lamp. At 160° no increase in decomposition was obtained using the narrower spectral region, whereas there was an increase of 1·8% in decomposition due to the full radiation. The decomposition, therefore, is caused principally by light of shorter wave-lengths (cf. Henri and Howell, A., 1930, 1088).

W. R. ANGUS.

Decomposition of potassium cobaltioxalate and sodium cobaltinitrite by light. W. V. BHAGWAT and N. R. DHAR (Z. anorg. Chem., 1931, 197, 18—28).—The temperature coefficient of the decomposition of potassium cobaltioxalate is 1·13 in sunlight, 1·85 in tungsten lamp radiation, and 3·7 in the dark, and that of sodium cobaltinitrite is 1·56 in sunlight and 2·7 in tungsten lamp radiation. Both reactions are strongly accelerated by short wave-length radiation. In sunlight the decomposition of potassium cobaltioxalate is a reaction of zero order, and the velocity is proportional to the square root of the intensity of the radiation, but in tungsten lamp radiation the linear relationship holds; the velocity coefficient in sunlight increases with increase of concentration of the solution. The quantum yield in unity in sunlight, but is less in tungsten lamp radiation; it increases with rise of temperature. The decomposition of sodium cobaltinitrite in sunlight is a semimolecular reaction, and the velocity is independent of the concentration; Einstein's law is invalid. Both reactions are unimolecular in tungsten lamp radiation. The following general equation has been derived for the velocity of a photochemical reaction: $dx/dt=KS^{n-1}I_0^n(1-e^{-il(a-x)^n})/l$, where S is the surface area exposed to radiation of intensity I_0, n is the order of the reaction, i is the molecular absorption coefficient, and K is a constant. It is shown theoretically that, in accordance with observation, n may vary from 0 to 1 and is related inversely to the quantity of light absorbed.

When prepared by Sorensen's method potassium cobaltioxalate contains 10 mols. of water, and not 3 mols. as reported by Sorensen. The absorption spectrum of the compound exhibits pronounced maxima at 6050 and 4250 Å. H. F. GILLBE.

Chemical origin of the colour changes of silicate and quartz glasses under the influence of radium radiation. J. HOFFMANN (Z. anorg. Chem., 1931, 197, 29—51).—The production of a grey coloration when various types of glass are subjected to the action of radium radiation is a complex process and is due to both atomic and ionic changes. A blue colour is produced in silicate glasses only when tervalent manganese is present; contrary to previous reports, sodium atoms cannot cause the effect. [Ra]dium or ultra-violet radiation thus affords a sensitive reagent for the manganic ion, although the blue colour fades after a time to a stable amethyst colour. The occurrence of multi-coloured parallel lines in irradiated glasses is ascribed to phase segregation. The brown coloration of glasses ascribed by Salaquada to iron and manganese can be caused only by manganous ions. The violet coloration of quartz glass is produced by ferrous and ferric ions in presence of titanium. H. F. GILLBE.

Relation between density, silver content, covering power, grain distribution, and grain size of developed photographic films. H. ARENS, J. EGGERT, and E. HEISENBERG (Z. wiss. Phot., 1931, 28, 356—366).—The relation $s=-x\log(1-ya)$ is theoretically deduced (cf. Nutting, Phil. Mag., 1913, 26, 423), where s=density, x=the number of grain layers, y=the number of grains per cm.^{2} of a one-grain layer, and a=the mean projection of a grain, in cm.^{2} The formula is experimentally proved for a one-grain layer. For many layers (*e.g.*, 20) in a film, the approximation $s-za/2\cdot3$ is obtained, where z=the number of grains per cm.^{2} of the whole film. The relation $\delta=k(f/d^{\frac{2}{3}})\mu^{-\frac{1}{3}}$ is calculated, where δ=covering power, d=the density of a grain, μ=the weight of a grain, and f is a factor dependent on the shape of the grain. Experimental results are compared; silver grains by physical development (d 10·5) give f 2·6, corresponding with crystalline leaflets, but by chemical development are probably spongy colloidal masses.

J. LEWKOWITSCH.

Separate [processes in] ripening. LÜPPO-CRAMER (Z. wiss. Phot., 1931, 28, 350—356).—By using 50% excess of bromide at emulsification, and no ripening, an emulsion may be prepared having large grains, but with small content of sensitive nuclei; its characteristic curve is very flat. $D_{max.}$ is small and does not increase with exposure. If plates are treated with Capri-blue solution, they are sensitised and give comparatively normal curves. The ripened emulsion is normal. The grain size of the unripened emulsion is unaltered by increase of the amount of gelatin present at emulsification (the final gelatin addition being reduced in proportion). The properties of fine-grain emulsions are compared. Grain growth and the formation of sensitive nuclei may be considered separately in relation to ripening processes.

J. LEWKOWITSCH.

Photonegative effect on [the conductivity of] silver bromide. E. A. KIRILLOV (Z. wiss. Phot., 1931, 28, 367–373; cf. A., 1929, 276).—After illumination (430 mμ) of silver bromide, its conductivity, measured in the dark, shows at first a decrease, superseded by an increase, which, in course of time, again slowly decreases. The primary negative effect is enhanced by previous treatment with sodium nitrite (photographic sensitiser), and inhibited by picric acid (desensitiser) which causes an immediate increase of conductivity on illumination of the silver bromide. Hence photonegative sensitivity is comparable to photographic sensitivity. Measurements of the resistance of silver bromide, by a method eliminating the influence of polarisation, show that it increases markedly after illumination. J. LEWKOWITSCH.

Different forms of silver bromide. A. REYCHLER (Bull. Soc. chim. Belg., 1931, 40, 12—17).—By placing a glass plate in a solution of silver nitrate rendered faintly turbid with potassium bromide solution an adherent deposit of silver bromide is formed within 15—20 hrs., and the plate behaves normally as regards exposure to light and development. By immersing a filter-paper in a similar turbid solution

it is readily sensitised; the time required for exposure to light is very short, and the resulting image after development, is clear and may be viewed from either side of the paper. The turbid solution is reduced immediately by an ordinary photographic developer, without previous exposure to light, on account of the fineness and reactivity of the silver bromide particles; this activity diminishes as the suspension ages, *e.g.*, during deposition on the plate or paper, and it is suggested that the action of light is to arrest this ageing process or to restore the initial condition of the halide. Experiments on the addition of gelatin to a silver bromide suspension demonstrate the mutual affinity of the halide and the gelatin, and indicate that after the micelles are formed the bromide associates to produce the form which is not reduced by a developer without exposure to light.

H. F. GILLBE.

Determinations on the size-frequency distribution of residual (undevelopable) grains of a photographic emulsion. E. C. JENSEN and A. P. H. TRIVELLI (J. Franklin Inst., 1931, **211**, 489—494).—An attempt to correlate exposure with the size-frequency distribution of residual grains has been unsuccessful. The log log frequency–size curves resemble parabolas, but the shape varies and shifts with the exposure in such a way as to preclude the existence of any simple relation.

J. LEWKOWITSCH.

Secondary reactions in latent image formation. Influence of free alkali halide. T. S. PRICE.—See B., 1931, 367.

Hydrolysis of acetone in ultra-violet light. M. QURESHI and N. A. TAHER (Nature, 1931, **127**, 522).—In the hydrolysis of acetone in ultra-violet light the velocity of reaction is directly proportional to the intensity of the incident light. Formaldehyde is also formed when an aqueous solution of acetone is exposed to the light of a quartz mercury lamp (cf. Bowen and Watts, A., 1926, 808).

L. S. THEOBALD.

Influence of wave-length in the irradiation of ergosterol. E. KISCH and T. REITER (Deut. med. Woch., 1930, 2034—2036; Chem. Zentr., 1931, i, 479).—The formation of malodorous products in the irradiation of milk and of inconstant products in that of ergosterol is avoided by using radiation of wave-length greater than 2800 Å.

A. A. ELDRIDGE.

Effect of radiation energy on the protein molecule. J. P. MISCHTSCHENKO (Strahlenther., 1928, **30**, 707—719; Chem. Zentr., 1930, ii, 3787).—Sunlight decomposes protein of low mol. wt.; eventually Bach's nitrate reaction for fission products fails. Peptone, nutrose, and horse serum are unaffected. Certain proteins suffer change in the dark; the change is much more rapid in sunlight. Protein of high mol. wt. is not decomposed by *X*- or radium rays in the doses employed; large doses cause in fresh solutions of proteins of low mol. wt. immediate diminution, in aged solutions almost always a diminution, of fission products, whilst small doses cause in fresh solutions an increase in fission products. Experiments on extracts of organs showed that the tissues can be grouped according to their content of protein fission products.

A. A. ELDRIDGE.

Photochemical decomposition of nicotine salts. I. PLOTNIKOV and K. WEBER (Chem.-Ztg., 1931, **55**, 237—239).—The decomposition of nicotine and nicotine salicylate, tartrate, and malonate solutions under the influence of prolonged exposure (up to 1 year) to sunlight, with or without catalysts (photo-active substances), has been studied. The best catalysts were dichromates, gold chloride, ferric nitrate, iodine, and chlorophyll; up to 85% decomposition was found. Experiments on tobaccos exposed to an arc lamp up to 8 days give lower and fluctuating results; the catalysts are difficult to apply in these cases.

J. LEWKOWITSCH.

Radiochemical equilibrium in mixtures of ammonia, nitrogen, and hydrogen. J. F. D'OLIESLAGER and J. C. JUNGERS (Bull. Soc. chim. Belg., 1931, **40**, 75—84).—The velocity of formation and decomposition of ammonia under the influence of α-rays at 24° has been investigated as a function of the pressure. The equilibrium mixture contains 4·7 vol.-% NH_3 when the other gases are present in stoicheiometric proportions. At constant pressure (500 mm.) the velocity of the reaction increases at first rapidly, then more slowly, and finally at an increasing rate as the concentration of the ammonia increases beyond the equilibrium point. The low value of the equilibrium concentration, compared with that calculated theoretically, is probably connected with the abnormal concentration of ammonia in the neighbourhood of each ion, due to the high dipole moment of ammonia.

H. F. GILLBE.

Solid polyiodides of potassium. N. S. GRACE (J.C.S., 1931, 594—609).—The effect of moisture on the m. p. of iodine–potassium iodide mixtures has been studied. The results suggested that potassium tri-iodide prepared from aqueous solution contained chemically combined water, and, moreover, that only the hydrated form was stable. This suggestion was confirmed by an investigation of the more concentrated solutions of the system iodine–potassium iodide–water which showed that at 25° the solid *hydrated iodides* KI_3,H_2O and KI_7,H_2O exist; no anhydrous polyiodide can be formed at this temperature. A study of the system iodine–potassium iodide–benzene indicated the formation of the *solvated hepta-iodide*, $KI_7,2C_6H_6$.

F. J. WILKINS.

Hypothetical potassium polyiodides. W. D. BANCROFT, G. A. SCHERER, and L. P. GOULD (J. Physical Chem., 1931, **35**, 764—785).—Mainly a discussion. Solid potassium tri-iodide does not occur as a stable phase at 25°; potassium iodide and iodine are the only solid phases which can be stable at this temperature. *X*-Ray measurements [by H. M. SOUTHWORTH] afford no evidence for the existence of potassium tri-iodide.

L. S. THEOBALD.

Chemical reactivity of the fused bases. I. Action of alkali amides on electropositive metals. W. C. FERNELIUS and F. W. BERGSTROM (J. Physical Chem., 1931, **35**, 740—755).—The reactions of the electropositive elements with fused potassamide at 375—400° are, in general, similar to the same reactions in liquid ammonia at the ordinary temperature. Magnesium, calcium, and aluminium form initially the free alkali metal which colours the fused mass blue.

Magnesium, beryllium, zinc, and calcium dissolve in the amide to give compounds of the type $M''(NHK)_2,2NH_3$ or $M''NK,2NH_3$; aluminium gives a white or grey mass insoluble in the fused mass and of indefinite composition, whilst germanium appears to be converted into a mixture of the compounds NGe·NHK and $Ge{:}NK,NH_3$. Mercury itself is apparently unattacked, but dissolves in the potassium which results from the slow decomposition of the amide into its elements. Cerium, thorium, cadmium (very slight), and manganese are only slightly attacked, and copper, thallium, titanium, zirconium (powder), tantalum, chromium, nickel, platinum, and iridium are not attacked after fusion for several hours. At 400° in fused sodium hydroxide, sodium dissolves to a slight extent, giving a blue colour to the fused mass, magnesium gives a blue colour around the strips of metal and then dissolves in a short time, whilst calcium, in an atmosphere of nitrogen, reacts to form a blue mass and ultimately a white precipitate, insoluble in the fused mass. Aluminium wire is apparently unattacked during 5 hrs.' treatment.

L. S. Theobald.

Action of sulphuric acid on copper. F. de Chaves (Anal. Fís. Quím., 1931, 29, 177—181).—By the action of concentrated sulphuric acid at 55° on copper there result, after 6 days, anhydrous cupric sulphate, free sulphur, sulphur dioxide, and a black deposit which contains Cu 69·73%, S 8·5%; the black substance yields sulphate ion on dissolution in hydrochloric acid. Its composition differs markedly from that of any natural or artificial substance previously reported, and it appears to be a more highly basic cupric sulphate than has been hitherto described.

H. F. Gillbe.

Carbonyls of copper halides. O. H. Wagner (Z. anorg. Chem., 1931, **196**, 364—373).—By the action of carbon monoxide on cuprous chloride and bromide at pressures up to 100—150 atm. the existence of $Cu_2Cl_2,2CO$ and $Cu_2Br_2,2CO$ has been established; the analogous iodide probably exists, but its formation takes place very slowly. Although the presence of water is not essential, it appears to have some catalytic influence on the progress of the reaction. Cuprous oxide or cyanide, or mixtures of copper and cupric sulphate, do not react with carbon monoxide. Vapour-pressure measurements show that equilibrium is established only very slowly; the vapour pressure of $Cu_2Cl_2,2CO$ attains 760 mm. at about 40° and that of $Cu_2Br_2,2CO$ at about 10°. The log p-$1/T$ curve is linear at temperatures above —20°, and the calculated mean heats of dissociation of the chloride and bromide complexes are 9·8 and 8·2 kg.-cal., respectively. The stability of these halide compounds follows the same order as that of the copper, silver, and gold ammoniates. Analogous silver complexes could not be prepared.

H. F. Gillbe.

Hydroxylamine as a precipitation agent. II. J. C. Roldan (Anal. Fís. Quím., 1931, 29, 158—161).—The precipitate resulting from the action of hydroxylamine on a solution of a cupric salt (A., 1930, 1547) is converted into the white form more rapidly in presence of an excess of copper, and is redissolved to a colourless solution by an excess of the reagent. Copper ferrocyanide is not formed in presence of hydroxylamine, but a white colloidal compound is slowly precipitated and the solution becomes orange-yellow and fluorescent; ammonia destroys the fluorescence. These results vary with the quantities and order of addition of the reagents. Hydroxylamine inhibits the precipitation of uranium ferrocyanide within certain concentration limits. H. F. Gillbe.

Thermal decomposition of silver subfluoride. R. Scholder and K. Traulsen (Z. anorg. Chem., 1931, **197**, 57—64).—Contrary to the report of Hettich (A., 1927, 1155), fluorine is not evolved when silver subfluoride is heated. The primary decomposition, which takes place at 100—150° is $Ag_2F=AgF+Ag$, and in presence of moisture this is followed by $4AgF+2H_2O=4Ag+4HF+O_2$. When silver subfluoride is heated in dry nitrogen or oxygen at 700°, there is a slow and progressive loss of weight, amounting to about 5% after 66 hrs., which is ascribed to volatilisation of silver fluoride. The subfluoride is partly re-formed when the mass is cooled. Silver subfluoride is slightly light-sensitive. H. F. Gillbe.

Composition of the cyanide complex radical of metals. II. Cadmium cyanide complex. K. Masaki (Bull. Chem. Soc. Japan, 1931, **6**, 60—64).—A simple titration method for the determination of the ratio of combined cyanide to cadmium in the complex ion has shown that the ion is probably $Cd(CN)_3'$ at all concentrations. The constant $K=[Cd(CN)_3']/[Cd''][CN']^3$ is evaluated as $5{\cdot}4\times10^{17}$.

E. S. Hedges.

Principles of genetic formation of substances. V. Chemistry and morphology of aluminium hydroxide. II, III. V. Kohlschutter [with W. Beutler] (Helv. Chim. Acta, 1931, **14**, 305—330, 330—354; cf. this vol., 444).—II. Three forms of aluminium hydroxide, α, β, and γ, have been recognised among the products of reaction of aluminium amalgam with water. None of these forms has a measurable solubility in conductivity water and the hydrogen-ion concentration of the liquid does not change during the reaction. The slight development of alkalinity which is observed when aluminium amalgam reacts with sodium chloride solution is due to an exchange reaction between the hydroxide and sodium chloride. Aluminium is also rendered active towards water by cathodic polarisation. The primary product of reaction of an aluminium cathode with water is α-aluminium hydroxide, which undergoes further transformation into the β- and γ-forms, depending largely on the nature of the foreign substances present, and the continuance of the reaction is due to the electrostatic repulsion of the negatively-charged hydroxide from the cathode. No evidence was obtained that the activation is due to an increase in the concentration of electrons in the metal, according to the theory of Smits. Experiments are described on the precipitation of aluminium hydroxide by mixing solutions of aluminium chloride or potassium or ammonium alum with solutions of sodium hydroxide or ammonia in such concentrations that suspensions containing about 0·1 g. of aluminium hydroxide per 100 c.c. were obtained. When equivalent quantities of the reagents were mixed the suspension always had an alkaline reaction, due to exchange adsorption.

The forms of aluminium hydroxide and basic salts produced in each case are described; increasing concentrations of ammonia solution accelerate the α–β transformation. When aluminium hydroxide was precipitated in the presence of alkali chlorides the precipitate had different properties in each case, but no simple correlation with the lyotropic series of cations was apparent; the greatest difference was produced by the presence of lithium chloride and the precipitate apparently contained lithium aluminate and basic salts. Aluminium hydroxide precipitated from more concentrated solutions of the reagents was less reactive. The properties of aluminium hydroxide prepared by the action of ammonia solution on crystals of ammonium alum are described. *X*-Ray spectrographic examination has established the presence of bauxite lines in the spectrum from the β-pseudomorph, whilst the γ-pseudomorph gives a bayerite spectrum; electrolytically prepared aluminium hydroxide gives an amorphous spectrum. The forms of aluminium hydroxide precipitated from aluminate solutions by ageing and by the addition of reagents are described.

III. Independently of the method of preparation, γ-aluminium hydroxide is always observed under the microscope to be in a somatoid form. *X*-Ray examination shows these to consist partly of amorphous material and partly of crystalline material giving a spectrum containing the lines of bayerite. The processes of gelation and syneresis enter into the formation of these structures. The results of a microscopical study of their forms of aggregation are described.

E. S. HEDGES.

Preparation of active aluminium chloride. K. BODENDORF (J. pr. Chem., 1931, [ii], **129**, 340).—Highly activated aluminium chloride for Friedel–Crafts reactions may be prepared *in situ* by passing dry hydrogen chloride into a boiling suspension of 5 g. of aluminium powder in 100 c.c. of benzene, toluene, or xylene, containing 1 g. of mercuric chloride and 0·5 g. of iodine as catalysts. J. W. BAKER.

Significance of the crystallographic transformations of silica for its reactivity in the solid state. I. Ferric oxide with quartz, tridymite, or cristobalite. J. A. HEDVALL and P. SJÖMAN (Z. Elektrochem., 1931, **37**, 130—142; cf. A., 1930, 1503).—Mixtures of finely-powdered quartz and ferric oxide, both of a high degree of purity, were heated at temperatures from 550° to 1350°, and the products examined by chemical and by *X*-ray analysis. No action occurs below 575°, the transition temperature of β- to α-quartz, at and above which temperature one or more compounds are formed. A similar change takes place more rapidly in the neighbourhood of 950°, corresponding with the conversion of α-quartz into cristobalite. At the higher temperature there is also formed a solid solution of ferric oxide in cristobalite, whereby the length of the unit cell is increased from 6·99 to 7·02 Å. Neither cristobalite nor tridymite reacts *per se* with ferric oxide, and the observed changes must therefore occur during the actual transition from one crystallographic form to another.

F. L. USHER.

Volatility of silica in water vapour. C. J. VAN NIEUWENBURG and H. B. BLUMENDAL (Rec. trav. chim., 1931, **50**, 338).—The statement made previously (A., 1930, 1262) that tridymite passes into cristobalite at 395° and 300 atm. is now corrected. A small amount of cristobalite was always formed under these conditions, but the amount was independent of the duration of the experiment and may have been formed as the initial metastable product from the vapour on cooling. J. W. SMITH.

Cerium sulphide. PICON (Compt. rend., 1931, **192**, 684—686).—Pure cerous sulphide is prepared by passing hydrogen sulphide over ceric oxide contained in a graphite boat for 1 hr. at 1000—1200°, and then for 30 min. at 1550—1600°. It is thus obtained as an apparently fused, cinnabar-red solid devoid of real crystal structure, 5·184. When heated in a vacuum it sinters at 2000°, and melts at 2200° with slow volatilisation and slight decomposition, which becomes rapid at 2300°. In hydrogen volatilisation and decomposition are slow even at 2400°. Chlorine at 250° converts it into cerous chloride. Oxygen above 400° and sulphur dioxide at 600° form cerous sulphate, accompanied by much ceric oxide. Water and hydrogen chloride separately have little action below 300°; together they attack it rapidly at the ordinary temperature, as also does moist bromine. Carbon dioxide at 800° reacts as follows: $Ce_2S_3+4CO_2=3S+4CO+2CeO_2$. Dilute (but not concentrated) sulphuric acid attacks it rapidly, and concentrated nitric acid forms the nitrate with no separation of sulphur. Hydrogen peroxide and potassium permanganate in the cold give cerous sulphate with some ceric oxide. It is unattacked up to 1000° by nitrogen, carbon monoxide, magnesium, sodium chloride, potassium cyanide, or the sulphides of lead, antimony, or bismuth. C. A. SILBERRAD.

Mechanism of precipitation processes. IV. Processes in which compounds of chlorine with lead are formed. Z. KARAOGLANOV [with D. TSCHAVDAROV] (Z. anorg. Chem., 1931, **196**, 384—394).—The precipitation of lead acetate solutions by the chloride ion has been investigated; the phenomena observed resemble those which occur with the bromide ion (A., 1930, 438). Lead chloride, lead hydroxychloride, or mixtures of the two, are formed, the mechanism of the process being probably $Pb(OAc)^{\cdot}+Cl' \rightleftharpoons Pb(OAc)Cl$ followed by $Pb(OAc)Cl+H_2O \rightleftharpoons Pb(OH)Cl+HOAc$. Experiments with lead nitrate solutions show that addition of potassium acetate to a solution from which the chloride is normally precipitated causes the production of the basic salt, probably as a result of the intermediate formation of the acetatochloride from $PbCl^{\cdot}$ and acetate ions. This view is confirmed by the precipitation of Pb(OH)Cl when potassium acetate solution is added to a saturated lead chloride solution. The hydroxychloride may also be obtained by addition of potassium chloride solution to a dilute solution of lead perchlorate. Lead hydroxychloride is only slightly hydrolysed by water, and its solubility (0·1—0·2 g. per litre) is markedly increased by the presence of carbon dioxide; unlike the corresponding bromine compound, it is not light-sensitive. Attempts to prepare pure lead acetatochloride were unsuccessful. Mixed halides of indefinite composition have been

prepared by the interaction of lead chloride and potassium bromide, potassium iodide, or lead bromide.
H. F. GILLBE.

Influence of p_H on formation and decomposition of chloro-derivatives of ammonia. R. M. CHAPIN (J. Amer. Chem. Soc., 1931, 53, 912—920; cf. A., 1929, 1026).—An interpretation of the stability of nitrogen trichloride towards 4—7*N*-sulphuric acid and the instability towards 2—5*N*-hydrochloric acid indicates that chlorine reacts with ammonium ion only after conversion into hypochlorous acid. Hydrogen ions, especially below a specific p_H, afford, by reaction with the chloro-derivatives, ammonium ions and hypochlorous acid which yields more highly-chlorinated derivatives. At p_H about 9, the principal reactions are $2NHCl_2+4OH' \longrightarrow 3Cl'+ClO'+3H_2O+N_2$; $2NCl_3+6OH' \longrightarrow 3Cl'+3ClO'+3H_2O+N_2$. With increasing dilution, and depending on the p_H, nitrous oxide, nitrite, and nitrate may be produced. Contrary to previous statements, oxygen is not liberated by passing chlorine into ammonia solutions.
J. G. A. GRIFFITHS.

Decomposition of nitrates and nitrites of metals of different valencies. I. Ferrous nitrate. C. MONTEMARTINI and E. VERNAZZA (Industria Chim., 1930, 5, 1260—1266; Chem. Zentr., 1931, i, 435).—The dehydration of ferrous nitrate hexahydrate at the ordinary temperature in an atmosphere of carbon dioxide is accompanied by evolution of nitric oxide: $3Fe(NO_3)_2+7H_2O \longrightarrow 3Fe(OH)_3+5HNO_3+NO$. Decomposition in boiling aqueous solution in an atmosphere of carbon dioxide is at first slow with formation of a reddish precipitate; it then suddenly becomes violent and continues to completion according to the above scheme. The preliminary period is shorter for more concentrated solutions or on addition of nitric or nitrous acid, but no definite relation between concentration and the formation of nitrogen dioxide, nitrous oxide, ammonia, etc. was found. The solid product is the hydrate Fe_2O_3,H_2O.
A. A. ELDRIDGE.

Loss of material and corrosion of apparatus during the evaporation of solutions of ammonium nitrate. L. WASILEWSKI and W. BADZYNSKI. —See B., 1931, 347.

Phosphoniates. II. Action of phosphine on aluminium and beryllium halides. R. HOLTJE and F. MEYER (Z. anorg. Chem., 1931, 197, 93—102).—Phosphine reacts with aluminium chloride if the latter be heated at 50—70°, yielding a white crystalline *compound* $AlCl_3,PH_3$, m. p. 81—83°; when heated in a vacuum it sublimes and at higher temperatures the phosphine molecule is evolved. At 34·1° the phosphine pressure is about 38 mm., and at 71°, 193 mm. At pressures up to 15 atm. no further compounds are formed. Aluminium bromide reacts readily with phosphine; the *compound* $AlBr_3,PH_3$ sublimes without decomposition at 60—70°, and has m. p. 114—118°. The total vapour pressure at 63·4° is 1·6 mm., and at 83°, 8·5 mm. Aluminium bromide and its phosphoniate are mutually soluble. Aluminium iodide reacts only at temperatures above 100°; the sole product is the *compound* AlI_3,PH_3, which has m. p. 145—150° and sublimes readily; the phosphine pressure at 81·7° is 4·9 mm., and at 115·1°, 30·6 mm. The stability of the phosphoniates is greater than that of the analogous thiohydrates, and increases in the order chloride, bromide, iodide. Beryllium halides do not combine with phosphine even at high temperatures and pressures. Theoretical considerations are discussed.
H. F. GILLBE.

Composition of hydrogen sulphide hydrate. (MLLE.) A. KORVEZEE and F. E. C. SCHEFFER (Rec. trav. chim., 1931, 50, 256—260).—By applying the relation between the slopes dP/dT of the curves and the compositions of the various phases at an invariant point (cf. this vol., 430) to the quadruple point hydrate–ice–liquid–gas of the system hydrogen sulphide–water the formula $H_2S,6H_2O$ is obtained for the hydrate.
O. J. WALKER.

Preparation and structure of lower oxides of tungsten. J. A. M. VAN LIEMPT (Rec. trav. chim., 1931, 50, 343—346).—The reduction of tungstic oxide by mixtures of carbon monoxide and carbon dioxide, and of hydrogen and water vapour, at various temperatures has been investigated. Of the lower oxides of tungsten only the brown WO_2 and the bluish-violet W_4O_{11} are stable, the so-called oxides of intermediate composition being either mixtures or mixed crystals. The oxide W_2O_5 does not exist. The conditions for the preparation of WO_2 and W_4O_{11} are given. The heats of combustion of the oxides to tungstic oxide are 64,520±0·5% g.-cal. and 61,380±4% g.-cal., respectively. These values are not in disagreement with the structural formulæ suggested by Spitzin and Kaschtanoff (A., 1927, 33).
J. W. SMITH.

Manganous acid. W. BILTZ [with O. RAHLFS] (Nachr. Ges. Wiss. Gottingen, 1930, 189—194; Chem. Zentr., 1931, i, 46).—The fact that natural manganese dioxide always contains basic oxide points to its acidic nature. Treatment of manganese dioxide containing water with liquid ammonia removes all the water except 1 mol. Moreover the existence of the compounds $(NH_4)_2MnO_3$ and NH_4HMnO_3 is indicated by the isothermal decomposition of the ammoniate.
A. A. ELDRIDGE.

Rhenium. I. NODDACK and W. NODDACK (Z. angew. Chem., 1931, 44, 215—220).—A survey of the chemical properties of rhenium and its compounds and of the detection of the metal by chemical, spectroscopic, and *X*-ray spectrographic methods. Details are given of the determination of rhenium in an alloy with tungsten and osmium by fusion with sodium hydroxide and nitrate, removal of the osmium as tetroxide, precipitation of the sulphides, and removal of the rhenium as heptoxide after oxidation with nitric acid. In per-rhenates the metal is most satisfactorily determined by isolation of the heptoxide, conversion into dioxide, and reduction to metal in a current of hydrogen, and in rhenium-molybdenum concentrates by fusion with alkali, precipitation of the sulphides from the solution of the mass, and isolation of the heptoxide. The preparation of perrhenic acid, rhenium dioxide, and of derivatives of quadrivalent rhenium, and the recovery of the metal from residues and its isolation from all other metals are described in detail.
H. F. GILLBE.

Reduction of potassium per-rhenate. H. V. A. BRISCOE, P. L. ROBINSON, and E. M. STODDART (J.C.S., 1931, 666—669).—The reduction of potassium per-rhenate gives rise initially to a yellow colloidal suspension, probably of the hydrated dioxide $ReO_2,2H_2O$; this suspension finally flocculates to precipitate the hydrated dioxide. This compound may be precipitated quantitatively and dehydrated without decomposition. No evidence of the formation of intermediate products, such as rhenic acid, has been obtained. F. J. WILKINS.

Reduction of iron oxide by carbon. H. H. MEYER (Mitt. Kaiser Wilh.-Inst. Eisenforsch., 1930, **12**, 1—5; Chem. Zentr., 1931, i, 435).—The reduction takes place in stages; there is a considerable difference in the temperature at which the reactions (in absence of oxygen) commence. The difference for ferric and ferrosoferric oxides is 300—370° according to the form of carbon used, and that for ferrosoferric and ferrous oxides 100°. The variation in the temperature of commencement of reduction according as wood charcoal, sugar charcoal, or coke is used is about 150°. The reduction of ferric to ferrosoferric oxide is quantitative, and may be used for the determination of the former in mixtures of oxides. A. A. ELDRIDGE.

Influence of p_H on the oxidation of ferrous sulphate. J. CORNOG and A. HERSHBERGER (Proc. Iowa Acad. Sci., 1929, **36**, 264—265).—Little ferrous sulphate was oxidised at p_H less than 5; in solutions buffered to p_H 5 the degree of oxidation increased with increasing iron concentration, but at p_H 10 it decreased with increasing iron concentration. The percentage, x, of iron oxidised by aeration of a solution of p_H 5 in T hrs. is given by $T=0{\cdot}032x-0{\cdot}01$. CHEMICAL ABSTRACTS.

Reactions of iron, manganese, and calcium sulphides with the oxides of iron. E. DIEPSCHLAG and E. HORN (Arch. Eisenhüttenw., 1930—1931, **4**, 375—382; Stahl u. Eisen, 1931, **51**, 329—330).—Interaction of ferrous sulphide and ferric oxide according to the equation $FeS+10Fe_2O_3=7Fe_3O_4+SO_2$ commences at 550° and is complete at 800—850°. Between 850 and 1100° no reaction occurs between ferrosoferric oxide and ferrous sulphide, but at higher temperatures the reaction $FeS+3Fe_3O_4=10FeO+SO_2$ takes place, 77·5% of the iron being converted into ferrous oxide at 1220°; above 1300° a small amount of free sulphur is formed and the solid product contains traces of metallic iron. Similar reactions occur when manganous sulphide replaces ferrous sulphide, but in this case ferrous oxide is found among the reaction products at temperatures above 975°, and at 1250° 95·5% of the iron is converted into ferrous oxide. With calcium sulphide the reaction $CaS+3Fe_2O_3=CaO+6FeO+SO_2$ commences at 720°, but the lime formed combines with the excess of ferric oxide to form ferrites. The following ferrites have been prepared: $2CaO,Fe_2O_3$, $5CaO,3Fe_2O_3$, and CaO,Fe_2O_3, and their reactions with ferrous and calcium sulphides studied; in all cases reduction of the ferrite proceeded directly to ferrous oxide without the intermediate formation of ferrosoferric oxide and commenced at 800° in a stream of nitrogen. The mixture $3CaO,Fe_2O_3$ reacts with calcium sulphide at 800°, but not with ferrous sulphide below 1150°; it is suggested that this is due to the decomposition of the ferrite $3CaO,Fe_2O_3$ into $2CaO,Fe_2O_3$ and free lime below 800°. Ferrous sulphide is oxidised by sulphur dioxide at 800° thus, $3FeS+2SO_2=Fe_3O_4+5S$. A. R. POWELL.

Iron titanates. B. PESCE (Gazzetta, 1931, **61**, 107—111).—By heating together at 900° in appropriate proportions titanium dioxide and ferrous oxalate, ilmenite and ferrous orthotitanate have been prepared. Ferric orthotitanate was obtained by heating at 1000° a mixture of titanium dioxide and ferric oxalate. Attempts to obtain metatitanates were unsuccessful. The chemical individuality of the above compounds was confirmed by an X-ray analysis. F. G. TRYHORN.

New methods in analytical chemistry. J. DICK (Z. anal. Chem., 1931, **83**, 105—107).—Polemical. A reply to the criticism of Moser and von Zombory (cf. A., 1930, 1149). A. R. POWELL.

Radioactivity method for investigating powdered substances. F. BEHOUNEK (Z. Physik, 1931, **68**, 284–285).—A criticism of Šebesta's paper (this vol., 449). A. J. MEE.

Use of Wood's light for the investigation of minerals. F. V. LUTATI (Industria Chim., 1930, 5, 1222—1225; Chem. Zentr., 1931, i, 490).—Fluorescence reactions on illumination with light of the hydrogen discharge are described. A. A. ELDRIDGE.

Nephelometric titrations. II. Standard solution end-point. C. R. JOHNSON (J. Physical Chem., 1931, **35**, 830—835; cf. this vol., 456).—An end-point, termed the standard solution end-point, is proposed as an alternative to the usual end-point employed in nephelometric at. wt. titrations. The chief advantages are that systems which are practically identical in composition are compared and that absolute instead of relative amounts of silver and halide ions are measured. L. S. THEOBALD.

Micro-acidimetric studies. I. J. MIKA (Mikrochem., 1931, **9**, 143—164).—Sources of error in micro-titrations are discussed and the theory of acid–alkali titration is examined from the microchemical point of view. For micro-chemical purposes strong acids should be titrated to p_H 4·8, thus giving a red colour to methyl-orange. The most favourable conditions of concentration and range of availability for the application of methyl-red, bromothymol-blue, phenol-red, phenolphthalein, thymolphthalein, and alizarin-yellow R as indicators for micro-titrations are given. E. S. HEDGES.

Acidity in non-aqueous solvents. Conductimetric and electrometric titrations of acids and bases in benzene. V. K. LA MER and H. C. DOWNES (J. Amer. Chem. Soc., 1931, **53**, 888—896; cf. Walden and Gloy, A., 1930, 37).—Equivalence points in the conductimetric titration of diethylamine with trichloroacetic acid in benzene correspond with regions of minimum conductivity. Electrometric titration curves obtained with cells of the type Pt|quinhydrone, tetra*iso*amylammonium iodide (sat.), trichloroacetic acid (0·165M), diethylamine (0·0413M)|tetra*iso*amyl-

ammonium iodide (sat.), trichloroacetic acid ($0{\cdot}165M$), diethylamine (x), quinhydrone|Pt, where x is increased by titration, are similar to those observed in strong acid–base titrations in aqueous solution. It is unlikely that the results are attributable to traces of water in the benzene. J. G. A. GRIFFITHS.

Use of the antimony–antimonous oxide electrode in the determination of the concentration of hydrogen ions and in potentiometric titrations. The Prideaux–Ward universal buffer mixture. H. T. S. BRITTON and R. A. ROBINSON (J.C.S., 1931, 458—473).—The scope of the antimony electrode as a titrimetric indicator and the extent to which the *E.M.F.* may be converted into accurate p_H values have been investigated. The values of the Prideaux–Ward universal buffer mixture have been confirmed and measured at a larger number of stages in the neutralisation, and then used to calibrate this electrode. A number of acids and bases have been titrated potentiometrically with this electrode and the p_K values calculated. The electrode has been employed successfully in the titration of hydrocyanic, sulphurous, selenious, selenic, and telluric acids which it has hitherto been impossible to titrate against the standard electrodes. The results obtained indicate that the electrode is capable of extended use in the determination of p_H values rapidly and with a moderately high degree of accuracy. F. J. WILKINS.

Measurement of hydrogen-ion concentration in unbuffered solutions. II. Application of the hydrogen electrode. III. Colorimetric method. I. M. KOLTHOFF and T. KAMEDA (J. Amer. Chem. Soc., 1931, 53, 821—824; 825—832).—II. No adsorption of cation or anion is observed when the previous experiments with platinised platinum (A., 1929, 1410) are repeated in an atmosphere of nitrogen. The preparation of a platinum electrode covered with a bright layer of the metal is described. Acids adsorbed by the electrode in presence of air are removed by water in an atmosphere of hydrogen. The electrode is easily poisoned, but gives reproducible results in unbuffered or slightly buffered solutions (cf. Beans and Hammett, A., 1925, ii, 694).

III. Pure indicators must be used. Conductimetric titration with sodium hydroxide affords evidence of their purity. The technique and corrections involved in the colorimetric determination of p_H are detailed (cf. Acree and Fawcett, A., 1930, 560). The p_H of pure water at 25° is 7·00—7·05, determined by means of isohydric bromothymol-blue and phenol-red, whilst the p_H of very dilute sodium hydroxide solutions have been determined to within 0·1 unit by means of isohydric thymol-blue and phenolphthalein. The p_H of $0{\cdot}05M$-potassium chloride, determined by means of bromothymol-blue and phenol-red, accords with the value derived by the hydrogen electrode.

J. G. A. GRIFFITHS.

Buffer mixtures from secondary sodium phosphate and citric acid. K. H. SLOTTA and W. FRANKE (Ber., 1931, 64, [*B*], 452—454).—Determinations of the p_H values of solutions of these substances are recorded. Between the acid limits 4·0 and 7·0, the data differ by as much as 0·19 unit from those recorded previously. H. WREN.

Use of dichroic indicators for the photometric determination of hydrogen-ion concentration. H. LINSER (Biochem. Z., 1931, 230, 285—289).—Dichroic indicators are not as suitable for these determinations as indicators giving a colour–colourless change. P. W. CLUTTERBUCK.

Determination of concentration of hydrogen ions with the Hellige comparator. J. GUILLAUME (Bull. Assoc. Chim. Sucr., 1930, 47, 450—454).—The liquid to be tested, contained in a glass cell and treated with an indicator of appropriate p_H range in prescribed amount, is matched against a series of coloured glasses mounted on a rotatable disc viewed through a second glass cell containing the liquid without indicator. The series of glasses on the disc correspond with p_H values differing by 0·2 unit over the useful range of the indicator, so that p_H values can be determined to 0·1 unit with liquids not too dark. Discs with coloured glasses are supplied for a variety of indicators covering different p_H ranges. The matching of the colours is facilitated by a prism which brings the fields of view into close juxtaposition.

J. H. LANE.

Determination of hydrogen in gaseous mixtures. G. N. SCHUTOV.—See B., 1931, 348.

Ebullioscopic method of determining water content of substances. S. BAKOWSKI (Rocz. Chem., 1931, 11, 49—64).—A known weight of substance is placed in an ebullioscope flask containing a known quantity of methyl alcohol or acetone, and the rise in b. p. of the solvent is determined; the water content of the azeotropic mixture in the flask is a function of the b. p. R. TRUSZKOWSKI.

Determination of hydrochloric acid in presence of hydrobromic and hydriodic acids. G. G. LONGINESCU and T. J. PIRTEA (Bul. Chim. Soc. Romane Stiin., 1928, 31, 77—87).—In Field's method for the determination of chlorine, bromine, and iodine in mixtures of the three incomplete conversion of the silver salts into bromide or iodide often occurs and leads to errors. Bromide and chloride may be determined in mixtures by precipitating the halogens as silver salts from two equal volumes of the solution, determining gravimetrically the total halogen in one precipitate, and converting the other precipitate wholly into bromide by digesting the precipitate with 50 c.c. of 7% ammonia solution, adding dilute potassium bromide or hydrobromic acid solution, acidifying the solution with nitric acid, and weighing the washed and dried precipitate. The difference in weight of the precipitate of mixed silver salts and that of the converted precipitate multiplied by 3·22402 gives the weight of silver chloride in the mixed halogen precipitate. Chloride and iodide may be determined by a similar method in which the potassium bromide or hydrobromic acid is replaced by potassium iodide; the difference in weight of the two precipitates, multiplied by 1·56724, gives the amount of silver chloride in the mixed precipitate. A corresponding method is applied to mixtures of bromide and iodide in solution. A combination of the three methods may be applied for the determination of chloride, bromide, and iodide in a solution. The factors used are calculated from the theoretical

increase in weight resulting from conversion of silver chloride into bromide or iodide and of silver bromide into iodide. A. H. EDWARDS.

Micro-determination of iodide in common salt. H. WERNER.—See B., 1931, 391.

Thermal reduction of sulphur in a hydrogen atmosphere applied to the analysis of iron and steel. Y. YAMAUCHI (Chikashige Anniv. Vol., 1930, 111—118).—Free sulphur covered with a layer of electrolytic iron is completely reduced to hydrogen sulphide by hydrogen at 600°. Barium sulphate (at 800°) and ferrous and nickelous sulphates also give quantitative yields of hydrogen sulphide if free iron is present; in absence of iron part of the sulphur escapes as sulphur dioxide. Manganous sulphate retains part of its sulphur as sulphide. Sulphur may be determined in iron and steel by reduction with hydrogen, passage of the gas through cadmium sulphate solution, and treatment of the residue with acid in a current of hydrogen in case any of the sulphur has been retained, as, *e g.*, with manganese steels. The method is comparatively rapid and gives trustworthy results. H. F. GILLBE.

Determination of small amounts of hydrogen sulphide. W. V. HARSHMAN, D. A. MCPHERSON, and F. H. EDMISTER (J. Elisha Mitchell Sci. Soc., 1930, **46**, 54—61).—A comparative study. Hydrogen sulphide produced by micro-organisms cannot yet be determined accurately. CHEMICAL ABSTRACTS.

Determination of hydrogen sulphide, methane, and hydrocarbon vapours in air. E. POSNER and R. A. MELIKOVA (J. Appl. Chem., Russia, 1930, **3**, 965—977).—Hydrogen sulphide is absorbed in sodium hydroxide solution; hydrocarbon vapours (other than methane, which is determined by combustion) are adsorbed on activated charcoal.

CHEMICAL ABSTRACTS.

Nephelometric micro-determination of sulphates as barium sulphate. CHATRON (J. Pharm. Chim., 1931, [viii], **13**, 321—327; cf. Denis and Reed, A., 1927, 167).—The solution (p_H 2·8) for titration (5 c.c., containing 0·0025—0·03 mg. S) is treated with 1 c.c. of a solution containing 100 c.c. of 5% aqueous gelatin, 5 g. of barium chloride, and 1 c.c. of *N*-hydrochloric acid per litre. After the first 15 min. the optical density remains constant for 24 hrs. and is proportional over a wide range to the sulphur content. It is not affected by the presence of sodium chloride, or of larger amounts of gelatin, but it increases slightly in more acid solutions.

H. E. F. NOTTON.

Volumetric determination of sulphates by the benzidine method. CHATRON (J. Pharm. Chim., 1931, [viii], **13**, 244—253).—A reaction of p_H 2·8, the presence of acetone, and the use of the benzidine hydrochloride solution of Fiske (A., 1921, ii, 556) are recommended for the precipitation of sulphate with benzidine. The technique includes filtration through sintered glass filters, washing the precipitate with 95% acetone, and titration at the b. p. following hydrolysis. An error of less than 4% is claimed.

F. O. HOWITT.

Volumetric determination of very small quantities of ammonia, especially in sea- and fresh-water. S. K. HAGEN (Z. anal. Chem., 1931, **83**, 164—175).—The water (250—350 c.c.) is distilled with magnesia or sodium hydroxide from a pyrex glass flask and the vapours are passed through a quartz condenser, the distillate (90—100 c.c.) being collected in 5 c.c. of *N*/140-hydrochloric acid and 0·5 c.c. of 96% alcohol containing 0·01% of methyl-red and 0·04% of bromothymol-blue. The solution is treated with a current of pure nitrogen for 1 hr. and then titrated with *N*/140-sodium hydroxide free from carbonate until the indicator becomes orange-yellow, treated with nitrogen for a further 20 min., and again titrated until the indicator becomes blue. The correct end-point is obtained by comparison with the colour of a buffer solution of p_H 6·8 to which is added 0·5 c.c. of indicator. An allowance of 0·09 c.c. is made for the indicator and a further correction, varying from 0·6 to 3·6 μg. of nitrogen for a total quantity of 5—500 μg., is deducted to compensate for hydrolysis errors. A. R. POWELL.

Use of acridine dyes for the determination of nitrites. W. M. RUBEL (Z. Unters. Lebensm., 1930, **60**, 588—592).—The red colour produced on addition of 0·5 c.c. of a 0·1% solution of rivanol (2-ethoxy-6 : 9-diaminoacridine hydrochloride) to 10 c.c. of the test solution in the presence of 0·5 c.c. of hydrochloric acid (*d* 1·06) is matched against that developed in a graded series of standards containing 0·001—0·1 mg. N_2O_3 in 10 c.c. The reaction, which is a diazotisation, has a limiting sensitiveness of 0·001 mg. N_2O_3, and is unaffected by sodium chloride (10%), nitrates, dextrose, lactic acid, phenol, and ammonium salts. Aldehydes and thymol suppress the colour, but to a smaller extent than in the Griess reaction, and free iodine produces a greenish-blue shade. Free ammonia inhibits the reaction by raising the p_H value, and should be neutralised. The reagent (solubility 1 in 260) is stable in the dark, and should be tested for colouring impurities by means of a nitrite-free control solution.

J. GRANT.

Determination of nitrite and sulphite in presence of one another in salt mixtures. E. SZABÓ.—See B., 1931, 391.

Determination of nitrate in drinking water. K. SCHERINGA.—See B., 1931, 420.

Quantitative analysis of phosphoric acid. V. Colorimetric determination. M. ISHIBASHI (Chikashige Anniv. Vol., 1930, 1—7; cf. A., 1929, 783).—To the solution is added a small quantity of a 10% solution of hydroxylamine hydrochloride, and the mixture is treated with an excess of a mixture of manganous chloride (1 mol.) and ammonium chloride (100 mols.); the p_H of the solution should be such that scarcely any precipitation results. The solution is heated to the b. p. and ammonia solution is added slowly and with stirring until precipitation is complete; the mixture is kept for 5 hrs. at the ordinary temperature in order to ensure conversion of the amorphous precipitate into crystalline manganous ammonium phosphate, which is removed and washed 2—4 times with a slightly alkaline *M*-solution of ammonium chloride containing 2 c.c. per litre of 10% hydroxylamine hydrochloride solution. The washed precipitate is treated with 4*N*-nitric acid and is

oxidised to permanganate by sodium bismuthate at 0°. The solution is removed by centrifuging, 0·5*N*-nitric acid being used for washing the residue, and is diluted to a definite volume, the permanganate content being determined colorimetrically. The permanganate concentration should be 0·001—0·0001*N*. In presence of only small quantities of phosphoric acid the precipitate consists of the normal manganous salt, and the double salt is produced only after prolonged contact with the solution; it is therefore necessary to ascertain that the precipitate is of the characteristic crystalline form before it is further treated. If the analysis is continued with the normal salt the empirical factor 0·3300 (theory 0·2997) should be used for calculation to P_2O_5. The error of the method is less than 2% (P_2O_5). H. F. GILLBE.

Determination of phosphates in presence of silica in boiler water. E. W. SCARRITT.—See B., 1931, 320.

Potassium permanganate as a reagent for the detection of lower oxides in phosphoric acid. J. W. SMITH (J.C.S., 1931, 528—529).—A colorimetric method for the determination of small quantities of phosphorous oxide in phosphoric oxide is sufficiently sensitive to detect the presence of 2 parts of the lower oxide in 10^6. F. J. WILKINS.

Rapid determination of small quantities of boric acid by the intensity of the flame coloration. W. STAHL (Z. anal. Chem., 1931, **83**, 340—344).—The substance is dissolved in 50 c.c. of a mixture of 100 vols. of methyl alcohol and 20 vols. of sulphuric acid (*d* 1·8); a current of air is passed through the solution at a definite rate and then into the non-luminous flame of a Bunsen. The colour so obtained is compared with that given by a solution containing a known weight of boric acid; if necessary either the standard or the test solution is diluted with more of the above acid-alcohol mixture until the flame colours match. A. R. POWELL.

Quantitative investigation of the boric acid–alcohol flame reaction. W. STAHL (Z. anal. Chem., 1931, **83**, 268—289).—Air dried with sulphuric acid is passed under similar conditions through three solutions in parallel, and through similar capillary tubes into the air inlets of shielded micro-burners giving similar flames. The solutions contain the sample and two suitable quantities (0·1—0·01 mg.) of a standard solution of boric acid, each in 15 c.c. of a mixture of methyl alcohol and sulphuric acid (5 : 1) at 60°. Curves from which these optimum conditions were derived show the relation between the colour intensity of the flame, the temperature, and the water and sulphuric acid contents. The colour varies linearly with temperature (—30° to 80°), and rises to a maximum and then falls with increasing amounts of sulphuric acid. Under the above conditions, using a small apparatus, and in the presence of less than 3% of water, the colours of the flames may be matched with a sensitiveness corresponding with 0·005 mg. of B_2O_3, *i.e.*, double that obtained at the ordinary temperature without the use of acid. With ethyl alcohol (optimum acid concentration 1 : 4) the sensitiveness is 0·02 mg., but decreases rapidly in the presence of small amounts of water, whilst with propyl alcohol it is about 0·05 mg. J. GRANT.

Analysis of ferrosilicon. G. H. GOODWIN.—See B., 1931, 298.

Analysis of gases and vapours which influence the rate of oxidation of phosphorus. J. TAUSZ and H. GORLACHER (Z. anal. Chem., 1931, **83**, 81—92).—By measuring the pressure at which phosphorus starts to glow in a mixture of air or oxygen and various hydrocarbons it is possible to determine the amount of hydrocarbon vapour in the mixture by reference to graphs or tables which are given for the following substances: benzene, *cyclo*hexane, acetylene, methyl*cyclo*hexane, ethylene, propylene, *cyclo*hexene, isoprene, and iron pentacarbonyl. A. R. POWELL.

Volumetric determination of carbon dioxide in carbonates. T. HECZKO.—See B., 1931, 293.

Systematic procedure for qualitative analysis with small quantities of cations. A. SCHEINKMANN (Z. anal. Chem., 1931, **83**, 176—188).—Details are given for the detection of the usual common elements of the five analytical groups using only 0·1—0·15 g. of material and making the confirmatory tests for each element with a few drops of solution only. The original must be consulted for the working directions, which comprise no novel procedures. A. R. POWELL.

Microscopic determination of minerals. M. BEREK (Z. Krist., 1931, **76**, 396—430).—The intensity of the light reflected by anisotropic materials is calculated for both perpendicular and oblique incidence. Methods for determining the amount of the various materials in a section depend on measurement of either the degree of polarisation or the intensity of the reflected light. C. A. SILBERRAD.

Lithium chloroplatinate and separation of potassium from sodium and lithium by the unmodified original Fresenius method. G. F. SMITH and A. C. SHEAD (J. Amer. Chem. Soc., 1931, **53**, 947—957; cf. Fresenius, A., 1877, ii, 220; 1882, ii, 1231).—Factors to which the empiricism of the Fresenius method for determining potassium may be attributed (cf. Dupre, A., 1897, ii, 232) are considered. When, instead of chloroplatinic acid, the reagent is a solution of lithium chloroplatinate prepared by conversion of lithium carbonate (twice precipitated from a solution of the hydrogen carbonate by boiling) into the chloroplatinate by means of chloroplatinic acid, the precipitated potassium chloroplatinate has the theoretical composition and is stable at 260°. J. G. A. GRIFFITHS.

Nickel uranyl acetate as a qualitative reagent for sodium. P. FELDSTEIN and A. M. WARD (Analyst, 1931, **56**, 245—248).—This reagent compares favourably with zinc, magnesium, or cobalt uranyl acetates and gives a pale green precipitate of sodium nickel uranyl acetate, consisting of microscopic octahedral crystals. Potassium forms yellow needle-shaped crystals of potassium uranyl acetate and, in excess, prevents the formation of the sodium salt. Magnesium and ammonium salts are without effect, but lithium gives crystals isomorphous with the triple

sodium salt, and phosphate gives an entirely different precipitate. High concentrations of sodium precipitate the double sodium uranyl acetate from either the nickel or zinc reagents. The triple sodium salt has the formula $NaNi(UO_2)_3(OAc)_9,6(?\,6\cdot5)H_2O$.

T. McLachlan.

Toxicological detection of silver. E. Meneghetti (Biochem. Terap. Sperim., 1930, **17**, 237—241; Chem. Zentr., 1931, i, 118—119).—The material is ignited with sodium carbonate and potassium nitrate, the residue being treated with nitric acid and evaporated to dryness. Silver is precipitated from an aqueous solution with hydrogen sulphide; the silver sulphide is evaporated with nitric acid and the silver determined gravimetrically as chloride.

A. A. Eldridge.

Micro-determination of calcium. L. Velluz and R. Deschaseaux (Compt. rend. Soc. Biol., 1930, **104**, 976; Chem. Zentr., 1931, i, 323—324).—The use of organic solvents for washing the calcium oxalate and oxidation in the cold with $N/150$-permanganate are proposed (cf. this vol., 641).

A. A. Eldridge.

Micro-determination of calcium and magnesium in the presence of each other. K. L. Maljarov (Mikrochem., 1931, **9**, 132—135).—The method described is specially suited for the analysis of magnesite, dolomite, etc. About 10 mg. of the material (in which calcium and magnesium are present only in the form of carbonates, oxides, and hydroxides and alkali carbonates are either absent or present only in traces) are ignited for 30 min. in a platinum crucible, cooled in a desiccator, and diluted with 60—80 c.c. of water, which is rapidly boiled in order to dissolve all the calcium oxide. The solution is filtered and calcium is determined in the filtrate by titration with $0\cdot05$—$0\cdot2N$-sulphuric acid, using methyl-orange. The precipitate of magnesium oxide is dissolved in excess of $0\cdot05$—$0\cdot2N$-sulphuric acid and the excess titrated back with standard sodium hydroxide solution. Iron or aluminium oxides, which may be present in the precipitate, are not dissolved by sulphuric acid of this concentration. The presence of calcium oxide diminishes the solubility of magnesium oxide in water.

E. S. Hedges.

Micro-determination of barium. R. R. McLaughlin (Biochem. J., 1931, **25**, 307—309).—A gravimetric method capable of dealing with 20 mg. of barium sulphate with a loss of not more than $0\cdot3\%$ is described.

S. S. Zilva.

Determination of magnesium in Portland cement and similar materials of the use of 8-hydroxyquinoline. J. C. Redmond and H. A. Bright.—See B., 1931, 396.

Electrolytic determination of lead as lead dioxide. W. T. Schrenk and P. H. Delano.—See B., 1931, 299.

Electrolytic separation of lead and antimony and its application to the determination of lead in tartar emetic. E. M. Collin and H. J. S. Sand (Analyst, 1931, **56**, 90—93).—The method depends on the fact that lead free from antimony is deposited by internal or external electrolysis on a copper-plated platinum cathode from alkaline tartrate solutions containing quinquevalent antimony. For the analysis of tartar emetic the salt is dissolved in water and the solution treated with 3 g. of potassium hydrogen carbonate, then with a slight excess of iodine followed by 4 g. of potassium hydroxide and 2—3 g. of tartaric acid; electrolysis is conducted with a rotating anode using an external current of 3 amp. or with a zinc anode immersed in 10% potassium cyanide solution in the anode compartment of Sand's internal electrolysis apparatus.

A. R. Powell.

Determination and separation of lead and bismuth by the filtration method. H. T. Bucherer and F. W. Meier (Z. anal. Chem., 1931, **83**, 351—361).—Good results for lead may be obtained by titrating the hot, slightly acid solution, containing an excess of sodium acetate, with potassium dichromate or with selenious acid and determining the end-point by the filtration method (cf. B., 1930, 1153). In the second case the lead is precipitated as white granular $PbSeO_4$, which settles and filters readily. The filtration method may also be used for the volumetric determination of bismuth in $0\cdot05$—$0\cdot08N$-nitric acid at 70°, using selenious acid as the precipitant; lead does not interfere and, if present, may be subsequently determined with selenious acid after addition of sodium acetate to the solution without removing the bismuth selenite precipitate.

A. R. Powell.

Separation cf bismuth from lead as oxychloride. W. Hertel (Metall u. Erz, 1930, **27**, 557—560; Chem. Zentr., 1931, i, 489).—The oxychloride method is more accurate than the sulphate method, and applicable at any bismuth content. A procedure for determining bismuth in lead in presence or absence of antimony is described.

A. A. Eldridge.

Luminescence analysis. II. Luminescence of white pigments. E. Beutel and A. Kutzelnigg.—See B., 1931, 403.

Cobalticyanide and chromicyanide anions as precipitating agents in potentiometric volumetric analysis. L. Czaporowski and J. Wierciński (Rocz. Chem., 1931, **11**, 95—102).—Hydrocobalticyanic acid, $H_3Co(CN)_6,5H_2O$, decomp. 50°, is prepared by saturating saturated aqueous potassium cobalticyanide with hydrogen chloride, and extracting the precipitate with alcohol, from which the free acid crystallises. The acid and its sodium or lithium salts are suitable reagents for the potentiometric titration of silver, cupric, and mercuric ions. Cupric sulphate should be titrated in presence of an equivalent amount of sodium acetate. Cobalt can be determined by conversion into cobalticyanide and titration with standard silver or mercuric solutions; this method is, however, not convenient. Chromicyanides are unsuitable for potentiometric analysis, as the titration curve varies according to the concentration of cations.

R. Truszkowski.

Determination of small amounts of mercury. A. Stock and H. Lux [with F. Cucuel and F. Gerstner] (Z. angew. Chem., 1931, **44**, 200—206).—Methods of determining quantities of mercury of the

order of 0·001 mg. by deposition on a copper wire, followed by distillation, conversion into chloride, and colorimetric determination, are untrustworthy because of incomplete deposition on the copper, and subsequent loss by evaporation. The mercury is deposited from the chloride solution (10—15 c.c.) on a copper wire, using a platinum anode, then distilled and condensed in a small capillary. After washing with alcohol, the amount is determined by microscopic measurement. If the mercury is contained in a larger volume of solution than 15 c.c. it is first concentrated by precipitation as sulphide in the presence of a copper salt, and reconversion into chloride by the action of chlorine. A. KEY.

Determination of small concentrations of mercury vapour in air. B. L. MOLDAVSKI (J. Appl. Chem., Russia, 1930, **3**, 955—964).—The mercury is combined with bromine vapour and the mercuric bromide dissolved in water.

CHEMICAL ABSTRACTS.

Determination of aluminium in ferrochromium and chromium. T. R. CUNNINGHAM.—See B., 1931, 298.

Determination of alumina in refractory clays. R. BIAZZO.—See B., 1931, 395.

Rhenium. II. Determination of rhenium as thallium per-rhenate. F. KRAUSS and H. STEINFELD (Z. anorg. Chem., 1931, **197**, 52—56; cf. this vol., 53).—Pure thallous per-rhenate may be prepared by adding, with stirring, a slight excess of thallous acetate or sulphate solution to a cold solution of potassium per-rhenate rendered slightly acid with acetic acid; the precipitate is collected, washed with glacial acetic acid, and dried at 140°. The compound forms white, anisotropic, apparently rhombic crystals. Its solubility is 0·085% at 10° and 0·16% at 26°, and is still lower in ethyl alcohol and dilute or concentrated acetic acid. For the determination of rhenium as thallous per-rhenate the sample (0·3—0·4 g.) is dissolved in 40 c.c. of hot water, 10 c.c. of glacial acetic acid are added, and the rhenium is precipitated by a slight excess of a solution of thallous carbonate in acetic acid. The solution is evaporated to 3—4 c.c. and after being cooled 10 c.c. of acetic acid are added and the precipitate is washed and dried. Halides must be absent. Results are somewhat low, probably as a result of volatilisation. H. F. GILLBE.

Determination of iron in water. O. MAYER.—See B., 1931, 320.

Separation of iron, titanium, and aluminium in tartaric acid solution. E. S. VON BERGKAMPF (Z. anal. Chem., 1931, **83**, 345—350).—The acid tartrate solution of the metals is treated with hydrogen sulphide to reduce ferric salts, and then with ammonia and hydrogen sulphide under pressure to precipitate ferrous sulphide. The filtrate is acidified with sulphuric acid and treated cold with 6% cupferron solution to remove the titanium; the filtrate is made ammoniacal again, and the aluminium precipitated with 8-hydroxyquinoline at 70°. Vanadium interferes in the separation; zirconium is precipitated with the titanium, and beryllium with the aluminium.

A. R. POWELL.

Influence of co-ordinated groups on the central iron atom of complex iron cyanides. O. BAUDISCH (Biochem. Z., 1931, **232**, 35—49).—Benzidine and guaiacol are oxidised both by ferric and by autoxidised pentacyanoaquoferroate ions. 5-Aminouracil reacts only with the ferroate at 3·8—8·0. Thioglycollic acid detects ferric and complex ferric ions, nitrosophenol detects ferrous ions. A reaction with dithio-oxamide is introduced for detection of pentacyanoaquoferroate ions. Ferroate is directly oxidised by 0·01N-hydrogen peroxide only in acid solutions. The reduction of ferriate to ferroate ions by a large number of substances is investigated (A., 1930, 41, 75). P. W. CLUTTERBUCK.

Gravimetric determination of iron in organic substances. G. SVEDENIUS (Acta paediatr., 1929, **9**, 1—8; Chem. Zentr., 1931, i, 323).—The ash is dissolved in hydrochloric acid, the solution nearly neutralised with ammonia, and the iron precipitated from the filtrate by four additions at 7—8 hr. intervals of 1-nitroso-β-naphthol, the precipitate being dried and ignited in a platinum crucible.

A. A. ELDRIDGE.

Determination of traces of chromium in steel. W. J. AGNEW.—See B., 1931, 297.

Determination of chromium and vanadium in ores and alloys after oxidation with perchloric acid. H. H. WILLARD and R. C. GIBSON.—See B., 1931, 299.

Determination of molybdenum. H. A. DOERNER (Metal Ind., London, 1930, **37**, 444—445; Chem. Zentr., 1931, i, 321).—The sample (1 g.) is fused with sodium carbonate and peroxide in an iron or nickel crucible; the hot aqueous extract is boiled for 10 min. with hydrogen peroxide and filtered. After acidification with hydrochloric acid and removal of carbon dioxide by boiling an alkali thiocyanate and zinc are added; a cherry-red colour appears in presence of molybdenum. For determination, 0·5—5 g. of finely pulverised material are digested with nitric (40 c.c.) and sulphuric (7 c.c.) acids, the soluble sulphates being dissolved by addition of water (50 c.c.). Tartaric acid (5 g.) is added and hydrogen sulphide passed; the filtrate is acidified with dilute sulphuric acid and the molybdenum sulphide collected. This is dissolved in aqua regia; the solution is neutralised with ammonia and heated with hydrochloric acid (7 c.c.), ammonium acetate (10 g.), and water (300 c.c.), lead acetate solution being added from a burette until a drop test with freshly prepared tannin solution gives no colour change. A slight excess is added, the lead molybdate being collected after heating for 30 min. and weighed as $PbMoO_4$.

A. A. ELDRIDGE.

Colorimetric determination of molybdenum in steel. T. R. CUNNINGHAM and H. L. HAMNER.—See B., 1931, 297.

Colorimetric determination of tungsten. G. HEYNE (Z. angew. Chem., 1931, **44**, 237—238).—The diluted ammoniacal solution of tungstic acid is treated with 0·5 c.c. of 10% potassium hydroxide solution, evaporated, and heated to fuming with 0·55 c.c. of sulphuric acid; if it is brown, potassium

persulphate is added. The liquid is cooled in a desiccator, treated with 1 c.c. of a solution of 10 g. of quinol in 100 c.c. of sulphuric acid, and the colour is matched with a standard solution of tungsten, for which 0·063 g. WO_3 is dissolved in 25 c.c. of 10% potassium hydroxide solution, evaporated to dryness, and dissolved in sulphuric acid to make 50 c.c. (1 c.c.$\equiv$ 0·001 g. W); 0·02—0·10 c.c. of this standard solution is mixed with solution of potassium sulphate in sulphuric acid and 1 c.c. of the quinol sulphate until the colours match. The determination is unaffected by small amounts of alkalis, phosphates, or nickel, but is affected by nitrates, iron, titanium, niobium, chromates, per-rhenates, and molybdates. In presence of molybdenum, the tungsten should be determined colorimetrically by means of rhodamine B.

D. WOODROFFE.

Reduction of tin and antimony prior to titration. B. S. EVANS (Analyst, 1931, **56**, 171—177).—Hypophosphorous acid may be employed for the reduction of stannic salts if the operation is carried out in hydrochloric acid solution (1 : 1) at the b. p. in an atmosphere of carbon dioxide, using mercuric chloride as a catalyst; starch, citric acid, and potassium iodide are added before titrating with 0·1*N*- or 0·01*N*-iodine solution. Antimony is reduced more rapidly and no catalyst is required, but ammonia is added in excess before titration. Lead, if present, is precipitated by sulphuric acid before reduction; with tin, cadmium, and bismuth, iodine is added to give a faint permanent blue colour to starch before the citric acid. Arsenic is reduced to the metallic state and may be filtered off. T. MCLACHLAN.

Lead reduction method for the volumetric determination of tin and the interference with it by copper and antimony. S. G. CLARKE (Analyst, 1931, **56**, 82—89).—Reduction of stannic chloride solutions by sheet lead leads to accurate results for tin provided that the reduction, cooling, and titration are carried out while a current of carbon dioxide is passed through the flask. An acidity of 50 c.c. of hydrochloric acid in a total volume of 250 c.c. and a time of reduction of 1·5 hrs. are recommended (cf. Powell, J.S.C.I., 1918, **37**, 285T). When the solution contains copper boiling with lead results in the deposition of a copper–tin compound as a black, flocculent precipitate, and hence low results for tin are obtained in the titration. If the solution contains antimony this is precipitated as a flocculent black precipitate by boiling with lead, and high results are obtained for tin if titration is carried out without filtration; if, however, the precipitate is removed and the filtrate again reduced and titrated the results for tin are low, as part of the tin is precipitated with the antimony. When both copper and antimony are present in the same solution, boiling with lead precipitates an antimony–copper compound in preference to a tin–copper compound, but the tin results are still slightly low.

A. R. POWELL.

Selenious acid method for determination of zirconium. S. G. SIMPSON [with W. C. SCHUMB] (J. Amer. Chem. Soc., 1931, **53**, 921—933; cf. Smith and James, A., 1920, ii, 710).—Zirconium (0·12 g. of ZrO_2) is precipitated quantitatively as the basic selenite by excess (20 c.c.) of 10% selenious acid from hot solutions (400 c.c.) containing not more than the optimum concentration, 0·6*N*, of hydrochloric acid or a lower concentration of nitric acid. Sulphuric acid causes very slow precipitation, affording the crystalline normal selenite which is insoluble in hot 6*N*-hydrochloric acid. Nitrates and chlorides do not interfere, but more than 0·5 g. of sodium sulphate prevents quantitative precipitation unless the acidity is diminished. The effect may be due to the formation of $[ZrOSO_4,SO_4]H_2$. Of many metallic ions investigated, only those of titanium, ceric cerium, and thorium are precipitated with zirconium (and hafnium) under the conditions adopted. 20 C.c. each of 12*N*-hydrochloric acid and alcohol are added to 100 c.c. of the nearly neutral solution free from phosphate, sulphate, niobium, and tantalum. The liquid is boiled, diluted to 500 c.c. and the selenites are precipitated. The precipitate is dissolved in 15 c.c. of 12*N*-hydrochloric acid. Thus, adsorption of vanadium and uranyl compounds is eliminated. Next, cerium and titanium are removed by the addition of 20 c.c. of 3% hydrogen peroxide followed by warming, dilution, and precipitation of zirconium (and thorium) selenite. Before the last process is repeated to remove the titanium completely, any thorium is separated quantitatively by double precipitation as oxalate from hydrochloric acid solution, sulphate being absent. The excess of oxalate is destroyed by evaporation with sulphuric acid, sulphate being eliminated by precipitation of thorium and zirconium with ammonia solution.

A rapid method for decomposing zirconium ores by fusion with sodium peroxide and sugar charcoal, and subsequent treatment for removal of niobium, tantalum, and phosphate, is detailed.

J. G. A. GRIFFITHS.

Determination of zirconium in steel. T. R. CUNNINGHAM and R. J. PRICE.—See B., 1931, 298.

Detection of gold, palladium, and silver with dimethylaminobenzylidenerhodanine. F. FEIGL, P. KRUMHOLZ, and E. RAJMANN (Mikrochem., 1931, **9**, 165—173).—The tests described may be carried out in a test-tube, shaking with ether to enrich the effect at the boundary, or by the spot method on filter-paper. One drop of a silver solution with one drop of 10% potassium cyanide and one drop of alcoholic *p*-dimethylaminobenzylidenerhodanine acidified with one drop of *N*-nitric acid produces a violet coloration. The test is sensitive at a dilution of 1 in 500,000 and succeeds in the presence of 1000 times the amount of mercury, 4000 times the amount of gold, and 300 times the amount of platinum or palladium. In the absence of potassium cyanide, gold compounds even at a dilution of 1 in 500,000 give a reddish-violet coloration with the reagent. Palladium gives a violet coloration at a dilution of 1 in 10^7 in neutral solution and 1 in 5×10^6 in 0·1*N*-acid solution. Special directions are given for the detection of palladium in the presence of platinum, iridium, silver, and gold. E. S. HEDGES.

Potentiometric determination of iridium. S. C. WOO and D. M. YOST (J. Amer. Chem. Soc.,

1931, **53**, 884—888; cf. this vol., 435; Delépine, A., 1917, ii, 537).—The chloroiridate in hydrochloric acid solution is reduced to the chloroiridite by standard titanous chloride which must be added slowly as the electrometric end-point is approached. The sharpness of the end-point is increased by the presence of sodium chloride. The iridium content of crystalline ammonium hexachloroiridate determined by the above method, the iodometric method in which the iodine–thiosulphate end-point is determined by means of benzene, and the gravimetric method accords, within $\pm 0.3\%$, with the formula $(NH_4)_2IrCl_6$.
J. G. A. Griffiths.

Conditions of precipitation of polonium; some of its complex derivatives. I. Study, by centrifugation, of the precipitation reactions of various compounds of polonium without addition of an entraining agent. M. Guillot (J. Chim. phys., 1931, **28**, 14—41).—The chemical reactions of polonium are reviewed, with special reference to their analytical significance. In the method of determination used the precipitated polonium (or its compound) was centrifuged at 6000 revs. per min. under standardised conditions, and the polonium removed from the walls of the tube in hot acid, and finally deposited on a silver plate, the radioactivity of which was then determined by the ionisation method (1 e.s.u. $= 1.6 \times 10^{-10}$ g. of polonium). The fixation of polonium on the walls of the tube and the formation of a centrifugable precipitate are parallel phenomena. Solutions in N-hydrochloric acid deposit polonium, by hydrolysis of the chloride, to a negligible extent, but hydrolysis begins with $0.1N$-solutions and is carried almost to completion in neutral solutions. In neutral or $0.01N$-media the curves relating the residual soluble polonium and the period of centrifuging appear to correspond with normal chemical precipitation. The properties of the hydrolysis product have been investigated, and indicate the formula $O:Po(OH)_2$. Similar experiments were carried out on the precipitation of polonium sulphide in N-hydrochloric acid, of polonium carbodithiodiethylamine in neutral solution, and of polonium by reduction with stannous chloride in N-hydrochloric acid. Satisfactory agreement exists between the results of these experiments and those hitherto studied in which precipitation is assisted by entraining agents, an insoluble, completely precipitable polonium derivative being formed, other conditions being the same, whether the entraining agent is present or absent. Entrainment may result from true syncrystallisation, due to isomorphism of the participating molecules, (1) when the polonium is in a soluble form and the entraining agent is crystalline, (2) when the polonium is insoluble and the entraining agent (a metallic compound) is insoluble in water, but soluble in and crystallisable from another neutral solvent. A compound of tervalent polonium may be totally entrained by the corresponding compound of a bivalent metal so long as both are insoluble.
J. Grant.

Difficulty of ensuring thermal insulation with solid insulator. P. Vernotte (Compt. rend., 1931, **192**, 340—341).—The quantity of heat passing in t sec. between the wall of the vessel in a calorimeter in which it is evolved and the insulating medium, counting time from the beginning of the evolution, and assuming such evolution to be sudden and to raise the temperature by is $Q = 2\sqrt{kc\rho t}T$ g.-cal. per cm.^{2}, where k is the conductivity of the insulating medium, c its specific heat, and ρ the density. If the medium is asbestos Q in 30 sec. amounts to $0.12T$ g.-cal. per cm.^{2}, whilst the normal flow is only $0.02T$. The best insulator is air, and a metal cushion is better than felt (cf. following abstract).
C. A. Silberrad.

Simple method of measuring specific heat of a solid [beryllium] at the ordinary temperature. P. Vernotte and A. Jeufroy (Compt. rend., 1931, **192**, 612—614; cf. preceding abstract).—The substance is suspended together with a thermometer in a thick-walled metal box in the actual place of experiment until it acquires the same temperature. The temperatures of this place and of the water in the calorimeter are such that the latter, even after the substance is dropped in, is well below that of its surroundings. The method applied to beryllium gives as the specific heat at 13° 0·397 g.-cal. per g. per degree.
C. A. Silberrad.

Thermostats. II. Electric relay and spark in thermoregulator. S. Kambara and M. Matsui (J. Soc. Chem. Ind. Japan, 1931, **34**, 94—99B).—In order to prevent sparking the current must not exceed 8 milliamp. at 100 volts and 20 milliamp. at 10 volts. A relay operated by smaller currents has been devised.
E. S. Hedges.

Thermostat regulator. E. Q. Adams (Rev. Sci. Instr., 1931, [ii], **2**, 187—188).—An inert atmosphere is maintained above the make-and-break contact of an electrically heated thermostat by means of a tungsten–mercury contact in hydrogen permanently enclosed in glass. With an auxiliary heater a temperature variation less than $\pm 0.001°$ was obtained.
N. M. Bligh.

Simple thermostat for 20° with temperature control independent of the room temperature. V. Čupr (Z. Elektrochem., 1931, **37**, 129—130).—The thermostat bath is fed continuously from the water main, the feed water passing over an electrically heated spiral operated by a relay of special construction. The temperature can be maintained within 0·02° of the desired point. Details and diagrams are given.
F. L. Usher.

Improved Fuessner type potentiometer. M. Eppley and W. R. Gray (Rev. Sci. Instr., 1931, [ii], **2**, 242—249).

Thermionic valve voltmeter. F. L. Hahn (Chem. Fabr., 1931, 121).—The circuit described is intended for microchemical titrations, and differs from circuits previously described in that the compensating rheostat utilises the full voltage of the filament battery and that a reduced voltage is applied to the filament in order to improve the constancy of the null point reading.
H. F. Gillbe.

Carborundum fractionating columns. E. C. Farnham (J. Physical Chem., 1931, **35**, 844—858). Midgley's results (A., 1929, 673) are confirmed. The

nature, as well as the physical structure, of the material filling the column affects fractional distillation in a specific manner. Thin plates are preferable to needles. Carborundum or micaceous hæmatite is better than glass beads or silver-plated glass films for the separation of benzene and pyridine. Ferrous sulphide is also preferable to glass beads, but needle ore, a form of hæmatite, and very finely-ground carborundum are not efficient. With alcohol and water, glass is preferable to micaceous hæmatite. Selective adsorption appears to be an important factor determining the efficiency of a fractionating column. L. S. THEOBALD.

Laboratory distillation apparatus. H. BURSTIN and J. WINKLER (Chem.-Ztg., 1931, **55**, 212).—The apparatus described was designed for the continuous vacuum distillation of oil residues, but is suitable also for the treatment of easily decomposable or foaming liquids, such as phenols and sulphonic acids, and for organic liquids containing water. It consists essentially of a heating chamber in which the liquid is vaporised as it enters through a needle valve, a dephlegmator packed with Raschig rings, and a condenser; the heating surface and vapour space are large compared with the quantity of material heated, and the latter is therefore maintained at a high temperature for only a short period.

H. F. GILLBE.

Storage and delivery apparatus for corrosive reagents. G. MIDDLETON (Analyst, 1931, **56**, 236—237).—A bottle is fitted with tubes having ground-glass and internal joints, so arranged that reagents such as antimony trichloride solution or bromine may be measured accurately and rapidly without coming into contact with the air.

T. McLACHLAN.

Apparatus for the measurement of ultra-violet light. E. WEYDE (Strahlenther., 1930, **38**, 378—390; Chem. Zentr., 1931, i, 115).

Filters for the reproduction of sunlight and daylight and the determination of colour temperature. R. DAVIS and K. S. GIBSON (U.S. Bur. Stand. Misc. Publ., 1931, No. 114, 165 pp.).—" Mean sun," *i.e.*, mean noon sunlight at Washington, is adopted as a white light standard in preference to 5000° Abs., since it represents the natural conditions of use of photographic materials and is more easily obtained from incandescence lights by means of filters. A series of filters has been prepared for conversion of the light of colour temperatures between 1600° and 20,000° Abs. into mean sun with accuracy both with regard to spectral energy distribution and colour match, over the range of wave-length 360—720 mμ. Filters for conversion of one colour temperature into another are also given. The filter consists of a two-compartment cell with three borosilicate crown glass windows (each 2·5 mm. thick, n_D 1·51), each cell being 10 mm. thick. The two cells contain respectively (A) a solution of equal weights of copper sulphate pentahydrate and mannitol, and 30 c.c. of pyridine, in distilled water to make 1000 c.c.; (B) a solution of copper sulphate, cobalt ammonium sulphate ($6H_2O$), and 10 c.c. of sulphuric acid (*d* 1·84), in distilled water to make 1000 c.c. The unstated amounts of the constituents vary with the purpose of the filters, which are standardised for use at 25°. A series of charts is given showing the composition of the filter, and the spectral energy distribution of the source with its filter compared with mean sun and the source and filter separately. The transmissions of the filters vary from 10 to 60%. Full investigations have been made of the permanence of the solutions and the variations due to temperature changes, impurity of materials, and other factors.

J. LEWKOWITSCH.

Laboratory apparatus. M. TROMBE (Bull. Soc. chim., 1931, [iv], **49**, 185—186).—A bubbler for washing a gas and a water bellows which works at high pressures are described. F. J. WILKINS.

Aerometer for the rapid determination of the density of liquids. G. BORGER (Munch. med. Woch., 1930, **77**, 2019; Chem. Zentr., 1931, i, 113).

Expansion hydrometer. E. HIEDEMANN (Physikal. Z., 1931, **32**, 223—225).—An apparatus for the determination of the coefficient of cubical expansion of liquids is described. A. J. MEE.

Hydrometer for determining the density of heavy liquids. A. C. TESTER (Science. 1931, **73**, 130—131).—An apparatus suitable for determining the density of liquids (5 c.c.) between 2 and 5 is described. L. S. THEOBALD.

Automatic constant-level device for liquid air. R. B. SCOTT and F. G. BRICKWEDDE (Rev. Sci. Instr., 1931, [ii], **2**, 171—172).—An electrically controlled apparatus for automatically maintaining a constant level in a bath of liquefied gas is described, and applied to a cryostat, using liquid air as the refrigerant.

N. M. BLIGH.

Apparatus for the evaporation of various materials in high vacua. C. H. CARTWRIGHT and J. STRONG (Rev. Sci. Instr., 1931, [ii], **2**, 189—193).—The substance to be evaporated is heated electrically in an evacuated bell-jar directly connected to a charcoal container cooled by liquid air, and is directed as a molecular beam on to the surface to be coated. Most metals and some non-metals could be deposited and the thickness of the film accurately controlled.

N. M. BLIGH.

Glass extraction apparatus. B. L. MANJUNATH (Mysore Univ. J., 1930, **4**, 243—244).—The substance to be extracted is contained in a Woulff's bottle which has an additional opening at the bottom. Solvent enters as vapour through one of the upper openings, and is prevented by a condenser from escaping through the other. By means of a two-way tap it can be caused either to run straight back to the still through the bottom opening or to accumulate until it reaches a certain height, when it automatically siphons back. Most of the joints are ground, and the use of rubber connexions is minimised.

C. W. GIBBY.

Apparatus for continuous extraction at raised temperatures. F. WREDE (Biochem. Z., 1931, **231**, 173—174).—An apparatus in which at least 5 kg. of solid material can be continuously extracted with solvents at any desired temperature is described.

W. McCARTNEY.

Filtering discs of sintered pyrex glass. W. F. Bruce and H. E. Bent (J. Amer. Chem. Soc., 1931, **53**, 990—992).—Details for making discs and sealing them to pyrex apparatus are given. A uniform layer, 1·5—2 mm. thick, of powdered pyrex glass of appropriate grain size is placed in a cylindrical nickel mould consisting of a piece of tube 1 cm. in diameter and 1 cm. high resting on a sheet of nickel (2·5×2·5 cm.). The covered mould is placed for about 2 min. in a muffle at a bright red heat.

J. G. A. Griffiths.

Measurement of permeability of porous alundum discs for water and oils. H. G. Botset (Rev. Sci. Instr., 1931, [ii], **2**, 84—95).—The rate of flow of distilled water through a porous alundum disc decreases with time if the water has been kept in contact with glass, on account of the presence of silicic acid produced by hydrolysis of the glass. Various petroleum fractions and crude oils also show a change in rate of flow with time, due to the oxidation of unsaturated hydrocarbons to gummy substances. Permeability measurements with oils containing unsaturated substances should be carried out in an inert atmosphere. C. W. Gibby.

Electrically heated muffle furnace. T. R. Ball (J. Chem. Educ., 1931, **8**, 355—357).—The top of the rectangular crucible furnace may be opened.

Chemical Abstracts.

Detection of slightly cloudy liquids. F. W. Meier (Chem.-Ztg., 1931, **55**, 146).—A lamp which assists in the examination of fine sediments and slightly cloudy liquids is described. E. Doctor.

Colorimeters, spectrophotometers, and nephelometers. C. Digaud (Ann. Chim. anal., 1931, [ii], **13**, 1—15, 33—54, 65—74).—An account of the theory, and an extensive description of types of apparatus available, including details of commercial photo-electric cells, thermoelements, colorimeters, photometers, spectrophotometers, nephelometers, opacimeters, and diffusimeters. H. F. Gillbe.

Plane-parallel plate refractometer. A. H. Pfund (J. Opt. Soc. Amer., 1931, **21**, 182—186).—A simple apparatus primarily for demonstration purposes is described.

Absorption apparatus. S. Reiner (Chem.-Ztg., 1931, **55**, 203).—An apparatus suitable for the study of the adsorption of solvent vapour on active material consists of a vacuum-tight H-shaped container, in the legs of which are placed bottles of solvent and adsorbent, respectively, with means for removing and replacing their stoppers without opening the vessel. H. E. F. Notton.

Application of the adiabatic microcalorimeter to the measurement of heats of adsorption and of vaporisation. W. Swientosławski and E. Bartoszewiczówna (Rocz. Chem., 1931, **11**, 78—89).—A microcalorimeter in which the galvanometer and leads from the thermocouple are placed within a recess in the thermostatic water-jacket within which the calorimeter vessel is suspended is described; in this way disturbances due to possible variations in the temperature of the environment are largely excluded. The construction of a special micro-calorimeter vessel for the determination of heats of vaporisation and adsorption of small quantities of liquid is described. R. Truszkowski.

Adiabatic microcalorimeter adapted to the determination of the specific heat of solid and liquid substances. W. Swientosławski, S. Rybicka, and W. Sołodkowska (Rocz. Chem., 1931, **11**, 65—77).—The microcalorimeter consists of a small copper or silver vessel containing the liquid under examination, and is suspended in a spherical vessel immersed in water of known invariable temperature. The substance is heated electrically, the heat supply being such that the rise of temperature amounts to 0·2—0·5° per hr. Where it is desired to determine the specific heat of a metal, the calorimeter vessel has to be made of this metal. Specific heats are determined by using two calorimeter sets, of which one has a known heat capacity. Evaporation or condensation of infinitesimal quantities of water on the calorimeter vessel gives heat effects sufficiently large to render the results inaccurate and the same applies to adsorption or desorption of gases; equilibrium should be attained in this respect before the commencement of determinations.

R. Truszkowski.

Prevention of foaming. L. Hart (Chemist Analyst, 1931, **20**, No. 1, 9).—Foaming during steam-distillation or distillation with xylene may be prevented by addition of sodium hydrogen sulphate (3—5 g.), rosin (2—5 g.), oleic acid (5 c.c.), paraffin, mineral oil, a soluble barium or calcium salt, or amyl alcohol. Chemical Abstracts.

Orsat apparatus for complete gas analysis. Anon. (Chem.-Ztg., 1931, **55**, 192).—A portable type of Orsat apparatus, comprising six absorption vessels in one wooden box and the burettes and their accessories in a second box, is described.

A. R. Powell.

Continuous dialyser. H. A. Aitken (J. Biol. Chem., 1931, **90**, 161—163).—An apparatus whereby a liquid (10 c.c. or upwards) may be subjected to continual dialysis against distilled water, the dialysing water being distilled and after condensation passed inside a parchment membrane on the outside of which is the liquid which is being dialysed, is described. By means of a siphon, the water inside the membrane is returned to the distillation flask, from which it is again distilled. W. O. Kermack.

Spring balance for measuring the water content of snow. G. D. Clyde (Science, 1931, **73**, 189—190). L. S. Theobald.

Micro-ebullioscopic determination of mol. wt. J. H. C. Smith and H. W. Milner (Mikrochem., 1931, **9**, 117—122).—The apparatus consists of a boiling tube, differential thermometer, and Cottrell pump. Satisfactory results can be obtained by using as little as 3 c.c. of solvent and 5—25 mg. of solute. The apparatus has three advantages over the micro-Beckmann apparatus: (1) it does not require a supply of platinum tetrahedra, (2) a differential thermometer is substituted for the expensive micro-Beckmann thermometer, (3) more accurate readings can be obtained. Some experimental results are given. E. S. Hedges.

Behaviour of "indifferent" electrodes when used for the determination of oxidation–reduction potentials in the presence of hydrogen. E. H. Lepper and C. J. Martin (Biochem. J., 1931, **25**, 45—48).—When a phosphate mixture is poised with 0·001*M*-indigo-carmine the gold electrode remains stable on substituting hydrogen for nitrogen, but when the concentration is made 0·0001*M* the potential rises by 8 millivolts. With a concentration of 0·002*M*-indigo-carmine the iridium electrode shows a rise of 10 millivolts, and with a concentration of 0·0001*M* reaches almost the potential of the hydrogen electrode by the end of 30 min. In unpoised buffer solutions when hydrogen is substituted for the nitrogen which previously expelled the air, there is a negative drift of 45 millivolts of the gold electrode at the end of 1·25 hrs., whereas the iridium electrode reaches the potential corresponding with the of the solution and remains steady at this level. The iridium electrode gives off hydrogen when the latter is displaced by nitrogen very slowly. When, however, oxygen is passed through the solution there is a rapid fall of potential in both electrodes. At the end of 30 min. the gold electrode gives again a steady potential, whilst the iridium electrode after the first sudden fall continues to show a slow positive drift. Gold electrodes give different results from iridium electrodes during the growth of organisms when hydrogen is evolved (cf. Lepper and Martin, Brit. J. Exp. Path., 1930, **11**, 100), because gold is relatively insensitive to hydrogen, whereas iridium becomes charged with hydrogen from the solutions and assumes the function of a hydrogen electrode.

S. S. Zilva.

Replacing the telephone by a loud speaker in conductivity measurements. L. Du Noüy (Nature, 1931, **127**, 441).—An arrangement is described.

L. S. Theobald.

Geochemistry.

Combined nitrogen in rain water. C. Srikantia (Mysore Univ. J., 1930, **4**, 195—198).—Tables showing the ammonia and nitric acid contents of rain water collected at Bangalore during nine months are given.

C. W. Gibby.

Content of krypton and xenon of some natural gases in Bulgaria. N. P. Pentchev (Compt. rend., 1931, **192**, 691—693; cf. A., 1928, 267; 1929, 1159).—As determined by the method of Moureu and Lepape (cf. A., 1922, ii, 394) the amounts of krypton and xenon per 100 vols. of gases from the thermal springs at Sulu-Dervent (Momina), Hissar (Chuluja), and Kovanlik are respectively 0·00021 and >0·000013; 0·00015 and 0·000013; and 0·00025 and 0·00002. The approximate constancy of the ratio supports Moureu and Lepape's nebular hypothesis of the solar system (cf. A., 1911, ii, 1134).

C. A. Silberrad.

Chromiferous pyroxene from Jagersfontein, S. Africa. H. O'Daniel (Z. Krist., 1930, **75**, 575; Chem. Zentr., 1931, i, 439).—The mineral contained SiO_2 53·53, Al_2O_3 1·30, Cr_2O_3 1·96, FeO 2·10, CaO 22·96, MgO 17·88%, corresponding with the formula $Mg(Ca.Fe)(SiO_3)_2,(Al,Cr)_2O_3$. It has n_D^α 1·6722, n_D^β 1·6847, n_D^γ 1·7015.

A. A. Eldridge.

Tarnowitzite. H. O'Daniel (Z. Krist., 1930, **75**, 576—577; Chem. Zentr., 1931, i, 439).—Tarnowitzite is a plumbiferous aragonite; the limit of lead oxide is higher than the earlier estimate of 5%.

A. A. Eldridge.

Thermal analysis of chlorite. J. Orcel (Bull. Soc. Franç. Min., 1930, **52**, 194—197; Chem. Zentr., 1931, i, 438).—The heating curve for a ripidolite in air was normal, with two maxima; in a vacuum and in nitrogen the curve shows a sharp maximum, corresponding with the exothermic reaction $2FeO+H_2O=Fe_2O_3+H_2$, at about 780°.

A. A. Eldridge.

Andesitic bread-crust bomb from Tusnádfürdö. V. Zsivny [with K. Emszt] (Math. Nat. Anz. Ungar. Akad. Wiss., 1929, **46**, 277—290; Chem. Zentr., 1930, ii, 3530).—The rock of the bread-crust bomb is an amphibole andesite poor in biotite. Analysis gave SiO_2 65·16, TiO_2 0·44, CaO 4·41, MgO 2·19, FeO 2·85, Fe_2O_3 1·57, Al_2O_3 16·13, Na_2O 3·02, K_2O 2·14, SrO 0 08, H_2O 1·52%.

A. A. Eldridge.

Eudialyte. B. Gossner (Zentr. Min. Geol., 1930, **A**, 449—450; Chem. Zentr., 1931, i, 438).—Polemical (cf. Zachariasen, Zentr. Min. Geol., 1930, **A**, 315).

A. A. Eldrdige.

Optical properties of manganese-poor grünerites and cummingtonites compared with those of manganiferous members. N. Sundius (Amer. J. Sci., 1931, [v], **21**, 330—344).—Analyses and optical properties of the following are given: grünerites from Lake Superior, Massachussetts, and Sodermanland, cummingtonite fron Saude (Norway) and from Storgruvan, Persberg, kupfferite from Bajkal and Ural.

C. W. Gibby.

Analysis of cyrtolite for lead and uranium. O. B. Muench (Amer. J. Sci., 1931, [v], **21**, 350—357).—A detailed account of the method used is given. 0·374% Pb and 7·29% U were found in a sample of cyrtolite rich in hafnium from Bedford, N.Y. Assuming no ordinary lead to be present, the age of the mineral is calculated to be 373×10^6 years.

C. W. Gibby.

Constitution of the scapolites. L. H. Borgstrom (Z. Krist., 1931, **76**, 481—499; cf. A., 1915, ii, 836).—By consideration of 52 analyses of scapolites it is shown that Tschermak's meionite ("oxide-meionite"), $(CaAl_2Si_2O_8)_3,CaO$, does not exist, but that the scapolites are isomorphous mixtures of the type $(NaAlSi_3O_8)_3,NaCl$, in which the albite molecule may be replaced by anorthite, $CaAl_2Si_2O_8$, and the NaCl by $CaCO_3$, $CaSO_4$, $0·5Na_2CO_3$, or $0·5Na_2SO_4$, sodium and calcium replacing each other atom for atom. The components found in the scapolites are: chloro-, sulphato-, and carbonato-marialites, respectively NaCl,X; $0·5Na_2SO_4$,X; and $0·5Na_2CO_3$,X [$X=(NaAlSi_3O_8)_3$], and carbonato-, sulphato- (sil-

vialite), and chloride-meionites, $CaCO_3,X$; $CaSO_4,X$; and $CaCl_2,X$ [$X=(CaAl_2Si_2O_8)_3$].

C. A. SILBERRAD.

Titaniferous augite from Chaudrawati, Sirohi State, Rajputana. A. L. COULSON (Rec. Geol. Survey India, 1931, **63**, 448—450).—Titaniferous augite, possibly triclinic, occurs in a contact metamorphic rock between olivine-gabbro and a calcic rock near Chaudrawati. It is black, but pleochroic in thin sections (mauve and greenish-brown), α 1·734, $\gamma-\alpha$ 0·0024, β variable; dispersion $\rho>\nu$.

C. A. SILBERRAD.

Sapphirine in the Vizagapatam district. H. CROOKSHANK (Rec. Geol. Survey India, 1930, **63**, 446—448).—Sapphirine has been found in several places 25 miles east of the place of first discovery (cf. Middlemiss, A., 1904, ii, 668), and is probably fairly common over most of the Eastern Ghats in the Vizagapatam district. The following additional optical properties are given: α 1·714, β 1·718, $\gamma-\alpha$ 0·006; $2V$ 62°. C. A. SILBERRAD.

Tremolite from near Jasidih, Behar, India. A. L. COULSON (Rec. Geol. Survey India, 1931, **63**, 444—446).—The tremolite is pale green, with minute twin lamellæ parallel to (001); d 3·05; α 1·6029, β 1·6175, $\gamma-\alpha$ 0·0271; $2V$ 85° 6′. Analysis of another sample gave SiO_2 58·50, Al_2O_3 2·82, ($FeO+Fe_2O_3$) 1·60, MnO trace, MgO 23·28, CaO 13·58, H_2O nil, total 99·78%. C. A. SILBERRAD.

Trap rocks of the Chitaldrug schist belt. C. S. PICHAMUTHU (Mysore Univ. J., 1930, **4**, 210—222).—The rocks are described and the mode of their occurrence is discussed. C. W. GIBBY.

Ephesite (soda-margarite) from Postmasburg, South Africa. F. C. PHILLIPS (Min. Mag., 1931, **22**, 482—485).—Pink micaceous plates with the characters of margarite occur in manganese ore. Analysis by H. G. WEALL gave SiO_2 29·4, TiO_2 0·1, Al_2O_3 50·6, Fe_2O_3 0·55, FeO 0·35, MnO 0·1, MgO 0·4, Na_2O 8·65, K_2O trace, Li_2O 1·5, H_2O+ 5·3, H_2O- 1·25, F 0·2, total 99·80%. The mineral is much richer in alumina than any mica and it corresponds with margarite with the calcium largely replaced by sodium, being a soda-margarite. L. J. SPENCER.

Grunerite from Pierrefitte, Hautes-Pyrenees, France. H. V. WARREN (Min. Mag., 1931, **22**, 477—481).—Grunerite forms a compact grunerite-schist overlying the ore-body and also occurs as needles in the lead and zinc ore. Analysis shows $FeSiO_3$ 81·4, $MnSiO_3$ 4·3, $MgSiO_3$ 10·6, $CaSiO_3$ 3·7%. The optical data for this material and for grunerite from other localities are correlated with the variations in chemical composition. L. J. SPENCER.

Distinction of analcime from leucite in rocks by *X*-ray methods. F. A. BANNISTER (Min. Mag., 1931, **22**, 469—476).—*X*-Ray powder photographs of analcime from Sicily and blairmorite from Portuguese East Africa give a unit cell of edge a 13·70 Å. Leucite from Vesuvius is pseudo-cubic with a body-centred cell of dimensions a 12·95, b 13·12, c 13·74 Å. It is thus possible by this method to distinguish between analcime and leucite and also both from the glassy groundmass in rocks. L. J. SPENCER.

Dolerite-chalk contact of Scawt Hill, Co. Antrim. Production of basic alkali-rocks by the assimilation of limestone by basaltic magma. C. E. TILLEY and H. F. HARWOOD (Min. Mag., 1931, **22**, 439—468).—The dolerite magma intruded into chalk absorbed some calcium carbonate with the production of pyroxenite, titanaugite-melilite-rocks, nepheline-dolerite, etc. Complementary to the precipitation of magnesium-rich pyroxene in the pyroxenite there was a segregation of a basic alkali residuum. Plagioclase was reabsorbed giving place to a titaniferous lime-augite rich in alumina, melilite, and nepheline. Several unusual minerals, including the new species larnite and scawtite, were formed by this interaction of dolerite magma and chalk. Analyses are given of the rocks and the pyroxenes.

L. J. SPENCER.

Enstatite and its relation to the pyroxenes and amphiboles. B. GOSSNER and F. MUSSGNUG (Z. Krist., 1929, **70**, 234—248; Chem. Zentr., 1930, ii, 1055).—Mixed crystals of bronzite and hypersthene show rhombic unit cells with a 8·93 and 8·84, b 18·2 and 18·23, and c 5·12 and 5·20 Å. for bronzite and hypersthene, respectively. (Enstatite gives no rotation diagram.) The cell probably contains 16 mols.; space-group probably V_h^{16}. The pyroxenes and amphiboles are discussed in the light of *X*-ray measurements. L. S. THEOBALD.

Formula of tourmaline. F. MACHATSCHKI (Z. Krist., 1929, **70**, 211—233; 1929, **71**, 45—46; Chem. Zentr., 1930, ii, 1054).—The formula $XY_9B_3Si_6H_xO_{31}$, where X is Ca, Na, and possibly $Mn^{\cdot\cdot}$, and Y is Li, Mg, Mn, Fe, and Al, is assigned to tourmaline. Apparently, aluminium can replace some silicon by means of the replacement of Na,Si by Ca,Al or of Si,Mg by Al,Al. Rotation photographs of black tourmaline from Grundesund, Norway, give a 16·02, c 7·22 Å.; the hexagonal unit cell contains 3 mols.

L. S. THEOBALD.

Heulandite. P. GAUBERT (Bull. Soc. Franç. Min., 1930, **52**, 162—194; Chem. Zentr., 1931, i, 49; cf. A., 1930, 718, 1017).—Different types of heulandite, associated with different optical properties, are produced by partial dehydration and rehydration. Differences in the speed of diffusion of various liquids into heulandite have been measured.

A. A. ELDRIDGE.

Klebelsbergite. V. ZSIVNY (Math. Nat. Anz. Ungar. Akad. Wiss., 1929, **46**, 19—24; Chem. Zentr., 1930, ii, 3530).—The new mineral from Felsobanya is a basic antimony sulphate. A. A. ELDRIDGE.

Minerals of the clay group. I. F. KASTNER and F. K. MAYER (Chem. Erde, 1931, **6**, 269—274).—A discussion of clays and the weathering of felspar. *X*-Ray powder photographs of samples referred to as nacrite, kaolin, and montmorillonite suggest that these are mixtures. L. J. SPENCER.

Formularisation of silicates. F. MACHATSCHKI (Chem. Erde, 1931, **6**, 253—254).—Further discussion on the formula of tourmaline (A., 1930, 315).

L. J. SPENCER.

Formularisation of silicates. W. KUNITZ (Chem. Erde, 1931, **6**, 255—256).—A reply to the above.

Origin of Schaumspat and dolomite. E. Köhler (Chem. Erde, 1931, 6, 257—268).—Analyses of Schaumspat (aphrite) from the dolomitic limestones and marls (Zechstein and Muschelkalk) of several localities in Thuringia show that the material consists of calcium carbonate with only traces of magnesia and ferric oxide. It is a pseudomorph of aragonite after gypsum. It can be produced artificially by the action of magnesium hydrogen carbonate solution on gypsum at 20° under carbon dioxide pressure, or with calcium hydrogen carbonate at a higher temperature (30°). Attempts to prepare dolomite by the action of magnesium sulphate solution on vaterite usually gave magnesite, but in the presence also of ammonium sulphate dolomite was formed. Dolomite-rock has been formed at certain depths in the earth's crust by the action of solutions of magnesium salts on limestone, and the calcium set free has been partly deposited as gypsum, which later became converted into aragonite, giving Schaumspat.

L. J. Spencer.

X-Ray examination of the modifications of calcium carbonate in gasteropod shells. F. K. Mayer (Chem. Erde, 1931, 6, 239—252).—In the embryonic forms of land and fresh-water snails the shell in the first stages consists of vaterite, which in later stages becomes converted into aragonite, and still later partly into calcite. L. J. Spencer.

Crystals of calcite from the coal mines of Hasard and of La Concorde formed by deposition on the lateral edges of scalenohedra d^2. Crystals from Binnen, with perfectly reflecting faces, having the notation d 13/11, associated with chalcedony. J. Mélon (Bull. Acad. roy. Belg., 1931, [v], 16, 1353—1363).—Crystallographic data are recorded. Both Hasard (yellowish) and La Concorde calcite are associated with chalcopyrite and ankerite. C. W. Gibby.

Mineral succession in regions of pneumatolytic-hydrothermal action. W. Kunitz (Z. Krist., 1931, 76, 462—463; cf. A., 1929, 965).—The order of crystallisation of minerals containing volatile acids is discussed according to a general scheme of fractional distillation. Thus in an acid granite pegmatite the silicates first separated, followed by the phosphates, and then by carbonates, sulphides, and fluorides. C. A. Silberrad.

Crystal habit of zinc blende with special reference to vicinal forms. G. Kalb (Z. Krist., 1931, 76, 386—395).—Examination of the vicinal forms of many samples confirms the reference of zinc blende to the octahedral isoharmonic type (cf. A., 1930, 1099). It further enables all blendes to be classified minerogenetically into an older cubo-octahedral type, usually black, rarely green, yellow, or colourless, and a younger dodecahedral type, usually red (ruby blende). C. A. Silberrad.

Genetic physico-chemical theory of formation of humus, peat, and coal. J. Zolcinski (Pflanzenbau, 1930, 4, 196—228; Chem. Zentr., 1931, i, 248—249).—Humification is not a bacterial process; hydrogen peroxide and aromatic compounds, having an antiseptic action, are formed simultaneously. The physico-chemical process proceeds the more vigorously the greater is the number of double linkings in the decomposing material. All biological factors employing stored chemical energy tend to convert organic compounds into those containing double linkings which are suitable for humification. Organic compounds, particularly aromatic, containing double linkings decompose even in the dark and with exclusion of air. A. A. Eldridge.

Soil erosion. Anon. (Imperial Bur. Soil Sci. Tech. Comm., Nos. 5 and 16).—A comprehensive summary of existing literature and bibliography.

A. G. Pollard.

Occurrence and distribution of salinity in a virgin Mallee soil. J. E. Thomas (J. Counc. Sci. Ind. Res. Australia, 1931, 4, 12—19).—Considerable variations in both the vertical and horizontal distribution of salt in the soil are recorded and correlated with relief, soil type, and type of vegetation.

A. G. Pollard.

Organic Chemistry.

Initial and other significant temperatures in the pyrolysis of pentanes and pentenes. G. Thomson (Abs. Theses Mass. Inst. Tech., 1931, 7, 51—53).—The decomposition temperatures of *n*- and *iso*-pentane, Δ^{a}- and Δ^{β}-pentene, and β-methyl-Δ^{β}-butene have been determined by heating a definite volume of the vapour at various temperatures until a temperature is attained at which appreciable expansion occurs within a prescribed period (1 hr.). By plotting the rate of expansion at this and at successively rising temperatures against temperature, and extrapolation of the resulting straight line to zero expansion the decomposition temperature is obtained. Complications arise owing to decomposition of intermediate products and, in the case of the unsaturated compounds, to polymerisation. The results indicate that the saturated branched-chain compounds are less stable than straight-chain compounds, and that the unsaturated compounds decompose more rapidly than the saturated compounds. The stability of the olefines is the greater the nearer is the double linking to the middle of the chain. A methyl group attached to an ethylenic carbon atom is firmly bound, and the stability increases with increase of the symmetry of the molecule. H. F. Gillbe.

Fission and condensation of hydrocarbons. I. Ethylene. E. Berl and W. Forst (Z. angew. Chem., 1931, 44, 193—197).—Ethylene was circulated through a porcelain tube heated at 800—900°, the heavy oils produced being precipitated electrolytically, the light oils absorbed in active carbon, and the gaseous products analysed when decomposition had ceased, usually after several hours. Up to 43% of liquid

products were obtained, their amount and the ratio of light to heavy oils being dependent on the temperature and velocity of circulation. Packing the tube with pieces of porcelain slightly increased the total yield, and also the proportion of light oil, whilst the presence of metals or metallic oxides greatly lowered the amount of liquid obtained because of their catalytic action on the decomposition of ethylene into its elements. The gaseous products were mainly lower aliphatic hydrocarbons and hydrogen, little ethylene remaining undecomposed. The liquids consist of benzene, naphthalene, anthracene, and their homologues, *cyclo*pentadiene being also detected. The mechanism of reaction is stated to be primarily the formation of unsaturated radicals, which either polymerise or unite with hydrogen. A. KEY.

Electromerides of Δ^{β}-pentene. R. H. CLARKE and E. G. HALLONQUIST (Trans. Roy. Soc. Canada, 1930, [iii], **24**, III, 115—119).—The two electromerides of Δ^{β}-pentene have m. p. $-149°$ (stable) and m. p. $-144°$ (metastable), respectively. A magnetic or electrostatic field had no effect on the product obtained by addition of hydrogen bromide to the metastable form. W. GOOD.

Catalysis of polymerisation by ozonides. R. C. HOUTZ and H. ADKINS (J. Amer. Chem. Soc., 1931, **53**, 1058—1063).—Ozonised mixtures of two di*iso*butylenes accelerate the polymerisation, both at the ordinary temperature and at 100°, and without solvent or in toluene solution, of styrene, indene, βγ-dimethyl-$\Delta^{\alpha\gamma}$-butadiene, methylpentadiene, and furfuryl alcohol, but are inactive towards stilbene, *o*-hydroxybenzyl alcohol, β-methyl-Δ^{β}-butene, and the original mixture of octylenes from which they were prepared. With styrene (and generally) the velocity of polymerisation increases with increasing concentration of the catalyst up to 2%, a period of induction of approximately 200 hrs. being observed when only 0·5% of the catalyst is used. The catalytic activity is inherent in the original ozonides and not in any decomposition products, since the activity diminishes rapidly on keeping. J. W. BAKER.

Oleastene, a hydrocarbon of the olive. G. SANI (Atti R. Accad. Lincei, 1930, [vi], **12**, 238—242 *Oleastene*, $(C_7H_{12})_x$, b. p. 300° (low pressure), $d^{17\cdot5}$ 0·8896, obtained during the separation of the cholesterol of the olive, forms an *ozonide*, $C_{21}H_{36}O_9$. T. H. POPE.

Vegetable dyes. XXIX. Symmetrical lycopene formula. Perhydrolycopene. P. KARRER, A. HELFENSTEIN, B. PIEPER, and A. WETTSTEIN (Helv. Chim. Acta, 1931, **14**, 435—438; cf. A., 1930, 1627).—Degradation of lycopene with ozone gives 1·6 mols. of acetone in accordance with the "symmetrical" formula (A., 1930, 1422), which is also supported by the close agreement in physical properties between perhydrolycopene and the hydrocarbon $C_{40}H_{82}$, b. p. 238—240°/0·3 mm., 212—214°/0·02 mm. (cf. A., 1929, 49), obtained from dihydrophytyl bromide by the Wurtz synthesis.

Squalene, which also possesses a symmetrical structure (cf. this vol., 333), gives 1·8 mols. of acetone under the same conditions. H. A. PIGGOTT.

Characterisation of alkyl halides and organo-magnesium halides. A. M. SCHWARTZ and J. R. JOHNSON (J. Amer. Chem. Soc., 1931, **53**, 1063—1068).—Alcohols and their halides are readily identified and characterised by conversion into the corresponding magnesium alkyl halide and conversion of these into crystalline acid anilides by interaction with a 10% ethereal solution of phenylcarbimide. With certain branched-chain alcohols isomerisation occurs (probably during conversion into the halide); thus methyl*iso*propylcarbinol and ββ-dimethylpropan-α-ol both afford ββ-dimethylbutyranilide. Magnesium allyl bromide affords a liquid anilide, probably impure vinylacetanilide. *d*-α-Bromo-octane affords only *dl*-β-methyloctanoanilide. J. W. BAKER.

Removal of hydrogen halide from organic halides. C. R. NOLLER and R. DINSMORE (J. Amer. Chem. Soc., 1931, **53**, 1185—1186).—The main reaction between alkyl halides and tertiary bases, especially pyridine, other than quaternary salt formation, appears to be the removal of hydrogen halide from the alkyl halide (cf. Semb and McElvain, this vol., 494). J. W. BAKER.

Activity of the halogens in some polyhalogeno-aliphatic derivatives. B. V. TRONOV and L. V. LADIGUINA (J. Russ. Phys. Chem. Soc., 1930, **62**, 2165—2171).—Activity is least in the case of chlorine and greatest in iodine. Halogen atom in a compound of the type $X[CH_2]_n{\cdot}X$ is more readily split off than in $H[CH_2]_n{\cdot}X$. In compounds of the former type, as the value of n increases, the activity begins to fall after an initial rise. This is attributed to two influences in the molecule. According to the theory of alternating polarity, the activity should alternately rise and fall, depending on the number of atoms separating the halogens. Counteracting this is the effect of the large effective positive charge of the halogen nucleus; under the influence of a strongly electronegative element all the atoms in the chain tend to become more electronegative. Both these forces weaken with increasing distance between the atoms, but the weakening proceeds along different lines. The force of direct action through the chain at first exceeds the periodic force, but afterwards diminishes more rapidly. E. B. UVAROV.

Preparation of chlorinated products of acetylene. S. LANGGUTH (Chim. et Ind., 1931, **25**, 22—25).—Laboratory details, with diagrams of apparatus, are given for the preparation of *s*-tetrachloroethane and *s*-dichloroethylene from acetylene and antimony pentachloride, and for converting the tetrachloroethane into trichloroethylene with potassium hydroxide. The preparation of α- and β-trianilinoethylene from aniline and the tetrachloride is described. L. J. HOOLEY.

Halogeno-compounds of the butane series. E. MULLER and F. HUTHER (Ber., 1931, **64**, [*B*], 589—600).—*s*-Tetrachloroethane loses chlorine when boiled for a considerable time and forms ααβγδδ-*hexachlorobutane*, m. p. 107°, which is contained in the residues of the technical distillation of crude tetrachloroethane. Irradiation of homogeneous tetrachloroethane with ultra-violet light causes loss of hydrogen chloride instead of chlorine and production

of *ααβγδδ-hexachloro-Δ^{β}-butene*, m. p. 80°. Removal of 2 mols. of hydrogen chloride from ααβγδδ-hexachlorobutane by means of calcium hydroxide leads to the production of two stereoisomeric forms of *αβγδ-tetrachloro-$\Delta^{\alpha\gamma}$-butadiene*, b. p. 188°, d^{15} 1·516, and m. p. 50°, respectively; both compounds are present in the residues obtained technically from crude trichloroethylene. Addition of chlorine to the tetrachlorobutadiene, m. p. 50°, gives *ααβγδδ-hexachloro-Δ^{β}-butene*, m. p. 80°, whereas the liquid tetrachloro-compound yields a liquid, *ααβγδδ-hexachloro-Δ^{β}-butene*, b. p. 97—98°/10 mm. Addition of bromine leads to *αβγδ-tetrachloro-αδ-dibromo-Δ^{β}-butene*, m. p. 105°, whereas the liquid modification of this compound cannot be distilled without decomposition in a vacuum. *αβγδ-Tetrachloro-αδ-dinitro-Δ^{β}-butene*, m. p. 131°, is obtained by the action of fuming nitric acid or nitrogen peroxide. αβγδ-Tetrachlorobutadiene can under certain conditions be regenerated from its additive compounds with chlorine and bromine.

H. WREN.

Addition of gaseous hydrogen bromide to acetylene and to gaseous vinyl bromide in presence of catalysts, and to vinyl and allyl bromides in the liquid phase. J. P. WIBAUT [with P. J. HUBERS, L. S. BROUWER, C. TER BRAAK, and J. P. WEDDEPOHL] (Rec. trav. chim., 1931, **50**, 313—337; cf. A., 1929, 1399).—The combination of gaseous hydrogen bromide and gaseous vinyl bromide has been carried out in a special apparatus, the relative proportions of the isomeric dibromoethanes formed being determined thermometrically and refractometrically. Although the results obtained are not always reproducible, the following generalisations may be made. Glass wool and asbestos are catalysts at 100° for the formation of ethylene bromide, whilst silica gel, bismuth and ferric bromides (without carriers) lead to ethylidene bromide. Metallic bromides on an asbestos support give mixtures of these isomerides, of variable composition, and the results are sometimes inexplicable. The effect of raising the temperature to 200° is to decrease the total yield, but to increase the proportion of ethylidene bromide. No interconversion of the two isomerides take place at 150°, with or without the above catalysts. Similar experiments with acetylene and hydrogen bromide show that the formation of dibromoethanes takes place with less ease, and it is concluded that the primary formation of vinyl bromide takes place with greater difficulty than its subsequent conversion into dibromoethanes. The formation of ethylene bromide by this process seems a practical possibility. Aqueous hydrogen bromide (*d* 1·6—1·7) with vinyl bromide at 100° leads to ethylidene bromide, but more concentrated solutions (*d* 1·82—1·86) give mixtures which contain 31—35% of ethylene bromide. Acetic acid solutions of hydrogen bromide, with or without the addition of metallic bromides or other contact substances, yield with vinyl bromide at 100° mainly ethylidene bromide. Acetic acid solutions of hydrogen bromide under a variety of conditions give only αβ-dibromopropane with allyl bromide, whereas in bright sunlight, liquid allyl bromide and anhydrous hydrogen bromide give mainly trimethylene bromide.

An explanation of the results, based on the hypothesis of "directed absorption" of Kruyt and van Duin (A., 1921, ii, 392; 1928, 849; 1929, 1399), is offered, but it is pointed out that the results are not in agreement with the theory of alternate polarities.

J. D. A. JOHNSON.

Addition of hydrogen bromide to allyl bromide in a magnetic and electrostatic field. R. H. CLARKE and K. R. GRAY (Trans. Roy. Soc. Canada, 1930, [iii], **24**, III, 111—114).—The composition of the product obtained on the addition of hydrogen bromide to allyl bromide in glacial acetic acid is greatly changed when the reaction is carried out in a magnetic field. W. GOOD.

Catalytic hydrogenation of organic compounds over copper chromite. H. ADKINS and R. CONNOR (J. Amer. Chem. Soc., 1931, **53**, 1091—1095).—Copper chromite, prepared by thermal decomposition of copper ammonium chromate, is a very effective hydrogenation catalyst, the reaction being exothermic. It is preferable to nickel, since it is much less readily deactivated, is less sensitive to sulphur and halogen poisons, and is less reactive towards a carbonyl group adjacent to benzenoid rings, reducing it only to the corresponding alcohol. J. W. BAKER.

Catalytic hydrogenation of esters to alcohols. H. ADKINS and K. FOLKERS (J. Amer. Chem. Soc., 1931, **53**, 1095—1097).—By use of a copper chromite catalyst (cf. preceding abstract) and hydrogen at 250°/220 atm., ethyl laurate, myristate, valerate, cinnamate, αα-dimethylpropionate, and succinate are reduced to the corresponding alcohols in 80—90% yield. Ethyl γ-hydroxy-ββ-dimethylbutyrate is reduced to the carbinol, but the molecule subsequently undergoes fission, yielding *iso*butyl and *n*-propyl alcohols. J. W. BAKER.

Formation of methyl alcohol by the direct oxidation of methane. W. A. BONE (Nature, 1931, **127**, 481).—Newitt and Haffner have obtained methyl alcohol by the interaction of oxygen and methane at 360°/100 atm. With a 9 : 1 mixture of methane and oxygen, the reaction is complete in a few min., 17% of the methane oxidised being recovered as methyl alcohol, 0·6% as formaldehyde, and the remainder as oxides of carbon and water vapour. No hydrogen and no trace of a peroxide is formed.

L. S. THEOBALD.

Ethylene chlorohydrin. E. D. G. FRAHM (Rec. trav. chim., 1931, **50**, 261—267).—The methods of preparation of ethylene chlorohydrin already described are critically discussed. The rate of formation is increased if the ethylene and chlorine are allowed to react in dilute aqueous solutions of suitable catalysts (copper chloride 0·1—1·0%, ferric chloride 0·1%, etc.), the simultaneous formation of ethylene chloride being diminished considerably. The catalysts used facilitate the decomposition of hypochlorous acid into hydrochloric acid and oxygen, and it is therefore suggested that the formation of ethylene chlorohydrin from ethylene and chlorine in aqueous media takes place by way of ethylene oxide, which is subsequently decomposed by hydrogen chloride.

J. D. A. JOHNSON.

Configurations of secondary carbinols of the *iso*propyl and *iso*butyl series. P. A. LEVENE and

R. E. Marker (J. Biol. Chem., 1931, **90**, 669—675).—The homologous *d-iso*butylcarbinols form a series in which the values of the mol. rotations fall with increasing mol. wt., whereas in the corresponding *d-iso*propyl alcohol series (Pickard and Kenyon, J.C.S., 1912, **101**, 620) the values rise; this is due to the differing distances, in the two series, of the *iso*propyl group from the asymmetric carbon atom. The following data are recorded, the values for $[\alpha]_D$ being for the homogeneous state in the case of the carbinols, and in absolute alcohol in the case of the esters: *d*-methyl*iso*butylcarbinol, b. p. 64°/60 mm., n_D^{25} 1·4100, $[\alpha]^{25}$ +20·85° (hydrogen phthalate, $[\alpha]_D^{25}$ +55·8°); *d*-ethyl*iso*butylcarbinol, b. p. 81°/60 mm., n_D^{25} 1·4171, $[\alpha]^{25}$ +21·23° (hydrogen phthalate, $[\alpha]_D^{25}$ +24·8°); *d-n*-propyl*iso*butylcarbinol, b. p. 80°/25 mm., n_D^{25} 1·4205, $[\alpha]_D^{25}$ +12·54° (hydrogen phthalate, $[\alpha]^{25}$ +13·0°); l-n-*butyl*iso*butylcarbinol*, b. p. 87°/20 mm., n_D^{25} 1·4258, $[\alpha]_D^{25}$ −9·48 (*hydrogen phthalate*, $[\alpha]^{30}$ −8·1°); d-n-iso*butylamylcarbinol*, b. p. 117°/40 mm., n^{25} 1·4302, $[\alpha]_D^{25}$ +7·22° (*hydrogen phthalate*, $[\alpha]_D^{30}$ +11·9°). A. Renfrew.

Butenols. J. Verhulst (Bull. Soc. chim. Belg., 1931, **40**, 85—90).—Δ^{γ}-Butenyl alcohol [the preparation of which by Pariselle's method (A., 1909, i, 282) is accompanied by a *by-product* $C_7H_{12}O$, b. p. 149—150°/745 mm., d_4^{20} 0·8570] or its acetate is not isomerised in the presence of sodium phenoxide, aniline, or other amines. If the product obtained by heating allylcarbinol, saturated with dry hydrogen chloride, in sealed tube is distilled, allyl chloride first passes over, followed by *γ-chlorobutyl alcohol*, b. p. 67—68°/15 mm., d_4^{20} 1·06218, n_D^{20} 1·44464, also obtained by the action of hydrogen chloride on αγ-dihydroxybutane. Δ^{γ}-Butenyl alcohol, b. p. 120—121°/755 mm., d_4^{20} 0·85306, n_D^{20} 1·42976, is produced (yield, 25%) by distilling the chlorohydrin, preferably in the presence of quinoline. The 6 fractions distilled between 115° and 122° give the same *phenylurethane*, m. p. 79·4—80°. The question of the formation of geometrical isomerides is therefore open. Δ^{γ}-Butenyl alcohol cannot be prepared by Charon's method (A., 1896, i, 407). A. Renfrew.

Preparation of carbon monoxide diethylacetal. A. E. Arbusov (Ber., 1931, **64**, [*B*], 698—700).—A criticism of Scheibler's work (A., 1926, 711; 1927, 338) on the preparation of diethoxymethylene (cf. Adickes, this vol., 196). H. Wren.

Dioxan and halogens. H. Rheinboldt and R. Boy (J. pr. Chem., 1931, [ii], **129**, 273—277).—In agreement with Wurtz (*ibid.*, 1863, 486) the view that the compound, m. p. 65—66°, obtained by the action of bromine on dioxan is the additive compound $(C_4H_8O_4),Br_2$, and not the oxonium perbromide $(C_4H_8O_4),HBr_3$, as stated by Kehrmann and Falke (A., 1925, i, 351), is confirmed by analysis of the corresponding additive *compounds* with iodine, m. p. 84—85°; iodine monochloride, m. p. 56—58°; and iodine monobromide, m. p. 65°. The iodine compound is the most stable of these derivatives. J. W. Baker.

Stannic halides and dioxan. H. Rheinboldt and R. Boy (J. pr. Chem., 1931, [ii], **129**, 268—272).—Dioxan reacts with stannic chloride itself or with its co-ordination compounds of the type $SnCl_4,2R$ ($R=Et_2O$, Ph·CHO, AcPh, and CHPh.CHAc) at 0° to give the co-ordination *compound* $SnCl_4$-----$(C_4H_8O)_2$, similar *compounds* being obtained with stannic bromide and iodide. The iodine compound is very unstable. J. W. Baker.

Condensations [of polyhydric alcohols] with acetone in presence of phosphoric oxide. L. Smith and J. Lindberg (Ber., 1931, **64**, [*B*], 505—516).—The polyhydric alcohol is kept well stirred with anhydrous acetone while a mixture of phosphoric oxide and sand or quartz powder is gradually added. The temperature is maintained between −10° and 30°, the optimum conditions being secured by keeping it as low as practicable. The upper acetone layer, containing the product of the reaction, is neutralised with anhydrous potassium carbonate and the acetone removed by distillation; mesityl oxide is formed in small amount. Ethylene glycol affords ethylene *iso*propylidene ether, b. p. 92—92·5°, d_4^{17} 0·9458, n_D^{17} 1·4009, in 50% yield and glycerol β-chlorohydrin yields its *iso*propylidene ether, b. p. 161·5—162·2° (corr.)/757 mm., d_4^{15} 1·1344, n_D^{15} 1·4487, in 71% yield (calculated on the chlorohydrin consumed in the reaction). With trimethylene glycol the yield of ether is 35%. With rise of temperature the αβ-ether from glycerol appears to be mixed with increasing amount of the αγ-isomeride. The acetonisation of arabinose (70%), rhamnose (85%), mannose (64%), galactose, lævulose (83%), and dextrose is described; the yields are recorded in parentheses. Mandelic acid condenses very readily with acetone in presence of phosphoric oxide. In the presence of hydrogen chloride, glycerol α-chlorohydrin condenses with acetone about thirteen times as rapidly as the β-chlorohydrin, whereas in presence of phosphoric oxide the ratio is about 5·6. The isolation of glycerol β-monochlorohydrin from its mixture with the α-isomeride is effected by acetonisation in presence of phosphoric oxide, followed by removal of the more volatile products. The residue is treated with acetone and hydrogen chloride, giving a residue containing 95% of the β-isomeride, which is purified by ether and finally by fractional distillation under very low pressure. Glycerol α-monochlorohydrin has b. p. 119°/14 mm., d_4^{20} 1·3214, n_D^{20} 1·4811, η^{20} 1·59, whereas the β-monochlorohydrin has b. p. 124°/14 mm., d_4^{20} 1·3219, n_D^{20} 1·4831, η^{20} 3·00. H. Wren.

Partial esterification of polyhydric alcohols. XI. Methyl ethers of glycerol. A. Fairbourne, G. P. Gibson, and D. W. Stephens (J.C.S., 1931, 445—458).—The five methyl ethers of glycerol (cf. Fairbourne, A., 1929, 1038, 1422; Hibbert and Whelen, *ibid.*, 908) are obtained by the methylation of sodium glyceroxides with methyl sulphate in glycerol, both α- and β-monomethyl ethers being separable from the monomethylation product. On further methylation, the β-monomethyl ether yields only glycerol trimethyl ether and *glycerol* ·*dimethyl ether*, b. p. 100°/40 mm., d_4^{15} 1·028, n_D^{15} 1·4249 (p-*nitrobenzoate*, m. p. 44°). By acetylation of the appropriate ethers, *β-acetoxy-αγ-dimethoxypropane*, b. p. 105—106°/40 mm., d_4^{25} 1·025, n_D^{25} 1·413; *γ-acetoxy-αβ-dimethoxypropane*, b. p. 108—109°/40 mm., d_4^{25} 1·027,

n_D^{25} 1·414; *αγ-diacetoxy-β-methoxypropane*, b. p. 144—145°/40 mm., d_4^{25} 1·100, n_D^{24} 1·424; *βγ-diacetoxy-α-methoxypropane*, b. p. 139—140°/40 mm., d_4^{25} 1·097, n_D^{25} 1·422, all hydrolysable to the parent ethers, and *βγ-diacetoxy-α-ethoxypropane*, b. p. 117—119°/10 mm., d_4^{25} 1·062, n_D^{25} 1·422; *β-acetoxy-αγ-diethoxypropane*, b. p. 127—129°/60 mm., d_4^{25} 0·980, n_D^{25} 1·415; *αγ-diphenoxy-β-acetoxypropane*, m. p. 33°; *αγ-di-o-tolyloxy-β-acetoxypropane*, b. p. 204—206°/2—3 mm., d_4^{25} 1·103, n_D^{25} 1·536; *αγ-di-m-tolyloxy-β-acetoxypropane*, b. p. 215—217°/2—3 mm., d_4^{25} 1·103, n_D^{25} 1·536; *αγ-di-p-tolyloxy-β-acetoxypropane*, m. p. 49°, are obtained. *β-Chloro-αγ-dimethoxypropane*, b. p. 155—156°, d_4^{25} 1·05, n_D^{25} 1·42; *glycerol αγ-diisopropyl ether*, b. p. 123—124°/60 mm., d_4^{25} 0·914, n_D^{25} 1·418; *glycidyl isopropyl ether*, b. p. 137—138°, d_4^{25} 0·924, n_D^{25} 1·408; *glycerol α-monobenzyl ether*, b. p. 164—166°/2—3 mm., d_4^{25} 1·130, n_D^{25} 1·530, and *glycerol αγ-dibenzyl ether*, b. p. 198—204°/2—3 mm., d_4^{25} 1·100, n^{25} 1·547, are prepared from the appropriate chlorohydrins and sodium alkoxides. The method of Newman, Trikojus, and Harker (A., 1927, 40) for esterification has been modified for the synthesis of *p-tolyl n-octoate*, b. p. 163—165°/10 mm., d_4^{25} 0·957, n_D^{25} 1·483. G. DISCOMBE.

Methylation of hexosemonophosphoric ester. E. J. KING, R. R. MCLAUGHLIN, and W. T. J. MORGAN (Biochem. J., 1931, **25**, 310—322).—The methylation of the aldosemonophosphate of Robison's fermentation hexosemonophosphate by Fischer's method at 18° and at 60° has yielded two distinct forms of methylhexosidemonophosphate. That produced by methylation at 18° is extremely sensitive to acids. With 0·1*N*-acid at 36° it is rapidly hydrolysed, yielding a reducing hexosemonophosphoric acid. The corresponding hexoside produced by methylation at 60° is stable in the presence of 0·1*N*-acid at 37°. Its rate of hydrolysis closely resembles that of α-methylglucoside under the conditions described.

S. S. ZILVA.

Soya-bean lecithins. II. Lecithins of the α-series. Y. YOKAYAMA and B. SUZUKI (Proc. Imp. Acad. Tokyo, 1931, **7**, 12—14).—By fractional extraction of the brominated α-lecithins of the soya bean (separated as their double salts with cadmium chloride; this vol., 401) with various solvents are isolated the *bromides* of *palmito-linoleo-*, *oleo-linoleo-*, *dioleo-*, and *dilinoleo-*, m. p. 113—114°, *-α-lecithin*. The structures are proved by hydrolysis to tetrabromostearic and palmitic; di- and tetra-bromostearic; dibromostearic; and tetrabromostearic acids, respectively. J. W. BAKER.

Isomeric isoprenesulphone. II. E. EIGENBERGER (J. pr. Chem., 1931, [ii], **129**, 312—326).—By the action of ultra-violet light (which of itself has no action) on a solution of the unimolecular isoprenesulphone *A* (A., 1930, 1405) in 0·5*N*-aqueous or alcoholic potassium hydroxide is obtained an isomeric *sulphone B*, m. p. 77·5—78° (mixed m. p. with *A* depressed to 30°), unchanged by heating at 200°, which forms no bromine additive compound even in a sealed tube at 100°, and is only slightly attacked by boiling *N*-potassium hydroxide. Oxidation with *N*-potassium permanganate (1 atom of oxygen) in neutral solution at 0° gave no crystalline products, 28% of the sulphone being recovered unchanged. The action of potassium on the sulphone *A* or *B* in anhydrous ether gives similar results, yielding the *potassium* salt of an unstable, readily polymerised, di-isoprenedisulphinic acid (*calcium* and *zinc* salts), most probably *γζ-dimethyl-Δ^{βζ}-octadiene-αθ-disulphinic acid*, since the potassium salt reacts with methyl iodide to give the corresponding *dimethylsulphone*, b. p. 130—140°/13—14 mm., and is oxidised with potassium permanganate (10 atoms of oxygen) at 0° giving carbon dioxide, sulphuric, formic, and oxalic acids and acetonylacetone (from the acid from *B*) and, in addition, acetic and tartaric acids in the case of the corresponding acid from *A*. No succinic acid could be detected. In moist ether potassium acts on the sulphone *A* to give a mixture of potassium salts in which γ-methyl-Δ^{β}-butene-α-sulphinic acid, obtained by reductive fission of the di-isoprenedisulphinic acid, is probably present, since oxidation of the *calcium* salt with potassium permanganate affords acetone. On the basis of these results it is suggested that the *A* and *B* sulphones are stereoisomerides, being, respectively, the *cis-* and *trans*-forms relative to the double linking in the ring. J. W. BAKER.

Structure of thiolmethanetrisulphonic acid. H. J. BACKER (Rec. trav. chim., 1931, **50**, 268—278). Oxidation of the potassium salt of the acid described as thiolmethanetrisulphonic acid (A., 1930, 1556) by a variety of reagents leads always to the potassium salt of methanetrisulphonic acid and not of the tetrasulphonic acid. In support of the view that no thiol group is present, it is found that no mercaptides are formed with alkali, the tripotassium salt is neutral, no precipitates are given by solutions of neutral salts of lead, copper, and mercury, the precipitate with silver nitrate is white and unstable, and the substance is odourless; however, a white precipitate is given with mercuric oxide. Colour reactions and the action of heat and hydrolytic reagents appear to indicate that the substance is disulphomethanemonothiosulphuric acid, $(SO_3H)_2CH{\cdot}S{\cdot}SO_3H$. Crystallographic data are given for the potassium, *ammonium* ($+2H_2O$), and *thallium* ($+2H_2O$) salts, which are isomorphous; the *sodium* salt ($+4H_2O$) is described.

J. D. A. JOHNSON.

Methylselenol. A. BARONI (Atti R. Accad. Lincei, 1930, [vi], **12**, 234—237).—*Methylselenol*, SeHMe, b. p. 12°/758 mm., is obtained by the action of methyl iodide on alcoholic sodium hydrogen selenide solution. The *mercuric*, *lead*, *silver*, *copper*, and *bismuth* derivatives were also prepared.

T. H. POPE.

Manufacture of carboxylic acids from nitriles. I. G. FARBENIND. A.-G.—See B., 1931, 289.

Identification of fatty acids. I. R. SEKA and R. H. MULLER (Monatsh., 1931, **57**, 97—105).—A slight excess of the fatty acid is heated with *o*-phenylenediamine at 140—150°, the reaction mixture neutralised with 10% alcoholic potassium hydroxide, the alcohol evaporated, and the residue extracted with benzene. The alkylbenziminazole so produced is purified by distillation and crystallisation. The following alkylbenziminazoles are described: 2-*n*-*propyl*-, b. p. about 220°/15 mm., m. p. 152—153°

(prepared from *n*-butyric acid); 2-n-*amyl*-, b. p. about 250°/15 mm., m. p. 155—156°; 2-n-*heptyl*-, b. p. about 280°/15 mm., m. p. 139—140°; 2-n-*nonyl*-, b. p. about 280°/15 mm., m. p. 114—115°; 2-n-*undecyl*-, b. p. about 300°/15 mm., m. p. 101—193°; 2-n-*pentadecyl*-, b. p. about 300°/15 mm., m. p. 91—92°; 2-n-*heptadecyl*-, b. p. about 310°/15 mm., m. p. 90—91°; 2-*isopropyl*-, b. p. about 180°/15 mm., m. p. 223—225° (from *iso*butyric acid), and 2-β-*methylamyl*-, b. p. about 230°/15 mm., m. p. 158—159° (from β-methylvaleric acid). The penta- and hepta-decyl derivatives are isolated by dissolving the reaction mixture in alcohol, removing the excess of palmitic or stearic acid as the barium salt, and crystallising the benziminazole from the mother-liquors. The m. p. of the above benziminazoles are compared with the m. p. of the corresponding fatty acid amides and anilides. H. BURTON.

Qualitative tests for acetic acid. E. TSCHIRCH (Oesterr. Chem.-Ztg., 1931, **34**, 38—40).—The formation of ethyl acetate, the reactions with ferric chloride and with *o*-phthalaldehyde and ammonia, and Benedict's reaction are of limited application; the ferric chloride reaction is masked by the presence of moderate amounts of sulphate. The cacodyl reaction is unsatisfactory. The blue coloration produced with iodine and lanthanous salts (cf. A., 1930, 62) is a very sensitive test for acetic acid, but inorganic salts, if present in quantity, should first be removed by extraction of the dry material with absolute alcohol (in which acetates are in general very soluble), oxalates and formates must be removed by oxidation with bromine, and if non-volatile organic acids are present in quantity, the acetic acid should be separated by distillation of the acidified solution. Benzoic acid and the homologues of acetic acid either give a similar coloration or inhibit the reaction.

H. A. PIGGOTT.

Mechanism of the allyl transformation. I. Reply to Burton. II. Tautomerism. C. PRÉVOST (Bull. Soc. chim., 1931, [iv], **49**, 261—268; cf. A., 1928, 1211; 1929, 169, 170).—No isomerisation of crotyl trichloroacetate or its isomeride could be detected on heating in toluene for 8 hrs. at 100°; with concentrated trichloroacetic acid as solvent the esters are partly resinified and partial isomerisation occurs, affording in the one case a 75 : 25 mixture and in the other 15 : 85. In the presence of 10% of water the ratios are 55 : 45 and 30 : 70, respectively, but considerably removed from the equilibrium and accordingly Burton's theory of isomerisation is considered inadequate. With 10% of water in the trichloroacetic acid partial hydrolysis also occurs, with subsequent formation of ethers. In the action of crotyl bromide on potassium trichloroacetate isomerisation is much too slow to account for the formation of mixed esters under the conditions employed. In support of Burton's theory is the isomerisation of the esters in boiling acetic anhydride. Support for the synionic theory is adduced from the absence of anomaly among allyl compounds and the absence of isomerisation in their preparation. The high dielectric constant of acetic anhydride explains the isomerism, mesomerides in such solvents being converted into desmotropes. Further evidence in support of the theory is supplied by the allelotrope of primary and secondary dichlorides obtained from Δ^{β}-penten-α-ol and Δ^{α}-penten-γ-ol, the chlorides being mesomeric at 140° in absence of solvent and isomerising at 175° or in presence of water at 100°. Esterification of ethylvinylcarbinol with aqueous hydrochloric acid at 0° yields 43—47% of primary chloride. Phosphorus trichloride at 45° yields 48—52% of primary chloride. The equilibrium mixture obtained after catalytic isomerisation by water at 100° contains almost equal amounts of the two chlorides, and the allelotrope at 175° under pressure in absence of solvent contains 53—55% of primary chloride and at 225°, 60—62%. These five points lie on the same curve, the desmotropic curve being thus a continuation of the mesomeric curve. Contrary to the observations with keto-enols, the influence of the medium is thus much less important than that of temperature, and the composition of the equilibrium mixture can vary widely with temperature.

R. BRIGHTMAN.

Electrolysis of trifluoroacetic acid and its salts. F. SWARTS (Bull. Acad. roy. Belg., 1931, [v], **17**, 27—28.)—Electrolysis of 4*N*-solutions of trifluoroacetic acid or its sodium salt with current density 0·2 amp./cm.² yields *hexafluorethane*, a colourless gas, b. p. −79°±0·5°/760 mm., m. p. −106·3°. The vapour pressure at the triple point is 234 mm.

J. R. I. HEPBURN.

Transformation of oleic into elaidic acid by sulphur. II. G. RANKOV (Ber., 1931, **64**, [*B*], 619—621; cf. A., 1930, 65).—Oleic acid is converted to the extent of 50% into elaidic acid, m. p. 44·4° (corr.), n_D^{100} 1·4308, when heated with 1% of sulphur at 200—220° in an open or closed vessel or in a current of carbon dioxide. If 3% of sulphur is employed, a crystalline compound of higher m. p. in which sulphur is present is also formed.

H. WREN.

Selective hydrogenation of unsaturated acids and their constitution. II. *iso*Linoleic acid of silkworm pupæ. Y. INOUE and B. SUZUKI (Proc. Imp. Acad. Tokyo, 1931, **7**, 15—18).—Oxidation of the methyl ester of *iso*linoleic acid, isolated from the oil of silkworm pupæ, with potassium permanganate in acetone affords oxalic, hexoic, and azelaic acids. After partial reduction with hydrogen and a palladium–barium sulphate catalyst in tetrahydronaphthalene, similar oxidation affords nonoic and azelaic acids. Hence, like linoleic acid, *iso*linoleic acid is also $\Delta^{\iota\mu}$-octadecadienoic acid, the two being stereoisomerides. Oxidation of partly reduced *iso*linoleic acid with alkaline potassium permanganate gives the dihydroxystearic acids, m. p. 130° and m. p. 100°, stearic acid, and elaidic acid, and the last-named is concluded to be the main constituent of the partly reduced acid. Since on partial reduction and subsequent oxidation linoleic acid affords the dihydroxystearic acid of m. p. 130° and oleic acid, this evidence suggests that around the ικ double linking linoleic and *iso*linoleic acids are *cis*- and *trans*-forms, respectively, a view which is supported by the observation that linoleic acid is hydrogenated much more rapidly than is *iso*linoleic acid.

J. W. BAKER.

Polymerisation of methyl esters of higher unsaturated fatty acids. VI. Hydrogenation of polymerised products. VII. Hydrogenation of linseed oil and of the methyl ester of liquid fatty acids of linseed oil. K. KINO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, **15**, 127—129, 130—136).—VI. The polymeride obtained by heating the methyl ester of a higher unsaturated fatty acid at 290—300° for 25 min. in hydrogen and removal of the methyl monocarboxylate, does not depolymerise when catalytically hydrogenated, alone at 180—200° for 5—7 hrs., or in glacial acetic acid at 90° for $2\frac{1}{4}$—$3\frac{1}{4}$ hrs. The saponification value and mol. wt. remain unaltered, but the iodine value falls. The amount of hydrogen absorbed is greater than that calculated from the decrease in the iodine value. The excess of hydrogen is probably used in rupturing the 4-membered carbon ring.

VII. The acetone-soluble and acetone-insoluble fractions of linseed oil, polymerised by heating for 5 hrs. at 290—300° in hydrogen, were saponified, and the monocarboxylic acids were removed. The mol. wts. of the residues were not altered by catalytic hydrogenation. By hydrogenating, in glacial acetic acid, the liquid fatty acids separated from the distillates, a product is formed the iodine value of which is not greatly reduced, although the calculated amount of hydrogen has been absorbed. Further, stearic acid (m. p. 69—70°) can be crystallised from the hydrogenated product of the liquid fatty acids of the acetone-insoluble fraction. Hydrogenation appears to rupture the intermolecular 4-membered carbon ring. The stearic acid obtained by Bauer and Hugel (B., 1925, 250) from the hydrogenated product of the acetone-insoluble fraction of perilla oil was probably formed in this way.

Similar results are obtained by catalytically hydrogenating the distillate and residue (after shaking with 99% methyl alcohol) from the vacuum distillation of the polymerised methyl ester of liquid fatty acids of linseed oil. A. RENFREW.

Separation of glycerides. XVI—XVIII. B. SUZUKI (Proc. Imp. Acad. Tokyo, 1931, **7**, 9—11).—XVI. [With Y. MASUDA.] By fractional extraction of the brominated bone oil of the common finbock (*Balænoptera physalus*) with various solvents are isolated the *bromides* of *dilinoleno-*, m. p. 65°, *clupanodonolinoleno-*, m. p. 132°, *stearolinoleo-*, *stearo-oleo-*, and *stearolinoleno-zoomarin*; *clupanodonoarachidono-*, m. p. 95°, and *arachidonolinoleno-*, m. p. 145°, *-olein*; *linoleno-*, and *oleo-dizoomarin*; *linoleodiolein*; *triarachidonin*, m. p. 218°; and $C_{20}H_{42}O$-*clupanodonolinolenin*, m. p. 123°.

XVII. [With S. OE and U. NISHIMOTO.] From the skin are similarly isolated: $C_{18}H_{27}O$-*linoleno-*, m. p. 122°, $(C_{18}H_{27}O)_2$-, m. p. 148°, *cetoleo-linoleo-*, m. p. 172°, and *tri-*, m. p. 192° (decomp.), *-stearidonin*; *distearidonozoomarin*, m. p. 168° (decomp.); triolein and (?) *dierucolinolein bromides*.

XVIII. [With R. YONEDA and U. NISHIMOTO.] From the internal organs are obtained the *bromides* of *clupanodono-*$C_{22}H_{35}O$-, m. p. 105°, and $C_{22}H_{35}O$-?-, m. p. 98°, *-linolenin*; *clupanodonostearidonozoomarin*, m. p. 193°; *diarachidonogadolein*, m. p. 220° (decomp.); and *linoleodizoomarin*. J. W. BAKER.

"Rhodanometry" of tung oil. J. VAN LOON (Z. Unters. Lebensm., 1930, **60**, 320—327).—When sufficient excess of reagent was used β-elæostearic acid gave a thiocyanogen–iodine value of 91·7, which is one third of the ordinary iodine value. (A suggested formula for the compound formed is given.) On storage in carbon dioxide for several days the acid gave low values unless a large excess of reagent was present. This is attributed to polymerisation. α-Elæostearic acid had a thiocyanogen–iodine value slightly above that of the β-isomeride. The theory is advanced that an unknown acid is present in the product. The thiocyanogen–iodine value of the α-acid is also lowered by polymerisation and oxidation. $\Delta^{\theta\kappa}$-Octadienoic acid, which has two double linkings similarly situated to two of those in elæostearic acid, gave the theoretical iodine value of 181, using Wijs' iodine or Kaufmann's bromine method, when an excess of 200—300% of halogen was present; the thiocyanogen–iodine value was 107·0—108·4. It is concluded that two isomerides are present which behave differently towards the thiocyanogen reagent. The thiocyanogen–iodine value of various tung oils unaltered by storage varied from 90·9 to 94·8, being much higher than the highest value (81) which corresponds with a mixture of glycerides of oleic and α(or β)-elæostearic acids with 5% of saturated acids. It is concluded that a hitherto unknown acid, γ-elæostearic acid, $C_{18}H_{30}O_2$, is present which adds thiocyanogen corresponding with two double linkings. Tung oil must contain about 15·5% of this substance. This conclusion is confirmed by the thiocyanogen–iodine values found for the total fatty acids. W. J. BOYD.

I. Constitution of the hydroxyoleic acid from ergot oil. II. Fission products of ricinoleic acid ozonide. H. MATTHES and O. H. KURSCHNER (Arch. Pharm., 1931, **269**, 88—101, 101—104).—I. The hydroxyoleic acid from ergot oil has the same chemical and physical constants as ricinoleic acid. It may be reduced through the corresponding bromooleic acid to stearic acid, is quantitatively oxidised by permanganate to two isomeric trihydroxystearic acids, and is, accordingly, chemically homogeneous. When ozonised, it gives results identical, except in the particulars mentioned below, with those obtained by Haller and Brochet (A., 1910, i, 216) for ricinoleic acid. The ozonides and ozonide peroxides of the ergot acid and its ethyl ester are viscous liquids, the crystalline products previously described being their hydrolysis products. The sodium hydrogen sulphite additive products of η-aldehydo-octoic acid and its ethyl ester are non-crystalline. The β-hydroxynonoic acid obtained together with traces of a liquid *acid*, (?) $C_8H_{16}(OH)\cdot CO_2H$, $[\alpha]_D$ −7·7°, from the ozonides, has m. p. 49·5—50·5°, b. p. 186°/17 mm., $[\alpha]_D^{15}$ −17·7°, not +2·5° as previously given. It is only partly dehydrated at 230—240°/760 mm. By heating with hydrochloric acid and subsequently with alcoholic potassium hydroxide it gives a Δ^{α}-nonenoic acid which has an abnormally low iodine value, but is identified by its ozonisation to heptoic acid and carbon dioxide.

II. The ozonisation products of ricinoleic acid are identical in all respects with those of the ergot acid. The two are therefore identical.

H. E. F. NOTTON.

Reactions of malonic esters with formaldehyde. II. K. N. WELCH (J.C.S., 1931, 653—657; cf. A., 1930, 452).—By aid of the method of integration of fractional parts (Noyes, A., 1896, ii, 158) the initial reaction between malonic ester and formaldehyde is shown to be of the second order at p_H 4·9, whilst the reaction velocity is inversely proportional to the hydrogen-ion concentration. Piperidine has a profound effect on the reaction velocity at p_H 4·9, methylamine has a similar but temporary effect, whilst ammonia and triethylamine are without effect. The results are explained by Lapworth's theory (A., 1930, 571), but the reaction takes a different course in the presence of piperidine. G. DISCOMBE.

Course of addition of sodium enol-alkylmalonic and -alkylcyanoacetic esters to unsaturated esters. A. MICHAEL and J. ROSS (J. Amer. Chem. Soc., 1931, **53**, 1150—1172).—The course of addition of the sodium enol of alkylmalonic esters to αβ-unsaturated esters agrees with the law of chemical neutralisation (A., 1900, i, 321), and in agreement, also, in the addition of the sodium enols of alkylmalonic ester to ethyl fumarate, the alkyl group migrates so that the addenda are alkyl and $\cdot C(CO_2Et)\colon C(ONa)\cdot OEt$. Thus in marked contrast to the formation of ethyl pentane-βγδδ-tetracarboxylate (*acid*, m. p. 166°) by methylation of *ethyl butane-βγδδ-tetracarboxylate* [described by Michael (A., 1901, 123) as the αβγγ-compound (*acid*, m. p. 176°)] formed by addition of ethyl sodiomethylmalonate to ethyl fumarate, *ethyl butane-αβγγ-tetracarboxylate*, b. p. 180°/3 mm. [obtained by methylation of ethyl propane-αβγγ-tetracarboxylate (*acid*, m. p. 153°), and hydrolysed to *butane-αβγγ-tetracarboxylic acid*, m. p. 170°], is converted by an ethereal suspension of dry sodium methoxide and methyl iodide into ethyl fumarate and the enol of ethyl sodiomethylmalonate, which is methylated to ethyl dimethylmalonate. Similarly, *ethyl pentane-αβγγ-tetracarboxylate*, b. p. 180°/3 mm. (*acid*, m. p. 177°), obtained by ethylation of ethyl propane-αβγγ-tetracarboxylate, is unchanged by treatment with cold sodium ethoxide and methyl iodide, whereas *ethyl pentane-ααβγ-tetracarboxylate* (*loc. cit.* described as the αβγγ-compound) [*acid*, m. p. 179° (decomp.)] is readily methylated to ethyl hexane-ββγδ-tetracarboxylate (*acid*, m. p. 170°), the ethyl group migrating during the addition. In the addition of the sodium enols of alkylcyanoacetic esters to ethyl crotonate the addenda are, similarly, alkyl and $\cdot C(CN)\colon C(ONa)\cdot OEt$ (cf. Thorpe, J.C.S., 1900, **77**, 923). Thus ethyl α-cyanopropionate condenses with ethyl crotonate in alcoholic sodium ethoxide to give *ethyl γ-cyano-αβ-dimethylglutarate*, b. p. 145—148°/3 mm. yield) [together with an *ester*, b. p. 182°/3 mm., which gives a ketonic *compound*, b. p. 50—120°/10 mm. (*semicarbazone*, m. p. 224°), on hydrolysis, the possible cyclic structure of which is discussed], which is apparently a stereoisomeride of the cyano-ester obtained by addition of ethyl sodiocyanoacetate to ethyl tiglate (this vol., 67), since it is hydrolysed by 20% potassium hydroxide to *γ-cyano-αβ-dimethylglutaric acid*, b. p. 145—148°/3 mm., hydrolysed by concentrated hydrochloric acid to give only a trace of αβ-dimethylglutarimide and, mainly, a liquid cyano-acid, further hydrolysed to *trans*-αβ-dimethylglutaric acid. Complete hydrolysis of the original cyano-ester with 20% potassium hydroxide affords a *γ-methylbutane-βδδ-tricarboxylic acid*, m. p. 142°, not identical, but probably stereoisomeric, with the corresponding product in the ethyl tiglate condensation. Ethyl sodioethylmalonate does not add to ethyl crotonate, but with ethyl sodio-α-cyanobutyrate the latter affords *ethyl γ-cyano-β-methyl-α-ethylglutarate*, b. p. 153°/3 mm. (33% yield) (together with an *ester*, b. p. 160—165°/3 mm.), hydrolysed by potassium hydroxide to the corresponding *cyano-acid*, m. p. 147°, further converted by boiling hydrochloric acid into a mixture of *cis*- and *trans*-β-methyl-α-ethylglutarimides, m. p. 92° (main product) and 102°, both hydrolysed to the same *cis*-β-methyl-α-ethylglutaric acid, m. p. 88°. Complete hydrolysis of the original cyano-ester with alkali gives *β-methylpentane-ααγ-tricarboxylic acid*, m. p. 143°. Similar addition of ethyl sodiocyanoacetate to ethyl α-ethylcrotonate gives a *stereoisomeride*, b. p. 154°/4 mm., of ethyl γ-cyano-β-methyl-α-ethylglutarate, hydrolysed by alcoholic potassium hydroxide to a *cyano-acid*, m. p. 132°, which with concentrated hydrochloric acid gives only a trace of the mixed glutarimides, the main product being the syrupy γ-cyano-β-methyl-α-ethylbutyric acid, completely hydrolysed to *trans*-β-methyl-α-ethylglutaric acid. Complete hydrolysis of the original cyano-ester affords a β-methylpentane-ααγ-tricarboxylic acid, m. p. 141°. For comparison, ethyl γ-cyano-β-methylglutarate was ethylated to *ethyl γ-cyano-β-methyl-γ-ethylglutarate*, b. p. 152°/4 mm., similarly hydrolysed to the corresponding *cyano-acid*, m. p. 139°, which with concentrated hydrochloric acid gives a very small quantity of the glutarimides and, mainly, a liquid cyano-acid (? γ-cyano-β-methyl-*n*-hexoic acid) hydrolysed to *trans*-β-methyl-α-ethylglutaric acid. Complete hydrolysis of the parent cyano-ester affords a liquid β-methylpentane-αγγ-tricarboxylic acid, further hydrolysed to a mixture of *cis*- and *trans*-β-methyl-α-ethylglutaric acid. These additive reactions appear to take place with selective synthesis of one of the stereoisomeric forms. Addition to the γ-carbon atom of βγ-unsaturated esters or nitriles has not been found possible, addition occurring to the αβ-form with migration of hydrogen. Thus ethyl sodio-cyanoacetate or -α-cyanopropionate and allyl cyanide afford *ethyl αγ-dicyano-β-methylbutyrate*, b. p. 160°/3 mm., and *ethyl αγ-dicyano-β-methyl-*n*-valerate*, b. p. 152°/3 mm., respectively. With ethyl γ-phenyl-Δ^{β}-butenoate and ethyl sodiocyanoacetate is obtained *ethyl γ-cyano-β-benzylglutarate*, b. p. 193°/3 mm., hydrolysed to β-benzylpropane-αγγ-tricarboxylic acid, m. p. 158° (possibly identical with the acid, m. p. 146°, obtained by Vorlander and Strunck, A., 1906, i, 362), and methylated to *ethyl γ-cyano-β-benzyl-γ-methylglutarate*, b. p. 194°/3 mm., from which *β-benzylbutane-αγγ-tricarboxylic acid*, m. p. 177°, and *β-benzyl-α-methylglutaric acid*, m. p. 139°, are obtained. Similarly, condensation of ethyl sodiomethylmalonate with ethyl γ-phenyl-Δ^{β}-butenoate affords *ethyl β-benzylbutane-ααγ-tricarboxylate*, b. p. 197°/3 mm., hydrolysed by alkali to *β-benzylbutane-ααγ-tricarboxylic acid*, m. p. 197°, and its *stereoisomeride*, m. p. 118°, converted, respectively, by loss of carbon dioxide, into two *forms*, m. p.

139° and m. p. 137°, of β-benzyl-α-methylglutaric acid, the former being identical with the acid obtained above. For comparison α-phenylpropaldehyde was condensed with malonic acid to give γ-phenyl-Δ^{β}-pentenoic acid, the *ethyl* ester, b. p. 156°/10 mm., of which {obtained together with *ethyl γ-phenyl-Δ^{β}-butene-αα-dicarboxylate*, b. p. 175—182°/10 mm. [acid, m. p. 151° (decomp.)]} condenses with ethyl sodiocyanoacetate to give *ethyl α-cyano-β-(α′-phenylethyl)glutarate*, b. p. 198°/3 mm., hydrolysed to β-(α′-*phenylethyl*)-*propane-ααγ-tricarboxylic acid*, m. p. 162°, which affords β-(α′-*phenylethyl*)*glutaric acid*, m. p. 88°, when heated. The mechanism of the retrograde Michael reaction is also discussed on the basis of the authors' views. J. W. BAKER.

Ethyl methylenedimalonate. K. N. WELCH (J.C.S., 1931, 673—674).—Ethyl methylenedimalonate is prepared by the interaction of paraformaldehyde and ethyl malonate in presence of alcoholic potassium hydroxide at the temperature of the water-bath. A yield of more than 90% (cf. A., 1930, 452) is obtained by destroying the catalyst with alcoholic hydrogen chloride before the ester is isolated.

G. DISCOMBE.

αβγ-Trimethylglutaric acids. F. E. RAY (J. Amer. Chem. Soc., 1931, **53**, 1174—1175).—Crystalline γ-methylpentane-ββδ-tricarboxylic acid, m. p. 144—145°, decomposes into αβγ-trimethylglutaric acid, m. p. 134° (A., 1928, 394), so that it cannot be identical with γ-methylbutane-ββγ-tricarboxylic acid, m. p. 145°, as suggested by Michael and Ross (this vol., 67). J. W. BAKER.

αβγ-Trimethylglutaric acids. A. MICHAEL and J. ROSS (J. Amer. Chem. Soc., 1931, **53**, 1175—1176).—A reply to Ray (preceding abstract).

J. W. BAKER.

Glutaconic acids. XXII. Optically active αγ-dimethylglutaconic acid. T. H. McCOMBS, J. PACKER, and J. F. THORPE (J.C.S., 1931, 547—560).—The peculiarities of glutaconic acids can be explained as a consequence of geometrical isomerism and three-carbon tautomerism (A., 1926, 820). *trans*-(normal)-αγ-Dimethylglutaconic acid can be resolved by repeated fractional precipitation of its *strychnine* salt from acetone solution, the l-*acid* having m. p. 132·5—133·5°, $[M]_D^{\text{or } 25}$ —100°, *strychnine hydrogen* salt, m. p. 208—209° (decomp. and resolidifying with m. p. 260—263°). Partial resolution is effected by refluxing the *r*-acid with strychnine in a small quantity of acetone, whilst strychnine or brucine in excess of boiling acetone displaces the equilibrium *l*-acid ⇌ *d*-acid in favour of the *l*-acid. Impure specimens of the *d*-acid are described. G. DISCOMBE.

Action of ozone on aldehydes. F. G. FISCHER, H. DÜLL, and J. L. VOLZ (Annalen, 1931, **486**, 80—94).—The ozonisation of undiluted aldehydes gives a mixture of the corresponding acid and peracid with the former in excess, the whole of the oxygen of the ozone being used, thus $2R·CHO+O_3 \longrightarrow R·CO_2H+R·CO_3H$ and $3R·CHO+O_3 \longrightarrow 3R·CO_2H$; the "aldehyde peroxides" of Harries and his collaborators appear to be mixtures of acid, peracid, and unchanged aldehyde. The second "nonylaldehyde peroxide," m. p. 73°, is actually *dihydroxynonyl peroxide* (cf. Riehe, "Alkylperoxide und Ozonide," 1931). *Dihydroxyheptyl peroxide* has m. p. 68—69°.

Ozonisation of an aldehyde in solution results in considerably more oxidation than is accounted for by the ozone used; this is not due to the action of oxygen alone, and the oxidation of aldehydes (by oxygen) is not catalysed by the acids or peracids. The ozone, therefore, must be regarded as the catalyst, and it is suggested than an ozonide is formed intermediately, which, in addition to decomposition according to the above equations, can react with oxygen as follows: $R·CHO,O_3+O_2 \longrightarrow R·CO_3H+O_3$. A similar behaviour is shown by olefinic substances in solution.

H. A. PIGGOTT.

Decomposition of aliphatic aldehydes by the Friedel–Crafts reaction. K. BODENDORF (J. pr. Chem., 1931, [ii], **129**, 337—339).—By addition of aliphatic aldehydes (1 mol.) to a suspension of aluminium chloride (1·2 mols.) in a large excess of benzene saturated with dry hydrogen chloride at 0° are obtained 50% yields of the corresponding diarylparaffins, the by-products being alkylbenzenes and resinous material. Thus from the appropriate aldehyde are obtained αα-diphenyl-ethane, -*n*-propane, and -*n*-butane, and αα-diphenyl-β-methyl-*n*-propane.

J. W. BAKER.

Condensation of ketones and aldehydes with ethyl chloroacetate. B. N. RUTOVSKI and N. A. DAJEV (Ber., 1931, **64**, [*B*], 693—698, and J. Russ. Phys. Chem. Soc., 1931, **62**, 2161—2164).—The reaction of ethyl chloroacetate with aliphatic aldehydes and ketones may be represented by the scheme

$$R·CO·CH_3 \xrightarrow{+NaNH_2} R·C(ONa)\!:\!CH_2 \xrightarrow{+CH_2Cl·CO_2Et}$$

$$R·CMe(ONa)·CHCl·CO_2Et \longrightarrow \begin{matrix} CH(CO_2Et) \\ | \\ CRMe \end{matrix}\!\!>O.$$

The preparation of the sodium derivative of acetone and its conversion into ethyl dimethylglycidate, together with the preparation of the last-named compound from acetone, sodium, and ethyl chloroacetate in the presence of ether, are described. Ethyl methylglycidate is obtained from acetaldehyde. With aromatic ketones and aldehydes condensation may occur through the medium of metallic ketyls or ester enolates. The successive action of benzaldehyde and ethyl chloroacetate on powdered sodium suspended in ether gives benzyl alcohol, phenylacetaldehyde, and α-chlorocinnamic acid; if the ether is replaced by toluene, the yield of α-chlorocinnamic acid is considerably increased. The sodium derivative of benzophenone and ethyl chloroacetate in ether afford benzhydrol and ethyl diphenylglycidate.

H. WREN.

Interaction of citronellaloxime and acetic anhydride. J. ZIMMERMANN (Rec. trav. chim., 1931, **50**, 283—286).—Citronellaloxime and acetic anhydride give the corresponding nitrile, amide, tarry material, and a base not identified. Hydrolysis of the nitrile with 0·5*N*-alcoholic potassium hydroxide leads to 7·1% of the amide. The determination of citronellal in crude specimens by the method of Dupont and Labaune (A., 1912, i, 880) is therefore impracticable. J. D. A. JOHNSON.

Enolic derivative of β-hydroxypropaldehyde; preparation of glyceraldehyde. H. O. L. FISCHER,

L. AHLSTROM, and H. RICHTER (Ber., 1931, 64, [B], 611—614).—The action of *p*-toluenesulphonyl chloride and pyridine on αγ-benzylideneglycerol affords *αγ-benzylideneglyceryl* β-*p-toluenesulphonate*, m. p. 125° (yield 86·7%), transformed by distillation with powdered potassium hydroxide into *benzylidene-*Δ^{α}*-propene-αγ-diol*, $CH{<}\genfrac{}{}{0pt}{}{CH_2\cdot O}{CH\cdot O}{>}CHPh$ b. p. 72—75°/0·1 mm., $d^{19\cdot3}$ 1·126, n_D^{20} 1·5408. Oxidation of the last-named compound with perbenzoic acid in chloroform at 0° followed by hydrolysis of the product with 12·5% acetic acid affords glyceraldehyde, m. p. 142°. Benzylidene-Δ^{α}-propene-αγ-diol is hydrogenated in presence of palladised barium sulphate to benzylidenepropane-αγ-diol, m. p. 49·5°, hydrolysed to trimethylene glycol. H. WREN.

Condensation between aliphatic esters and ketones. S. G. POWELL and K. H. SEYMOUR (J. Amer. Chem. Soc., 1931, 53, 1049—1051).—Reaction through the methylene group could not be detected in condensation between esters and ketones of the type $Me\cdot CO\cdot CH_2R$ under the conditions of Claisen and Ehrhardt (A., 1889, 850) and modifications thereof. Thus βδ-diketohexane is obtained from ethyl acetate and methyl ethyl ketone or from ethyl propionate and acetone; γε-diketo-*n*-octane from ethyl propionate and methyl *n*-propyl ketone or from ethyl butyrate and methyl ethyl ketone; and γε-diketo-β-methyl-*n*-hexane from ethyl acetate and methyl *iso*propyl ketone or from ethyl *iso*butyrate and acetone.
J. W. BAKER.

Relation of the structure of ketones to their reactivity and affinity in acetal formation. II. G. J. PFEIFFER and H. ADKINS (J. Amer. Chem. Soc., 1931, 53, 1043—1048).—Re-determination of the amount of ethyl formate present in a mixture of this substance with alcohol, ethyl orthoformate, a ketone, and its acetal by Carswell and Adkins' method (A., 1928, 274) shows that the ratio of carbon monoxide formed to the ethyl formate, $3H\cdot CO_2Et+4Na=2CO+MeONa+3EtONa$, is independent of the amounts of ethyl orthoformate and ketone acetal present, but is a function of the amount of sodium ethoxide and of the amount and nature of the ketone. The presence of sodium ethoxide presumably facilitates the reactions, $H\cdot CO_2Et+Me_2CO=EtOH+COMe\cdot CH{:}CH\cdot OH$ and $H\cdot CO_2Et+Ph_2CO=OH\cdot CPh_2\cdot CO_2Et$, between the ketone and ethyl formate. The amount of ethyl formate equivalent to a given volume of carbon monoxide has been determined. The extent of acetal formation under the conditions previously used (0·136% alcoholic hydrogen chloride at 25°), with acetone, acetophenone, benzophenone, methyl ethyl, methyl β-phenylethyl, methyl neopentyl, di*iso*propyl, methyl *tert.*-butyl, ethyl *tert.*-butyl, *iso*propyl *tert.*-butyl, and di-*tert.*-butyl ketones, is found to be 94·8, 36·2, 33·7, 90·1, 89·1, 84·0, 65·4, 50·1, 36·2, 25·8, and 2%, respectively. The corresponding values of the equilibrium coefficient $k_E\times10^2$ are given. In general, substitution of one of the hydrogen atoms of the methyl groups in acetone results in a decrease in the amount of acetal formed. J. W. BAKER.

Preparation of telluroketones. R. E. LYONS and E. D. SCUDDER (Ber., 1931, 64, [B], 530—532; cf. A., 1927, 449).—Telluroketones are prepared by the action of hydrogen telluride, from aluminium telluride and hydrochloric acid, on a cooled mixture of the requisite ketone and concentrated hydrochloric acid. *Dimethyl telluroketone*, b. p. 55—58°/10—13 mm., d_4^{15} 0·8578, n_D^{25} 1·48825, *methyl ethyl telluroketone*, b. p. 63—66°/9—10 mm., d_4^{15} 0·8711, n^{25} 1·5055, *diethyl telluroketone*, b. p. 69—72°/8—11 mm., d_4^{15} 0·8821, n_D^{25} 1·5480, and the unstable dipropyl telluroketone are described. Benzil and benzophenone do not appear to react.
H. WREN.

Dioximes. LXXIII. G. PONZIO and G. BERTINI (Gazzetta, 1931, 61, 51—59).—Chloro-derivatives of the type $R\cdot C({:}N\cdot OH)\cdot C({:}N\cdot OH)\cdot Cl$ are converted into the corresponding cyano-derivatives when an ethereal solution is added slowly to ice-cold aqueous potassium cyanide solution. The product is isolated, after acidification, by extraction with ether. Chloro-oximinoacetone yields *cyano-oximinoacetone*, m. p. 84° [*benzoyl* derivative, m. p. 138—139°; *phenylhydrazone*, m. p. 177° (decomp.)]. Methylchloroglyoxime yields *methylcyanoglyoxime*, m. p. 154—155° ($+2H_2O$) and m. p. 164—165° (anhydrous) [*nickel* salt ($+2H_2O$); *diacetyl* derivative, m. p. 92—93°; *dibenzoyl* derivative, m. p. 236—237°; *peroxide*, an oil], which is also obtained by the action of hydroxylamine on cyano-oximinoacetone. The interaction of hydroxylamine and methylcyanoglyoxime yields *α-amino-αβγ-trioximinobutane*, m. p. 170—172° (decomp.) (*nickel* salt), which is converted by acetic anhydride into *2-amino-3-acetoximinoacetylfurazan*, m. p. 137—138°. Hydrolysis of the last-named compound yields *2-amino-3-acetylfurazanoxime*, m. p. 199—200° (*benzoyl* derivative, m. p. 168—169°), from which, or its acetyl derivative, there is obtained by complete hydrolysis *aminoacetylfurazan*, m. p. 96—97° [*benzoyl* derivative, m. p. 136—137°; *semicarbazone*, m. p. 242—243° (decomp. from 210°); *phenylhydrazone*, m. p. 142—143°]. R. K. CALLOW.

Oxidative decomposition of sugars. X. Formation of methylglyoxal from sugars and related substances under the action of hydrogen peroxide. XI. Formation of phenols. XII. Formation of higher fatty acids. K. BERNHAUER (Biochem. Z., 1931, 230, 484—492, 493—500, 501—504).—X. [With H. TSCHINKEL.] Under the action of hydrogen peroxide sugars and related substances (especially γ-methylglucoside) in acid solution and in presence of ferrous sulphate yield methylglyoxal, whereas in absence of ferrous sulphate considerable amounts of acids (chiefly formic) are formed.

XI. [With J. NEPP.] The formation of phenols on fusion of various sugars and related substances with potassium hydroxide is comparatively investigated. By the action of potassium formate on phenol, salicylic and *m*-hydroxybenzoic acids, and on pyrocatechol, protocatechuic acid were obtained.

XII. [With J. NEPP.] When lactic acid and sugars are autoclaved with potassium hydroxide, formic, acetic, and propionic but not higher acids are formed.
P. W. CLUTTERBUCK.

Cellobiosan and cellulose. K. HESS and E. GARTHE (Naturwiss., 1930, 18, 180).—The observ-

ations of Freudenberg (A., 1930, 198) are ascribed to unsuitable experimental conditions. B. LEVIN.

Æsculin. R. SEKA and P. KALLIR (Ber., 1931, **64**, [*B*], 622—627).—Æsculin, m. p. 204°, $[\alpha]_{D}^{18}$ −38·5° in pyridine, is transformed by diazomethane in methyl alcohol into *æsculin methyl ether*, m. p. 225°, hydrolysed by 2·5% sulphuric acid to æsculetin monomethyl ether, m. p. 185°. The last-named compound is identified as 6-hydroxy-7-methoxycoumarin by the following method. *p*-Aminoguaiacol hydrochloride is warmed with sulphuric acid until the hydrogen chloride is completely expelled, and the resulting solution is diluted with water, diazotised, and boiled, thus giving 2 : 5-*dihydroxyanisole*, m. p. 79°, in 41·7% yield. Treatment of this compound in ether with zinc chloride, hydrogen cyanide, and hydrogen chloride leads to the isolation of 2 : 5-*dihydroxy-4-methoxybenzaldehyde*, m. p. 206° (decomp.) (*phenylhydrazone*, m. p. 166°), transformed by acetic anhydride and sodium acetate into 6-*acetoxy-7-methoxycoumarin*, hydrolysed to 6-*hydroxy-7-methoxycoumarin*, m. p. 184·5°.

Treatment of æsculetin with diazomethane followed by fractional extraction of an ethereal solution of the product with 0·1*N*-alkali hydroxide leads to the isolation of 6 : 7-*dimethoxycoumarin*, m. p. 144°, and 6-hydroxy-7-methoxycoumarin, m. p. 184—185° (*benzoate*, m. p. 211°); the isomeric 7-hydroxy-6-methoxycoumarin does not appear to be produced. H. WREN.

Strophanthin. XIX. Dehydrogenation of strophanthidin and gitoxigenin. W. A. JACOBS and E. E. FLECK (Science, 1931, **73**, 133—134).—Preliminary details of the fractionated products obtained after dehydrogenation of strophanthidin and gitoxigenin with selenium are recorded. L. S. THEOBALD.

Isolation of phytosterolin from wheat embryo. N. NAKAMURA and A. ICHIBA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, **15**, 137—141).—The insoluble material separated from the oil obtained by extracting air-dried wheat embryo powder with ether gives phytosterolin (Power and Salway, J.C.S., 1913, **103**, 399, 1022), m. p. 285—290° (*acetate*, m. p. 168° uncorr., $[\alpha]_D$ −22·4° in chloroform; *benzoate*, m. p. 198° uncorr., $[\alpha]_D$ +17·24° in chloroform), hydrolysed to phytosterol and dextrose. A. RENFREW.

Bacterial decomposition and constitution of starch. H. PRINGSHEIM (Woch. Brau., 1931, **48**, 73—78, 83—86).—A lecture.

Cellulose butyrate. G. VON FRANK and H. COHN (Cellulosechem., 1931, **12**, 68—70).—Cellulose butyrate, giving on hydrolysis 65—66% of butyric acid, and therefore intermediate in composition between the di- and tri-esters, is obtained by first steeping cellulose in 80—95% aqueous formic acid for 24 hrs. at the ordinary temperature, then esterifying with butyric anhydride, butyric acid, and zinc chloride, and finally removing the formyl group by hydrolysis with 93% butyric acid. The product sinters at 172°, becomes clear at 208°, and begins to decompose at 225°. It is soluble in the usual solvents, forming highly viscous solutions. In the form of films or fine threads it has a much lower tensile strength and greater plasticity than cellulose acetate. H. A. PIGGOTT.

Preparation of cellulose nitrate with mixtures of nitric and phosphoric acids. E. BERL and G. RUEFF (Cellulosechem., 1931, **12**, 53—62).—An expanded description of results already published (cf. this vol., 203). The maximum content of nitrogen in the product (14·14%, corresponding with the pure trinitrate) is obtained with nitric and phosphoric acids in the ratio 1 : 1, the value falling more rapidly with excess of nitric acid on account of hydrolysis; under suitable conditions a product containing 11·3% N can be obtained with an acid mixture containing only 0·8% of nitric acid and 4·85% of water. H. A. PIGGOTT.

Chemical composition of wood of the red beech (*Fagus sylvatica*). E. SCHMIDT (Cellulosechem., 1931, **12**, 62—67).—Delignification of the wood of the red beech (and other deciduous trees) by chlorine dioxide yields the partly decomposed "skeletal substances" of the cell-wall, from which may be isolated by treatment with alkali of successively increasing concentrations an easily soluble xylan, a polymeric carboxylic acid, a sparingly soluble xylan, and cellulose. The stoicheiometric ratio of 1 : 3 is found for the xylose anhydride in the sparingly soluble xylan and the glucose anhydride in the cellulose. If deacetylation be avoided by the use of milder conditions, a further ratio of 1 : 1 for the acetyl group and xylose anhydride is observed. These proportions are constant, and unaffected by the age or habitat of the tree. The water-soluble products from this degradation contain decomposition products of the lignin and the "galactose constituents," *i.e.*, products that may be regarded as built up from *d*-galactose and its simple transformation products. The view is advanced that the skeletal substance, which forms about 78% of the cell-wall, is a compound of ester type derived from the four constituents isolated by chlorine dioxide treatment, physically incorporated with the lignin and the galactose constituents, the proportion of lignin increasing somewhat with the age of the tree. H. A. PIGGOTT.

Determination of choline and acetylcholine; decomposition of acetylcholine. L. LEMATTE, G. BOINOT, E. KAHANE, and (MME.) M. KAHANE (J. Pharm. Chim., 1931, [viii], **13**, 371—385).—Methods for the gravimetric determinations of choline and acetylcholine with either phosphotungstic or silicotungstic acid are described and also a method by which a measure of the decomposition of the acetylcholine may be calculated from the weight of the ignited precipitate. E. H. SHARPLES.

Salts of glycine. J. V. DUBSKÝ and A. RABAS (Coll. Czech. Chem. Comm., 1931, **3**, 135—154).—Aqueous solutions of the zinc salt of glycine deposit 21% of the zinc as hydroxide when heated at 65—70°, and 32% when boiled, during 2 hrs. Further precipitation occurs when the filtrate is boiled with sodium carbonate solution. Precipitation of zinc hydroxide in the former cases is prevented by addition of glycine. The following *salts* are described

(GH = glycine): $G_2Zn,3GH,H_2O$, decomp. 245°; $ZnSO_4,GH,5H_2O$, m. p. 82°, decomp. 320°; $HCl,G_2Cu,CuCl_2$, decomp. 190°; $CuCl_2,2GH,2HCl,2H_2O$, m. p. 96°, decomp. 120°.

J. D. A. JOHNSON.

Identity of Fischer's "glycylglycinecarboxylic acid" and carbamidodiacetic acid. R. LOCQUIN and V. CERCHEZ (Bull. Soc. chim., 1931, [iv], **49**, 318—324).—The isomeric "glycylglycinecarboxylic ester," m. p. 146—148°, obtained by Fischer (A., 1901, i, 675; 1902, i, 350; 1903, i, 607) is ethyl carbamidodiacetate, yielding hydantoin-3-acetic acid when boiled with hydrochloric acid. Esterification of the residue from the alkaline hydrolysis of α-carbethoxyglycylglycine ester, m. p. 87°, yields ethyl hydantoin-3-acetate, and since hydrolysis of α-carbethoxyglycylglycine ester, m. p. 87°, with hydrochloric acid yields glycine hydrochloride or with alcoholic hydrochloric acid ethyl aminoacetate, m. p. 144°, hydrochloric acid has no isomerising action, but only decomposes α-carbethoxyglycylglycine ester into glycine. Accordingly, isomerisation of the latter must occur in its alkaline hydrolysis and not later. The true glycylglycinecarboxylic acid has not been isolated. Since the two terminal carbethoxy-groups in α-carbethoxyglycylglycine ester are not equivalent, tautomerism of the type —CO·NH— —C(OH):N— is suggested, although the final result represents a more profound transformation, probably in accordance with the tendency of organic molecules to assume the most symmetrical form.

R. BRIGHTMAN.

Isomerisation of Fischer's "carbethoxydiglycylglycine ester." V. CERCHEZ (Bull. Soc. chim., 1931, [iv], **49**, 324—328; cf. preceding abstract).—α-Carbethoxydiglycylglycine ester, m. p. 160—161°, on hydrolysis yielded a small amount of the acid, m. p. 206° (decomp.), not identical with carbamidodiacetic acid, and the existence of diglycylglycinecarboxylic acid is regarded as probable. On esterification this acid yielded an ethyl ester of m. p. 149—150°. There appears to be no analogy in the isomerisation of diglycylglycinecarboxylic acid and of glycylglycinecarboxylic acid. R. BRIGHTMAN.

Decomposition of cystine and cysteine during irradiation. F. LIEBEN and E. MOLNAR (Biochem. Z., 1931, **230**, 347—352).—In diffused daylight cystine is decomposed in alkaline and cysteine in acid medium in presence of a sensitiser such as hæmatoporphyrin. The decomposition proceeds readily without addition of sensitiser when the substances are irradiated with ultra-violet light. Addition to tryptophan of irradiated cystine does, but of cysteine does not, decrease its Voisenet colour reaction. Investigation of the action of diffused daylight on the reduction of methylene-blue by cysteine showed that the reduction times in the light and dark tests increase with decreasing p_H, and the difference between the reduction times of light and dark tests also increases. P. W. CLUTTERBUCK.

Glutathione. V. Spontaneous cleavage of glutathione in aqueous solution. H. L. MASON (J. Biol. Chem., 1931, **90**, 25—32).—When glutathione is kept in an aqueous solution at 37—62° it undergoes cleavage into pyrrolidonecarboxylic acid and cysteinylglycine. With Sullivan's test for cysteine, cysteinylglycine gives a purplish-red colour resembling, but not identical with, that given by cysteine. The view put forward by Meldrum and Dixon (cf. A., 1930, 803) on the basis of a positive Sullivan test, that glutathione is frequently contaminated with cysteine and that this latter compound is responsible for autoxidation, is considered to be erroneous, the contaminant being probably cysteinylglycine. Erepsin does not attack glutathione, but hydrolyses the cysteinylglycine after the glutamyl radical has been split off as pyrrolidonecarboxylic acid. W. O. KERMACK.

Constitution of so-called cyanoacetoacetic ester and a disputed synthesis of citric acid. G. FAVREL and C. PRÉVOST (Bull. Soc. chim., 1931, [iv], **49**, 243—261).—Chlorination of ethyl acetoacetate always yields the α-chloro-derivative, and Haller and Held's ester (A., 1882, 1280; 1889, 588; 1891, 171; 1892, 697) consisted entirely of the α-chloro-ester. Ethyl γ-chloroacetoacetate obtained by Lespieau's method with potassium cyanide yields 80—90% of ethyl succinosuccinate, m. p. 127—128°, and not the γ-cyanoacetoacetate. Haller and Held's B derivative, b. p. 142—144°/43—45 mm., also obtained from pure ethyl α-chloroacetoacetate and aqueous potassium cyanide in 32% yield (minimum), has no enolic structure, since it gives no coloration with ferric chloride. With alcohol and hydrochloric acid about 50% of ethyl α-chloroacetoacetate is regenerated. No trace of ethyl acetonedicarboxylate was detected but 40% of an *acid*, $C_5H_7O_2Cl$, m. p. 147—149° (m. p. 105—106°, hydrated), also obtained by the action of potassium cyanide on ethyl α-chloroacetoacetate in presence of hydrochloric acid or sulphuric acid, which is regarded as *α-chloropropan-β-ol-αβ-dicarboxylic acid*.

The structure, is accordingly assigned to the B compound of Haller and Held. Hydrolysis of this cyano-glycidic ester with 4*N*-potassium hydroxide and precipitation of the potassium as sulphate yields a syrup which decomposes at 160°, yielding traces of hydrogen cyanide, carbon dioxide, formaldehyde, acrylonitrile, and a little water. The hydration product, $CN{\cdot}CMe(OH){\cdot}CH(OH){\cdot}CO_2H$, is obtained by addition of a slight excess (1%) of sulphuric acid in neutralising after hydrolysis with potassium hydroxide as a syrup, stable below 140°, slow decomp. at 145—160°, decomp. at 185°, hydrolysed by potassium hydroxide to ammonia and a dicarboxylic acid. Hydrolysis of the cyanoglycidic ester at 70° with 0·25*N*-potassium hydroxide affords a methyltartaric acid, m. p. 100° (*lead* and *silver* salts), which with copper sulphate, ferric salts, resorcinol and sulphuric acid, and β-naphthol and sulphuric acid gives reactions resembling those of tartaric acid. The acid $Ac{\cdot}CH(OH){\cdot}CO_2H$, obtained by hydrolysis of ethyl *O*-acetyl-α-hydroxyacetoacetate, by addition of hydrogen cyanide and hydrolysis yields a similar methyltartaric acid. None of these compounds is capable of yielding citric acid, as claimed by Haller and Held. The mobility of the α-halogen in α-halogeno-ketones is contrary to the feeble mobility which would be

expected, and the mobility of the halogen is regarded as affording an index of complex reactions appearing with the ketonic group, double decomposition and replacement of the halogen by a fresh radical being usually abnormal. R. BRIGHTMAN.

Structure of the glutaconic acids and esters. I. Cyanoglutaconic esters. G. A. R. KON and H. R. NANJI (J.C.S., 1931, 560—575).—The α-cyanoglutaconic esters form equilibrium mixtures of the αβ- and αγ-forms. Ethyl α-cyano-β-methylglutaconate (Rogerson and Thorpe, *ibid.*, 1905, 87, 1685) forms a otassium compound from which by the action of enzoic acid or hydrogen chloride in non-polar solvents is obtained *ethyl α-cyano-β-methyl-Δ^{α}-propene-αγ-dicarboxylate*, b. p. 178—180°/22 mm., $d_4^{19.5}$ 1·0918, $n_D^{19.5}$ 1·47409, converted by sodium ethoxide into the equilibrium mixture containing about 23% of its αβ-isomeride, and yielding on alkylation with the corresponding alkyl halide *ethyl α-cyano-βγ-dimethyl-Δ^{α}-propene-αγ-dicarboxylate*, b. p. 162°/14 mm., d_4^{18} 1·0456, n^{18} 1·46619, and *ethyl α-cyano-γ-benzyl-β-methyl-Δ^{α}-propene-αγ-dicarboxylate*, b. p. 213°/15 mm., $d_4^{19.2}$ 1·0997, $n_D^{19.2}$ 1·51800, both yielding the equilibrium ester with sodium ethoxide. *Ethyl α-cyano-βγ-dimethyl-Δ^{β}-propene-αγ-dicarboxylate*, b. p. 154°/9 mm., d_4^{20} 1·0729, n_D^{20} 1·46916, is obtained by decomposing the potassium derivative of ethyl α-cyano-βγ-dimethylglutaconate with benzoic acid in ether. *Ethyl α-cyano-α-methyl-Δ^{β}-propene-αγ-dicarboxylate*, b.p. 160—161°/16 mm., d_4^{20} 1·0662, n_D^{20} 1·45543, and its *α-ethyl* analogue, b. p. 158—160°/11 mm., d_4^{20} 1·0503, n_D^{20} 1·5323, are obtained by alkylation of ethyl sodio-α-cyanoglutaconate with methyl and ethyl iodides, whilst *ethyl α-cyano-αγ-dimethyl-Δ^{β}-propene-αγ-dicarboxylate*, b. p. 176—177°/22 mm., d_4^{20} 1·0729, n_D^{20} 1·46818, is obtained by similar alkylation of ethyl α-cyano-γ-methylglutaconate, and with sodium ethoxide yields *ethyl α-cyano-αγ-dimethylcrotonate*, b. p. 103°/12 mm. Attempts to apply Linstead and May's iodometric method (A., 1927, 1167) to these esters under standard conditions were partly successful. G. DISCOMBE.

Constitution of acid amides and thioamides. A. HANTZSCH (Ber., 1931, 64, [*B*], 661—667).—Comparison of the ultra-violet absorption of trichloroacetamide, trichloroacetpiperidide, and the ether $CCl_3\cdot C(OMe){:}NH$ in methyl alcohol, water, and chloroform establishes the close similarity of the two last-named compounds and shows that the equilibrium $CCl_3\cdot CO\cdot NH_2 \rightleftharpoons CCl_3\cdot C(OH){:}NH$ is displaced extensively towards the right in chloroform and further in water. The curve for benzamide in alcohol is almost identical in its most characteristic portion with that of benzimino ethyl ether and markedly different from that of benzdimethylamide; benzamide is almost completely dissolved as the iminohydrin $Ph\cdot C(OH){:}NH$. Comparison of the b. p. of the amides, methylamides, dimethylamides, and iminoethers shows that the two first-named types exist mainly in the iminohydrin form $R\cdot C(OH){:}NH$ and $R\cdot C(OH){:}NMe$. The anomalies in the b. p. of the "amides and methylamides" are attributed to association caused by the presence of the hydroxyl groups and consequent greater difficulty in passing into the unimolecular condition. The b. p. is essentially the temperature of decomposition of the dimolar or more highly associated iminohydrin into the unimolecular form.

In all solvents the absorption spectrum of thioacetamide is so similar to that of thioacetpiperidide and different from that of the thioether, $CH_3\cdot C(SEt){:}NH$, that it is regarded as exclusively or almost exclusively present in chloroform or ether as the true thioamide $CH_3\cdot CS\cdot NH_2$ and only to a minor extent as the iminothioether in water. Similar conclusions are reached for xanthamide and its derivatives. The optical results are confirmed cryoscopically, since xanthdiethylamide and the thioether, $OEt\cdot C(SMe){:}NH$, are unimolecular in benzene, whereas xanthamide becomes partly associated with increasing concentration owing to the action of the thiol groups developed in the equilibrium $OEt\cdot CS\cdot NH_2 \rightleftharpoons OEt\cdot C(SH){:}NH$. H. WREN.

So-called imido- and amido-chlorides, the salts of nitriles and acid amides, and the chemistry of the transformation of nitriles into acid amides. A. HANTZSCH (Ber., 1931, 64, [*B*], 667—678).—Preparative work combined with measurements of mol. wt. and observations of the optical behaviour of nitriles and amides in concentrated sulphuric acid leads the author to the following conclusions. The additive products from hydrogen halides and nitriles are identical with the products obtained from amides and phosphorus pentachloride and regarded hitherto as imide chlorides, $R\cdot CCl{:}NH$, and amide chlorides, $R\cdot CCl_2\cdot NH_2$. They are actually nitrilium salts, the former being monohalides, $[R\cdot C{\equiv}NH]Cl$, and the latter dihalides, $[R\cdot C{\equiv}NH]Cl,HCl$, in which the second acid molecule is not structurally combined. All these compounds decompose spontaneously or when treated with water into hydrogen halide and nitrile, which may pass secondarily into the amide. Determinations of mol. wt. in absolute sulphuric acid show the nitriles to be present as completely dissociated sulphates, $[R\cdot C{\equiv}NH]SO_4H$. A solid *sulphate* has been obtained from triphenylacetonitrile; the datum that this nitrile is converted by sulphuric acid into a dissociated cyanide, $CPh_3\cdot CN'$, and exhibits "polarity isomerism" is erroneous. Acid amides are similarly dissolved by concentrated sulphuric acid to dissociated sulphates which absorb light more strongly than the corresponding nitriles. The salt formation weakens the absorption of the aliphatic nitriles and amides, whereas that of the aromatic analogues is strengthened by the chromophoric benzene residue. The aromatic compounds are optically almost completely identical with the compounds of the benzimino-ethers, $[Ar\cdot C(OEt){:}NH_2]\cdot SO_4H$, and therefore contain iminohydrinium salts, $[Ar\cdot C(OH){:}NH_2]\cdot SO_4H$, in harmony with the observation that the free primary "acid amides" are preponderatingly iminohydrins, $R\cdot C(OH){:}NH$. Since the true tertiary acid amides, $Ar\cdot CO\cdot NR_2$, form the analogously constituted dialkyliminohydrinium salts, $[Ar\cdot C(OH)\cdot NH_2]\cdot SO_4H$, isomeric acylammonium salts, $[Ar\cdot CO\cdot NH_3]\cdot SO_4H$ and $[Ar\cdot CO\cdot NMe_2H]\cdot SO_4H$, do not exist. The heats of dissolution of the nitriles and amides in sulphuric acid are essentially the heats of formation of their salts, and since those of the amides are much greater than those of the corresponding nitriles

the latter are much weaker base anhydrides than the former. The exothermal transformation of nitrilium sulphate into iminohydrinium sulphate occurs slowly but completely at the ordinary temperature. In aqueous solution the conversion of nitrile into amide is not a consequence of the catalytic acceleration of the addition of water by the acid, since addition of acid to the nitrile is the primary change; the nitrilium salts pass by addition of water into acid amides or, more accurately, into iminohydrinium salts, which are hydrolysed to "acid amides" and acids or to their hydroxonium salts: $[R\cdot C{\equiv}NH]X+H\cdot OH \longrightarrow [R\cdot C(OH){:}NH_2]\cdot X+nH_2O \longrightarrow R\cdot C(OH){:}NH+[H(OH_2)_n]\cdot X$. The processes occur in accordance with the author's chemical theory of acids, the strength of which is determined by their differing tendency towards salt formation. The strongest acids have their most marked action as such and are weakest as their ions in aqueous solution. Their so-called catalytic action depends on their salt formation. They are weakest in dilute aqueous solution, since they are then present exclusively as hydroxonium salts. The increase in activity with rise of temperature in aqueous solution depends on increasing decomposition into water and acid.

The following compounds are prepared, generally by the action of the hydrogen halide on the nitrile dissolved in anhydrous ether or benzene: *dihydrochlorides* of cinnamonitrile and *p*-toluonitrile; *monohydrobromides* of trichloroacetonitrile, phenylacetonitrile, and cinnamonitrile; *dihydrobromides* of benzonitrile, *p*-toluonitrile, acetonitrile, and trichloroacetonitrile; *dihydroiodides* of *p*-toluonitrile, phenylacetonitrile, and acetonitrile. All are very unstable.

H. WREN.

Preparation of bisacetamide hydrochloride and its use as an acetylating agent. H. STEPHEN (J.C.S., 1931, 672—673).—Bisacetamide hydrochloride (yield 66%) and acetonitrile are obtained from thionyl chloride and dry ethereal acetamide. On fusion of equimolecular proportions of bisacetamide hydrochloride and the hydrochloride of an aromatic primary amine, acetylation of the base occurs with formation of small quantities of an amidine. The reaction probably involves the intermediate formation of acetyl chloride and diacetamide (cf. Brunner and others, A., 1927, 867). G. DISCOMBE.

Structure of the carbamide molecule. L. EBERT (Ber., 1931, 64, [*B*], 679—681).—In reply to Devoto (A., 1930, 1358), it is pointed out that analysis of the dielectric polarisation of aqueous solutions affords no valid evidence of an unusually strongly polar form of the carbamide molecule. The crystalline structure of carbamide can be reconciled only with the symmetrical diamide formula. In thiocarbamide the two amido-groups are strictly equivalent. H. WREN.

Nitroso- and oximino-ferropentacyanides derived from nitroprusside. L. CAMBI [with A. CAGNASSO and T. RICCI] (Gazzetta, 1931, 61, 3—13).—The formation of highly-coloured complex compounds, probably of the general formula $K_4[(CN)_5Fe\cdot NO{:}CRR']$, has been demonstrated when a further series of compounds with mobile hydrogen atoms able to react with nitrous acid to form nitroso- or oximino-derivatives are treated with potassium nitroprusside and potassium methoxide in methyl alcohol (cf. A., 1914, i, 967; 1927, 346; 1930, 905). Spontaneous isomerisation to the less highly-coloured compounds, $K_4[(CN)_5Fe\cdot O\cdot N{:}CRR']$, takes place, and hydrolysis with dilute sulphuric acid then yields the oximino-compounds. In this way the oximino-derivatives of nitroethane, ethyl cyanoacetate, phenylacetonitrile, and *p*-nitrophenylacetonitrile have been obtained. Indole yields the *compound* $K_4[(CN)_5Fe\cdot NO{:}C_8H_6N]$. Spectrographic data for the highly-coloured compounds from acetone, acetylacetone, acetophenone, pyruvic acid, indole, and nitrosobenzene show a general resemblance.

R. K. CALLOW.

Preparation of tri-*n*-alkylbismuthines. W. C. DAVIES, I. NORVICK, and W. J. JONES (Bull. Soc. chim., 1931, [iv], 49, 187—194).—When a solution of bismuth chloride in ether is added to about 6 mols. of magnesium *n*-propyl bromide in an atmosphere of hydrogen, the mixture finally decomposed with ammonium chloride, and distilled in vacuum, *tri*-n-*propylbismuthine*, b. p. 86—87°/8 mm., d^{17} 1·621, is obtained together with a little hexane. *Tri*-n-*butylbismuthine*, b. p. 124°/7 mm., d_4^{17} 1·456, and *tri*-n-*amylbismuthine*, b. p. 157—158°/7 mm., d^{17} 1·381, are similarly obtained. With a smaller proportion of Grignard reagent, by-products are obtained, magnesium amyl bromide (3 mols.) with bismuth chloride (1 mol.) affording a greenish *liquid*, b. p. 165—185°/6 mm., d_4^{17} 1·67. The trialkylbismuthines oxidise readily in air and no methiodides could be prepared.

R. BRIGHTMAN.

Autoxidation of *cyclo*hexene. H. N. STEPHENS (Ber., 1931, 64, [*B*], 637—638).—The author's experiments (A., 1928, 401) show that the product obtained by Zelinski and Borissov (A., 1930, 1422) is not the simple *cyclo*hexene peroxide, but probably a mixture of complex products of which the main component is a higher polymeride of the peroxide. H. WREN.

Oscillating, puckered, centroid model for the benzene ring. M. L. HUGGINS (J. Amer. Chem. Soc., 1931, 53, 1182—1183).—Recent chemical and *X*-ray evidence may be explained by the author's electronic model for benzene (A., 1922, i, 928) if the tetrahedra are sufficiently distorted and there is a frequent or continuous oscillation between such a puckered form and its mirror image. J. W. BAKER.

Effect of substituents on certain physical properties of benzene picrate. O. L. BARIL and E. S. HAUBER (J. Amer. Chem. Soc., 1931, 53, 1087—1091).—The *picrates* of the following aromatic hydrocarbons and their derivatives have been prepared by gently melting an equimolecular mixture of picric acid and the compound, and cooling to determine the f. p. (recorded after each) of the compound so formed: toluene, 88·2°; ethyl-, 96·6°, and propyl-, 103·5°, -benzene; *o*-, 88·5°, *m*-, 90—91·5°, and *p*-, 90·5°, -xylene; hemimellithene, 89·5°; pseudocumene, 96—97°; mesitylene, 96·6°; 1 : 2 : 3 : 4-tetra-, 92—95°; penta-, 131°, and hexa-, 170°, -methylbenzene; phenol, 83·1°; pyrocatechol, 122°; resorcinol, 89—90°; quinol, 115—117°; pyrogallol, 128—129°; hydroxy-

quinol, 96°; phloroglucinol, 101—103°; *o*-, 88°; *m*-, 61·6°, and *p*-, 64—65°, -cresol; orcinol, 92°; 1 : 2 : 4-, 83·8°, 1 : 3 : 2-, 50—53°, and 1 : 4 : 2-, 81—82°, -xylenol; 1-, 140—141°, and 2-, 115—116°, -methyl-; 1-, 97·4°, and 2-, 69—70°, -ethyl-; 1-, 140—141°, and 2-, 89—90°, -propyl-; 1-, 104—105°, and 2-, 71—73°, -butyl-; 1 : 4-, 139—140°, and 2 : 6-, 141—142°, -dimethyl-; 1 : 2 : 6-trimethyl-, 121—122°, -naphthalene; α-, 188·5°, and β-, 155·5°, -naphthol; anthracene, 138°; hexamethylanthracene, 203°; phenanthrene, 132·8°; acenaphthene, 160·5°; stilbene, 90—91°; fluorene, 77°; and pyrene, 220°. The colour of the picrate is deepened and the f. p. raised by substitution of methyl groups into benzene, the side-chain, or naphthalene, whilst the colour is deepened but the f. p. lowered by introduction of hydroxyl groups into benzene. J. W. BAKER.

Induction of the reaction between chlorine and benzene by ethylene. T. D. STEWART and M. H. HANSON (J. Amer. Chem. Soc., 1931, **53**, 1121—1128).—In homogeneous solution in benzene the ratio of total chlorine reacting to ethylene reacting varies from 1·7 to 2·2 when the chlorine concentration varies between 0·3 and 0·42*M*, and the ethylene concentration changes from the initial value 0·042*M* to zero, but in one experiment in which the initial ethylene concentration was 0·013*M*, the value was as high as 10. A large amount of benzene substitution occurs even at high concentrations, the ethylene having a low induction efficiency. When ethylene is passed into a benzene solution of chlorine in the dark, benzene hexachloride (mixture of stereoisomerides in which the α-form, m. p. 157°, predominates) is formed, comparatively little substitution occurring. Under these conditions the mol. ratio of total chlorine reacting to total ethylene reacting varies from 2 to 11, being the greater the lower is the partial pressure of the ethylene. These results are provisionally explained on the basis of chain mechanisms for both the ethylene–chlorine and benzene–chlorine reactions, the latter being induced by, and acting as an inhibitor of, the former. No evidence of a Friedel-Crafts type of reaction between the (assumed) intermediate activated ethylene chloride and benzene could be detected, nor is any benzophenone formed when ethylene is introduced into a mixture of benzene, benzoyl chloride, and chlorine. J. W. BAKER.

Magnesium phenyl fluoride. H. GILMAN and L. L. HECK (J. Amer. Chem. Soc., 1931, **53**, 377—378).—When fluorobenzene is treated with activated magnesium-copper alloy in ether during 18 months at the ordinary temperature, magnesium phenyl fluoride is formed. H. BURTON.

Velocity of nitration of certain derivatives of the benzene series by nitric acid in nitrobenzene solution. B. V. TRONOV and G. J. BER (J. Russ. Phys. Chem. Soc., 1930, **62**, 2337—2345).—The effect of substituents in the nucleus on the velocity of nitration varies at different stages of the reaction. E. B. UVAROV.

Nitration of benzene by ethyl nitrate in the presence of catalysts. B. V. TRONOV and N. C. SIBGATULLIN (J. Russ. Phys. Chem. Soc., 1930, **62**, 2267—2272).—Aluminium chloride is the best catalyst in this reaction. An explanation of the mechanism of the catalyst is based on the formation of a complex salt between the catalyst and ethyl nitrate. E. B. UVAROV.

Nitration of *m*-dichlorobenzene. H. S. JOIS and B. L. MANJUNATH (Mysore Univ. J., 1930, **4**, 239—240; cf. Dann, A., 1930, 79).—Nitration of *m*-dichlorobenzene by Nietzki and Schedler's method (A., 1897, i, 464) gives mainly 1 : 3-dichloro-4 : 6-dinitrobenzene (I). The mixture of dinitro-derivatives formed (cf. Davies and Hickox, J.C.S., 1922, **121**, 2649) consists of I and 1 : 3-dichloro-2 : 4-dinitrobenzene, m. p. 70—71°; separation is best effected by Dann's method (*loc. cit.*). H. BURTON.

Reactions of nitrosulphonyl chlorides. II. Separation of nitrosulphonyl chlorides by means of hydrazine hydrate. W. DAVIES, F. R. STORRIE, and S. H. TUCKER (J.C.S., 1931, 624—629).—The method of Dann and Davies (A., 1929, 921) has been extended to the nitrobenzenesulphonyl chlorides. A mixture of *o*- and *p*-nitrobenzenesulphonyl chlorides gives with hydrazine hydrate at 35° *o*-nitrobenzenesulphinic acid and p-*nitrobenzenesulphonhydrazide*, m. p. 150—152° (decomp.). The *o*- and *m*-nitrobenzenesulphonyl chlorides at 50° yield *o*-nitrobenzenesulphinic acid, and the *m*- and *p*-sulphonyl chlorides at 55° form *p*-nitrobenzenesulphinic acid. The mixture of the three isomerides is separated by removing the *o*-nitro-isomeride as sulphinic acid, and the resulting mixture separated at 40—45°. 2-Chloro-5-nitro-*p*-toluenesulphonyl chloride and 2-chloro-6-nitro-*p*-toluenesulphonyl chloride were separated in the same way at 60°. 2 : 4-*Dinitrobenzenesulphonhydrazide*, m. p. 110° (decomp.), is prepared at −10°. Nitrobenzenesulphonhydrazides form hydrazones with aldehydes and ketones. p-*Nitrobenzenesulphonhydrazones* of acetone, m. p. 169—171°; benzaldehyde, m. p. 142—144°; piperonal, m. p. 189—190°; *o*-nitrobenzenesulphonhydrazides of acetone, m. p. 147—148° (decomp.); piperonal, m. p. 177—179° (decomp.). m-*Nitrobenzenesulphonhydrazones* of acetone, m. p. 148—150° (decomp.); methyl ethyl ketone, m. p. 124—125° (decomp.); benzaldehyde, m. p. 150—151° (decomp.); piperonal, m. p. 173—175° (decomp.), are described. The reactivities of the isomeric chloronitrobenzenes towards sodium disulphide is shown to be in the order $o,p > m$ (Sprung, A., 1930, 759). G. DISCOMBE.

Preparation of *o*-chlorotoluene from toluene-*p*-sulphonyl chloride. L. MCMASTER and J. CAROL (Ind. Eng. Chem., 1931, **23**, 218—219).—*o*-Chlorotoluene is obtained in 90% yield by chlorinating toluene-*p*-sulphonyl chloride at 70—80° in presence of antimony trichloride as catalyst [cf. G.P. 133,000 (A., 1903, i, 331); iron is unsatisfactory], and hydrolysing the *o*-chlorotoluene-*p*-sulphonyl chloride formed first with 10% and then with 80% sulphuric acid. H. A. PIGGOTT.

Chlorination of *o*- and *p*-nitrotoluenes. 3 : 4 : 6-Trichloro-2-nitrotoluene and 2 : 6-dichloro-4-nitrotoluene. L. F. LEVY and H. STEPHEN (J.C.S., 1931, 76—79).—Chlorination of *o*-nitrotoluene in presence of antimony pentachloride gives 3 : 4 : 6-*tri-*

chloro-2-nitrotoluene, m. p. 93—94°, identified by conversion on nitration into 3 : 4 : 6-trichloro-2 : 5-dinitrotoluene, m. p. 229·5° (Seelig, A., 1887, 362). It is reduced by stannous chloride and hydrochloric acid to 3 : 4 : 6-*trichloro-o-toluidine*, m. p. 89° (*acetyl*, m. p. 199°, and *benzoyl* derivative, m. p. 230°). Chlorination of *p*-nitrotoluene beyond the monochloro-stage is slow and gives 2 : 6-*dichloro-4-nitrotoluene*, m. p. 63—64°, the orientation of which depends on its reduction to 2 : 6-*dichloro*-p-*toluidine*, m. p. 55° (*acetyl*, m. p. 215°, and *benzoyl*, m. p. 179°, derivatives), identified by difference, and nitration to 2 : 6-*dichloro-3 : 4-dinitrotoluene*, m. p. 130°, the reduction product of which has the properties of an *o*-diamine.

H. A. PIGGOTT.

Fluorination of organic compounds. I. Action of lead tetrafluoride on organic compounds. O. DIMROTH and W. BOCKEMÜLLER (Ber., 1931, **64**, [*B*], 516—522).—αα-Diphenylethylene reacts with lead tetra-acetate and anhydrous hydrogen fluoride (4 mols.) in chloroform at 0° with production of *αβ-difluoro-αα-diphenylethane*, m. p. 66°, b. p. 135—145°/14 mm. (slight decomp.). Reaction does not proceed smoothly, a portion of the material being unchanged and a portion resinified. Excess of hydrogen fluoride increases the resinification, which appears characteristic of fluorination. Treatment of αα-diphenylethylene with 40% aqueous hydrofluoric acid and lead tetra-acetate gives deoxybenzoin. With alcoholic potassium hydroxide αβ-difluoro-αα-diphenylethane yields *β-fluoro-αα-diphenylethylene*, m. p. 93·5°. Addition of fluorine does not occur with stilbene, cinnamic acid, ethyl cinnamate, and *p*-benzoquinone. Anisole and quinol dimethyl ether absorb two atoms of fluorine from lead tetrafluoride, but do not undergo substitution; a portion of the material remains unchanged, whilst the remainder is converted into a resin free from fluorine. Acetanilide is transformed into *p*-fluoroacetanilide in 10% yield. Fluoro-derivatives of anthracene, phenanthrene, or naphthalene could not be obtained; the last-named substance appears to be polymerised and oxidised.

H. WREN.

Fluorination of organic compounds. II. Action of aryl iododifluorides on organic compounds. W. BOCKEMÜLLER (Ber., 1931, **64**, [*B*], 522—530; cf. preceding abstract).—αα-Diphenylethylene does not react with aryl iododifluorides in chloroform or nitrobenzene at the ordinary temperature. In the presence of a little anhydrous hydrogen fluoride or silicon tetrafluoride formation of αβ-difluoro-αα-diphenylethane occurs in 60% yield, accompanied by production of oily material which evolves hydrogen fluoride when distilled and of non-distillable, dark resin. The fluorine appears to abstract a portion of the hydrogen from the hydrocarbon, and the resulting unsaturated residues undergo condensation or fluorination. In the presence of a trace of moisture, deoxybenzoin is produced by the " hydrogen fluoride process." The optimal conditions for the reaction are thorough cooling, exclusion of moisture, and a not excessive amount of hydrogen fluoride or silicon tetrafluoride. αα-Diphenyl-Δ^{α}-propene is smoothly transformed into *αβ-difluoro-αα-diphenylpropane*, b. p. 115—120°/2 mm. Stilbene, α-methylstilbene, anthracene, and phenanthrene give resins or oils containing fluorine from which individual substances cannot be isolated. Phenanthrene and phenyl iododifluoride, in absence of hydrogen fluoride or silicon tetrafluoride, give a very unstable molecular *compound*. Diethylaniline is transformed into p-*fluorodiethylaniline*, b. p. 214°/atmospheric pressure, and tetraethylbenzidine, m. p. 89·5—90°.

Iodosobenzene is converted by a solution of potassium hydrogen fluoride in 40% hydrofluoric acid into *phenyl iododifluoride*. The following iododifluorides are prepared analogously: *p*-tolyl, m. p. 107—109° (decomp.); m-*nitrophenyl*, m. p. 115° (slight decomp. after softening at 113°; p-*nitrophenyl*, m. p. 173·5° (decomp.); p-*chlorophenyl*, m. p. 99°.

H. WREN.

Isolation of an intermediate form during an acetylene isomerisation. M. BOURGUEL (Compt. rend., 1931, **192**, 686—688).—The conversion of α-phenyl-Δ^{α}-propinene (I) into α-phenyl-Δ^{β}-propinene (II) by potassium hydroxide and the reverse reaction under the influence of sodamide lead to the intermediate formation of the *sodium* derivative of a *hydrocarbon*, b. p. 72°/17 mm., d^{20} 0·939, n_D^{20} 1·5642, inactive to cuprous chloride, and not hydrated by sulphuric acid and mercuric salts, converted by sodamide into I and by potassium hydroxide above 40° into II. On atmospheric oxidation it yields *α-phenylpropane-αβ-dione*, adds two atoms of iodine, reduces mercuric acetate to mercury, polymerises to a resin at 60°, and is hydrogenated to α-phenylpropane.

G. DISCOMBE.

Acenaphthenesulphonic acids. I. Derivatives of acenaphthene-3-sulphonic acid. K. DZIEWOŃSKI, B. GRÜNBERG, and (MLLE) J. SCHOENÓWNA (Bull. Acad. Polonaise, 1930, **A**, 518—528).—Acenaphthene is converted by chlorosulphonic acid at 125—130° into its 3-sulphonic acid (A., 1924, i, 1178) and 3 : 3'-*diacenaphthylsulphone*, m. p. 230—232°, converted by oxidation with potassium dichromate and acetic acid into the *compound* $(O{<}^{CO}_{CO}{>}C_{10}H_5\cdot)_2SO_2$, m. p. above 420°. Sodium acenaphthene-3-sulphonate [*aniline* salt, m. p. 284—286° (decomp.)] reacts with phosphorus pentachloride to give the corresponding *sulphonyl chloride*, m. p. 113—114°, reduced by zinc dust in moist ether to *acenaphthene-3-sulphinic acid*, m. p. 148—149°, and by zinc dust and dilute sulphuric acid to 3-*thiolacenaphthene*, m. p. 68° (*picrate*, m. p. 117°; coloured *lead* and *mercury* salts). This is oxidised by air in alcoholic ammonia to *diacenaphthyl* 3 : 3'-*disulphide*, m. p. 141—142°, and reacts with sodium chloroacetate in alkaline solution to give *acenaphthyl-3-thiolacetic acid*, m. p. 142° (*sodium* salt). Reduction of either the " α " (amide, m. p. 237—238°, not 137° as given in error) or " β " 5-bromoacenaphthenesulphonic acids (A., 1930, 600) with zinc dust and 35% sodium hydroxide or with sodium amalgam in alcoholic solution affords the same acenaphthene-3-sulphonic acid, so that the α and β acids are 5-bromoacenaphthene-3- and -8-sulphonic acids. The α-sulphonyl chloride is reduced by zinc dust and dilute sulphuric acid to 5-*bromo*-3(or 8)-*thiolacenaphthene*, m. p. 59—60° (*lead* and *mercury* salts), converted as above into 5 : 5'-*dibromodiacenaphthyl* 3 : 3'(or 8 : 8')-

disulphide, m. p. 147—148°, and 5-*bromoacenaphthyl-3(or 8)-thiolacetic acid*, m. p. 154—156°.

J. W. BAKER.

Anthracene derivatives. IV. E. DE B. BARNETT and F. C. MARRISON (Ber., 1931, 64, [*B*], 535—541; cf. this vol., 341).—Phthalic anhydride is condensed with *o*-xylene to *o*-3 : 4-dimethylbenzoylbenzoic acid, which is reduced by ammonia and activated zinc dust to *o*-3 : 4-dimethylbenzylbenzoic acid, m. p. 136°. Treatment of the benzoylbenzoic acid with concentrated sulphuric acid yields a mixture of 2 : 3-dimethylanthraquinone, m. p. 210°, and 1 : 2-dimethylanthraquinone, m. p. 156° (not completely free from the 2 : 3-isomeride). 2 : 3-*Dimethylanthrone*, m. p. 158°, is obtained from the anthraquinone and tin and hydrochloric acid in presence of glacial acetic acid or from the benzylbenzoic acid and 80% sulphuric acid at 100°. 2 : 3-*Dimethylanthranyl acetate* has m. p. 171°. With magnesium methyl iodide, 2 : 3-dimethylanthrone affords 2 : 3 : 9-*trimethylanthracene*, m. p. 125°, in poor yield. 9-*Benzyl*-2 : 3-*dimethylanthracene*, m. p. 149°, is transformed by bromine in carbon disulphide into 10-*bromo*-9-*benzyl*-2 : 3-*dimethylanthracene*, m. p. 158°, which is unchanged by piperidine in boiling chloroform. The following derivatives of 2 : 3-dimethylanthrone are described: 10-*bromo*-, m. p. 125—128° (decomp.); 10-*piperidino*-, m. p. 174° after softening, which gives a dark orange colour with alkali; 10-*anilino*-, m. p. about 186° (decomp.) according to the rate of heating; 10-p-*dimethylaminophenyl*-, m. p. 235° (decomp.); 10-*methoxy*-, m. p. 102° (10-*methoxy*-2 : 3-*dimethylanthranyl acetate*, m. p. 109°); 10-*phenyl*-, m. p. 207° after becoming red (10-*phenyl*-2 : 3-*dimethylanthranyl acetate*, m. p. 168°). 9-*Methoxy*-10-*phenyl*-2 : 3-*dimethylanthracene*, m. p. 151°, is obtained from 10-phenyl-2 : 3-dimethylanthrone, potassium hydroxide, and methyl *p*-toluenesulphonate in boiling alcohol. 10-*Phenyl*-2 : 3 : 9-*trimethylanthracene*, m. p. 119°, and 10-*phenyl*-9-*benzyl*-2 : 3-*dimethylanthracene*, m. p. 163°, are described. Reduction of 2 : 3-dimethylanthrone with zinc dust and ammonia yields 2 : 3-dimethylanthracene, m. p. 252°, converted by bromine in carbon disulphide into 9 : 10-*dibromo*-2 : 3-*dimethylanthracene*, m. p. 207°.

H. WREN.

Polycyclic aromatic hydrocarbons. II. Non-existence of 1 : 2 : 7 : 8-dibenzanthracene. III. Derivatives of 1 : 2 : 5 : 6-dibenzanthracene. IV. Condensed derivatives of 1 : 2-benzanthracene. J. W. COOK (J.C.S., 1931, 487—489, 489—499, 499—507).—II, III. The 1 : 2 : 7 : 8-dibenzanthracene of Clar (A., 1929, 435) and of Fieser and Dietz (*ibid.*, 1055) obtained by the pyrolysis of 2-methyl-1 : 1′-dinaphthyl ketone is identical with 1 : 2 : 5 : 6-dibenzanthracene (I). Carcinogenetic substances derived from 1 : 2 : 5 : 6-dibenzanthracene are described. Dinaphthyl ketones are obtained by the Friedel–Crafts reaction, and submitted to pyrolysis at 440—450°. 2 : 4′-*Dimethyl*-1 : 1′-*dinaphthyl ketone*, m. p. 120—121°, yields I on pyrolysis; 2 : 6-*dimethyl*-1 : 1′-*dinaphthyl ketone*, m. p. 162—163°, and 2 : 6 : 4′-*trimethyl*-1 : 1′-*dinaphthyl ketone* yield 3′-methyldibenzanthracene, whilst 2 : 7-*dimethyl*-1 : 2′- and 2 : 7-*dimethyl*-1 : 1′-*dinaphthyl ketones*, m. p. 113·5—114·5° and 161—162°, respectively, and 4 : 7 : 2′-*trimethyl*-1 : 1′-*dinaphthyl ketone* (an oil) yield 2′-*methyl*-1 : 2 : 5 : 6-*dibenzanthracene*, m. p. 256—257·5°, the trimethyl ketones by demethylation at the position α to a closed ring (A., 1930, 903). 1 : 2 : 5 : 6-Dibenzanthraquinone (Clar, *loc. cit.*) is converted by Grignard reagents into 9 : 10-*dihydroxy*-9 : 10-*dialkyl*-9 : 10-*dihydro*-1 : 2 : 5 : 6-*dibenzanthracenes* (*dimethyl* compound, m. p. 245—250°; *di*-n-*butyl*, m. p. 214—215°; *dibenzyl*, m. p. 249—251°), reduced, according to conditions, to 9 : 10-*dialkyl*-1 : 2 : 5 : 6-*dibenzanthracenes* [*dimethyl*, m. p. 205·5—206·5°; *di*-n-*butyl*, m. p. 143·5—144·5°; *dibenzyl* compound, m. p. 195—201° (decomp.)] or to 9 : 10-dialkyl-9 : 10-dihydrodibenzanthracene (cis-*dimethyl* compound, m. p. 207—209°, trans-*dimethyl*, m. p. 277—278°). By reduction of I with sodium in amyl alcohol an *octahydro*-derivative, m. p. 188—190°, is obtained. 4-*Benzoyl*-1 : 6-*dimethylnaphthalene*, m. p. 77—78°, is described.

The high-boiling constituents of coal tar contain chrysene, a *substance* m. p. 153—156°, with fluorescence similar to that of the product from tetrahydronaphthalene and aluminium chloride, and a mixture of substances oxidisable to quinones.

IV. Unsubstituted carcinogenetic hydrocarbons are described (cf. above). By pyrolysis of 4 : 4′-*di*-α-*naphthoyl*-3 : 3′-*dimethyldiphenyl*, m. p. 159·5—160·5°, 1 : 2 : 1′ : 2′-*dibenz*-6 : 6′(or 7 : 7′)-*dianthryl*, m. p. above 310° (decomp.), is formed, whilst 5-(2′-*methyl*-1′-*naphthoyl*)*hydrindene* (an oil) yields 5 : 6(or 6 : 7)-cyclo*penteno*-1 : 2-*benzanthracene*, m. p. 199—200°, 3-(2′-*methyl*-1′-*naphthoyl*)*acenaphthene*, m. p. 184—185°, forms *phenanthra-acenaphthene*, m. p. 231—232°, 2-(2′-*methyl*-1′-*naphthoyl*)*fluorene*, m. p. 169—170°, yields 2 : 3-*phenanthra*-3′ : 2′(or 1′ : 2′)-*fluorene*, m. p. 302—304°, 3-(2′-*methyl*-1′-*naphthoyl*)-*phenanthrene*, m. p. 341—343°, forms 2′ : 3′-*phenanthra*-2 : 3-*phenanthrene*, m. p. 341—343°, with an isomeric *hydrocarbon*, m. p. 245—248°; and 1-(2′-*methyl*-1′-*naphthoyl*)*anthracene* (an oil), forms 2′ : 3′-*phenanthra*-1 : 2-*anthracene*, m. p. 281—282° (decomp.). 1-*Benzoyl*-5-(1′-*naphthoyl*)-2 : 6-*dimethylnaphthalene*, m. p. 206—208°, and 1-*benzoyl*-5-(2′-*naphthoyl*)-2 : 6-*dimethylnaphthalene*, m. p. 222—223°, both yield 4 : 5-*benz*-10 : 11-(1′ : 2′-*naphtha*)*chrysene*, m. p. 435—440° (decomp.). 2-*Methyl*-5′ : 6′ : 7′ : 8′-*tetrahydro*-1 : 2′-*dinaphthyl ketone*, m. p. 122·5—123·5°, from tetrahydronaphthalene and 2-methyl-1-naphthoyl chloride, on pyrolysis loses hydrogen and forms 1 : 2 : 5 : 6-dibenzanthracene.

G. DISCOMBE.

Fluosilicates of organic bases. II. C. A. JACOBSON (J. Amer. Chem. Soc., 1931, 53, 1011—1015).—By the method previously used (A., 1929, 57) the characteristically crystalline *fluosilicates* of *o*-tolidine (AB), m. p. 268—269° (0·013); α-, m. p. 218° (decomp.) (0·1504), and β-, m. p. 263·3° (0·0816), -naphthylamine; *m*-nitroaniline, m. p. 200° (0·1210); diphenylamine, m. p. 169° (2·4492); *m*- (AB), m. p. 243—244° (0·065), and *p*- (AB) (decomp.) (0 014), -phenylenediamine; ethylaniline, m. p. 165·3° (0·979); nitrosodiphenylamine, m. p. 124·5° (decomp.) (0·84); *p*-aminoazobenzene, m. p. 220° (decomp.) (0·187); and *p*-aminobenzoic acid, m. p. 240—245° (0·91), have been prepared. All these are of the type

AB_2 except where otherwise indicated. The figures in parentheses are the solubilities in 95% alcohol at 25°. J. W. BAKER.

p-Bromoanilides of *iso*butyric and *iso*valeric acids. M. KUEHN and S. M. MCELVAIN (J. Amer. Chem. Soc., 1931, **53**, 1173—1174).—By a modification of Robertson's method (J.C.S., 1919, **115**, 1210) *p*-bromo-*iso*butyr-, m. p. 150—151° (lit., m. p. 128°), and -iso-*valer*-, m. p. 128—129°, -*anilides* are prepared. J. W. BAKER.

Action of amines on 2-substituted semicarbazones. J. CHAPMAN and F. J. WILSON (J.C.S., 1931, 507—514; cf. A., 1928, 1247).—Those 2-substituted semicarbazones which decompose at moderate temperatures to give hydrazones and cyanic acid afford, when heated with an amine, hydrazones and substituted carbamides, the latter arising from the action of the amine on the cyanic acid. Others more stable to heat give 2 : 4-disubstituted semicarbazones, which may react with further quantities of amine, yielding hydrazones and substituted carbamides. Acetone-2-phenylsemicarbazone heated at 140—145° gives acetonephenylhydrazone and cyanuric acid. Acetonephenylhydrazone and *s*-disubstituted carbamides were obtained from the interaction of acetone-2-phenylsemicarbazone and benzylamine, aniline, *p*-toluidine, β-phenylethylamine, and *n*-heptylamine. Benzylamine gave also some monobenzylcarbamide, whilst aniline and *p*-toluidine gave small quantities of *solids*, m. p. 133° and 162°, respectively. Acetophenone-2-phenylsemicarbazone (m. p. 126°) and aniline gave acetophenonephenylhydrazone and *s*-diphenylcarbamide. Benzaldehyde-2-benzylsemicarbazone yielded with aniline benzaldehyde-4-phenyl-2-benzylsemicarbazone; with *p*-toluidine *benzaldehyde-4-p-tolyl-2-benzylsemicarbazone*, m. p. 172°; and with benzylamine *benzaldehyde-2 : 4-dibenzylsemicarbazone*, m. p. 124°, together with *s*-dibenzylcarbamide. Benzaldehyde-2-methylsemicarbazone gave with aniline benzaldehyde-4-phenyl-2-methylsemicarbazone, and with benzylamine *s*-dibenzylcarbamide, *benzaldehyde-4-benzyl-2-methylsemicarbazone*, m. p. 106°, a *substance* $C_{11}H_{12}O_3N_2$, m. p. 207°, and (by prolonged action) a *substance* $C_{17}H_{20}O_2N_2$, m. p. 63°. A. A. LEVI.

Effects of substituents in the formation of thiocarbanilides. L. C. RAIFORD and G. M. MCNULTY (Proc. Iowa Acad. Sci., 1929, **36**, 269).—The presence of a methyl group *meta* to the amino-group diminishes the velocity of reaction of monoacetyl-*p*-phenylenediamine with carbon disulphide by about 33%; if either or both *m*-positions are occupied by bromine atoms the reaction does not take place. An *o*-bromine atom also causes inhibition. The acetyl group could not be removed from the thiocarbanilides produced. CHEMICAL ABSTRACTS.

Monoacetylation and monodiazotisation of diphenylene [2 : 4′-diaminodiphenyl]. C. FINZI (Gazzetta, 1931, **61**, 33—42).—When 2 : 4′-diaminodiphenyl in aqueous alcohol is treated with acetic anhydride the diacetyl derivative formed is accompanied by *2-amino-4′-acetamidodiphenyl*, m. p. 176—177°, the constitution of which has been proved by its conversion into 4-acetamido-, 4-amino-, and 4-hydroxydiphenyl, successively, and also into *4′-acetamido-2-hydroxydiphenyl*, m. p. 199°, 4-amino-2-hydroxy-, and 2-hydroxy-diphenyl, successively. Monodiazotisation, on the other hand, yields the 2-diazonium compound, for the product may be converted either into 4′-amino-2-hydroxy- and 2-hydroxy-diphenyl, successively, or into 4-amino- and 4-hydroxy-diphenyl, successively. R. K. CALLOW.

Catalytic reduction of benzidine. F. BALAŠ and P. ŠEVČENKO (Coll. Czech. Chem. Comm., 1931, **3**, 171—176).—Hydrogenation of benzidine in presence of colloidal platinum gives *perhydrobenzidine* (4 : 4′-*diaminodicyclohexyl*), m. p. 59°, b. p. 120°/0·8 mm. (*dihydrochloride*, decomp. 290°; *dipicrate*, decomp. 247°), in small yield. J. D. A. JOHNSON.

Molecular compounds of hydroxyazo-compounds with acid halides. W. M. FISCHER and A. TAURINSCH (Ber., 1931, **64**, [*B*], 236—239).—All hydroxyazo-compounds yield adducts with the chlorides and bromides of carboxylic and inorganic acids in ether, benzene, light petroleum, or carbon disulphide. The molecular compounds of many of the azo-derivatives of phenols are solvatised by these media; in these cases the adducts can be prepared without use of solvent. Azo-hydrocarbons and alkylated and acylated hydroxyazo-compounds do not yield molecular compounds, so that the formation from the hydroxy-compounds appears due to the residual valency of the hydrogen atom of the hydroxyl group. The compounds are formed most readily when the hydroxyl group is in the *para*-position to the azo-complex, less readily when it is in the *ortho*-position. The presence of a substituent in the *para*-position in the non-hydroxylated nucleus appears to impede reaction. The adducts are remarkably stable towards air. In benzene, they appear to be dissociated almost completely into their components. The following individuals are described, the ratio of the components (hydroxyazo-compound : halide) being given in parentheses: p-*benzeneazophenol–acetyl chloride* (1 : 1), m. p. 172°; *–propionyl chloride* (1 : 1), m. p. 162°; *–isovaleryl chloride* (1 : 1), m. p. 165°; *–benzoyl chloride*, (1 : 1), m. p. 166°; *–phenylacetyl chloride* (1 : 1), m. p. 166°; *–p*-nitrobenzoyl chloride (1 : 2), m. p. 177°; *–bromoacetyl chloride* (2 : 3), m. p. 165°; *–oxalyl chloride* (2 : 1), m. p. 175°; *–phthalyl chloride* (2 : 1), m. p. 166°; *–carbonyl chloride* (5 : 2), m. p. 165°; *–acetyl bromide* (4 : 5), m. p. 165°; *–benzoyl bromide* (1 : 2), m. p. 158°; *–sulphuryl chloride* (2 : 1), m. p. 138°; *–thionyl chloride* (2 : 1), m. p. 173°; *–phosphorus trichloride* (3 : 1), m. p. 173°; *–phosphoryl chloride* (3 : 1), m. p. 165°; *benzeneazo-o-cresol–acetyl chloride* (1 : 1), m. p. 175°; *–propionyl chloride* (2 : 3), m. p. 172°; *–benzoyl bromide* (1 : 2), m. p. 166°; *–carbonyl chloride* (2 : 1), m. p. 167°; 4-p-*nitrobenzeneazophenol–acetyl chloride* (3 : 2), m. p. 164°; *–benzoyl bromide* (2 : 3), m. p. 146°: *benzeneazo-p-cresol–benzoyl bromide*, unstable: p-*nitrobenzeneazoresorcinol–propionyl chloride* (1 : 1), m. p. 158°; *–benzoyl bromide* (1 : 2), m. p. 131°; p-*tolueneazosalicylic acid–propionyl chloride* (1 : 1), m. p. 205°; *–benzoyl bromide* (1 : 1), m. p. 210°; *benzeneazo-α-naphthol–acetyl chloride* (2 : 1), m. p. 183°; *–propionyl chloride* (2 : 1), m. p. 193°; *–benzoyl*

bromide (4 : 3), m. p. 183°; *–thionyl chloride* (4 : 1), m. p. 187°; *–tin tetrachloride* (2 : 1), m. p. 248°; *benzeneazo-β-naphthol–benzoyl bromide* (1 : 1), m. p. 126°; *4-α-naphthaleneazophenol–acetyl chloride* (1 : 1), m. p. 148°; *–propionyl chloride* (1 : 1), m. p. 155°; *–benzoyl bromide* (1 : 2), m. p. 146°; 4-β-*naphthalene-azophenol–propionyl chloride*, m. p. 165°. The behaviour of α-naphthaleneazo-α-naphthol, α-naphthaleneazo-β-naphthol, 2 : 4 : 6-tribromobenzeneazo-β-naphthol, *o*-nitrobenzeneazo-α-naphthol, and 2 : 4-dinitrobenzeneazo-β-naphthol has been investigated qualitatively. H. WREN.

Carbylamines. XVII. Reactions with nitroso-derivatives. M. PASSERINI [with N. ZITA] (Gazzetta, 1931, **61**, 26–33).—Interaction of 1-nitroso-β-naphthol with phenylcarbylamine in benzene yields no crystalline product, but with *p*-carbylamino-azobenzene there is formed, with evolution of carbon monoxide and dioxide, *carbonyl-α-amino-β-naphthol-*p*-benzeneazoanil*, m. p. 241—243° (decomp.). This is reduced by brief treatment with tin and hydrochloric acid to the p-*aminoanil*, m. p. 220—221° (darkens) (*benzylidene* compound, m. p. 205—208°) (by-product, m. p. 165°), but when the reaction is prolonged hydrolysis occurs with the formation of carbonyl-α-amino-β-naphthol and a basic by-product, m. p. 92—95° (decomp.). The *p*-aminoanil yields *p*-phenylenediamine when fused with potassium hydroxide.

Reaction between *p*-carbylaminoazobenzene and 2-nitroso-α-naphthol yields di-*p*-benzeneazophenyl-formamidine, formyl-*p*-aminoazobenzene, and a dark-coloured material of high m. p. R. K. CALLOW.

Constitution of normal diazotates. A. HANTZSCH and E. STRASSER (Ber., 1931, **64**, [*B*], 655—660; cf. A., 1930, 1032).—A refutation of the formula advanced by Angeli (A., 1930, 1428) for the normal diazotates. H. WREN.

2-Phenyl-1-methyl*cyclo*hexanol and its transformations. S. I. SERGIEVSKAJA (J. Russ. Phys. Chem. Soc., 1930, **62**, 2187—2192).—The action of sulphuric acid on 2-*phenyl*-1-*methyl*cyclo*hexanol*, b. p. 131—132°/8 mm., d_4^{20} 1·0283, gives 2-*phenyl*-1-*methyl*cyclo*hexane*, b. p. 115—118°/12 mm., d_4^{20} 0·9699 (*oxide*, b. p. 136—138°/19 mm., d_4^{20} 1·0266; 2-*phenyl*-1-*methyl*cyclo*hexanediol*, b. p. 139—140°/2·02 mm). The product of the pinacolin rearrangement of the glycol gives two *semicarbazones*, m. p. 226—227° (decomp.) and m. p. 172—175°; sulphuric acid treatment of these gives two *ketones*, an oil, b. p. 137—140°/16 mm., and a crystalline substance, m. p. 51·5°. E. B. UVAROV.

Thermal behaviour of phenols. III. A. HAGEMANN.—See this vol., 577.

Nitration of phenol and the role of nitrous acid. A. V. KARTASCHEV (J. Russ. Phys. Chem. Soc., 1930, **62**, 2129—2160).—A definite initial temperature dependent entirely on the solvent and concentration of nitric acid is required. The reaction in ethyl acetate solution proceeds in two stages, a deepening in colour being followed by a rise in temperature. At the commencement of the second stage there is a slight fall in temperature attributed to a simultaneous endothermic reaction. Nitrous acid is essential to commence the reaction, but acts as a positive catalyst only within certain temperature limits, outside which it hinders nitration and gives rise to a small amount of a green solid the nature of which was not established. The whole reaction between nitric acid and phenol is stated to proceed thus: $HNO_3 \longrightarrow HNO_2 + O$; $PhOH + HNO_2 \longrightarrow NO{\cdot}C_6H_4{\cdot}OH + H_2O$; $NO{\cdot}C_6H_4{\cdot}OH + HNO_3 \longrightarrow NO_2{\cdot}C_6H_4{\cdot}OH + HNO_2$. E. B. UVAROV.

Halogenated nitrophenols. II. Preparation of 2-chloro-3-nitrophenol from phenacetin. H. VAN ERP (J. pr. Chem., 1931, [ii], **129**, 327—336).—The action of 15% nitric acid on phenacetin (A., 1930, 1176) gives 12% of the 2-nitro-derivative in addition to the 3-nitro-compound. The latter is converted by sodium chlorate and acetic acid into 2-*chloro*-3-*nitrophenacetin*, m. p. 184·5° (together with an *N*-chlorinated *substance*, decomp. 130°, separated by its solubility in chloroform), hydrolysed by concentrated sulphuric acid to 2-*chloro*-3-*nitro*-p-*aminophenol*, m. p. 165·5°, and by dilute sulphuric acid to 3-*chloro*-2-*nitro*-p-*phenetidine*, m. p. 74°. This is converted successively into 2-chloro-3-nitrophenetole and 2-chloro-3-nitrophenol, both identical with the specimens previously obtained (*loc. cit.*), but the ether depressed the m. p. of 5-*chloro*-3-*nitrophenetole*, m. p. 47°, prepared for comparison by the action of potassium carbonate, potassium ethyl sulphate, and glycerol on the corresponding phenol. J. W. BAKER.

Condensations of dimethylolcarbamide with derivatives of benzene and naphthalene. H. DE DIESBACH, O. WANGER, and A. VON STOCKALPER (Helv. Chim. Acta, 1931, **14**, 355—368).—Prolonged interaction of 1 mol. of dimethylolcarbamide (*s*-dihydroxydimethylcarbamide) (I) (Einhorn and Hamburger, A., 1908, i, 141) with 2 mols. of *o*-nitrophenol in acetic and sulphuric acids at 15—20° gives *α-3-nitro-4-hydroxybenzyl-γ-hydroxymethylcarbamide*, decomp. 128° without melting, or a mixture of s-*di*-(3-*nitro*-4-*hydroxybenzyl*)*carbamide*, m. p. 216°, a *dinitrodihydroxydiphenylmethane*, m. p. 228°, and (?) polymeric dinitrodihydroxydiphenylmethane, m. p. 200° (cf. G.P. 76,490), according to the amounts of acids used. Equimolecular quantities of *p*-nitrophenol and I in sulphuric acid afford α-5-*nitro*-2-*hydroxybenzyl-γ-hydroxymethylcarbamide*, m. p. 181°; with 2 mols. of the phenol in sulphuric and acetic acids, s-*di*-(5-*nitro*-2-*hydroxybenzyl*)*carbamide*, m. p. 198°, results. *p*-Cresol condenses with I in 60% alcohol saturated with hydrogen chloride forming s-*di*-(2-*hydroxy*-5-*methylbenzyl*)*carbamide*, m. p. 165—167°; when an excess of *p*-cresol is used in more dilute alcohol, an equimolecular *compound* of the carbamide and cresol is obtained. The following carbamides are prepared (usually in presence of acetic and sulphuric acids): s-*di*-(3-*nitro*-2-*hydroxy*-5-*methylbenzyl*)-, m. p. 229—230° (equimolecular *compound*, m. p. 223—224°, with 3-nitro-*p*-cresol); s-*di*-(3-*nitro*-4-*methoxybenzyl*)-, m. p. 223°; s-*di*-(4-*hydroxy*-3-*carboxybenzyl*)-; s-*di*-(2 : 4-*dihydroxybenzyl*)-; s-*di*-(p-*acetamidobenzyl*)-, m. p. 242° (decomp.), and s-*di*-(5-*acetamido*-2-*methylbenzyl*)-*carbamide*, m. p. 270°. Quinol condenses with I in cold, dilute hydrochloric acid forming

methylenebis-2 : 5-*dihydroxybenzylcarbamide* (II), $[(OH)_2C_6H_3\cdot CH_2\cdot NH\cdot CO\cdot NH]_2CH_2$, probably formed thus: $2(OH)_2C_6H_3\cdot CH_2\cdot NH\cdot CO\cdot NH\cdot CH_2\cdot OH \longrightarrow II + CH_2O + H_2O$. Dissolution of II in moist acetone and evaporation of the solution in a vacuum gives a *compound*, probably $[(OH)_2C_6H_3\cdot CH_2\cdot NH\cdot CO\cdot NH]_2CH\cdot CMe_2\cdot OH$, which when heated at 105—110° loses 1 mol. of water forming the iso*propylidene* derivative of II, (?) $[(OH)_2C_6H_3\cdot CH_2\cdot NH\cdot CO\cdot NH]_2C\colon CMe_2$.

Condensation of *N*-methylolchloroacetamide with 3-hydroxy-2-naphthoic acid in alcohol saturated with hydrogen chloride gives 3-*hydroxy*-4-*chloroacetamidomethyl*-2-*naphthoic acid*, m. p. 239—240°; 3-*hydroxy*-4-*benzamidomethyl*-2-*naphthoic acid*, m. p. 219—220°, is prepared similarly using *N*-methylolbenzamide. 1-Hydroxy-2-naphthoic acid is converted similarly into 1-*hydroxy*-4-*chloroacetamidomethyl*-2-*naphthoic acid*, m. p. 219—220°, and 1-*hydroxy*-4 : 8(?)-*di*(*benzamidomethyl*)-2-*naphthoic acid*, m. p. 219°. Hydrolysis of 1-chloroacetamidomethyl-β-naphthol (Einhorn, A., 1906, i, 245; 1908, i, 608) with boiling hydrochloric acid gives mainly di-(2-hydroxy-α-naphthyl)methane, also formed when 1-aminomethyl-β-naphthol (*loc. cit.*) is boiled with sodium hydroxide solution. β-Naphthol and I condense in 50% alcohol saturated with hydrogen chloride forming s-*di*-(2-*hydroxy*-α-*naphthylmethyl*)*carbamide*, m. p. 205°, converted by boiling hydrochloric acid into αβ-di-(2-hydroxy-α-naphthyl)ethane. s-*Di*-(2-*hydroxy*-3-*carboxy*-α-*naphthylmethyl*)*carbamide*, m. p. 264—265° (*ethyl* ester, m. p. 261°), prepared from 3-hydroxy-2-naphthoic acid (and the ethyl ester), is hydrolysed by alcoholic hydrochloric acid to αβ-*di*-(2-*hydroxy*-α-*naphthyl*)*ethane*-3 : 3′-*carboxylic acid* ($+H_2O$), m. p. 295°.

Equimolecular quantities of α-naphthol and I in 50—70% alcohol saturated with hydrogen chloride give α-(1-*hydroxy*-β-*naphthylmethyl*)-γ-*hydroxymethylcarbamide*, m. p. 211° (decomp.), oxidised by alkaline potassium permanganate to 1-hydroxy-2-naphthoic acid and hydrolysed by hydrochloric acid to αβ-*di*-(1-*hydroxy*-β-*naphthyl*)*ethane*, anhydrous and $+2H_2O$, not melted at 330° [*diacetate* ($+H_2O$), m. p. 178°, m. p. (anhydrous) 278°]. When the above condensation is effected with 2 mols. of α-naphthol, a *substance*, $C_{36}H_{32}O_7N_4$, probably derived from 2 mols. of I and 3 mols. of α-naphthol, is produced. s-*Di*-(4-*hydroxy*-3-*carboxy*-α-*naphthylmethyl*)*carbamide*, m. p. 239°, obtained together with other products from 1-hydroxy-2-naphthoic acid and I, is hydrolysed to αβ-*di*-(4-*hydroxy*-3-*carboxy*-α-*naphthyl*)*ethane*, m. p. 266°. In many of the above condensations small amounts of diarylmethane derivatives are produced.

The production of ethane derivatives by hydrolysis of the condensation products of dimethylolcarbamide and naphthol derivatives is compared with the formation of such derivatives in the anthraquinone series (cf. this vol., 226). The amido-groups appear to be eliminated, not as ammonia but as nitrogen.

H. BURTON.

Acyl derivatives of o-aminophenol. VI. C. B. POLLARD and R. E. NELSON (J. Amer. Chem. Soc., 1931, **53**, 996—1001).—From the *O*- and *N*-acyl derivatives of *o*-aminophenol the diacyl derivatives have been prepared by the action of the appropriate acyl chlorides, of which one was always phenylacetyl chloride, whilst the other was varied, and the *N*-acyl derivative, obtained by hydrolysis of the product with 10% potassium hydroxide, was identified to ascertain the effects of the relative acidity and mol. wt. of the acyl groups in determining any rearrangement during hydrolysis. No rearrangement occurs on hydrolysis of o-*phenylacetamidophenyl* n-*butyrate*, m. p. 91—92°, o-n-*butyramidophenyl phenylacetate*, m. p. 46—48°, or o-n-*valeramidophenyl phenylacetate*, m. p. 71—72°; of the products o-n-*butyramidophenol*, m. p. 80—81°, is new. Hydrolysis of o-*phenylacetamidophenyl* n-*valerate*, m. p. 80—82°, affords a mixture of *o*-phenylacetamidophenol (65%) and *o*-*n*-valeramidophenol (35%), whilst o-*carbomethoxylamidophenyl phenylacetate*, m. p. 105—106°, gives a 50% mixture of *o*-phenylacetamido- and *o*-carbomethoxylamido-phenol. Rearrangement occurs in all the following cases: o-*phenylacetamidophenyl acetate*, m. p. 101—102°; o-*acetamidophenyl phenylacetate*, m. p. 99—100°; o-*phenylacetamidophenyl propionate*, m. p. 98—99°; o-*propionamidophenyl phenylacetate*, m. p. 71—72°; o-*phenylacetamidophenyl monochloroacetate*, m. p. 113—114°; o-*phenylacetamidophenyl benzoate*, m. p. 110—111°; and *benzamidophenyl phenylacetate*, m. p. 108—109°, all give o-*phenylacetamidophenol*, m. p. 149—150°, on hydrolysis: o-*phenylacetamidophenyl* iso*valerate*, m. p. 87—88°, and o-iso*valeramidophenyl phenylacetate*, m. p. 56—57°, both give *o*-*iso*valeramidophenol: o-*phenylacetamidophenyl* m-*chlorobenzoate*, m. p. 146—148°, and o-(m-*chlorobenzamido*)*phenyl phenylacetate*, m. p. 150—152°, both give o-(m-*chlorobenzamido*)*phenol*, m. p. 156—158°: o-(m-*bromobenzamido*)*phenyl phenylacetate*, m. p. 157—159° (isomeride could not be obtained), gives o-(m-*bromobenzamido*)*phenol*, m. p. 180°: o-*carbethoxy*-, m. p. 62—63°, and o-*carbobutoxy*-, m. p. 72—73°, -*amidophenyl phenylacetate* each give the corresponding *o*-carbalkoxyamidophenol.

J. W. BAKER.

Derivatives of 3-amino-4-methoxytoluene. L. C. RAIFORD and O. GROSZ (Proc. Iowa Acad. Sci., 1929, **36**, 268).—6-Bromo-3-amino-4-methoxytoluene (*N*-acetyl and benzoyl derivatives) has been prepared.

CHEMICAL ABSTRACTS.

Bromine derivatives of certain mixed ethers and some of their reactions. L. C. RAIFORD and L. H. HOWLAND (J. Amer. Chem. Soc., 1931, **53**, 1051—1057).—Fission of various tri-, and pentabromophenyl alkyl ethers has been investigated by the following methods: (1) heating with phosphorus tribromide in acetic acid with gradual addition of the calculated amount of water; (2) as in the previous method but heated in a sealed tube at 135—150°; (3) addition of bromine to a benzene solution of the ether containing iodine as a catalyst, and (4) keeping a mixture of the ether, excess of bromine, and 1% of aluminium bromide at the ordinary temperature. Of these (2) is the most generally effective, whilst with (4) the percentage of phenol formed depends largely on the alkyl radical present in the ether. The observation (Raiford and Birosel, A., 1929, 923) that phenyl allyl ether is converted by excess of bromine in chloroform into 2 : 4-dibromophenyl

βγ-dibromopropyl ether is confirmed by the following observations. 2 : 4-*Dichloro-*, b. p. 144—145°/25 mm. (prepared by Claisen's method, A., 1913, i, 1175, from 2 : 6-dichlorophenol and allyl bromide), and 2 : 6-*dibromo-*, b. p. 132—133°/10 mm., *-phenyl allyl ether* are similarly brominated to 2 : 4-*dichlorophenyl*, b. p. 188°/10 mm., and 2 : 6-*dibromophenyl*, m. p. 48—49°, *βγ-dibromopropyl ether*, respectively, whilst 3 : 5-*dibromophenyl allyl ether*, b. p. 145°/10 mm., is converted into 2 : 3 : 4 : 5-*tetrabromophenyl βγ-dibromopropyl ether*, m. p. 96°. Thus when any two of the *ortho* and *para* positions in a phenyl allyl ether are substituted by bromine no further bromination of the nucleus occurs under the conditions used. *Pentabromophenyl allyl ether*, m. p. 167—168°, is similarly converted into *pentabromophenyl βγ-dibromopropyl ether*, m. p. 122—123°. Phenyl allyl ethers containing two or more bromine atoms in the nucleus could not be rearranged to the corresponding phenols by heat. The phenyl αβ-dibromopropyl ethers are very hygroscopic and are converted by the action of alcoholic potassium hydroxide into phenyl propargyl ethers and thus are obtained: 2 : 4-*dichloro-*, liquid (*silver* salt); 2 : 4-, m. p. 65° (*silver, cuprous*, and *mercuric* salts), and 2 : 6-, m. p. 58—60° (*silver* salt), *-dibromo-*; and 2 : 4 : 6-*tribromo-*, m. p. 136—137° (*silver, cuprous*, and *mercuric* salts), *-phenyl propargyl ether*.
J. W. Baker.

Synthesis of pharmacologically important amines. II. β-Arylethylamines from aromatic aldehydes and carboxylic acids. K. Kindler (Arch. Pharm., 1931, **269**, 70—78).—High yields of β-arylethylamines are obtained from α-acetoxyarylacetonitriles only when the reaction is completed as rapidly as possible by gradual addition of the nitrile in acetic acid to palladium-black in sulphuric and acetic acids in presence of hydrogen at 3—4 atm. By this means β-*p*-anisylethylamine (95% of the theoretical yield) (I) is obtained from *α-acetoxy-*p*-anisylacetonitrile*, m. p. 38—39°, and β-3 : 4-methylenedioxyphenylethylamine (75%) (II), β-3 : 4-dimethoxyphenylethylamine (80%) (III), and β-3 : 4-methylenedioxy-5-methoxyphenylethylamine (73%) from the corresponding nitriles. *p*-Anisoyl cyanide is hydrogenated, similarly, to I. Although these β-arylethylamines are not obtainable by the usual technique of the Hofmann process, I, II, and III are formed in 90%, 77%, and 73%, respectively, of the theoretical yield when the requisite β-arylpropionamides are dissolved in alkaline potassium hypochlorite solution at 0° to form the *N*-chloroamide and the product is added slowly to boiling 50% aqueous potassium hydroxide.
H. E. F. Notton.

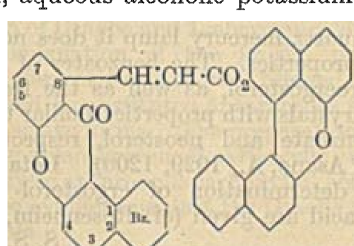
Diphenyl ether series. II. Preparation and structure of some sulphonic acids and related derivatives. C. M. Suter (J. Amer. Chem. Soc., 1931, **53**, 1112—1116).—The structure of diphenyl ether-4 : 4′-disulphonic acid obtained by sulphonation of diphenyl ether is proved by bromination of its barium salt in aqueous solution first to 4-bromodiphenyl ether-4′-sulphonic acid (isolated as its *sodium* salt; p-*toluidine* salt, m. p. 245—247°) and then further to 4 : 4′-dibromodiphenyl ether (Le Fevre and others, A., 1927, 660). Diphenyl ether is converted by chlorosulphonic acid in acetic acid or by 95% sulphuric acid and acetic anhydride into its 4-sulphonic acid [p-*toluidine* salt, m. p. 221—222°; *sulphonyl chloride*, b. p. 205—207°/12 mm., m. p. 45—46°; amide, m. p. 128—129° (lit. m. p. 88°)] identical with the product obtained by Quilico (A., 1928, 407) and also converted by bromination into 4 : 4′-dibromodiphenyl ether. Attempts to prepare 4-hydroxydiphenyl ether by fusion of the monosulphonic acid with alkali were unsuccessful. 4-Bromodiphenyl ether is converted by 95% sulphuric acid at 100° into its 4′-sulphonic acid and by chlorosulphonic acid into the 4′-*sulphonyl chloride*, m. p. 81—82° (also by bromination of diphenyl ether-4-sulphonyl chloride: *amide*, m. p. 131—132°; *anilide*, m. p. 108—109°). Excess of chlorosulphonic acid converts diphenyl ether into its 4 : 4′-*disulphonyl chloride*, m. p. 128—129° (*diamide*, m. p. 158—160°). Diphenyl ether-4-sulphonyl chloride is reduced by sodium sulphite to the unstable 4-*sulphinic acid*, darkens above 180°, and by zinc dust and sulphuric acid to 4-*thioldiphenyl ether*, b. p. 178—180°/20 mm., m. p. 19—22°, oxidised by iodine to the *disulphide*, m. p. 47—48°.
J. W. Baker.

Substitution products of 2-nitro- and 2-acetamido-diphenyl ethers, and the corresponding diphenylene oxides. H. McCombie, W. G. MacMillan, and H. A. Scarborough (J.C.S., 1931, 529—537).—Nitration of 2-acetamidodiphenyl ether with nitric acid, *d* 1·42, gives 5-*nitro-2-acetamidodiphenyl ether*, m. p. 180°, hydrolysed by alcoholic hydrochloric acid to 5-*nitro-2-aminodiphenyl ether*, m. p. 116°, which on diazotisation and treatment with 50% sulphuric acid gives 2-nitrodiphenylene oxide. Further nitration of 5-nitro-2-acetamidodiphenyl ether with more concentrated acid gives 5 : 4′(?)-*dinitro-2-acetamidodiphenyl ether*, m. p. 190°, from which 5 : 4′(?)-*dinitro-2-aminodiphenyl ether*, m. p. 192°, is obtained on hydrolysis as above. 2-Chloro-2′-nitrodiphenyl ether (from the condensation of *o*-chloronitrobenzene and potassium *o*-chlorophenoxide) on reduction and acetylation gives 2-*chloro-2′-acetamidodiphenyl ether*, m. p. 104°. This by a similar series of reactions gives 2-*chloro-5′-nitro-2′-acetamido-*, m. p. 142°, 2-*chloro-5′-nitro-2′-amino-*, m. p. 125°, 2-*chloro-4(?) : 5′-dinitro-2′-acetamido-*, m. p. 176°, and 2-*chloro-4(?) : 5′-dinitro-2′-amino-diphenyl ether*, m. p. 202°. 2 : 5-Dichloronitrobenzene condenses with sodium phenoxide to 4-*chloro-2-nitrodiphenyl ether*, b. p. 211°/20 mm., reduced to 4-*chloro-2-aminodiphenyl ether*, b. p. 215°/20 mm., m. p. 44° (*hydrochloride*, m. p. 192°). This when diazotised and treated with 50% sulphuric acid gives 3-*chlorodiphenylene oxide*, m. p. 106°. Chlorination of 2-nitrodiphenyl ether gives 4-chloro-2′-nitrodiphenyl ether (also from potassium *p*-chlorophenoxide and *o*-chloronitrobenzene), reduced to 4-chloro-2′-aminodiphenyl ether (*hydrochloride*, m. p. 181°; *acetyl*, m. p. 99°, *diacetyl* derivative, m. p. 106°), giving 3-chlorodiphenylene oxide when treated as above. From the monoacetyl derivative by the methods described above 4-*chloro-5′-nitro-2′-acetamido-*, m. p. 203°, 4-*chloro-5′-nitro-2′-amino-*, m. p. 123°, and 4-*chloro-2(?) : 5′-dinitro-2′-acetamido-diphenyl ether*, m. p. 198°, and 3-*chloro-7-nitrodiphenylene oxide*, m. p. 226°, were prepared. Potassium

p-chlorophenoxide condenses with 2 : 5-dichloronitrobenzene to 4 : 4′-dichloro-2-nitrodiphenyl ether, reduction of which yields 4 : 4′-dichloro-2-aminodiphenyl ether (*hydrochloride*, m. p. 145°; *acetyl* derivative, m. p. 109°; 3 : 6-*dichlorodiphenylene oxide*, m. p. 190°). Nitration of the above acetyl derivative gives 4 : 4′-*dichloro-5-nitro-2-acetamido-*, m. p. 159°, and 4 : 4′-*dichloro-2′(?)*:5-*dinitro-2′-acetamido-diphenyl ether*, m. p. 212°. Bromination of 5-nitro-2-acetamidodiphenyl ether or nitration of 4′-bromo-2-acetamidodiphenyl ether gives 4′-*bromo-5-nitro-2-acetamidodiphenyl ether*, m. p. 208°, hydrolysed to -*bromo*-5-*nitro-2-aminodiphenyl ether*, m. p. 133°, which is deaminated to give 4′-bromo-3-nitrodiphenyl ether. 5-Bromo-2-aminodiphenyl ether by the diazotisation method gives 2-*bromodiphenylene oxide*, m. p. 120°. Similarly, 4-bromo- or 4′-bromo-2-aminodiphenyl ether gives 3-bromodiphenylene oxide, also obtained by direct bromination of diphenylene oxide; further bromination of this gives 3 : 6-*dibromodiphenylene oxide*, m. p. 195°, also obtained from 4 : 4′-dibromo-2-aminodiphenyl ether. 4′ : 5-Dibromo-2-aminodiphenyl ether gives 2 : 6-*dibromodiphenylene oxide*, m. p. 176°. 4-Chloro-4′-bromo-2-nitrodiphenyl ether is obtained by bromination of 4-chloro-2-nitrodiphenyl ether, or by synthesis from potassium *p*-bromophenoxide and 2 : 5-dichloronitrobenzene. Interaction of iodine monochloride with 2-nitrodiphenyl ether gives 4-iodo-2′-nitrodiphenyl ether, m. p. 86° (*dichloride*, m. p. 96°), reduced to 4-iodo-2′-aminodiphenyl ether (*hydrochloride*, m. p. 219°; *acetyl* derivative, m. p. 115°; *diacetyl* derivative, m. p. 94°). A. A. LEVI.

Substitution in resorcinol derivatives. Bromo-derivatives from β-resorcylaldehyde and their orientation. M. S. IYENGAR and H. S. JOIS (Mysore Univ. J., 1930, **4**, 199—201).—Treatment of 5-nitro-2 : 4-dimethoxy-benzaldehyde or -benzoic acid with bromine in acetic acid containing a little iodine gives 6-*bromo-4-nitroresorcinol dimethyl ether*, m. p. 140—141°. 4-*Bromo-6-nitroresorcinol* 1-*methyl* 3-*ethyl ether*, m. p. 119—121°, is obtained similarly from 5-nitro-4-methoxy-2-ethoxy-benzaldehyde or -benzoic acid. H. BURTON.

Oxidation of β-dinaphthol. A. RIECHE and K. JUNGHOLT (Ber., 1931, **64**, [*B*], 578—589).—β-Dinaphthol (25 g.) in aqueous alkaline solution is oxidised by potassium ferricyanide (90 g.) at 70—80° within 30 min. to the *hydroxydinaphthylene oxide* ester of 1 : 2-*benzoxanthone*-8-*acrylic acid* (I), m. p. 248° (also $+C_6H_6$ and $+C_6H_5Cl$), hydrolysed by concentrated, aqueous alcoholic potassium hydroxide to



(I.)

hydroxydinaphthylene oxide and 1 : 2-*benzoxanthone*-8-*acrylic acid*, m. p. 256° (decomp.)(*sodium* salt). The acid may also be prepared directly by the oxidation of β-dinaphthol with potassium ferricyanide or potassium permanganate; it affords an unstable tetrabromo-compound and adds 2 mols. of iodine chloride. It is oxidised by alkaline permanganate to 1 : 2-*benzoxanthone*-8-*carboxylic acid*, m. p. 263—264° (*sodium* salt), also prepared by the oxidation of β-dinaphthol in alkaline solution with potassium permanganate. It is prepared synthetically by condensing tetrachlorophthalic anhydride with β-naphthol in presence of *s*-tetrachloroethane and aluminium chloride to 3 : 4 : 5 : 6-*tetrachloro*-2-2′-*hydroxy*-1′-*naphthoylbenzoic acid*, which under the influence of alkali passes into 5 : 6 : 7-*trichloro*-1 : 2-*benzoxanthone*-8-*carboxylic acid*, m. p. 297° (also +AcOH, m. p. 301°), catalytically reduced in presence of palladised calcium carbonate to 1 : 2-benzoxanthone-8-carboxylic acid. Alternatively, tetrachlorophthalic anhydride and β-naphthyl methyl ether are condensed to 3 : 4 : 5 : 6-*tetrachloro* - 2 - 2′ - *methoxy*-1′-*naphthoylbenzoic acid*, m. p. 204° and m. p. 222° after re-solidification, reduced to 1 : 2-benzoxanthone-8-carboxylic acid. H. WREN.

Synthesis of ethylpyrogallol. F. MAUTHNER (J. pr. Chem., 1931, [ii], **129**, 281—284).—Reduction of trimethylgallacetophenone (A., 1910, i, 680) by Clemmensen's method affords 3 : 4 : 5-*trimethoxyethylbenzene*, b. p. 149°/12 mm., hydrolysed by boiling hydriodic acid (*d* 1·96) to 3 : 4 : 5-*trihydroxyethylbenzene*, m. p. 86—87°. Reduction of 3 : 4 : 5-trimethoxybenzoyl chloride (prepared from the acid) with hydrogen and palladised barium sulphate in toluene affords 3 : 4 : 5-trimethoxybenzaldehyde (Spath, A., 1919, i, 548), which by treatment with amalgamated zinc and hydrochloric acid gives only resinous products. J. W. BAKER.

β-2 : 4 : 5-Trimethoxyphenylethylamine, an isomeride of mescaline. M. P. J. M. JANSEN (Rec. trav. chim., 1931, **50**, 291—312).—An account of syntheses of substances related to mescaline, with which β-2 : 4 : 5-trimethoxyphenylethylamine (I) is similar in pharmacological action. p-*Methoxyphenylpropionhydrazide*, m. p. 129° (*anisylidene* derivative, m. p. 134·5°), is converted through the azide into *methyl* and *ethyl* β-p-*methoxyphenylethylcarbamate*, m. p. 63—64° and 49·5°, respectively, and s-*di*-β-p-*methoxyphenylethylcarbamide*, m. p. 162°. Hydrolysis of the last two compounds gives β-p-methoxyphenylethylamine. Asarone on ozonolysis to asaraldehyde (2 : 4 : 5-trimethoxybenzaldehyde) (II) gives as by-product 2 : 5-dimethoxybenzoquinone. Reduction of 2 : 4 : 5-trimethoxycinnamic acid with sodium amalgam gives 2 : 4 : 5-*trimethoxyphenylpropionic acid*, m. p. 98° (*methyl* ester, m. p. 52°, b. p. 325—327°), the corresponding *hydrazide*, m. p. 114° (*anisylidene* derivative, m. p. 153·5°), being converted by the Curtius reaction into *ethyl* β-2 : 4 : 5-*trimethoxyphenylethylcarbamate*, m. p. 63—64° (and a by-product, m. p. 180°, s-di-2 : 4 : 5-trimethoxyphenylethylcarbamide), hydrolysed by concentrated hydrochloric acid to I, which was also obtained from β-2 : 4 : 5-*trimethoxyphenylpropionamide*, m. p. 130°, by the Hofmann reaction. Asaraldehyde condenses with nitromethane to 2 : 4 : 5-*trimethoxy*-ω-*nitrostyrene*, m. p. 127—128° (red and yellow forms), which is re-

duced chemically or electrolytically to I. I was also obtained by decarboxylation of 2 : 4 : 5-trimethoxyphenylalanine, m. p. 226° (decomp.) [lit. 217° (decomp.)], obtained from 2 : 4 : 5-trimethoxybenzylidenehydantoin, m. p. 274—276 (lit. 274°), through 2 : 4 : 5-trimethoxybenzylhydantoin.

J. D. A. JOHNSON.

[Action of aminoacetal on pyrogallolsulphonic acid.] O. HINSBERG and R. MAYER (Ber., 1931, 64, [*B*], 702).—The compound obtained from pyrogallolsulphonic acid and aminoacetal (A., 1927, 1071) has the composition $C_6H_4<\begin{matrix}{}^{(4)}SO_2\cdot O\\ {}_{(3)}\text{——}CH\cdot CH_2\cdot NH_2\end{matrix}$

H. WREN.

Ready methylation of alcoholic hydroxyls. K. VON AUWERS (Ber., 1931, 64, [*B*], 533—534).—Readiness of etherification is shown, not only by benzyl alcohol (cf. von Braun and others, this vol., 85), but also by benzhydrol, triphenylcarbinol, and hydroxybenzyl alcohols containing several bromine atoms or methyl groups in the molecule. Since the halogen atom in the corresponding halides is unusually reactive, it follows that the union of the halogen atom or hydroxyl group with the hydrocarbon residue is feeble and that etherification is represented by the scheme: $R\cdot CH_2\cdots OH+HOR'=R\cdot CH_2\cdots OR'+H_2O$. In von Braun's experiments, methyl sulphate is regarded as becoming partly hydrolysed; in the presence of the alkali hydroxide, the methyl alcohol etherifies the benzyl alcohol.

H. WREN.

***p*-Tolylallylcarbinol.** A. KARTASCHEV (J. Russ. Phys. Chem. Soc., 1930, 62, 1883—1884).—*p-Tolylallylcarbinol*, synthesised by the Grignard reaction, using allyl iodide and *p*-tolylaldehyde, has b. p. 236—242° (decomp.), 194°/160 mm., 149—150°/42 mm. d_{20}^{20} 0·99071. Attempts to synthesise phenylallylcarbinol using benzaldehyde and allyl iodide were unsuccessful. Apart from benzaldehyde, aldehydes and ketones gave satisfactory results.

E. B. UVAROV.

Propargyl ethers of phenol. C. D. HURD and F. L. COHEN (J. Amer. Chem. Soc., 1931, 53, 1068—1077).—Phenyl phenylethinyl ketone, m. p. 65—66° (Nef, A., 1900, i, 20, gives m. p. 53—55°), is also prepared from phenylpropiolyl chloride by conversion into ethyl phenylpropiolate and treatment of this with 1 mol. of magnesium phenyl bromide. Triphenylpropargyl alcohol is best prepared by Nef's method (*loc. cit.*), but the yield may be increased to 65—70% by careful purification of the initial reaction materials. Methylacetylene reacts with magnesium ethyl bromide in ether to give ethane and magnesium methylethinyl bromide which, with acetone, affords *trimethylpropargyl alcohol* (*β-methyl-Δ^γ-pentinen-β-ol*), b. p. 75—77°/15 mm., n_D^{20} 1·4193, in 47% yield, together with some of its dehydration product *β-methyl-Δ^β-penten-Δ^γ-inene* $CH_2{:}CMe\cdot C{:}CMe$, b. p. 75—77°, n_D^{20} 1·4002. γ-Methylpropargyl alcohol, b. p. 137—140°, n_D^{20} 1·4497, was obtained by Yvon's method (A., 1925, i, 514). 1-*Phenylethinyl*cyclo*hexan*-1-*ol*, b. p. 166—169°/14 mm., m. p. 58—60°, is obtained by the action of sodium phenylacetylide on *cyclo*hexanone and hydrolysis of the product with dilute hydrochloric acid, whilst *αγ-diphenyl-α-(p-dimethylaminophenyl)propargyl alcohol*, m. p. 144—145°, is similarly obtained from *p*-dimethylaminobenzophenone. Three of these alcohols are converted into their chlorides by the action of phosphorus trichloride in ether or benzene and thus are obtained: triphenyl-, *trimethyl-* (*β-chloro-β-methyl-Δ^γ-pentinene*), b. p. 57—61°/47 mm., n_D^{20} 1·4143, and *γ-methyl-* (*α-chloro-Δ^β-butinene*), b. p. 81—84°, *-propargyl chloride*. These are converted either by the action of sodium phenoxide or by refluxing with phenol and potassium carbonate in acetone into the corresponding ethers and thus are prepared: *phenyl triphenyl-*, m. p. 90—90·5°, *trimethyl-*, n_D^{20} 1·3408, and *γ-methyl-*, b. p. 123—126°/25 mm., n_D^{20} 1·3894, *-propargyl ether*. Pyrolysis of the triphenylpropargyl ether at 310° affords phenol and *-phenylethinylfluorene* $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CH\cdot C{:}CPh$, m. p. 98—100°, identical with a specimen synthesised either by the action of sodium phenylacetylide on 9-chlorofluorene, or by interaction of 9-hydroxyfluorene and phenylacetylene in the presence of concentrated sulphuric acid in dry ether at 5—10°. Decomposition of the trimethylpropargyl ether occurs at 160°, giving β-methyl-Δ^β-penten-Δ^γ-inene (above), phenol, and much tarry material. Decomposition of the γ-methylpropargyl ether at 215—220° affords mainly a tarry product, probably a trimeride, and only a trace of phenol.

J. W. BAKER.

Combinations among certain dye radicals. M. REBEK (Coll. Czech. Chem. Comm., 1931, 3, 155—170).—The interactions of 2 : 4 : 2′ : 4′ : 2″ : 4″-hexanitrotriphenylmethane and 2 : 4 : 6 : 2′ : 4′ : 6′-hexanitrodiphenylamine with the base of crystal-violet in acetone and nitrobenzene solutions, of piperidine with hexanitrotriphenylmethane, and of *p*-nitrodiphenylamine with the base of crystal-violet in acetone have been followed by conductivity measurements. The compounds *hexanitrotriphenylmethane—crystal-violet base*+3 *mols. acetone* and *hexanitrodiphenylamine—crystal-violet base*+1 *mol. acetone*, which are considered to be true dye salts, were isolated. These compounds (free from acetone) exhibited identical absorption spectra in the yellow and green.

J. D. A. JOHNSON.

Occurrence of α-dihydroergosterol as an impurity in yeast-ergosterol. R. K. CALLOW (Biochem. J., 1931, 25, 87—94).—α-Dihydroergosterol has been isolated by fractionation of the benzoates from yeast-ergosterol followed by a process of partial bromination which destroys the ergosterol preferentially. It has been identified and characterised by the preparation of derivatives. On irradiation by an unscreened quartz mercury lamp it does not acquire antirachitic properties. The benzoates of ergosterol and α-dihydroergosterol, as well as the free sterols, form mixed crystals with properties similar to those of neosteryl benzoate and neosterol, respectively (cf. Wieland and Asano, A., 1929, 1200). Details for the colorimetric determination of ergosterol with trichloroacetic acid are given (cf. Rosenheim, A., 1929, 359).

S. S. ZILVA.

Purification of ergosterol. R. K. CALLOW Biochem. J., 1931, 25, 79—86).—Distillation of ergosterol and recrystallisation of ethyl ergosteryl

carbonate are unsatisfactory methods for purifying ergosterol, and recrystallisation from alcohol–benzene (2 : 1) does not invariably yield a pure product. A high degree of purity is, however, attained by benzoylation of ergosterol, recrystallisation of the benzoate, which is trimorphic, from ethyl acetate at 37°, and hydrolysis. There is no variation in the properties of purified yeast-ergosterol from different sources and no evidence of the existence of natural isomerides (cf. Bills and Cox, A., 1930, 84, 1286). When ergosterol is kept over a dehydrating agent in air it takes up five atoms of oxygen. This oxidation is rapid with distilled material but also takes place with recrystallised hydrated material after an induction period.

S. S. Zilva.

Constitution of cholesterol. XIV. Cholesterylbenzoin. E. Montignie (Bull. Soc. chim., 1931, [iv], **49**, 274—275).—When cholesterol is heated with benzoin in chloroform at 50° in presence of hydrogen chloride O-*cholesterylbenzoin*, m. p. 117° (*bromide*, m. p. 96—97°; *phenylhydrazone*, m. p. 104°; *oxime*, m. p. 125°; *semicarbazone*, m. p. 143°), is obtained, converted by boiling with alcoholic potassium hydroxide into cholesterol, potassium benzoate, and benzyl alcohol, and by nitric acid into benzil and nitrocholesterol. Reduction in alcohol with zinc and hydrogen chloride affords cholesterol and deoxybenzoin. R. Brightman.

Nitration of benzoic acid in magnetic and in electrostatic fields. R. H. Clark and R. M. Archibald (Trans. Roy. Soc. Canada, 1930, [iii], **24**, III, 121—124).—No change outside experimental error was found in the proportion of mononitrobenzoic acids obtained by nitration of benzoic acid when the nitration was carried out in a magnetic or in an electrostatic field. W. Good.

Detonation of benzoyl peroxide. S. S. Nametkin and L. S. Kitchkina (J. Russ. Phys. Chem. Soc., 1930, **62**, 2193—2194).—A case of spontaneous detonation of benzoyl peroxide is reported.

E. B. Uvarov.

Preparation of *N*-*o*-chlorobenzoyl-*o*-chlorobenzenesulphonamide. R. Wertheim (J. Amer. Chem. Soc., 1931, **53**, 1172—1173).—This *compound*, m. p. 154—155°, is obtained by the action of *o*-chlorobenzoyl chloride on *o*-chlorobenzenesulphonamide at 180—190°. J. W. Baker.

Optical activity of derivatives of anthracene. H. Goudet (Helv. Chim. Acta, 1931, **14**, 379—396).—Armstrong's formula (Proc. C.S., 1890, 101) for anthracene is preferred to the usual bridged representation of Graebe and Liebermann, since it offers a better explanation of the known properties of anthracene derivatives. If the bridged formula is correct, α- and β-substituted anthracenes should exist in optically active forms. The preparation of inactive 9(or 10)-benzylanthracene-2-carboxylic acids from active benzyloxanthrone-2-carboxylic acids is considered to be evidence against the Graebe and Liebermann formula.

Anthraquinone-2-carboxylic acid is reduced with sodium hyposulphite in ammonium carbonate solution in a current of carbon dioxide, and the resultant solution treated with benzyl chloride and sodium hydroxide, whereby two *benzyloxanthrone-2-carboxylic acids*, (*a*) m. p. 227° and (*b*) m. p. 210°, are obtained; these are separable owing to their differing solubilities in benzene. These acids are resolved by brucine into the corresponding *l*-acids, (*a*) $[\alpha]^{20}$ −71·5° in alcohol (brucine salt, m. p. 176°, $[\alpha]_{D}^{1}$ −42·8° in chloroform) and (*b*) $[\alpha]_{D}^{20}$ −81° in alcohol (brucine salt, m. p. 219°, $[\alpha]^{1}$ −74·8° in chloroform), which when reduced with zinc dust and ammonia afford optically inactive *benzylanthracene-2-carboxylic acids*, (*a*) m. p. 264° and (*b*) m. p. 238°. Intermediate benzylhydranthranolcarboxylic acids could not be isolated. The possibility of racemisation occurring through the use of an alkaline reducing agent is noted.

Reduction of sodium anthraquinone-2-sulphonate with aqueous sodium hyposulphite and treatment of the product with ethyl bromide, sodium hydroxide, and a small amount of iodine gives *sodium* 9 : 10-*diethoxyanthracene-2-sulphonate*. Anthrahydroquinone-2-carboxylic acid is converted by ethyl bromide and potassium hydroxide solution into a mixture of 9 : 10-*diethoxyanthracene-2-carboxylic acid*, m. p. 180°, and *ethyloxanthrone-2-carboxylic acid*, m. p. 210° (*benzoyl* derivative, m. p. 355°). The last-named acid is reduced by zinc and ammonia to 9(or 10)-*ethylanthracene-2-carboxylic acid*, m. p. 187°.

H. Burton.

Asymmetric syntheses. IX. Preparation of optically active substituted glycollic acids from *l*-menthyl and *l*-bornyl α-naphthoylformates. A. McKenzie and P. D. Ritchie (Biochem. Z., 1931, **231**, 412—422).—l-*Menthyl α-naphthoylformate*, m. p. 88·5—89°, $[\alpha]^{25}_{5461}$ −23·8° in ethyl alcohol, prepared by passing hydrogen chloride through a hot mixture of α-naphthoylformamide and menthol, undergoes mutarotation in propyl and *iso*butyl alcohols provided that mineral acids are absent, equilibrium being reached in 12—14 hrs. When magnesium phenyl bromide acts on the ester a mixture of the *l*-menthyl esters of *d*- and *l*-phenyl-α-naphthylglycollic acids is formed. This mixture contains more of the second acid than of the first and hence on hydrolysis yields *l*-phenyl-α-naphthylglycollic acid. *l*-Methyl- and -ethyl-α-naphthylglycollic acids can be prepared in a similar way. From α-naphthoylformamide and *l*-borneol, l-*bornyl α-naphthoylformate*, m. p. 69·5—70·5°, $[\alpha]_{5461}$ −23° in benzene, is prepared and from this ester, which likewise undergoes mutarotation in ethyl alcohol, *l*-methyl-α-naphthylglycollic acid is obtained by Grignard synthesis.

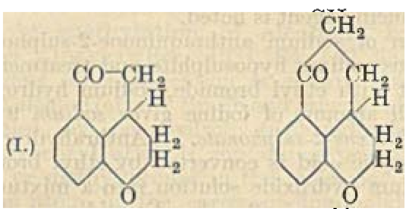
W. McCartney.

Action of hydroxylamine on ethyl phthalimide-*N*-carboxylate. N. I. Putochin (J. Russ. Phys. Chem. Soc., 1930, **62**, 2203—2208).—The action of potassium phthalimide on ethyl chlorformate gives *ethyl phthalimide*-N-*carboxylate*, m. p. 86°, which reacts with hydroxylamine giving *phthaloylhydroxylamine*, m. p. 230° (*potassium* salt; *silver* salt; *ethyl*, m. p. 103°, and *acetyl* derivative, m. p. 181°).

E. B. Uvarov.

Attempted synthesis of a tricyclic system present in morphine. R. H. Manske (J. Amer. Chem. Soc., 1931, **53**, 1104—1111).—Ethyl phenylsuccinate (improved details for preparation given) is reduced by sodium and alcohol to β-*phenylbutane-αδ*-

diol, b. p. 165°/4 mm. (*bisphenylurethane*, m. p. 113°), converted by dry hydrogen bromide in acetic anhydride into *αδ-dibromo-β-phenylbutane*, b. p. 173—175°/16 mm. This with aqueous-alcoholic sodium cyanide affords the dinitrile, b. p. 190—200°/4 mm., hydrolysed without purification to *β-phenyladipic acid*, m. p. 146°. This with phosphorus pentachloride gives the acid chloride, which with aluminium chloride in carbon disulphide affords 1-*keto*-1 : 2 : 3 : 4-*tetrahydronaphthalene-4-acetic acid* (not obtained pure but probably contaminated with the isomeric keto-acid), together with 4 : 9-*diketo*-1 : 2 : 3 : 4-*tetrahydroacenaphthene* (I), m. p. 149°. Similarly, ethyl


(I.) (II.)

β-phenylglutarate is converted successively into *γ-phenylpentane-αε-diol*, b. p. 174°/4 mm. (*bisphenylurethane*, m. p. 112—113°), *αε-dibromo-γ-phenylpentane*, b. p. 177—182°/16 mm. (converted by aqueous-alcoholic sodium phenoxide into *αε-diphenoxy-γ-phenylpentane*, m. p. 72°), the dinitrile, b. p. 200—215°/4 mm., and *γ-phenylpimelic acid*, m. p. 83—84°. This is similarly converted into β-(1-*keto*-1 : 2 : 3 : 4-*tetrahydronaphthyl*-4-)*propionic acid*, m. p. 108—109° (*methyl* ester), together with the tricyclic *dione* (II), m. p. 111° [*dioxime*, m. p. 253—254° (decomp.)]. β-Phenylglutaric acid is converted by treatment through the (isolated) acid chloride into *α-hydrindone-3-acetic acid*, m. p. 155° (*methyl* ester, m. p. 54°, b. p. 175—180°/18 mm.). Ethyl δ-phenoxyvalerate is reduced by sodium and alcohol to ε-phenoxyamyl alcohol (75% yield), whilst similar reduction of a specimen of ethyl γ-phenoxybutyrate which contained γ-phenoxybutyronitrile gave δ-phenoxybutylamine and *γ-phenoxybutyr-δ-phenoxybutylamide*, $CH_2(OPh)\cdot[CH_2]_2\cdot CO\cdot NH\cdot[CH_2]_3\cdot CH_2\cdot OPh$, m. p. 94—95°. All m. p. are corrected. J. W. BAKER.

Condensation of aromatic aldehydes with phenylacetonitrile. (MISS) T. DE KIEWIET and H. STEPHEN (J.C.S., 1931, 639—640; cf. A., 1889, 597).—Condensation of hydroxy- and methoxy-benzaldehydes with phenylacetonitrile in presence of sodium ethoxide or alkali gives derivatives of cinnamonitrile (except *o*-hydroxyaldehydes, which give coumarins) (cf. A., 1904, i, 893). The following are described; 2 : 4-*dimethoxy*, m. p. 95°; 3 : 4-*dimethoxy*-, m. p. 88°; 4-*hydroxy-2-methoxy*-, m. p. 195°; 2-*methoxy-4-acetoxy*-, m. p. 158°, and 4 *hydroxy-2-methoxy-α-phenylcinnamonitrile*, m. p. 99°; 8-*methoxy-3-phenylcoumarin*, m. p. 155·5°. A. A. LEVI.

***cyclo*Propene series. I. Diphenyl*cyclo*propenedicarboxylic acid.** S. F. DARLING and E. W. SPANAGEL (J. Amer. Chem. Soc., 1931, 53, 1117—1120).—Methyl γ-nitro-αγ-diphenylethylmalonate (Kohler and Barrett, A., 1926, 849) is converted by sodium methoxide and bromine in methyl alcohol into the corresponding *α-bromomalonate*, m. p. 117—118°, converted by heating with methyl-alcoholic potassium acetate into *methyl 2-nitro-2 : 3-diphenyl*-cyclo*propane-1 : 1-dicarboxylate*, m. p. 129°. This is converted, with loss of nitrous acid, by boiling with methyl-alcoholic sodium methoxide into *methyl 2 : 3-diphenyl-Δ*²-cyclo*propene-1 : 1-dicarboxylate*, m. p. 140—142° (cf. Kohler and Darling, A., 1930, 933), the structure of which is proved by oxidation of the corresponding dicarboxylic *acid*, m. p. about 190° (decomp.; see below), with alkaline potassium permanganate, dibenzoylmethane being formed. The *cyclo*propene acid is converted by bromine in carbon tetrachloride into 2 : 3-*dibromo-2 : 3-diphenyl*cyclo*propane-1 : 1-dicarboxylic acid*, m. p. 194—195° (decomp.), and when heated above its m. p. it is converted not into the corresponding monobasic acid but into the *lactone*, m. p. 149—151°, of 3-*hydroxy-2 : 3-diphenyl*cyclo*propanecarboxylic acid*, m. p. 146—148°, which is obtained by hydrolysis of the lactone with aqueous methyl-alcoholic potassium hydroxide, and is only slightly attacked by ozone. No benzoin, which would result from ozonolysis of the other possible structure for the lactone, $\begin{matrix}CPh\cdot CHPh\\ CH——CO\end{matrix}\!>\!O$ could be detected. J. W. BAKER.

Action of cyanoacetic acid on triphenylcarbinol. Syntheses of α-cyano-βββ-triphenylpropionic and *N*-triphenylmethylmalonamic acids. R. FOSSE (Bull. Soc. chim., 1931, [iv], 49, 159—173; cf. A., 1907, i, 764).—The "isomeric" substance, B, m. p. 175° (decomp.), obtained with α-cyano-βββ-triphenylpropionic acid, m. p. 155° (decomp.), when triphenylcarbinol is heated with cyanoacetic acid is now shown to be N-*triphenylmethylmalonamic acid*, since on fusion at 220° it is converted into acet-triphenylmethylamide, m. p. 211°, also obtained from triphenylcarbinol and acetamide at 210—240°, and hydrolysed by 90% sulphuric acid to triphenylcarbinol, ammonia, and acetic acid. The structure of α-cyano-βββ-triphenylpropionic acid is confirmed by its conversion at 160—170° into α-cyano-βββ-triphenylethane, m. p. 140° (also obtained by heating triphenylcarbinol and cyanoacetic acid at 110—115°), hydrolysed to βββ-triphenylpropionic acid, m. p. 178—179 (*silver* salt). R. BRIGHTMAN.

Action of hydrogen peroxide on 6 : 7-benz-2 : 3-diketo-2 : 3-dihydrothionaphthen in sodium hydroxide solution. R. STOLLE and W. BADSTUBNER (J. pr. Chem., 1931, [ii], 129, 309—311).—This compound (A., 1925, i, 1146) is converted by 3% hydrogen peroxide in sodium hydroxide solution into 1 : 1′-*dinaphthyl disulphide-2 : 2′-dicarboxylic acid*, m. p. 156°. With alkali this titrates normally as a dibasic acid, but with excess of alkali the reaction is: $2[C_{10}H_6(CO_2H)\cdot S\cdot]_2 + 8KOH = C_{10}H_6(CO_2K)\cdot SO_2K + 3C_{10}H_6(CO_2K)\cdot SK + 6H_2O$. J. W. BAKER.

Syntheses in the *cyclo*butanol series. L. BLANCHARD (Bull. Soc. chim., 1931, [iv], 49, 279—309).—When *s*-dibromohydrin or chlorobromohydrin is first converted into ethers, the condensation with ethyl sodiomalonate yields *cyclo*butane derivatives without difficulty, formation of ethylene oxides being avoided. Thus, αγ-dibromo-β-amyloxypropane, obtained from magnesium butyl bromide and chloro-

methyl $\alpha\gamma$-dibromopropyl ether, yields 45—50% of *ethyl 3-amyloxy*cyclo*butane*-1 : 1-*dicarboxylate*, b. p. 175/12 mm., d^{15} 1·011, n_D 1·44361 (free *acid*; *copper* salt, $+H_2O$; *chloride*, b. p. 143—145°/15 mm.; *amide*, m. p. 177·5°; *anilide*, m. p. 175°). The chloride condenses with carbamide to give *amyloxy*cyclo*butane*spiro*barbituric acid*, m. p. 222—223°, $C_5H_{11}O\cdot CH{<}{}^{CH_2}_{CH}{>}C{<}{}^{CO\cdot NH}_{CO\cdot NH}{>}CO$ At 120°, 3-amyloxy*cyclo*butane-1 : 1-dicarboxylic acid is converted into 3-*amyloxy*cyclo*butane*-1-*carboxylic acid*, b. p. 164—166°/10 mm., *d* 1·003, n_D 1·45412 (*silver* salt; *amide*, m. p. 131—132°; *chloride*, b. p. 100—120°/14 mm.). The corresponding methoxyhalogenopropanes are less suitable for the condensation owing to the proximity of their b. p. to that of the corresponding alcohol. Purification of *ethyl 3-methoxy*cyclo*butane*-1 : 1-*dicarboxylate*, b. p. 130°/10 mm., d^{13} 1·076, n_D 1·441, obtained from α-chloro-γ-bromo-β-methoxypropane, is difficult owing to the presence of the formal, $CH_2Cl\cdot CH(OMe)\cdot CH_2\cdot CH(CO_2Et)_2$, b. p. 157°/13 mm. α-Chloro-γ-bromo-β-amyloxypropane and ethyl sodiomalonate yield *ethyl 3-amyloxymethoxy*cyclo*butane*-1 : 1-*dicarboxylate*, b. p. 190—195°/18 mm., d^{14} 1·04, n_D 1·44481, together with a residue, b. p. 210—240°/18 mm. The corresponding *acid* and its *copper* salt are described. Acid hydrolysis converts the acid into amyl alcohol, amylformal, b. p. 250°, d^{15} 0·843, and 3-*hydroxy*cyclo*butane*-1 : 1-*dicarboxylic acid*, m. p. 125° (*barium* salt, $+3H_2O$). The amyl and methyl ethers of this acid and the amyl ether of ethyl 3-hydroxy-1-cyano*cyclo*butane-1-carboxylic acid show an abnormal molecular refraction attributed to the double linking, *e.g.*, $>\dot{C}—C—O$, in conjunction with the *cyclo*butane ring.

Treatment of chloromethyl $\alpha\gamma$-dibromo*iso*propyl ether with methyl alcohol yields methyl chloromethyl ether and $\alpha\gamma$-dibromohydrin, the methoxymethyl ether first formed being decomposed by the hydrogen chloride liberated. Addition of chloromethyl amyl ether to epichlorohydrin yields the same formal as that obtained by the action of magnesium ethyl bromide on $\alpha\gamma$-dichlorohydrin, to form the intermediate $(CH_2Cl)_2{:}CH\cdot OMgBr$, followed by reaction with chloromethyl amyl ether, and accordingly in the former case opening of the oxide ring must occur thus: $\underset{\quad O-}{CH_2Cl\cdot CH\cdot CH_2-}$ The following formals have been prepared by this method: *methoxymethyl $\alpha\gamma$-dichloro*iso*propyl ether*, b. p. 80—81°/11 mm., d^{18} 1·237, *n* 1·45412; *ethoxymethyl $\alpha\gamma$-dichloro*iso*propyl ether*, b. p. 90—91°/12 mm., d^{17} 1·182, *n* 1·44912, and *amyloxymethyl $\alpha\gamma$-dichloro*iso*propyl ether*, b. p. 133—135°/19 mm., d^{18} 1·09, *n* 1·4506. The chloromethyl methyl ether, b. p. 60°, and ethyl ether, b. p. 80°, are not readily obtained pure; chloromethyl amyl ether, b. p. 150°, 50—55°/18 mm., is obtained in 87% yield by saturating amyl alcohol with hydrogen chloride and adding trioxymethylene. *Ethoxymethyl α-chloro-γ-bromo*iso*propyl ether*, b. p. 110—112°/20 mm., d^{22} 1·409, *n* 1·46954 (from *bromomethyl ethyl ether*, b. p. 107°), *amyloxymethyl α-chloro-γ-bromo*iso*propyl* b. p. 142—144°/20 mm., d^{13} 1·277, *n* 1·46856, and *ethoxymethyl α-chloro-γ-iodo*iso*propyl ether*, b. p. 124—/18 mm., d^{18} 1·6528, *n* 1·50882 (from *iodomethyl ethyl ether*, b. p. 70°/70 mm.), are similarly obtained. *Methoxymethyl α-chloro-γ-amyloxy*iso*propyl ether*, b. p. 118°/12 mm., d^{15} 1·01, *n* 1·43587, is obtained from epiamyline and methyl chloromethyl ether.

When a mixed formal, *e.g.*, amyloxymethyl α-chloro-γ-bromo*iso*propyl ether, is heated at 170°, a mixture of the symmetrical formals, amylformal, and α-chloro-γ-bromo*iso*propylformal is obtained. Chloromethyl ethers and the corresponding alcohol also give a symmetrical formal if the hydrochloric acid formed is eliminated with a sparingly soluble hydroxide, *e.g.*, magnesium hydroxide. The following have been obtained thus from the corresponding hydrins: *methylene bis-$\alpha\gamma$-dichloro*iso*propyl ether*, m. p. 51°; *methylene bis-α-chloro-γ-bromo*iso*propyl ether*, m. p. 54—55°; *methylene bis-α-chloro-γ-iodo*iso*propyl ether*, m. p. 60°; *methylene bis-$\alpha\gamma$-dibromo*iso*propyl ether*, m. p. 68—69°. Methyl α-chloro-γ-bromo*iso*propyl ether condenses with ethyl sodiomalonate giving *ethyl δ-chloro-γ-methoxybutanedicarboxylate*, b. p. 157°/13 mm., d^{13} 1·135, n_D 1·44682, in 30% yield. In presence of iodine the ester yields on bromination 70% of *ethyl δ-chloro-α-bromo-γ-methoxybutanedicarboxylate*, b. p. 178—180°/13 mm., d^{15} 1·393, n_D 1·47544. Attempts to prepare the δ-chloro-γ-hydroxy-ester failed, but hydrolysis with 50% hydrochloric acid yields *δ-chloro-γ-methoxybutanedicarboxylic acid* (*barium* salt).

R. BRIGHTMAN.

Use of tetramethylene dibromide in synthetical formation of closed carbon chains. L. J. GOLDSWORTHY (J.C.S., 1931, 482—486).—Treatment of tetramethylene dibromide (improved preparation) with ethyl sodiomalonate gives ethyl *cyclo*pentane-1 : 1-dicarboxylate. With ethyl sodioethanetetracarboxylate, ethyl *cyclo*hexane-1 : 1 : 2 : 2-tetracarboxylate is obtained, converted by heat into *cis*- and *trans*-hexahydrophthalic acid. The products of the action of tetramethylene dibromide on ethyl sodiopropanetetracarboxylate are ethyl *cyclo*pentane-1 : 1-dicarboxylate and the polymeride of ethyl methylenemalonate.

A. A. LEVI.

Synthesis of *m*-glucosidoxybenzaldehyde. F. MAUTHNER (J. pr. Chem., 1931, [ii], **129**, 278—280).—*m*-Tetra-acetylglucosidoxybenzaldehyde (best prepared by the action of tetra-acetylglucosidyl bromide on *m*-hydroxybenzaldehyde in acetone with addition of 9% aqueous sodium hydroxide below 16°) is readily hydrolysed to m-*glucosidoxybenzaldehyde*, m. p. 160—161°, by 2·5% aqueous ammonia in the cold, although unsatisfactory results are obtained with barium hydroxide. It is not identical with picrin (A., 1914, i, 195).

J. W. BAKER.

New *p*-bromophenacyl esters. S. G. POWELL (J. Amer. Chem. Soc., 1931, **53**, 1172).—By Reid and Judefind's method (A., 1920, i, 480) are obtained p-*bromophenacyl $\alpha\alpha$-dimethylpropionate*, m. p. 76·5°, iso*hexoate*, m. p. 77·3°, n-, m. p. 69·2°, and iso-, m. p. 75·5°, -*heptoate*, and n-*nonoate*, m. p. 63·5°.

J. W. BAKER.

Oximes of $\alpha\beta$-unsaturated ketones and the Beckmann rearrangement. A. H. BLATT (J. Amer. Chem. Soc., 1931, **53**, 1133—1141).—The stable oxime of benzylideneacetophenone, obtained from the ketone by the action of hydroxylamine in the presence of alkali, is not the *anti*-oxime as stated

by Henrich (A., 1911, i, 650), but is 3 : 5-*diphenyl*-iso*oxazoline*, , since it gives no methane with magnesium methyl iodide. The following evidence shows that the labile oxime of benzylideneacetophenone (and of the αβ-unsaturated ketones studied) is not the *syn*-form as suggested by Henrich (*loc. cit.*), but is the *anti*-form, the Beckmann rearrangement to cinnamanilide involving a *trans*-migration. *Benzylidene*-o-*chloroacetophenone* is converted by hydroxylamine hydrochloride in boiling aqueous alcohol into its anti-*oxime*, m. p. 110—124° even when carefully purified, converted by a Beckmann change into *cinnam*-o-*chloroanilide*, m. p. 136—137°, but unchanged by prolonged heating with alcoholic potassium hydroxide which would be expected to convert it into a benz*iso*oxazole if it possessed the *syn*-configuration. Similarly benzylidene-*p*-bromoacetophenone affords its anti-*oxime*, m. p. 138—150° (cf. above), not converted into the *iso*oxazoline with alcoholic potassium hydroxide, giving *cinnam*-p-*bromoanilide*, m. p. 191°, by a Beckmann rearrangement, and converted by bromine in chloroform into a *dibromide*, m. p. 155° (decomp.). This is converted, with loss of hydrogen bromide, either by alcoholic alkali or by heating either alone or in acetic acid into 3-p-*bromophenyl*-5-*phenyl*iso-*oxazole*, $CH<\genfrac{}{}{0pt}{}{C(C_6H_4Br):N}{CPh——O}$ m. p. 178—179°, identical with a specimen prepared by the action of alcoholic hydroxylamine hydrochloride and potassium hydroxide on the dibromide of *benzylidene*-p-*bromoacetophenone*. This ring closure is explicable only on the *anti*-configuration for the oxime. The *anti*-oximes are not intermediates in the formation of the *iso*oxazolines, since the *anti*-oximes of dypnone and benzylidene-*p*-bromoacetophenone are unaltered by further treatment with hydroxylamine hydrochloride and excess of alkali. The *iso*oxazolines are not formed by 1 : 4-addition of hydroxylamine to the unsaturated ketones followed by ring closure, since dypnone affords 3 : 5-diphenyl-5-methyl*iso*oxazoline (also obtained from the *anti*-oxime by rearrangement with concentrated sulphuric acid) and not the isomeric compound $CH<\genfrac{}{}{0pt}{}{CPhMe\cdot NH}{CPh——O}$, since the product is inert towards the Grignard reagent. Similarly benzylidene-*p*-bromoacetophenone affords 3-p-*bromophenyl*-5-*phenyl*iso*oxazoline*, $CH_2<\genfrac{}{}{0pt}{}{C(C_6H_4Br):N}{CHPh——O}$, m. p. 138—139° (also obtained by the action of concentrated sulphuric acid on the *anti*-oxime), oxidised by chromic oxide in glacial acetic acid at 80° to the *iso*oxazole, m. p. 178—179° (above). The rearrangement of the *anti*-oximes into *iso*oxazolines under the influence of sulphuric acid is the best method of preparing these derivatives, and may involve halochromic salt formation by the oxime followed by rearrangement of the cation in the strongly acid medium to yield a more basic product. J. W. BAKER.

Action of phenol on benzoyldiphenylmethyl bromide. C. F. KOELSCH (J. Amer. Chem. Soc., 1931, 53, 1147—1150).—The product of the interaction of phenol and phenyl diphenylbromomethyl ketone is not phenylbenzoin monophenyl ether as stated by Schuster (A., 1930, 1576), but phenyl diphenylmethyl ketone, identical with a specimen prepared by Orekhov's method (A., 1919, i, 272), *p*-bromophenol also being formed. This is confirmed by fission of the resulting ketone into potassium benzoate and diphenylmethane with hot alcoholic potassium hydroxide; its conversion by acetic anhydride and a few drops of concentrated sulphuric acid at 60—70° into triphenylvinyl acetate; and by the formation, on treatment with magnesium phenyl bromide, of ααββ-tetraphenylethyl alcohol, m. p. 232—233° (Schuster, *loc. cit.* described it as benzopinacone monomethyl ether, m. p. 219°), which is hydrolysed by alcoholic potassium hydroxide to diphenylmethane and benzophenone. J. W. BAKER.

Synthesis of antiseptic derivatives of indan-1 : 3-dione. II. Interaction of alkylmalonyl chlorides with *p*-tolyl methyl ether. T. K. WALKER, A. J. SUTHERS, L. L. ROE, and H. SHAW (J.C.S., 1931, 514—520; cf. this vol., 487).—Interaction of *p*-cresol, or its methyl ether, and suitably substituted malonyl chlorides in presence of aluminium chloride gives 4-*hydroxy*-7-*methylindan*-1 : 3-*dione*, m.p. 258° (50% yield), and the following derivatives of this compound: 2-*methyl*-, m. p. 253° (sinters 243°); 2-*ethyl*- (III), m. p. 197°; 2 : 2-*diethyl*-, m. p. 199—200°; 2-n-*propyl*-, m. p. 187° (theoretical yield); 2-n-*butyl*-, m. p. 165° (theoretical yield); 2-n-*amyl*-, m. p. 146° (29% yield); 2-n-*hexyl*-, m. p. 136° (31% yield); 2-n-*heptyl*-, m. p. 124° (50% yield); 2-iso*propyl*-, m. p. 224° (16% yield); 2-iso*butyl*-, m. p. 152·5° (47% yield); 2-iso*amyl*-, m. p. 142° (44% yield). 4-*Methoxy*-7-*methyl*-2 : 2-*diethylindan*-1 : 3-*dione* (oily) with aluminium chloride gave III. Improved conditions for carrying out the condensation are described. Ferric chloride can be used in place of aluminium chloride.

The substances are graded in order of antiseptic activity, maximum efficiency being obtained with *n*-heptyl and *n*-hexyl derivatives. Branched-chain compounds are less effective. A. A. LEVI.

Fluorene series. Synthesis of two ketones: 2-fluoryl methyl ketone and 2 : 7-fluoryl dimethyl diketone. K. DZIEWONSKI and J. SCHNAYDER (Bull. Acad. Polonaise, 1930, A, 529—535).—Fluorene condenses with acetyl chloride in the presence of aluminium chloride in carbon disulphide solution to give 2-*fluoryl methyl ketone*, b. p. 323—328°/20 mm., m. p. 132° (*phenylhydrazone*, m. p. 216—218°; *oxime*, m. p. 196—197°), and 2 : 7-*fluoryl dimethyl diketone* (2 : 7-*diacetylfluorene*), m. p. 182—184° (*phenylhydrazone*, m. p. 233—235°; *dioxime*, m. p. 258°). 2-Fluoryl methyl ketoxime is converted by a Beckmann change when heated with dry hydrogen chloride in acetic anhydride and acetic acid solution in a sealed tube at 100° into 2-*acetamidofluorene*, m. p. 192—193°, hydrolysed by heating with 6% hydrochloric acid to 2-*aminofluorene*, m. p. 127—129°. Oxidation of 2-fluoryl methyl ketone with potassium dichromate and acetic acid converts it into fluorenone-2-carboxylic acid, identical with a specimen prepared from fluorenone-1 : 7-dicarboxylic acid (Bamberger and Hooker,

A., 1885, i, 905). Similarly, the dioxime of the diketone is converted into 2 : 7-*diacetamido*-, m. p. 274°, hydrolysed to 2 : 7-*diamino*-, m. p. 162—163°, -*fluorene*. J. W. BAKER.

Formation of chloranil from aromatic compounds, and use of the reaction in analysis. R. P. P. COLMANT (Ann. Soc. Sci. Bruxelles, 1931, [B], 51, 27—39).—About 130 aromatic compounds were tested for the formation of chloranil, by heating with hydrochloric acid, *d* 1·08, and potassium chlorate on a water-bath. Neither benzene nor its halogeno-, nitro-, azo-, or sulphonic derivatives, nor those containing groups linked by carbon to the nucleus give chloranil, but the compound is given by benzene substituted by the amino-group and its alkyl or acyl derivatives, the hydrazine group, the pyrazole group, and the hydroxyl group and its ethers. The presence of a single active group makes the reaction possible. If more than two substituents are present, one of which is an alkylated chain, no chloranil is formed. When two active substituents are present they must be in the *p*-position if reaction is to take place. With more than two active substituents no chloranil is formed. The analytical application of the reaction is exemplified by tests on the reduction products of nitro-compounds. The introduction into phenol or aniline of any inactive substituent decreases the yield of chloranil. In phenols the nitro-group decreases the yield more than the carboxyl group, which in turn reduces the yield more than the methyl group. For aniline the order is reversed. *p*-Amino-derivatives give greater yields than *o*-amino-derivatives, but *o*-phenol derivatives give greater yields than *p*-phenol derivatives. Phenol ethers give smaller yields than phenol. Cresol ethers give no chloranil. A. RENFREW.

Reduction potentials of some higher benzologues of the quinones. L. F. FIESER and E. M. DIETZ (J. Amer. Chem. Soc., 1931, 53, 1128—1133).—The normal reduction potentials of 1 : 2-benzanthra-, 1 : 2 : 7 : 8- and 1 : 2 : 5 : 6-dibenzanthra-, 1 : 2-(3-methylbenz)-1 : 2 : 5 : 6-dibenzanthra-, 5 : 6- and 6 : 12-chryso-, 12-hydroxy- and 12-ethoxy-5 : 6-chryso-, 1 : 2-benz-3 : 4-anthra-, and picene-quinones have been determined, generally by catalytic reduction and potentiometric titration of the reductant with a suitable oxidising agent : the values are, respectively, 0·228, 0·264, 0·268, 0·257, 0·465, 0·392, 0·391, 0·418, 0·430, and 0·474 ±0·01 volt. The significance of these results is discussed and the potentials of benz- and dibenz-anthraquinones lend support to the *o*-quinonoid theory of the structure of anthracene (cf. Fieser and Ames, A., 1927, 1198), and are not readily harmonised with the *p*-linking structure which a symmetrical structure. Contrary to the assumption of Beschke and Diehm (A., 1911, i, 889) the stable *o*-quinonoid structure of hydroxy*amphi*chrysoquinone is the one possessing the higher reduction potential, and this compound thus forms an exception to the rule (*loc. cit.*) that when a quinone can exist in two tautomeric forms the one with the lower potential will be the stable form. J. W. BAKER.

New *p*-2-carboxybenzoylbenzenesulphonic acids and the corresponding anthraquinone compounds. I. GUBELMANN, H. J. WEILAND, and O. STALLMANN (J. Amer. Chem. Soc., 1931, 53, 1033—1036).—Nitration of *p*-2-carboxybenzoylbenzenesulphonic acid (as its sodium salt) with mixed acids at 15—35° affords p-(4-*nitro-2-carboxybenzoyl*)-*benzenesulphonic acid* (I) (as its sodium salt), converted by heating in 25% oleum at 150° into 2-nitroanthraquinone-7-sulphonic acid. This is converted by sodium chlorate in boiling hydrochloric acid solution into 7-*chloro-2-nitroanthraquinone*, m. p. 251—252°, reduced by sodium sulphide in alkaline solution to the corresponding 2-*amino*-derivative, m. p. 302—303°. Reduction of the original nitrosulphonic acid (I) with iron and glacial acetic acid affords p-(4-*amino-2-carboxybenzoyl*)*benzenesulphonic acid*, similarly converted into 2-aminoanthraquinone-7-sulphonic acid, which on heating with ammonia and arsenic acid at 180° gives 2 : 7-diaminoanthraquinone, converted into the corresponding dihydroxy- and diacetoxy-derivatives in the usual manner.
J. W. BAKER.

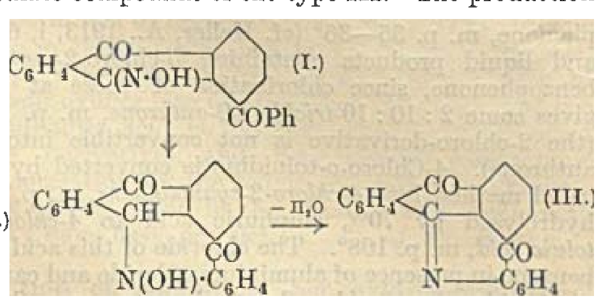
Chlorination of derivatives of *o*-methylbenzophenone. H. DE DIESBACH and P. DOBBELMANN (Helv. Chim. Acta, 1931, 14, 369—378; cf. A., 1925, i, 1435).—Treatment of *o*-methylbenzophenone with chlorine at 120° during 24 hrs. gives mainly 10 : 10-dichloro-9-anthrone (cf. Thorner and Zincke, A., 1878, 231). The product formed after 2 hrs. contains 2 atoms of chlorine per mol., and is not converted into anthraquinone when moistened and then kept in a vacuum (whereby hydrogen chloride is eliminated); boiling with alcohol, however, leads to the formation of anthraquinone and *o*-benzoylbenzoic acid. Chlorination at 180° during 4 hrs. gives a quantitative yield of 10 : 10-dichloro-9-anthrone, which is probably formed by loss of hydrogen chloride from the intermediate trichloromethyl derivative. 4-*Chloro-2′-methylbenzophenone*, b. p. 194°/14 mm., from *o*-toluoyl chloride and chlorobenzene in presence of aluminium chloride, is converted by chlorine at 130° into 3 : 10 : 10-*trichloro-9-anthrone*, m. p. 137°, which when boiled with alcohol gives 2-chloroanthraquinone. 2 : 5-*Dichloro-2′-methylbenzophenone*, b. p. 203°/13 mm., m. p. 63·5°, from *o*-toluoyl chloride and *p*-dichlorobenzene, does not undergo ring closure when chlorinated, probably owing to a steric hindrance effect; the resulting trichloromethyl derivative is converted by dissolution in sulphuric acid into 2 : 5-dichlorobenzophenone-2′-carboxylic acid. Condensation of benzoyl chloride and *p*-chlorotoluene gives 2-chloro-5-methylbenzophenone, m. p. 35—36° (cf. Heller, A., 1913, i, 631), and liquid products containing 5-chloro-2-methylbenzophenone, since chlorination of these at 180° gives some 2 : 10 : 10-*trichloro-9-anthrone*, m. p. 162° (the 2-chloro-derivative is not convertible into an anthrone). 4-Chloro-*o*-toluidine is converted by the usual method into 4-*chloro-2-cyanotoluene*, m. p. 48°, hydrolysed by 70% sulphuric acid to 4-*chloro-o-toluic acid*, m. p. 168°. The chloride of this acid and benzene in presence of aluminium chloride and carbon disulphide give 5-*chloro-2-methylbenzophenone*, b. p. 191°/12 mm., m. p. 41°, chlorinated to 2 : 10 : 10-trichloro-9-anthrone. 2 : 4-*Dichloro-5-methylbenzophenone*, b. p. 202—203°/12 mm., m. p. 78°, from

2 : 4-dichlorotoluene and benzoyl chloride, is chlorinated at 180° to the *monochloromethyl* derivative, which after treatment with sulphuric acid at 35° and subsequent oxidation with alkaline potassium permanganate affords 2 : 4-*dichlorobenzophenone*-5-*carboxylic acid*, m. p. 167°. Chlorination of 2 : 5-dibenzoyl-*p*-xylene in a small amount of trichlorobenzene at 140—150° gives slightly impure 2 : 5-*dibenzoyl*-1 : 4-*di*(*trichloromethyl*)*benzene*, m. p. 205·5°, which when heated in nitrobenzene or trichlorobenzene at 180° passes into 7 : 7 : 14 : 14-*tetrachloro*-5 : 12-*diketopentacene*, decomp. 200° without melting. Chlorination of 2 : 5-dimethylbenzophenone at 180° gives mainly 2-*chloromethyl*-5-*trichloromethylbenzophenone*, which when moistened and then kept in a vacuum eliminates 1 mol. of hydrogen chloride, and is converted by water at 150° into 2-*hydroxymethylbenzophenone*-5-*carboxylic acid*, m. p. 198—200°. When the above tetrachloro-derivative is heated with alcohol for several days, unexpectedly 2-*trichloromethylanthraquinone*, m. p. 154°, is produced. This is converted by sulphuric acid at 35° into anthraquinone-2-carboxylic acid, and when boiled with nitrobenzene affords di-2-anthraquinonylacetylene, also formed when the trichloromethyl derivative is treated with amyl-alcoholic sodium hydroxide; reduction with alkaline hyposulphite gives αβ-di-2-anthraquinonylethylene. H. BURTON.

Morpholquinone. L. F. FIESER (Ber., 1931, **64**, [*B*], 701—702).—Fuller details are given of the synthesis of morpholquinone from 3-hydroxyphenanthrene (cf. A., 1929, 567). H. WREN.

[**Action of aluminium chloride on *o*-dihydroxybenzil.**] P. K. BRASS (Ber., 1931, **64**, [*B*], 700—701; cf. Brass and others, A., 1930, 1589).—The synthesis of morpholquinone by Fieser (A., 1929, 567) has been overlooked. H. WREN.

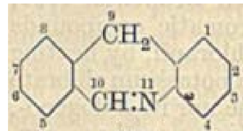
Reaction of aromatic 1 : 4-diketonemonoximes occurring in place of the Beckmann transformation. IV. Benzoylenemorphanthridone and benzoylenemorphanthridine. R. SCHOLL and J. MÜLLER [with J. DONAT] (Ber., 1931, **64**, [*B*], 639—655; cf. this vol., 488).—Oximation of 1-aroylanthraquinones leads to 1-aroylanthraquinone-9-oximes (I), probably mixed with small amounts of easily removed isomerides. Dehydration of the oximes to the benzoylenemorphanthridones (II) takes place by loss of water probably through the intermediate compounds of the type III. The production



(I.) (II.) (III.)

of anthraquinone-1-carboxyarylides or anthraquinone-1-carboxylic acid and arylamines with aqueous or alcoholic hydrochloric acid at an elevated temperature is a consequence of an isomerisation of the oximes into anthraquinone-9-anil-1-carboxylic acids, $C_6H_4{<}{\genfrac{}{}{0pt}{}{CO\text{———}}{C(:NPh)}}{>}C_6H_3{\cdot}CO_2H$; the reaction occurs in place of the normal Beckmann transformation of quinoneoximes.

It is proposed to designate the structure IV by the name "morphanthridine," partly by reason of its relationship to phenanthridine and partly of its kinship to Knorr's morphine formula.



(IV.)

Benzoylenemorphanthridone III (anhydro-compound of phenyl anthraquinonyl ketoxime) is converted by fusion with potassium hydroxide into *anthraquinoneanil*-o-*carboxylic acid*, $C_6H_4{<}{\genfrac{}{}{0pt}{}{CO\text{————}}{C(:N{\cdot}C_6H_4{\cdot}CO_2H)}}{>}C_6H_4$, m. p. 222° (after softening) (very readily converted by acids into anthraquinone and anthranilic acid), 1 : 2-phthalylacridone, not molten below 350°, and acridone, m. p. 349—350°. Anthraquinoneanil-*o*-carboxylic acid is obtained synthetically from *ms*-dibromoanthrone and anthranilic acid in boiling toluene. It is mainly unchanged by concentrated sulphuric acid at 80—90° and converted into anthraquinone and anthranilic acid at 130—140°; treatment of its chloride with aluminium chloride in benzene gives anthraquinone and *o*-aminobenzophenone.

Anthranol-1-carboxylic acid, m. p. 248° varying with the rate of heating, is converted by bromine in boiling chlorobenzene into 9-*bromoanthrone*-1-*carboxylic acid*, $C_6H_4{<}{\genfrac{}{}{0pt}{}{CO}{CHBr}}{>}C_6H_3{\cdot}CO_2H$, decomp. 225° when rapidly heated, transformed by aniline in benzene into 9-*anilinoanthrone*-1-*carboxylic acid*, m. p. indef. 160—163°. The last-named compound does not give benzoylenemorphanthridone when treated with nitrobenzene containing hydrogen chloride. It is converted by potassium ferricyanide in alcoholic alkaline solution followed by very cautious addition of acetic acid into *anthraquinone*-9-*anil*-1-*carboxylic acid*, m. p. 171—172° (decomp.), readily hydrolysed to aniline and anthraquinone-1-carboxylic acid; attempts to transform it into benzoylenemorphanthridone were unsuccessful.

Protracted ebullition of anthraquinone and hydroxylamine in alcoholic alkaline solution gives anthraquinonemonoxime in only 2·5% yield; this may be increased to about 50% if anthraquinol is used as initial material. The application of the method to the production of 1-benzoylanthraquinone-9-oxime is described.

[With E. STIX.] Benzoylenemorphanthridone is converted by sodium amalgam in boiling absolute alcohol and repeated crystallisation of the product from alcohol into *benzoylenemorphanthridine*, m. p. 218°. H. WREN.

Constitution of amyrins. H. DIETERLE (Arch. Pharm., 1931, **269**, 78—87).—α-Amyrin (cf. Horrmann, A., 1930, 216; Vesterberg, A., 1922, i, 825) is oxidised by chromic and acetic acids in a current of steam to carbon dioxide, acetone, α-amyrone [*hydrazone*, m. p. 252° (decomp.)], and a *ketone*, $C_{21}H_{34}O$,

m. p. 89—90° $[\alpha]^{20}$ +123·2° (all rotations in chloroform) (*hydrazone*, m. p. 224°). α-Amyrin has therefore a side-chain of nine carbon atoms which contains an *iso*propyl group. With boiling nitric acid (*d* 1·46) it yields *substances*, $C_{20}H_{27}(NO_2)_2(CO_2H)_3$, m. p. 171°, $[\alpha]_D^{0}$ +29·6°, and $C_{20}H_{29}(NO_2)_2(CO_2H)_3$, m. p. 185—186°, $[\alpha]_D^{0}$ +54·3°. The former is reduced by zinc dust and acetic acid to the corresponding *diamine*, m. p. 196°. The oily *ozonide* of α-amyrin yields when heated an *acid*, $C_{20}H_{36}(CO_2H)_2$, $[\alpha]_D^{20}$ +88·0°, and when treated with water an *acid*, $C_{20}H_{33}(CO_2H)_3$, $[\alpha]^{20}$ +104·5°. Both acids are saturated. Dehydrogenation of α-amyrin with selenium gives *hydrocarbons*, $C_{21}H_{36}$, m. p. 184°, $[\alpha]_D^{20}$ +41·7°; $C_{14}H_{22}$, b. p. 140°/15 mm., $[\alpha]_D^{20}$ +34·6°, and $C_{14}H_{14}$, b. p. 170°/15 mm. (*picrate*, m. p. 134°). α-Amyrin is not isomerised by boiling formic or hydrobromic acid, but β-amyrin yields a *formate*, m. p. 210°, which is hydrolysed to *γ-amyrin*, $C_{30}H_{50}O$, m. p. 145°, $[\alpha]_D^{0}$ +42°. This is dehydrated by phosphorus pentachloride to *γ-amyrilene*, $C_{30}H_{48}$, $[\alpha]_D^{20}$ +54·1°. α-Amyrin is reduced by hydriodic acid to *amyrene*, $C_{30}H_{50}$, b. p. 120°/15 mm., $[\alpha]_D^{20}$ +44·9°. H E F. NOTTON.

Cannabis indica resin. II. R. S. CAHN (J.C.S., 1931, 630—638).—The active principle of *Cannabis indica* resin (hashish etc.) is contained in a high-boiling resin, from which cannabinol (I), trinitrocannabinol (II), a hydrocarbon (III), and nitrocannabinolactone (IV) (cf. A., 1930, 913) have been prepared. The statements of Wood, Spivey, and Easterfield (J.C.S., 1899, **75**, 20) on the isolation of I are confirmed. "Crude cannabinol" is ether-soluble, b. p. about 265°/25 mm., and yields when treated with acetyl chloride in pyridine a crystalline *acetylcannabinol*, $C_{21}H_{25}O_2Ac$, m. p. 75°, which on hydrolysis affords pure cannabinol, b. p. 263°/20 mm. (uncrystallisable). The cannabinol unless prepared from the acetyl derivative is a mixture. Nitration of cannabinol with cold fuming nitric acid yields II, oxidised by hot nitric acid to IV. II forms a *methyl ether*, m. p. 150°, most conveniently prepared with dry methyl iodide and silver oxide, in absence of a solvent, and hydrolysed by warm pyridine and a little water, showing that methylation occurs at the hydroxyl group; the *benzenesulphonyl* derivative of II has m. p. 196—197°. II contains two benzene nuclei, one in the residue giving IV, the other carrying two nitro-groups and a phenolic hydroxyl group. The objection of Bergel (A., 1930, 1431) to the structure previously proposed for IV (*loc. cit.*) is refuted. The main constituent of III is probably *n*-nonacosane.

F. R. SHAW.

[Constituents of] euphorbium resin. L. SCHMID and M. K. ZACKERL (Monatsh., 1931, **57**, 177—200).—The light petroleum extractive of the resin is hydrolysed with alcoholic alkali, the alkaline solution added to 30—40% alcohol, and the euphorbone purified further by various solvents. Euphorbone can only be obtained crystalline from benzene (in which it is very soluble) or light petroleum (b. p. 20—50°; from which it separates with m. p. 67—68°). When euphorbone of m. p. 67—68° is heated at 40°/high vac. it becomes amorphous (m. p. 70—114°). The more fusible form can be isolated directly from the resin by extraction with light petroleum. The carbon content of euphorbone varies from 79 to 83% according to the number of crystallisations. Euphorbone gives an ill-defined acetate, m. p. 96°, a *benzoate*, m. p. 118° (*dibromo*-derivative), and an *anisate*, m. p. 159—160° (hydrolysed by alcoholic alkali to the original material, m. p. 67—68°). Catalytic hydrogenation of euphorbone affords a *hydroeuphorbone*, m. p. 109° (*acetate*, m. p. 99°). Aldehydic substances are obtained by ozonolysis of euphorbone, which is probably a mixture.

Euphorbol, probably $C_{26}H_{48}O$, m. p. 118°, extracted from the resin by Bauer and Schenkel's method (B., 1929, 137), gives an *anisate*, m. p. 159°, which appears to be identical with euphorbone anisate. Euphorbol acetate gives an amorphous *dibromide*. H. BURTON.

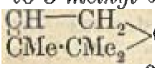
Optical activity and polarity of substituent groups. XVII. *l*-Menthyl hydrogen naphthalate, its alkali salts, and methyl ester. H. G. RULE and A. MCLEAN (J.C.S., 1931, 669—672).—Sodium menthoxide and naphthalic anhydride yield l-*menthyl hydrogen naphthalate*, m. p. 141° (solidifies and remelts at about 271°) (*sodium*, *potassium*, and *lithium* salts, and l-*menthyl methyl naphthalate*, m. p. 96·5—97° (slight decomp.) (from the silver salt and methyl iodide). With the exception of the methyl ester all are unstable even at the ordinary temperature. The rotatory powers for the methyl and hydrogen esters in benzene and acetonitrile for different wavelengths are given (the free hydrogen ester has a high dextrorotation in benzene); that of the hydrogen ester in methyl alcohol ($[M]_{5461}$ −383°, c=4) falls to small positive values in the form of the salts, the depressions being in the order K>Na>Li. F. R. SHAW.

Optically active α-pinenes. F. H. THURBER and R. C. THIELKE (J. Amer. Chem. Soc., 1931, **53**, 1030—1032).—Optically pure specimens of *d*-, b. p. 155—156°/760 mm., $[\alpha]_D^{20}$ +51·14°, d^{20} 0·8591, n_D^{20} 1·4663; *l*-, b. p. 155—156°/760 mm., $[\alpha]_D^{20}$ −51·28°, *d* 0·8590, n_D^{20} 1·4662; and *dl*-, b. p. 155—156°/760 mm. $[\alpha]_D^{20}$ 0·00, d^{20} 0·8592, n_D^{20} 1·4664, -α-pinene are prepared by the action of dimethylaniline on their nitrosochlorides (preparation described), *d*-, m. p. 89·5°, $[\alpha]_D^{20}$ +396·2°; *l*-, m. p. 90·0°, $[\alpha]_D^{20}$ −366·8° in benzene; and *dl*-, m. p. 115°. Contrary to statements in the literature, the pinenes are converted normally into *d*-, $[\alpha]_D^{20}$ +33·52°, *l*-, $[\alpha]_D^{20}$ −33·24°, in 1% alcoholic solution, and *dl*-, all m. p. 132°, -α-pinene hydrochloride, respectively. J. W. BAKER.

Degradation of 4-methylcamphor to methyl-*iso*camphoronic acid. M. BREDT-SAVELSBERG and J. BUCHKREMER (Ber., 1931, **64**, [*B*], 600—610).—The methylcamphor derived from fenchone or camphor (A., 1919, i, 125) is identified as 4-methylcamphor.

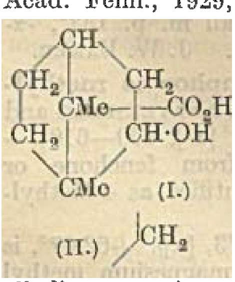
Fenchone, b. p. 190°, $d_D^{18·5}$ 0·9473, $[\alpha]_D^{21}$ +62·07°, is converted by a small excess of magnesium methyl iodide into *tert.*-methylfenchol, b. p. 88—89°/12 mm., m. p. 61°, $[\alpha]_D^{21}$ +5·14° in ethyl alcohol, transformed by acetic anhydride at 150° into a mixture of hydrocarbons $C_{11}H_{18}$ from which optically inactive 4-*methylisobornyl acetate*, b. p. 106—107°/12 mm., is obtained by means of glacial acetic and sulphuric acids.

4-*Methyl*iso*borneol*, m. p. 192—193° (*phenylurethane*, m. p. 102—103°), is oxidised by potassium dichromate and sulphuric acid to 4-*methylcamphor*, m. p. 168° (*semicarbazone*, decomp. 255—257°; *oxime*, m. p. 132—133°). Boiling sulphuric acid (d 1·18) converts the oxime into 5-*methyl-α-campholenonitrile*, b. p. 115—118°/18 mm., d_4^{18} 0·9217, n_D^{18} 1·47221, hydrolysed to 5-*methyl-α-campholenic acid*,



CMe·CH$_2$·CO$_2$H, b. p. 150—151·5°/12 mm., m. p. 36·5—37°, d_4^{40} 0·9841, n_D^{40} 1·64982 (*ammonium* salt; corresponding *amide*, m. p. 99—100°). Successive treatment of methyl-α-campholenic acid with permanganate in alkaline solution and chromic acid and sulphuric acid gives *methyl*iso*camphoronic acid*, $CO_2H\cdot CMe_2\cdot CMe(CH_2\cdot CO_2H)_2$, m. p. 180—182° (decomp.) (*barium* and *monohydrated silver* salts), and *methyl*iso*ketocamphoric acid* [*silver* and *barium* salts; corresponding *dilactone*, $C_{11}H_{16}O_4$, m. p. 240—242°, and the *compounds* decomp. 224—225°, and $C_{13}H_{22}O_4N_6$, m. p. 244—245° (decomp.), formed therefrom with one and two mols. of semicarbazide, respectively]. [*iso*Ketocamphoric acid is transformed by acetyl chloride into a similar *dilactone*, $C_{10}H_{14}O_4$, m. p. (indef.) 180—185°.] The dilactone is oxidised by alkaline hypobromite to methyl*iso*camphoronic acid. H. WREN.

π-Camphor derivatives. II. Identity of dihydroteresantalic acid with π-*apo*camphane-7-carboxylic acid. T. HASSELSTROM (J. Amer. Chem. Soc., 1931, **53**, 1097—1103).—The structure of teresantalic acid (Ruzicka and Liebe, A., 1926, 400) is confirmed by the following observations. Methyl teresantalate is converted by 90% formic acid into the lactone of 2-hydroxy-π-*apo*camphane-7-carboxylic acid (I), which is obtained by hydrolysis of the lactone with 2% sodium hydroxide and has the carboxyl group in the bridge and not in the ring, both products being identical with those obtained by Semmler and Bartelt (A., 1907, i, 1062). Oxidation of the hydroxy-acid with alkaline permanganate affords the corresponding 2-*keto*-π-apo*camphane*-7-*carboxylic acid* (ketodihydroteresantalic acid), m. p. 269—270°, $[\alpha]_D^{20}$ −55° in 10% alcohol solution, the *semicarbazone*, m. p. 204—205°, of which is reduced by Wolff's method to dihydroteresantalic acid identical with π-*apo*camphane-7-carboxylic acid (II) previously synthesised (Ann. Acad. Fenn., 1929, **30**, 12). The mixed (probably stereoisomeric) methyl chlorodihydroteresantalates obtained by Rupe and Tomi's method (A., 1917, i, 138) are reduced by aluminium amalgam and moist ether, followed by sodium and alcohol, to dihydroteresantalol, oxidised by potassium dichromate and sulphuric acid to dihydroteresantalal, further oxidised by alkaline potassium permanganate to dihydroteresantalic acid identical with the specimen obtained above. Teresantalol is converted by a saturated methyl-alcoholic solution of anhydrous hydrogen chloride in a freezing mixture into a mixture of solid and liquid chlorodihydroteresantalol, the solid product being reduced by sodium and alcohol to dihydroteresantalol. Such side reactions as are here observed may be due either to the formation of stereoisomerides or to a rearrangement of the teresantalene to the santene skeleton. J. W. BAKER.



(I.) (II.)

Action of substituted aromatic amines on camphoric anhydride. Rotatory powers of some disubstituted camphoranilic acids. M. SINGH and D. SINGH (J.C.S., 1931, 478—482).—In presence of sodium acetate, from camphoric anhydride and the appropriate amine are obtained: 2′ : 3′-, m. p. 190—192°, 2′ : 6′-, m. p. 236—238°, 2′ : 5′-*dimethyl*-, m. p. 203—204°, 5′-*nitro-2′-methoxy*-, m. p. 162—163°, 4′-*nitro-2′-methoxy*-, m. p. 185—186°, 5′-*nitro-2′-methyl*-, m. p. 220—221°, 3′-*nitro-4′-methyl*-, m. p. 204—205°, 2′-*nitro-4′-methyl*-, m. p. 187°, and 4′-*nitro-2′-methyl-camphoranilic acids*, m. p. 229—230°. Nitration of the corresponding acids gives 4′-*chloro-2′-nitro*-, m. p. 204—205°, 4′-bromo-2′-nitro-, m. p. 212°, (Wootton, J.C.S., 1910, **97**, 405, gives m. p. 204—206°, and describes it as 3′-nitro-), 2′ : 6′-*dinitro-4′-methoxy*-, m. p. 228—229°, and 2′ : 6′-*dinitro-4′-ethoxy-camphoranilic acids*, m. p. 189—190°. The rotatory power of these acids in different solvents has been examined, and it is shown that, in accordance with Rule's statement (A., 1924, ii, 645), groups of like polarity reinforce, and of opposite polarity neutralise, each other when they are in the *p*-position with respect to each other. A nitro-group in the *o*-position causes considerable rise in the rotatory power, accompanied by reversal of sign. F. R. SHAW.

Solubility of salts of camphorcarboxylic acid. M. PICON (J. Pharm. Chim., 1931, [viii], **13**, 185—196, 233—243, and Bull. Soc. chim., 1931, [iv], **49**, 399—423; cf. Bruhl, A., 1903, i, 4).—The solubility in water and organic solvents of the following camphorcarboxylates is discussed: sodium, calcium, *magnesium*, *zinc*, *neodymium*, *cerium*, normal (monohydrate and anhydrous) and basic *copper*, *gold*, *lead*, bismuth, *uranyl*. F. O. HOWITT.

α-Carboxycamphocean-β-acrylic and -β-propionic acids. Synthesis of β-homocamphor. F. SALMON-LEGAGNEUR (Compt. rend., 1931, **192**, 748—750).—Camphoceanaldehydic acid (Bredt, A., 1917, i, 560) by successive action of thionyl chloride and methyl alcohol gave the *methyl* ester, b. p. 135—136°/12 mm. (*semicarbazone*, m. p. 184°). This with ethyl bromoacetate gave *methyl ethyl α-carboxycamphocean-β-acrylate*, m. p. 52—53°, $[\alpha]_D^{23}$ −92·2° in methyl alcohol, hydrolysis of which gave the *acid*, m. p. 174—176°, $[\alpha]_D^{23}$ +58·8° in methyl alcohol. This was reduced in presence of platinum oxide to α-carboxycamphocean-β-propionic acid, m. p. 150—151°, $[\alpha]_D^{19}$ +38·1°, in methyl alcohol, the lead or thorium salt of which, when heated, gave β-*homocamphor*, m. p. 202—204°, $[\alpha]_D^{13}$ +111·2° in methyl alcohol (*oxime*, m. p. 104—105°; *semicarbazone*, m. p. 245°). A. A. LEVI.

Structure of nitrofuran and the mechanism of nitration in the furan series. B. T. FREURE and J. R. JOHNSON (J. Amer. Chem. Soc., 1931, **53**, 1142—1147).—The nitrofuran obtained by the action of nitric and acetic acids on furan is not the 3-nitro-

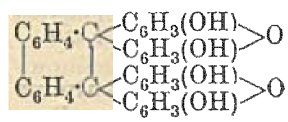
derivative (Marquis, A., 1905, i, 224), but is 2-*nitrofuran* (microcrystallographic examination by Mc'Clellan), also obtained by decarboxylation of 5-nitrofuroic acid (Hill and White, A., 1902, i, 388). Nitration of methyl furoate affords a *nitroacetate*, m. p. 96·3° (corr.) (together with an unidentified oil), which is converted by warm pyridine into methyl 5-nitrofuroate, m. p. 81·6° (corr.) (Marquis, *loc. cit.* gives m. p. 78·5°), and is probably the acetate of either the 2 : 3-, $\substack{CH(OAc)\cdot CH(NO_2)\\ CH{=\!=\!=}C(CO_2Me)}>O$, or the corresponding 2 : 5-additive product of the ester and nitric acid. Such addition is tentatively suggested as the mechanism of nitration of furan derivatives, the observation that no intermediate nitroacetates can be isolated in the nitration of the free acid being explained by the greater lability of these intermediates.

J. W. Baker.

Stability of the furan nucleus. N. A. Orlov and V. V. Tischtschenko (J. Russ. Phys. Chem. Soc., 1930, **62**, 2243—2248).—When coumarin is passed through a tube heated at 860°, coumarone is obtained; xanthone at 880° gives diphenyl ether; dimethylpyrone gives a tar with a furan reaction, carbon monoxide being evolved in each case. These reactions show the stability of the furan nucleus at high temperatures.

E. B. Uvarov.

Condensation of ketones with resorcinol. II. R. N. Sen, N. C. Chattopadhya, and S. C. Sen-Gupta (J. Indian Chem. Soc., 1930, **7**, 997—1006).—A mixture of the ketone (1 mol.) and resorcinol (2 mols.) is heated until molten and treated with hydrogen chloride after addition of anhydrous zinc chloride at 180—190°. The condensation products are all coloured and possess dyeing properties in varying degree, although a quinonoid formulation appears impossible. Thus benzophenone and resorcinol afford 4 : 4-*diphenyl*-2 : 3-5 : 6-*dihydroxybenzopyran*, $OH\cdot C_6H_4<\substack{-O-\\ CPh_2}>C_6H_4\cdot OH$, m. p. 125—127° (*dipotassium* salt; *dibromo*-derivative, m. p. 175°; *dibenzoyl* compound). Fluorenone affords the *substance* $C_{25}H_{16}O_3$, m. p. 220° (*chloroacetyl* compound, m. p. 182°), and benzil yields 4-*phenyl*-4-*benzoyl*-2 : 3-5 : 6-*dihydroxybenzopyran*, m. p. 215° (*dipotassium* salt). The following compounds are analogously obtained: 4-*phenyl*-4-*trihydroxyphenyl*-2 : 3-5 : 6-*dihydroxybenzopyran*, not molten below 280°, from trihydroxybenzophenone; 4-*phenyl*-4-*methyl*-2 : 3-5 : 6-*dihydroxybenzopyran*, m. p. 152° (from acetophenone) (*dibromo*-derivative, m. p. 160°; *dibenzoyl* compound, m. p. 115°); 4 : 4-*dimethyl*-2 : 3-5 : 6-*dihydroxybenzopyran*, m. p. 165°, from acetone (*dibromo*-derivative, m. p. 153°); the *substance* $C_9H_{16}{:}C<\substack{C_6H_3(OH)\\ C_6H_3(OH)}>O$, m. p. 200°, from camphor (*dipotassium* salt; *dibenzoyl* compound, m. p. 120°; *dibromo*-derivative, not molten below 280°); the *compound* $C_6H_{10}<\substack{C_6H_3(OH)\\ C_6H_3(OH)}>O$, softening and decomposing at 213°, from *cyclo*hexanone (*dipotassium* and *barium* salts; *dibenzoyl* derivative, softening at 202—203°; *dibromo*-compound, not molten below 280°); the *substance* $C_{11}H_{12}N_2<\substack{C_6H_3(OH)\\ C_6H_3(OH)}>O$, m. p. 150°, from antipyrine (*dibromo*-derivative, m. p. 190°). *cyclo*Hexanone and pyrogallol give the *compound* $C_6H_{10}<\substack{C_6H_2(OH)_2\\ C_6H_2(OH)_2}>O$, unchanged below 280° (*tetrapotassium* and *dibarium* salts). With resorcinol (1 mol.), phenanthraquinone affords the *compound* $C_6H_4<\substack{C_6H_4\\ -CO-}>C<\substack{C_6H_3(OH)\\ C_6H_3(OH)}>O$, m. p. 160° (*dibenzoyl* derivative, m. p. 148°), whereas 2 mols. of the phenol give the *substance* (I) unchanged below 290° (*tetrabenzoyl* derivative, m. p. 173°; *tetrapotassium* salt).



(I.)

H. Wren.

Fluoran derivatives. II. Mixed hydroxyfluorans and their bromo-derivatives. III. Di- and tetra-methylfluorans and their nitro-derivatives. M. Dominikiewicz (Rocz. Chem., 1931, **11**, 103—112, 113—123).—II. 6-Hydroxyfluoran gives a 7-*nitro*-, m. p. 140° (decomp.), and a 5 : 7-*dibromo*-, m. p. 189°, -derivative. 6-*Hydroxyfluoran*-4-, -3-, and -2-*carboxylic acids*, all decomp. 360°, are prepared by condensation, respectively, of 2-, 3-, and 4-hydroxybenzoic acid with 2 : 4-dihydroxybenzoyl-*o*-benzoic acid. 5 : 7-*Dibromo*-6-*hydroxy*-1 : 2- and -3 : 4-*phenylenefluoran*, m. p. 175° and 172°, are prepared by bromination of the appropriate phenylenehydroxyfluorans. 3 : 6-*Dihydroxy*-1 : 2-*phenylenefluoran*, m. p. 294° (4 : 5 : 7-*tribromo*-derivative, m. p. 308°), and 4 : 6-dihydroxy-2 : 3-phenylenefluoran, m. p. above 350°, are prepared by condensation with dihydroxybenzoyl-*o*-benzoic acid, respectively, of naphthoresorcinol and 1 : 2-dihydroxynaphthalene. 6-*Hydroxy*-1 : 2- and -3 : 4-*pyridinofluoran*, m. p. 285° and above 360° (5 : 7-*dibromo*-derivatives, m. p. 307° and above 360°), are prepared by condensation with dihydroxybenzoyl-*o*-benzoic acid, respectively, of 6- and 8-hydroxyquinoline. The mercuri-acetate and -hydroxy-derivatives of the pyridine derivatives have a bactericidal action equal to that of phenol in equivalent concentrations. The above products are dyes of the fluorescein type, whilst the bromo-derivatives correspond with the eosins.

III. 2 : 3 : 6 : 7-, 2 : 4 : 5 : 7-, and 1 : 3 : 6 : 8-*Tetramethylfluoran*, m. p. 269°, 271°, and 275°, respectively, are prepared by condensing *o*-4-, *m*-4-, and *m*-5-xylenol with phthalic anhydride, whilst *p*-2-xylenol yields 3 : 6-*dihydroxy*-1 : 4 : 6 : 8-*tetramethylphthalophenone*, m. p. 285—287°. The following are described: 4-*nitro*-2 : 7-*dimethyl*-, m. p. 206° (decomp.), 4 : 5-*dinitro*-2 : 7- and -3 : 6-*dimethyl*-, m. p. 302° and 210° (decomp.), 2 : 4 : 5 : 7-*tetranitro*-3 : 6-*dimethyl*-, m. p. 330° (decomp.), 1 : 8-, 3 : 6-, and 1 : 6-*dinitro*-2 : 4 : 5 : 7-*tetramethyl*-, m. p. 188°, 335°, and 255° (decomp.), 4 : 5-*dinitro*-1 : 3 : 6 : 8-*tetramethyl*-, m. p. 195° (decomp.), 2 : 4 : 5 : 7-*tetranitro*-1 : 3 : 6 : 8-*tetramethyl*-, m. p. 344° (decomp.), and 4 : 5-*dinitro*-2 : 3 : 6 : 7-*tetramethyl-fluoran*, m. p. 340° (decomp.).

R. Truszkowski.

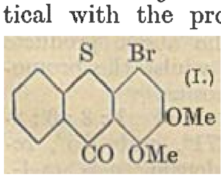
Constitution of tea-tannin. M. Tsujimura (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, **15**, 155—159; cf. A., 1930, 1295).—Tea-tannin on methylation gives a *heptamethyl* derivative,

$C_{22}H_{11}O_3(OMe)_7(+\frac{1}{2}H_2O)$, $[\alpha]_D$ $-135°$ in acetone. Oxidation gave gallic acid trimethyl ether and veratric acid. The trimethyl ether of galloyl chloride condensed with tetramethyl-tea-catechin (A., 1929, 934) gave *tetramethyl-tea-catechin galloate trimethyl ether*, $C_{22}H_{11}O_3(OMe)_7$, m. p. 140°, the absorption spectrum of which is identical with that of heptamethyl-tea-tannin. The demethylated product resembles tea-tannin. A. A. Levi.

Attempted asymmetric synthesis of sulphur compounds. B. K. Menon and P. C. Guha (Ber., 1931, **64**, [*B*], 544—546).—2-Methyltetrahydrothiophen, b. p. 130°/685 mm., is converted by *l*-menthyl bromoacetate into the *ester*, $\begin{matrix}CH_2\cdot CH_2 \\ CH_2\cdot CHMe\end{matrix}\!>\!SBr\cdot CH_2\cdot CO_2C_{10}H_{19}$, m. p. 107°, $[\alpha]^{25}$ $+43\cdot4°$ in alcohol, which yields an optically inactive product after removal of the *l*-menthyl group.

Propyl mercaptan is converted by ethyl bromoacetate and subsequent hydrolysis into *propylthiolacetic acid*, b. p. 244—245°/685 mm. The corresponding *brucine* salt, m. p. 114°, is transformed by ethyl iodide into propylthiolacetic acid and *brucine ethiodide*. H. Wren.

Derivatives of 1 : 2-dihydroxythioxanthone. A. A. Levi and S. Smiles (J.C.S., 1931, 520—527).—4-Bromoveratrole and chlorosulphonic acid give 4-bromoveratrole-5-sulphonyl chloride (analysed as the *amide*, m. p. 236°), which is converted (*a*) into veratrole-4-sulphonamide, (*b*) by vigorous reduction into the thiol, which oxidises to *diveratryl* 4-*disulphide*, m. p. 94°, (*c*) by sodium sulphite into 4-*bromoveratrole*-5-*sulphinic acid*, m. p. 122°, which with hydriodic acid gives *di*-4-*bromoveratryl* 5-*disulphide*, m. p. 118—119°. The thiol derived from the sulphonyl chloride with 2-bromobenzoic acid affords 2-*bromo*-4 : 5-*dimethoxy*-2′-*carboxydiphenyl sulphide*, m. p. 211—212°, which by dehydration gives 4-*bromo*-1 : 2-*dimethoxythioxanthone* (I), m. p. 159—160°, identical with the product from 4-bromoveratrole and



2-thiolbenzoic acid. 5-Bromoguaiacol condenses with 2-thiolbenzoic acid to form 4-*bromo*-2-*hydroxy*-1-*methoxy*-, m. p. 208°, methylated to give I, and demethylated to 4-*bromo*-1 : 2-*dihydroxy-thioxanthone*, m. p. 212°. I is hydrolysed to 4-*bromo*-1-*hydroxy*-2-*methoxythioxanthone*, m. p. 191° (*diacetoborate*), also obtained by the condensation of 4-bromoguaiacol and 2-thiolbenzoic acid. 1-*Hydroxy*-2-*methoxy*-, m. p. 173—174° (*diacetoborate*), from creosol, yields 1 : 2-*dimethoxy*-4-*methylthioxanthone*, m. p. 125° (*dihydrochloride*). Oxidation with hydrogen peroxide gives 4-*bromo*-1-*hydroxy*-2-*methoxy*-, m. p. 243°, 1-*hydroxy*-2-*methoxy*-4-*methyl*-, m. p. 190° (*diacetoborate*, m. p. 222°), 1 : 2-*dimethoxy*-4-*methyl*-, m. p. 154°, 4-*bromo*-1 : 2-*dimethoxy*-, m. p. 165° (by methylation of the corresponding 1-hydroxy-derivative), and 1 : 2-*dimethoxy-thioxanthone dioxide*, m. p. 246° (by oxidation of I). 2-Thiolbenzoic acid and *p*-cresol condense to 4-*hydroxy*-1-*methyl*-, m. p. 245°; and 1-*hydroxy*-4-*methyl-thioxanthone*, m. p. 160° (*diacetoborate*, m. p. 236°), is formed by (*a*) hydrolysis of 1-methoxy-, (*b*) diazotisation of 1-amino-4-methylthioxanthone, and (*c*) the condensation of *p*-tolyl carbonate with 2-thiolbenzoic acid, in small yield.

Study of the basic character of these substances supports the chelate structure previously assigned to the cations of the 1-methoxy-compounds (A., 1929, 934). The relative stabilities of diacetoborates derived from 1-hydroxy-compounds follow in similar order to those of salts of 1-methoxythioxanthones, and corroborative evidence is adduced from the characters of the dioxides. In the presence of other methoxyl groups, the process of demethylation of 1-methoxy-groups is easily accomplished and is selective. F. R. Shaw.

Configuration of the doubly-linked tervalent nitrogen atom. IV. Resolution of β-methyltrimethylene dithiolcarbonate carboxyphenylhydrazone. W. H. Mills and B. C. Saunders (J.C.S., 1931, 537—546).—With the object of obtaining an optically active compound, the molecular dissymmetry of which could be due only to the non-planar arrangement of the valencies of a doubly-linked tervalent nitrogen atom, the 2′-*carboxyphenylhydrazone* of β-*methyltrimethylene dithiolcarbonate* (I) has been prepared and examined. β-Methyltrimethylene dibromide is converted by sodium trithiocarbonate into β-*methyltrimethylene trithiocarbonate*, m. p. 74°, which when boiled with phenylhydrazine in alcohol gives β-*methyltrimethylene dithiolcarbonate phenylhydrazone*, m. p. 89°, and when boiled with *methyl phenylhydrazine*-o-*carboxylate*, m. p. 48° (from methyl anthranilate), affords the *methyl* ester of I, m. p. 91·5—93°, from which the free acid I, m. p. 202°, is obtained. *Trimethylene trithiocarbonate*, m. p. 80°, and *trimethylene dithiolcarbonate* o-*carboxyphenylhydrazone*, m. p. 212° (*methyl* ester, m. p. 139—140°), are similarly prepared.

I is resolved by quinine into the d-, m. p. 199°, $[\alpha]^{17}_{5461}$ $+12\cdot4°$ in chloroform (sodium salt, $+10\cdot6°$; *quinine* salt, m. p. 184—185°, $[\alpha]^{17}_{5461}$ $-255°$ in chloroform), and l-*isomerides*, m. p. 199°, $[\alpha]^{17}_{5461}$ $-12\cdot8°$ in chloroform. The active compounds possess considerable optical stability, solutions in chloroform showing an induction period of several days before racemisation occurs; in acid and alkaline media racemisation occurs on boiling. The structure of the compound is discussed and the conclusion reached that it must be represented by $\begin{matrix}H \\ Me\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\cdot S \\ CH_2\cdot S\end{matrix}\!>\!C\colon N\cdot NH\cdot C_6H_4\cdot CO_2H$. The acid differs from its salts and esters in being bright yellow, and is doubtless an internal ammonium salt, $CHMe<(CH_2\cdot S)_2>C\colon N\cdot NH_2\cdot C_6H_4\cdot CO_2$. The optical stability may be accounted for by co-ordination between the hydrogen atom of the NH group and one of the sulphur atoms, but this could not determine the displacement of the group $\cdot NH\cdot C_6H_4\cdot CO_2H$ from the median plane of the cyclic residue on which dissymmetry depends, nor give stable optical activity associated with the asymmetry acquired, in consequence, by the sulphur atom. F. R. Shaw.

Derivatives of the pyrrolidine ring. N. I. Putochin (J. Russ. Phys. Chem. Soc., 1930, **62**, 2209—2215).—Racemic proline was prepared by hydrolysis of gelatin with sulphuric acid and precipit-

ated as the copper salt. Action of acetic anhydride on its amide gave the *amide* of N-*acetylproline*, m. p. 178—180°; the *acetyl* derivative of the latter, m. p. 142°, and the *nitrile* of N-*acetylpyrrolidine* were prepared by further action of acetic anhydride. 2-*Pyrrolidylmethylamine*, b. p. 50°/7 mm., was prepared by reducing the nitrile, whilst reduction of proline-amide gave 2-*pyrrolidylcarbinol*, b. p. 110°/7 mm.

E. B. UVAROV.

Catalytic reduction of pyrrole and its derivatives. Preparation of 2-pyrrolidylmethylamine and proline. N. I. PUTOCHIN (J. Russ. Phys. Chem. Soc., 1930, **62**, 2216—2225).—The reductions were carried out by passing hydrogen through a solution in glacial acetic acid and absolute alcohol, using platinum oxide and ferric chloride as catalyst. Reduction of 2-pyrrylmethylamine gave 2-*pyrrolidylmethylamine*, b. p. 50°/7 mm.; pyrrole-2-carboxylic acid gave proline. The use of palladium oxide gave poor yields.

E. B. UVAROV.

Action of nitrous acid on 2-pyrrylmethylamine and 2-pyrrolidylmethylamine. N. I. PUTOCHIN (J. Russ. Phys. Chem. Soc., 1930, **62**, 2226—2234).—Action of nitrous acid on 2-pyrrylmethylamine and 2-pyrrolidylmethylamine gives pyridine and piperidine respectively.

E. B. UVAROV.

Local anæsthetics in the pyrrole series. II. F. F. BLICKE and E. S. BLAKE (J. Amer. Chem. Soc., 1931, **53**, 1015—1025).—Various analogues of novocaine, stovaine, and β-eucaine have been synthesised and their anæsthetic action has been investigated qualitatively. Potassium pyrrole reacts with β-chloroethyl acetate (from ethylene chlorohydrin and acetyl chloride) to give the *acetate*, b. p. 222—225°/740 mm., hydrolysed to β-(1-*pyrryl*)*ethyl alcohol*, b. p. 110—113°/12 mm. [*benzoate* (I), m. p. 53—55°; p-*nitrobenzoate*, m. p. 92—94°, reduced with hydrogen at 4 atm. and a platinum oxide catalyst in alcohol, to the p-*amino-benzoate* (II), m. p. 87—88°; and 2-*pyrrylcarboxylate* (III), m. p. 73—74°; all prepared by the action of the appropriate acyl chloride on the potassium derivative of the alcohol]. β-Chloroethyl *p*-aminobenzoate with pyrrolidine in a sealed tube at 115—120° affords β-(1-pyrrolidyl)ethyl *p*-aminobenzoate (IV). Similarly from γ-chloropropyl acetate, b. p. 168—173° (lit. b. p. 160—166°; from trimethylene chlorohydrin and acetyl chloride), is prepared γ-(1-*pyrryl*)*propyl alcohol*, b. p. 229—231°/743 mm. [*acetate*, b. p. 127—135°/13 mm.; *benzoate* (V), b. p. 165—170°/5 mm. (probably not pure); p-*nitrobenzoate*, m. p. 68—70°, reduced to the p-*aminobenzoate* (VI), m. p. 114—116°; and 2-*pyrrylcarboxylate*, m. p. 69—70°), whilst γ-*chloropropyl* p-*aminobenzoate*, m. p. 86—87° (from trimethylene chlorohydrin and *p*-aminobenzoic acid), is converted into γ-(1-*pyrrolidyl*)*propyl* p-*aminobenzoate* (VIII), m. p. 84—85°. Of these novocaine analogues, I—VIII, all but I and V produce local anæsthesia in alcoholic solution, but aqueous solutions of the hydrochlorides of IV and VIII are without action. Stovaine may be conveniently prepared by interaction of the potassium derivative of dimethylaminomethylethylcarbinol with benzoyl chloride, the 2-*pyrrylcarboxylate*, m. p. 194—195° (IX), of the carbinol being similarly prepared. Chloromethylmethylethylcarbinol is converted by heating with pyrrolidine in a sealed tube at 115—120° into the oily 1-*pyrrolidylmethylmethylethylcarbinol* (oily *benzoate*, X). Ethyl chloroacetate and potassium pyrrole give *ethyl* 1-*pyrrylacetate*, b. p. 110—115°/16 mm. (free *acid*, m. p. 94—95°), converted by the appropriate Grignard reagent into 1-*pyrrylmethyldimethyl*-, b. p. 86—88°/2—3 mm., and -*diethyl*-, b. p. 108—116°/1 mm., -*carbinol*. Similarly, from ethyl β-bromopropionate is prepared *ethyl* β-(1-*pyrryl*)-*propionate*, b. p. 119—122°/14 mm. (*acid*, m. p. 62—64°), and hence 1-*pyrrylethyldiethylcarbinol*, b. p. 125—128°/4—5 mm. Of these stovaine analogues both the free bases IX and X and their hydrochlorides are local anæsthetics. Diacetoneamine hydrogen oxalate can be reduced directly to 4-hydroxy-2 : 2 : 6-trimethylpiperidine, separated into the stable and unstable forms and these methylated as described by Harries (A., 1919, i, 131). The methylated stable and labile forms are each converted through their potassium derivatives into their 4-2-*pyrrylcarboxylate*, m. p. 106—107° and 106—107°, respectively (mixed m. p. 80—83°; *picrate* of stable form, m. p. 192—193°). Of these the stable form is active and the labile form is inactive as a local anæsthetic. Thus the local anæsthetic action of these derivatives is retained by substitution of the 2-pyrrylcarboxylate for the benzoate or *p*-aminobenzoate, and by replacement of the dimethyl- or diethyl-amino-group by the 1-pyrryl or 1-pyrrolidyl nuclei. Improved details for the preparation of intermediates in the synthesis of pyrrolidine are given.

J. W. BAKER.

Preparation of 2-alkylpiperidines. I. 2-Amylpiperidine. A. FRANKE and W. PRODINGER (Ber., 1931, **64**, [*B*], 542—543).—αε-Dibromodecane, obtained from αε-oxidodecane and saturated hydrobromic acid at 100°, is converted by treatment with *p*-toluenesulphonamide and potassium hydroxide in boiling alcohol into 2-amylpiperidine isolated as the *chloroplatinate*, m. p. 117° after softening at 114°.

H. WREN.

Interaction of sulphonates and sulphonamides with piperidine. F. BELL (J.C.S., 1931, 609—615).—In contrast to the mononitro-compounds, the scission of 2 : 4-dinitrophenyl *p*-toluenesulphonate with piperidine gives (*a*) 2 : 4-dinitrophenol and *p*-toluenesulphonylpiperidine and, at the same time, (*b*) 2 : 4-dinitro-1-phenylpiperidine. 2 : 4-Dinitrophenol is not an intermediate, since it forms a stable *piperidine* salt, m. p. 171°, and *pyridine* salt, m. p. about 85°. The reaction (*b*) seems to require the intermediate production of an additive compound in which the nitro-group loses its normal electrical character. Disulphonamides (including dinitro-compounds) react with piperidine to give the monosulphonamides, and the mechanism of this change is discussed. Nitroamines react with difficulty, if at all, with *p*-toluenesulphonyl chloride in pyridine, but the corresponding nitrosulphonamides are easily converted into disulphonamides, *di*-p-*toluenesulphon*-2 : 4-*dinitroanilide*, m. p. 217°, and 3 : 5-*dinitro*-4-p-*toluenesulphonamidodiphenyl*, m. p. 249°, being formed. 3 : 5-*Dibromo*-4-p-*toluenesulphonamidodiphenyl*, m. p. 196°, is obtained from the corresponding disulphonamide and piperidine. Although polynitrophenols

are usually converted into the chloro-compounds by the action of *p*-toluenesulphonyl chloride (cf. Ullmann, A., 1908, 525), sulphonates are probably intermediate products. The following are described: *piperidine picrate*, m. p. 150° (*piperidine* compound, m. p. about 135°), *picrylpyridinium*-p-*toluenesulphonate*, m. p. 197°, *pyridine* salt of 3 : 5 : 4′-trinitro-4-hydroxydiphenyl, m. p. 198°, and *piperidine* salt of *p*-toluenesulphon-*p*′-nitroanilide, m. p. 138°.
F. R. SHAW.

Pyridine bases from tar. M. P. OPARINA (Ber., 1931, **64**, [*B*], 562—569).—Fractional distillation of the mixture of bases followed by treatment of the fractions with picric acid leads to the isolation of 4-methyl-, 2 : 6-, 2 : 5-, and 2 : 4-dimethyl-, 2 : 4 : 6-, 2 : 3 : 6-, 2 : 3 : 5-, and 2 : 4 : 5-trimethyl-pyridine. The following observations appear to be new: 2 : 3 : 5-*trimethylpyridine*, b. p. 183—185°, d_4^{15} 0·9377 (*chloroplatinate*, m. p. 227—228°; *chloroaurate*, m. p. 146—147°), oxidised to pyridine-2 : 3 : 5-carboxylic acid, m. p. 307—308°; 2 : 3 : 6-trimethylpyridine, b. p. 173—174°, d_4^{1} 0·9299 (picrate, m. p. 146°; chloroplatinate, m. p. 228°; chloroaurate, m. p. 146—147°), oxidised to (?) 2-*methylpyridine*-3 : 6-*dicarboxylic acid*, m. p. 247° (decomp.) (*silver* salt), and *pyridine*-2 : 3 : 6-*tricarboxylic acid*, m. p. 245° (decomp.); 2 : 4 : 5-trimethylpyridine, b. p. 188—190° (*picrate*, m. p. 159—160°; chloroplatinate (+$2H_2O$), m. p. 191—192° (decomp.); *chloroaurate*, m. p. 107—108°), oxidised to 4-*methylpyridine*-2 : 5-*dicarboxylic acid*, m. p. 237° (*silver* salt), and *pyridine*-2 : 4 : 5-*tricarboxylic acid* (+$2H_2O$), m. p. 242° (*silver* salt).
H. WREN.

Condensation of mixtures of aldehydes and ketones with ammonia in presence of aluminium hydroxide as contact substance. M. P. OPARINA (Ber., 1931, **64**, [*B*], 569—577).—Passage of a mixture of acetone (1 mol.) and paracetaldehyde (2 mols.) with excess of ammonia over aluminium oxide in a coppered tube at 340—350° leads to the formation of 2 : 4-dimethylpyridine (picrate, m. p. 181°); the production of 2 : 6-dimethylpyridine could not be detected. Formaldehyde (1 mol.) and acetone (2 mols.) give 2 : 6-dimethylpyridine with a small proportion of the 2 : 4-isomeride. 2 : 3 : 6-Trimethyl- and (?) 2 : 3 : 5 : 6-tetramethyl-pyridine are obtained from molar proportions of acetone, methyl ethyl ketone, and formaldehyde; the tetramethyl base is the main product from methyl ethyl ketone (2 mols.) and formaldehyde (1 mol.). Acetaldehyde (2 mols.) and methyl ethyl ketone (1 mol.) afford 2 : 3 : 4-trimethylpyridine. The base is prepared synthetically in the following manner: γ-methylpentane-βδ-dione is condensed with ethyl cyanoacetate and ammonia to 3-cyano-2-hydroxy-4 : 5 : 6-trimethylpyridine, m. p. 304—305°, which is converted by boiling sulphuric acid into 2-*hydroxy*-4 : 5 : 6-*trimethylpyridine*, m. p. 252° (*potassium* salt), reduced by zinc dust to 2 : 3 : 4-trimethylpyridine in poor yield. The hydroxy-compound is therefore transformed by phosphorus pentachloride into 2-*chloro*-4 : 5 : 6-*trimethylpyridine*, b. p. 118—119°/20 mm., m. p. 49° (*picrate*, m. p. 105°), reduced by hydriodic acid at 180° or by the acid and zinc dust at 40° to 2 : 3 : 4-trimethylpyridine, b. p. 192—193°, d_4^{15} 0·9566 (*picrate*, m. p. 164·5°; *chloroplatinate*, m. p. 259°; *chloroaurate*, m. p. 182—183°). Oxidation of the base with potassium permanganate gives pyridine-2 : 3 : 4-tricarboxylic acid (+$1·5H_2O$), m. p. 249° (*trimethyl* ester, m. p. 101—102°), and 2-methylpyridine-3 : 4-dicarboxylic acid, m. p. (indef.) 260—268° (anhydride, m. p. 118—119°). Successive treatment of 2 : 3 : 4-trimethylpyridine with 30% formaldehyde and nitric acid (*d* 1·4) affords 3-*methylpyridine*-2 : 4-*dicarboxylic acid*, m. p. 216—217°. The preparation of 4-*methylpyridine*-2 : 3-*dicarboxylic acid*, m. p. 190°, is incidentally described. H. WREN.

Polyhalogenated ketones of indole. G. SANNA (Gazzetta, 1931, **61**, 60—74).—Dichloroacetyl chloride and the magnesium derivative of 2-methylindole give 3-*dichloroacetyl*-2-*methylindole*, m. p. 195°. The chlorine is feebly reactive. The compound is unaffected by boiling water. A (?) *diacetate* is obtained after prolonged boiling with alcoholic potassium acetate solution, and the *dibromo*-compound, m. p. 178°, is slowly formed by the action of alcoholic potassium bromide. The action of potassium iodide is slow and incomplete. Boiling 5% potassium hydroxide solution yields 2-*methylindole*-3-*glycollic acid*, m. p. 90° (decomp.) (*barium* salt; *silver* salt, m. p. 247°), converted by fusion into 3-(2-*methyl*)*indolylcarbinol*, m. p. 196°. When heated with ammonia at 100° in a sealed tube it yields 2-*methylindole*-3-*carboxylamide*, m. p. 218°.

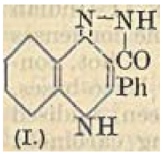
3-*Trichloroacetyl*-2-*methylindole*, m. p. 167°, is obtained from the magnesium derivative of 2-methylindole and trichloroacetyl chloride. It is very slowly attacked by boiling aqueous potassium hydroxide. Alcoholic potassium hydroxide yields 2-*methylindole*-3-*carboxylic acid*, m. p. 186° (decomp.). Potassium bromide or ammonia solutions have no action.

The m. p. of the chlorinated 3-acetylindoles show a variation with the number of chlorine atoms parallel with that of the m. p. of the chlorinated acetophenones. R. K. CALLOW.

Methoxylated 2-phenyl-4-quinolones (4-hydroxy-2-phenylquinolines). R. SEKA and W. FUCHS (Monatsh., 1931, **57**, 52—62).—Various improvements in the Just method (A., 1886, 149, 161) of preparing ethyl 4-hydroxy-2-phenylquinoline-3-carboxylate are described, and used in the synthesis of hydroxymethoxyphenylquinolines. Treatment of benz-*p*-anisidide with phosphorus pentachloride at 70—75° and distillation of the mixture gives the corresponding iminochloride, b. p. 220°/20 mm., m. p. 63—64° (80·6% yield), which with dry ethyl sodiomalonate in ether at 100—120° affords 26·5% of the theoretical amount of *ethyl* 4-*hydroxy*-6-*methoxy*-2-*phenylquinoline*-3-*carboxylate*, m. p. 245°. The free *acid* (+H_2O), m. p. 235°, when heated in a vacuum gives 4-*hydroxy*-6-*methoxy*-2-*phenylquinoline*, m. p. 287°. The iminochloride from anis-*p*-anisidide and ethyl sodiomalonate in ether at 80—90° afford *ethyl* 4-*hydroxy*-6-*methoxy*-2-*anisylquinoline*-3-*carboxylate*, m. p. 265—266°, converted by way of the free *acid*, m. p. 252°, into 4-*hydroxy*-6-*methoxy*-2-*anisylquinoline*, m. p. 295°. Quinoline derivatives could not be prepared by the above method from the benzoyl and anisoyl derivatives of 3 : 5-dimethoxyaniline, 3 : 4 : 5-

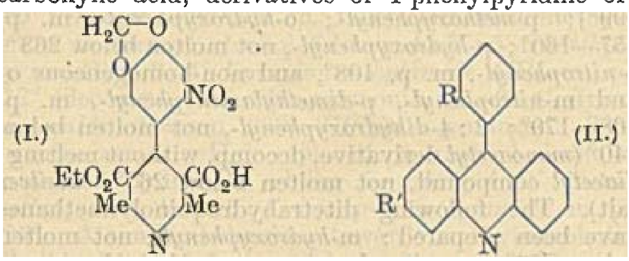
trimethoxybenzanilide, or *benz*-3 : 4 : 5-*trimethoxyanilide*, m. p. 138·5°.

Treatment of ethyl 4-hydroxy-2-phenylquinoline-3-carboxylate, prepared as above from the iminochloride from benzanilide, with phosphorus pentachloride in phosphoryl chloride, removal of the phosphoryl chloride in a vacuum, and treatment of the residue with ammonia and hydrazine gives 4-*hydroxy*-2-*phenylquinoline*-3-*carboxylamide*, m. p. 208°, and the *compound* (I), m. p. 317°, respectively.



H. BURTON.

Stereochemistry of derivatives of diphenyl and its analogues. F. LIONS (J. Amer. Chem. Soc., 1931, **53**, 1176—1179).—Attempts to resolve the methosulphate of 2-(*o*-carboxyphenyl)pyridine-3-carboxylic acid, derivatives of 4-phenylpyridine of



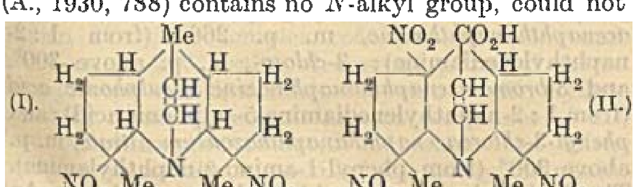
type I, and acridine derivatives of type II (R= Cl or Me; R′=H or Me) have proved unsuccessful.

J. W. BAKER.

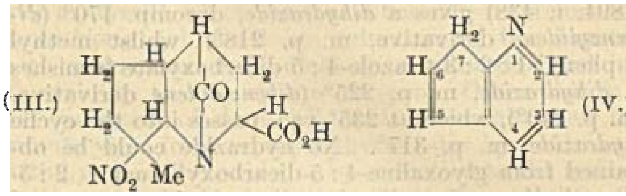
Carbazole derivatives. E. GHIGI (Gazzetta, 1931, **61**, 43—46).—The compound (revised m. p. 100°) obtained by the action of sulphuric acid on β-tetralonephenylhydrazone (A., 1930, 787) is 3 : 4-*benzo*-1 : 2-*dihydrocarbazole*, since distillation over lead oxide yields 3 : 4-benzocarbazole. β-Tetralonephenylhydrazone and zinc chloride in alcohol may give either 3 : 4-benzo-1 : 2-dihydrocarbazole or 1 : 2-*benzocarbazole*, m. p. 229° (*picrate*, m. p. 185—186°; *acetyl* derivative, m. p. 289—290°), also obtainable by dehydrogenating 1 : 2-benzo-3 : 4-dihydrocarbazole.

R. K. CALLOW.

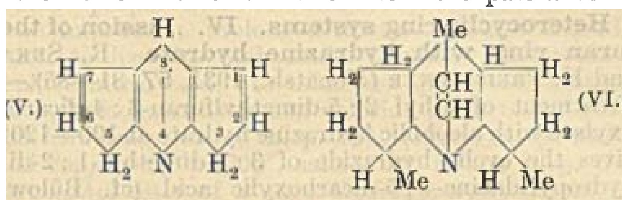
Nitrogen compounds in petroleum distillates. III. Structure of a hydroaromatic base $C_{16}H_{25}N$. W. C. THOMPSON and J. R. BAILEY (J. Amer. Chem. Soc., 1931, **53**, 1002—1011).—The "naphthenic" base $C_{16}H_{25}N$, b. p. 278·2°/746 mm., d_4^{20} 0·9391, n_D 1·5129 (*picrate*, m. p. 151°; *hydrogen sulphate*, m. p. 196°; *hydrochloride*, m. p. 251°; *nitrate* $+H_2O$, m. p. 79°, and anhydrous, m. p. 141°; *chloroplatinate*, decomp. 240°; *methiodide*, softens at 250°, decomp. without melting; zinc chloride, m. p. 171°, and mercuric chloride, m. p. 157·5°, double *salts*), isolated from the crude kerosene distillate of California petroleum (A., 1930, 788) contains no *N*-alkyl group, could not



be brominated, dehydrogenated, or reduced, and is very stable towards alkaline permanganate. Oxidation with nitric acid at 170° gives the following products: 3 : 5-*dinitro*-3 : 5 : 8-*trimethyldecahydro*-4 : 8-*ethylenopyrindacine* (I), m. p. 116·5° (*picrate*, m. p. 231°); 3 : 5 : 7a-*trinitro*-3 : 5-*dimethyldecahydro*-4 : 8-*ethylenopyrindacine*-8-*carboxylic acid* (II), m. p. 347° (decomp.); 7-*nitro*-7-*methyloctahydro*-1 : 4-*keto*-*pyrindine*-3-*carboxylic acid* (III), m. p. 189—190°



(decomp.); and pyridine-2 : 4 : 5-tricarboxylic acid. The nomenclature is derived from the parent com-



pounds pyrindine (IV) and pyrindacine (V). The structure VI is chosen for the naphthene base $C_{16}H_{25}N$, from various possible structures.

J. W. BAKER.

Conversion of compounds of the carbamidodiacetic acid type into the hydantoin-3-acetic acid type and the inverse process. R. LOCQUIN and V. CERCHEZ (Bull. Soc. chim., 1931, [iv], **49**, 309—318).—Contrary to the assertion of Granacher and Landolt (A., 1928, 74) the nature of the alkali used does not affect the position at which the ring is ruptured in hydantoin-3-acetic acid. With ammonia or with alkali hydroxide rupture always occurs between positions 3 and 4, yielding carbamidodiacetic acid or derivatives. Thus ethyl hydantoin 3-acetate, m. p. 120°, with concentrated aqueous ammonia at 0° affords mainly ethyl carbamidodiacetamide, decomp. begins at 240°, m. p. 260° with carbonisation, and a little hydantoin-3-acetamide, m. p. 225—226°, whilst heating with *N*-sodium hydroxide gives a 66% yield of carbamidodiacetic acid, m. p. 230° (decomp.) (sinters at 200—210° when heated slowly), converted on esterification into ethyl carbamidodiacetate, m. p. 147—148°, and not into ethyl glycylglycinecarboxylate, m. p. 87° (Fischer, A., 1902, i, 350), as assumed by Granacher and Landolt. Hydrolysis with 3% barium hydroxide also affords carbamidodiacetic acid.

When refluxed with alcoholic hydrogen chloride ethyl carbamidodiacetate gives ethyl hydantoin-3-acetate, also obtained by esterifying hydantoin-3-acetic acid (from ethyl carbamidodimalonate). Water at 170—180° converts hydantoin-3-acetic acid and carbamidodiacetic acid or their esters into carbon dioxide and glycine (cf. Wessely and John, A., 1928, 530).

R. BRIGHTMAN.

Heterocyclic ring systems. III. Ring closure reactions of heterocyclic *o*-dicarboxylic acids. R. SEKA and H. PREISSECKER (Monatsh., 1931, **57**, 71—80; cf. A., 1925, i, 57, 1298).—The behaviour of various heterocyclic *o*-dicarboxylic esters towards hydrazine is investigated. Ethyl 2 : 5-diphenyl-

furan-3 : 4-dicarboxylate and hydrazine hydrate at 100—120° give a cyclic *hydrazide*; ethyl 2 : 5-dimethyl- and 2 : 5-diphenyl-pyrrole-3 : 4-dicarboxylates and hydrazine hydrate (containing a little alcohol) at 140—150° afford cyclic *hydrazides*, decomp. 359° after charring at 295° and m. p. 324°, respectively. Ethyl pyrazolinedicarboxylate (von Pechmann, A., 1894, i, 438) gives a *dihydrazide*, decomp. 170° (*dibenzylidene* derivative, m. p. 218°), whilst methyl 2-phenyl-1 : 2 : 3-triazole-4 : 5-dicarboxylate furnishes a *dihydrazide*, m. p. 225° (*dibenzylidene* derivative, m. p. 240°), which at 235°/vac. passes into the cyclic *hydrazide*, m. p. 317°. No hydrazide could be obtained from glyoxaline-4 : 5-dicarboxylic acid; 2 : 5-dimethylfuran-3 : 4-dicarboxylic acid is decomposed by treatment with hydrazine hydrate. H. BURTON.

Heterocyclic ring systems. IV. Fission of the furan ring with hydrazine hydrate. R. SEKA and H. PREISSECKER (Monatsh., 1931, **57**, 81—85).—Treatment of ethyl 2 : 5-dimethylfuran-3 : 4-dicarboxylate with alcoholic hydrazine hydrate at 100—120° gives the cyclic hydrazide of 3 : 6-dimethyl-1 : 2-dihydropyridazine-4 : 5-dicarboxylic acid (cf. Bülow, A., 1904, i, 272). The same compound (*tetra-acetyl* derivative, m. p. 140°; *tetrabenzoyl* derivative, m. p. 190°) is also obtained from ethyl αα′-diacetylsuccinate and hydrazine hydrate. H. BURTON.

Pyrimidines. CXX. Action of ozone on uracil. CXXI. Action of ozone on some derivatives of uracil. T. B. JOHNSON and R. B. FLINT (J. Amer. Chem. Soc., 1931, **53**, 1077—1081, 1082—1087).—CXX. Ozonolysis of uracil gives mainly *formylglyoxylcarbamide* (I), m. p. 162° (with phenylhydrazine it gives either formylphenylhydrazine or a *substance*, decomp. 221°, according to conditions), and oxaluric acid (II), whilst traces of an unidentified pyrimidine, and complete degradation products, carbamide, oxalic and formic acids, are also obtained. The formation of these products: $CO{<}\genfrac{}{}{0pt}{}{NH\cdot CO}{NH\cdot CH}{>}CH \longrightarrow CO{<}\genfrac{}{}{0pt}{}{NH\cdot CO}{NH\cdot CH}{>}\genfrac{}{}{0pt}{}{CH}{O_3} \longrightarrow CHO\cdot NH\cdot CO\cdot NH\cdot CO\cdot CHO$ (I) $\longrightarrow CHO\cdot NH\cdot CO\cdot NH\cdot CO\cdot CO_2H \longrightarrow NH_2\cdot CO\cdot NH\cdot CO\cdot CO_2H$ (II), indicates that uracil forms an unstable ozonide.

CXXI. Ozone attacks a suspension of 4-methyl- and 4-phenyl-uracil in acetic acid to give *acetyl-*, m. p. 150° (64% yield), and *benzoyl-*, m. p. 168° (with phenylhydrazine gives the same substance, decomp. 221°, as was obtained with formylglyoxylcarbamide), *-glyoxylcarbamide*, together with traces of carbamide and oxalic acid. Thymine gives formylcarbamide (40% yield); 5-bromouracil gives parabanic acid, whilst 5-nitrouracil gives this acid and oxaluric acid. 5-Bromo-1 : 3-dimethyluracil affords *dimethyloxaluric acid*, m. p. 124—125°. Carbamide and oxalic acid are also formed in each case. J. W. BAKER.

2 : 2′-Dipyridyl from pyridine by catalytic dehydrogenation under pressure. J. P. WIBAUT and H. D. T. WILLINK (Rec. trav. chim., 1931, **50**, 287—290).—Pyridine when heated at 320—325° in presence of nickel during 5—6 hrs. gives 2 : 2′-dipyridyl [14—20% (pure) on the pyridine transformed]. J. D. A. JOHNSON.

Triphenylmethane dyes derived from quinoline, tetrahydroquinoline, diphenylamine, and carbazole. R. N. SEN and B. N. SEN (J. Indian Chem. Soc., 1930, **7**, 965—972).—Quinoline condenses with aromatic aldehydes in the presence of hot, concentrated hydrochloric acid, giving leuco-bases, analogous in constitution to malachite-green, oxidised by lead peroxide to the corresponding carbinols. Since 6-nitroquinoline fails to react, it is assumed that the hydrogen atom attached to the 6-carbon atom suffers replacement. Tetrahydroquinoline behaves analogously and its residue appears to exert a stronger auxochromic influence than that of quinoline. The following diquinolylmethanes are described: *phenyl-* [*chloroplatinate*, m. p. 230° (decomp.); *picrate*, m. p. 199°]; p-*methoxyphenyl-*; o-*hydroxyphenyl-*, m. p. 157—160°; p-*hydroxyphenyl-*, not molten below 263°; p-*nitrophenyl-*, m. p. 108°, and non-homogeneous o- and m-*nitrophenyl-*, p-*dimethylaminophenyl-*, m. p. 168—170°; 2 : 4-*dihydroxyphenyl-*, not molten below 240° (*monoacetyl* derivative, decomp. without melting; *diacetyl* compound, not molten below 267°; *disilver* salt). The following ditetrahydroquinolylmethanes have been prepared: m-*hydroxyphenyl-*, not molten below 256°; m-*nitrophenyl-*, m. p. 212° (decomp.); *furfuryl-*, decomp. without melting; p-*methoxyphenyl-*; o-*hydroxyphenyl-*, m. p. 163—164°; p-*hydroxyphenyl-*, m. p. 255°; p-*dimethylaminophenyl-*; 2 : 4-*dihydroxyphenyl-*, not molten below 253°. *Di-1-methyltetrahydroquinolylmethane* and *phenyldi-1-methyltetrahydroquinolylmethane*, m. p. 100° after softening at 90°, have been prepared. The following dyes are obtained from diphenylamine or carbazole: *di-*p-*anilinotriphenylmethane* and its *disulphonic acid*; *di-*p-*methylanilinotriphenylmethane*, m. p. 144—146°; *phenyldicarbazolylmethane*, not molten below 260°; *phenyldi-1-methylcarbazolylmethane*, m. p. 148° after softening at 140°; *di-*p-*anilinodiphenylmethane*; *di-*p-*methylanilinodiphenylmethane*; 4′ : 4″-*dianilino-2-hydroxytriphenylmethane*; 4′ : 4″-*dianilino-3 : 4-methylenedioxytriphenylmethane*. H. WREN.

Dyes derived from acenaphthenequinone. II. Azine and azonium derivatives. S. K. GUHA (J.C.S., 1931, 582—586).—The following were prepared by condensing 3-chloro- and 3-bromo-acenaphthenequinones with o-diamines: 3-*chloro-*, m. p. 278°, and 3-bromo-acenaphthaphenazine, m. p. 272° (from o-phenylenediamine); 3-*chloro-*, m. p. 256°, and 3-*bromo-acenaphthatolazine*, m. p. 270° (from 3 : 4-tolylenediamine); 3-*chloro-* and 3-*bromo-acenaphthaphenazinazine* (do not melt; from 2 : 3-diaminophenazine); 3-*chloro-*, m. p. 274°, and 3-*bromo-acenaphthanaphthazine*, m. p. 266° (from 1 : 2-naphthylenediamine); 3-*chloro-*, m. p. above 300°, and 3-*bromo-acenaphthanaphthazine-5-sulphonic acid* (from 1 : 2-naphthylenediamine-5-sulphonic acid); and *phenyl-3-chloroacenaphthanaphthazonium nitrate*, m. p. above 300° (from phenyl-1-amino-β-naphthylamine). The dyeing shades on wool have been examined. An improved method for preparing 3-bromoacenaphthenequinone is described. F. R. SHAW.

Reaction of aliphatic iminoethers with hydrazine. W. Oberhummer (Monatsh., 1931, **57**, 106—111).—Prolonged treatment of formiminoether hydrochloride with dry ethereal hydrazine gives 25—30% of the theoretical amount of 1-amino-1 : 3 : 4-triazole, also produced from the ether hydrochloride and a hydrazine salt in alcohol. H. Burton.

Constitution of bile pigments. III. Derivatives of coproporphyrin I, and synthesis of hydroxypyrromethenes. H. Fischer and W. Frowis (Z. physiol. Chem., 1931, **195**, 49—80; cf. A., 1924, i, 319).—An improved method of preparation of methyl 5-bromo-4 : 3′ : 5′-trimethylpyrromethene-3 : 4′-dipropionate (I; cf. A., 1926, 1261) is described. The bromine is readily replaced by aniline, giving *methyl* 5-*anilino*-4 : 3′ : 5′-*trimethylpyrromethene*-3 : 4′-*dipropionate*, m. p. 145° (complex *copper* salt, m. p. 120°; *hydrobromide*, m. p. 186°), but with methylamine in methyl alcohol 5-*bromo*-4 : 3′ : 5′-*trimethylpyrromethene*-3 : 4′-*dipropionmethylamide* (II), m. p. 212° (decomp.), and with ammonia the -3 : 4′-*dipropionamide*, decomp. 260—270°, are produced. The bromine atom in II is replaced by methyl-alcoholic potassium hydroxide, giving 5-*methoxy*-4 : 3′ : 5′-*trimethylpyrromethene*-3 : 4′-*dipropionmethylamide*, m. p. 225°. A similar behaviour towards methyl-alcoholic alkali is shown by I, the product, after re-esterification with methyl sulphate, being *methyl* 5-*methoxy*-4 : 3′ : 5′-*trimethylpyrromethene*-3 : 4′-*dipropionate* (III), m. p. 88°. With silver acetate in acetic acid, however, the 5-*hydroxy*-compound, m. p. 180°, is produced; this is readily obtained from III by fusion with resorcinol, or by complete demethylation with methyl-alcoholic sodium methoxide at 170—180°, followed by re-esterification with methyl sulphate; the last process leads to the same result when applied to I. The 5-hydroxy-compound may be detected by the deep violet coloration it gives with acidified aqueous diazobenzenesulphonic acid. Coproporphyrin is produced from III by the action of hydrogen bromide in acetic acid at 170—180°, and a colourless, readily oxidised substance, possibly the methane, by reduction with sodium amalgam. 5-*Methoxy*-4 : 3′ : 5′-*trimethyl*-3 : 4′-*diethylpyrromethene*, m. p. 70°, is readily prepared from the bromo-compound, and gives the corresponding 5-*hydroxy*-compound, m. p. 243°, on fusion with resorcinol.

The mother-liquors from the preparation of 5-bromo-4 : 3′ : 5′-trimethylpyrromethene-3 : 4′-dipropionic acid (*loc. cit.*) after long keeping contain coproporphyrin I, which may be isolated as its tetraethyl ester; this porphyrin also appears to be formed in small yield from the methene and concentrated sulphuric acid. Fusion of I with citric acid gives, in addition to coproporphyrin I, a little coproporphyrin IV. The complex *cobalt*, m. p. 270°, and *silver*, m. p. 286°, salts of coproporphyrin I tetramethyl ester are described; they are readily hydrolysed by dilute aqueous alkali to complexes of the free porphincarboxylic acid, of which the *silver* complex is readily re-esterified by methyl sulphate. Potassium cyanide and acetic acid regenerate the ester from its silver complex; ferrous acetate in acetic acid replaces the silver with formation of *coprohæmin tetramethyl* ester, m. p. 245°, converted in the usual way, and possibly also by silver acetate, into the *hæmatin*, m. p. 215°. The *cobalt* salt, m. p. 316°, decomp. 320—325°, of *iso*uroporphyrin II octamethyl ester is described.

Long exposure of a colloidal aqueous solution of coproporphyrin to bright sunlight gives a *chlorin* (not analysed), which behaves differently from normal *coprochlorin* (obtained by reduction of the hæmin with sodium and amyl alcohol) on reduction and in its stability to atmospheric oxygen. Other chlorin-like products of doubtful identity are obtained in minute yield from coproporphyrin ester by oxidation with hydrogen peroxide, or by reduction to the leuco-compound (zinc and acetic acid) and oxidation of this with ferric chloride.

The preparation of dinitrocoproporphyrin has been improved; prolonged nitration causes degradation to hæmatic anhydride. Sodium nitrite may replace nitric acid, but offers no special advantage. Methyl-alcoholic hydrogen chloride gives in the cold the *tetramethyl* ester, m. p. 191° (*silver*, m. p. 240°, and *copper*, m. p. 200°, salts), but at the b. p. the *tetramethyl* ester of a *nitrodihydroxyporphyrin*, m. p. 206° (*copper* salt, m. p. 245°), is formed (cf. Hilger, A., 1926, 189). Reduction gives coproporphyrin and a *mononitro*-derivative (isolated as *tetramethyl* ester, m. p. 204°), which also appears to be formed by incomplete nitration. Coproporphyrin tetrahydrazide (A., 1928, 1384; the *iron* salt is very sensitive to atmospheric oxidation) is converted by nitrous acid into the *tetrazide*, decomp. 90° (explodes), which with boiling methyl alcohol gives the *tetramethylurethane*, m. p. 190°. H. A. Piggott.

Porphyrins. XXVII. Mechanism of the introduction of iron into porphyrins and isolation of crystalline hæms. H. Fischer, A. Treibs, and K. Zeile (Z. physiol. Chem., 1931, **195**, 1—27).—The introduction of iron into porphyrins by ferrous salts in absence of air is unaccompanied by evolution of hydrogen or by reduction of the solvent or porphyrin, even when the latter is readily reducible; thus derivatives of mesoporphyrin are completely absent from the product of interaction of ferrous salts with protoporphyrin. The products obtained are not hæmins, however, but ferrous compounds in which two pyrrole nuclei are linked by an atom of iron (>N·Fe·N<). The spectra of their solutions are almost indistinguishable from those of the corresponding hæmins, but differences are more readily observed in their "powder spectra." These new complex salts, for which the name "hæm" is proposed, are readily converted by mineral acids into the original porphyrin and a ferrous salt, and are readily oxidised, even by air, particularly in presence of chloride ions, to the hæmin, the order of ease of oxidation being ætio- < meso- < proto-hæm, and combine with pyridine to form hæmochromogens. The final property is shown in a much smaller degree by hæmins, which, however, readily combine with pyridine in the presence of reducing agents.

The hæms are necessary intermediates in the formation of hæmins, and ferric chloride is unable to convert mesoporphyrin ester into the hæmin under

the usual conditions (in presence of acetic acid and an alkali acetate) if a stream of air is passed through the solution; in the absence of the air stream, and particularly in presence of a little ferrous salt, hæmin formation is rapid and complete. Reduction of hæmins by ferrous salts in acid solution regenerates the porphyrin, owing to the decomposition of the intermediately formed hæm by the free acid. A further consequence of the ready reversibility of hæm formation is the need of the presence of sodium acetate or a similar salt in preparing hæmins by interaction of ferric chloride and a porphyrin, but alternative methods of removing the hydrochloric acid produced, *e.g.*, use of boiling butyric acid in an open vessel as solvent, are equally effective. The presence of 3 atoms of active hydrogen in hæmin, determined by Zerevitinov's method, and the formation during the reaction of ionic chlorine, are due to reduction to hæmochromogen, which may be detected spectroscopically; this conclusion is confirmed by the value of 0·3 observed with mesoesterhæm and 1·2 with dimethylhæmatin.

Crystalline *ætio-*, *proto-*, *meso-*, and *mesoester-hæms* are readily prepared from the porphyrin and ferrous acetate in acetic acid solution in a current of pure nitrogen. The last forms with pyridine a crystalline hæmochromogen, which is relatively stable to atmospheric oxidation and contains 2 mols. of base, one of which is lost at 55°, and the other only on oxidation to the hæmatin (in chloroform). A *substance*, m. p. 230°, apparently the acetoxyhæmin, is found in the mother-liquors from the preparation of mesoesterhæm. The oxidation of mesoporphyrin-ester with ferric chloride and potassium ferricyanide gives the corresponding *xanthoporphinogen*, m. p. 295°, readily reconverted into the original porphyrin by reduction. The occasional formation of a crystalline form of protohæmin, which shows parallel extinction, is reported. H. A. PIGGOTT.

Chlorophyll formation. K. NOACK and W. KIESSLING (Z. angew. Chem., 1931, 44, 93—96).——Protophæophytin (from gourd skins) is converted by 30% methyl-alcoholic hydrogen chloride into a *trimethyl* ester (I), $C_{36(37)}H_{42}O_6N_4$ (3 OMe groups), m. p. 234—235° (absorption spectrum: bands at 637—630, 593—576, 558—549, and 525—507 in order of increasing intensity), hydrolysis of which or of the parent phytin affords protophæophorbide, $C_{34(35)}H_{38}O_6N_4$ (1 OMe group). Reduction of methylphæophorbid with iron and 80% formic acid affords *methylprotophæophorbide*, $C_{35(36)}H_{38}O_5N_4$ (2 OMe groups), but reduction of chlorophyll itself always involves fission of the phytol group, the main product being an alkali-soluble substance, spectrally identical with methylprotophæophorbide, both of which give the same trimethyl ester I. The view that phylloerythrin is an acid anhydride receives support from the observation that it is hydrolysed in *iso*propyl alcohol by 10% aqueous potassium hydroxide to a free carboxylic *acid*, $C_{33(34)}H_{34}O_5N_4$, the absorption spectrum of which (bands at 632—624, 585—569, 550—539, and 517—500, in order of increasing intensity) is very similar to that of I: this acid is of the blood-porphyrin type, and gives, with diazomethane, a *trimethyl* ester, m. p. 232—233°, spectrally identical with the acid and probably isomeric with I. The structural and biological inter-relationships of these products are discussed. The protochlorophyll series of derivatives must be photo-oxidisable to the corresponding derivatives of the chlorophyll series, and is related to the latter by the deficiency of one oxygen atom. The formation of phylloerythrin in animals involves deoxidation of chlorophyll, combination with fission of magnesium, hydrolysis and anhydride formation, this compound forming a physiological bridge between the leaf and blood colouring matters. J. W. BAKER.

Dehydrogenation of chlorophyll and the mechanism of photosynthesis. J. B. CONANT, E. M. DIETZ, and S. E. KAMERLING (Science, 1931, 73, 268).—Methyl phæophorbide *a* is oxidised by potassium molybdicyanide in pyridine and acetone solution to the corresponding dehydrophæophorbide which yields the same hydrolysis products with hot alkali as allomerised phæophorbide. These results support the view (this vol., 368) that the allomerisation of chlorophyll is essentially a dehydrogenation. The mechanism for photosynthesis now suggested can be represented by the scheme: dark reaction, chlorophyll+CO_2+enzyme⟶dehydrochlorophyll+dextrose+water, and light reaction, dehydrochlorophyll+light+water⟶chlorophyll+oxygen. L. S. THEOBALD.

Ring closure of *o*-thiocarbamidobenzoic acids. Isomerism. T. N. GHOSH (J. Indian Chem. Soc., 1930, 7, 981—984).—Anthranilic acid condenses with phenylthiocarbimide in boiling alcohol with formation of 2-*thio*-4-*keto*-3-*phenyl*-1 : 2 : 3 : 4-*tetrahydroquinazoline*, m. p. above 300° (corresponding *disulphide*, $C_{28}H_{18}O_2N_4S_2$, m. p. 250—252°), the intermediate *o*-thiocarbamidobenzoic acid not being isolable. The corresponding -3-p-*tolyl*-, m. p. 310°, -3-o-*tolyl*-, m. p. 268—270° (*disulphide*, m. p. 215° after shrinking at 200°), -3-1′ : 3′ : 4′-xylyl-, m. p. 259—260°, and -3-*allyl*-, m. p. 206—207°, compounds are similarly prepared. 2-Thio-4-keto-3-phenyl-1 : 2 : 3 : 4- tetrahydroquinazoline is converted by concentrated sulphuric acid at 125—130° into 2-*anilino*-6-*keto*-4 : 5-*benzo*-1 : 3-*thiazine*, m. p. 184—185°, also prepared from *o*-phenylthiocarbamidobenzoic acid. 2-p-*Toluidino*-6-*keto*-4 : 5-*benzo*-1 : 3-*thiazine*, m. p. 235°, is similarly obtained. Boiling hydrochloric acid (*d* 1·19) transforms 2-thio-4-keto-3-allyl-1 : 2 : 3 : 4-tetrahydroquinazoline into 2-*allylamino*-6-*keto*-4 : 5-*benzo*-1 : 3-*thiazine*, m. p. 115° (*hydrochloride*, m. p. 231—232°), whereas with concentrated sulphuric acid a *compound*, m. p. 207°, results in very small yield. H. WREN.

Thiodiazines. VII. Condensation of ethyl chloroacetate with thiosemicarbazides. P. K. BOSE and B. K. NANDI (J. Indian Chem. Soc., 1930, 7, 961—964).—Thiodiazines are prepared from ethyl chloroacetate and the requisite thiosemicarbazide (1 : 1) in boiling alcohol. Their acetylation is effected with boiling acetic anhydride containing a little pyridine and their methylation with methyl iodide and methyl-alcoholic potassium hydroxide. The following compounds are described: 2-*amino*-5-

hydroxy-1 : 3 : 4-*thiodiazine*, m. p. 284° (decomp.) (*acetyl* derivative, m. p. 205°; *benzoyl* compound, m. p. 260°; *adduct* with phenylthiocarbimide, m. p. 195°); 2-*methylamino*-5-*hydroxy*-1 : 3 : 4-*thiodiazine*, m. p. 282° (decomp.) (*acetyl* derivative, m. p. 198°; non-crystalline *methyl* compound); 2-*ethylamino*-5-*hydroxy*-1 : 3 : 4-*thiodiazine*, m. p. 225° (*acetyl* derivative, m. p. 169°); 2-iso*butylamino*-5-*hydroxy*-1 : 3 : 4-*thiodiazine*, m. p. 210° (*acetyl* derivative, m. p. 199°; *methyl* compound, m. p. 135°); 2-*anilino*-5-*hydroxy*-1 : 3 : 4-*thiodiazine*, m. p. 184° (*acetyl*, m. p. 172°, and *methyl*, m. p. 265°, derivatives); 2-o-*toluidino*-5-*hydroxy*-1 : 3 : 4-*thiodiazine*, m. p. 183° (*acetyl* derivative, m. p. 210°); 2-p-*toluidino*-5-*hydroxy*-1 : 3 : 4-*thiodiazine*, m. p. 195° (*acetyl* derivative, m. p. 218°).
H. WREN.

Lupinine. C. SCHOPF, E. SCHMIDT, and W. BRAUN (Ber., 1931, **64**, [*B*], 683—691; cf. A., 1928, 1144).—The mixture of (—)-lupinic and (+)-*epi*lupinic ester obtained by the successive oxidation and esterification of lupinine is converted by boiling hydrochloric acid mainly into (—)-lupinic acid and (+)-*epi*lupinic ester hydrochloride; hydrolysis with boiling alkali hydroxide permits the isolation of (+)-epi*lupinic acid hydrochloride*, m. p. 233—235°, $[\alpha]_D^{18}$ +27·2° in methyl alcohol. The hydrochloride is transformed by ethereal magnesium phenyl bromide into the *carbinol*, $\begin{array}{l}CH_2{\cdot}CH_2{\cdot}CH{\cdot}CH(CPh_2{\cdot}OH){\cdot}CH_2\\ CH_2{\cdot}CH_2{\cdot}N{-}CH_2{-}{-}{-}{-}CH_2\end{array}$, m. p. 170—171°, which yields two *methiodides*, m. p. 250—252° (decomp.) and (+H_2O), m. p. 140° (decomp.). The possibility of stereoisomerism appears to be conditioned by the passage of nitrogen from the tervalent to the co-ordinatively quadrivalent state (contrast Winterfeld, this vol., 370). The ketone $\begin{array}{l}CH_2{\cdot}CH_2{\cdot}CH{\cdot}CHBz{\cdot}CH_2\\ CH_2{\cdot}CH_2{\cdot}N{-}CH_2{-}CH_2\end{array}$ (' *c. c*) [preparation given from (—)-lupinyl chloride, benzene, and aluminium chloride] yields an amorphous *methiodide* (corresponding *methopicrate*, m. p. 153—154°) which is very readily transformed by 20% sodium hydroxide into the *base* $\begin{array}{l}CH_2{\cdot}CH_2{\cdot}CH{:}CBz{-}CH_2\\ CH_2{\cdot}CH_2{\cdot}NMe{\cdot}CH_2{\cdot}CH_2\end{array}$, b. p. 143 145 / 1 mm. [*picrate* (anhydrous), m. p. 142—143°, (monohydrated), m. p. 120—121°], catalytically hydrogenated to the dihydro-*base* (*picrate*, m. p. 159—160°). The ease with which the Hofmann degradation occurs is typical of β-amino-ketones. Confirmation is thus afforded to Karrer's formula for lupinine.

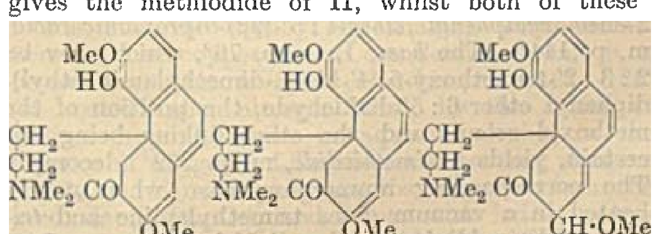
The work of Winterfeld and Holschneider (*loc. cit.*) is criticised in detail. Re-examination of lupinene, m. p. 68—69°, and its benzoyl derivative fails to give evidence of non-uniformity.
H. WREN.

[**Lupinene.**] K. WINTERFELD (Ber., 1931, **64**, [*B*], 692—693; cf. this vol., 370).—A reply to Schopf and others (preceding abstract). The isolation of 2-methylpyridine-6-carboxylic acid and the acid $C_{10}H_{13}O_2N$ was effected from a sample of lupinene, m. p. 63—65°, but not from that of m. p. 68—69°.
H. WREN.

Reactions of harmine. O. FERNANDEZ and F. E. RAURICH (Anal. Fís. Quím., 1931, **29**, 74—76).—The following reactions are sensitive and characteristic. (i) Harmine is oxidised to *m*-nitroanisic acid by evaporation with nitric acid. By reduction with stannous chloride, diazotisation, and addition of an ammoniacal solution of β-naphthol a purple coloration is obtained. (ii) Harmine is reduced by sodium and amyl alcohol to tetrahydroharmine, and water is added. The addition of *p*-nitrobenzenediazonium chloride solution gives a carmine-red coloration, whilst a hydrochloric acid solution of vanillin gives a permanganate-purple coloration.
R. K. CALLOW.

Sinomenine and disinomenine. XXIII. Identity of β-tetrahydrodeoxycodeine and dihydrothebacodine. K. GOTO and S. MITSUI (Bull. Chem. Soc. Japan, 1931, **6**, 33—39).—The identity of *d*-dihydrothebacodine (Speyer and Siebert, A., 1921, i, 685), dehydroxytetrahydrocodeine, and deoxytetrahydrosinomenine (deoxydemethoxydihydrosinomenine) (Kondo and Ochiai, A., 1930, 625) is supported by experiments on the reduction of sinomenine and its derivatives by various methods. Only the one substance corresponding with the above was isolated. Further, the de-*N*-methyl base and the nitrogen-free substance obtained from deoxytetrahydrosinomenine melt at the same temperatures as the corresponding products from dihydrothebacodine. The name "dihydroeuthebainan" is proposed in place of "dihydrothebainan" suggested by Kondo and Ochiai (*loc. cit.*), since the methylaminoethyl side-chain is probably differently linked from that in thebainone.
A. A. LEVI.

Sinomenine and disimonenine. XXV. Three different sinomeninemethines. K. GOTO and H. SHISHIDO (Bull. Chem. Soc. Japan, 1931, **6**, 79—87; cf. A., 1926, 1160).—The Hofmann degradation of sinomenine has been re-examined. Sinomenine methiodide with 2% sodium hydroxide gives sinomenine-achromethine (I) (*N*-methylsinomeninium base, *loc. cit.*), m. p. 179°, $[\alpha]_D^{16}$ +72·58° in chloroform [methiodide, m. p. 212°, $[\alpha]_D^{17}$ −33·00° in water; *hydriodide*, m. p. 115—118° (not sharp); *oxime*, loses water at 120°, decomp. 204—205°]. This substance slowly changes into sinomenine-roseomethine (β-methylsinomeninemethine, *loc. cit.*) (II), m. p. 163°, $[\alpha]_D$ +135·70° in chloroform (methiodide, m. p. 276°, $[\alpha]_D^{15}$ −48·26° in water), also obtained from sinomenine methiodide and cold 5% sodium hydroxide. The achromethine with cold 10% sodium hydroxide gives sinomenine-violeomethine (α-methylsinomeninemethine, *loc. cit.*) (III), m. p. 172—173°, $[\alpha]_D^{15}$ +434·78° in chloroform (methiodide, m. p. 209°, $[\alpha]_D^{17}$ +373·36° in water). The methiodide of I with sodium hydrogen carbonate in methyl alcohol gives the methiodide of II, whilst both of these



(I.) (II.) (III.)

methiodides yield that of III in cold 10% sodium hydroxide. In several cases sinomeninol (and disino-

meninol) were obtained by heating the above substances with alkali. The prefixes to the new names refer to the colours produced by the substances and their derivatives with concentrated mineral acids. The constitutions I, II, and III are suggested.

A. A. Levi.

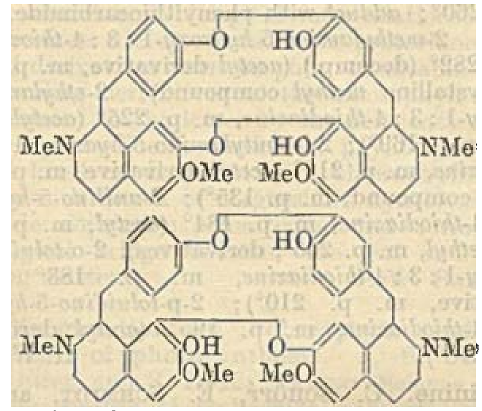
Oxonitin. T. A. Henry and T. M. Sharp (J.C.S., 1931, 581—582).—In the oxidation of aconitine, to oxonitin, acetaldehyde is produced and the methyl group attached to nitrogen is lost; oxonitin cannot therefore contain more than 31 carbon atoms. The present work indicates $C_{31}H_{41}O_{12}N$ as the probable formula rather than $C_{32}H_{43}O_{12}N$ (cf. Spath and Galinovsky, this vol., 243).

F. R. Shaw.

Aconitine from *Aconitum chasmanthum*, Kashmir. K. H. Bauer and T. C. Radjhan (Pharm. Zentr., 1931, 72, 145—152).—*Aconitine*-chasmanthum, $C_{21}H_{27}O_2N(OAc)(OBz)(OMe)_4$, m. p. 197·5°, $[\alpha]_D$ +20·0° (*hydrobromide*, $[\alpha]_D^{20}$ −18·1°; *hydrochloride*, $[\alpha]_D^{20}$ −15·3°; *chloroaurate*, m. p. 135°), from the ether extract of the root, differs from indaconitine, isolated from the same species (Dunstan, J.C.S., 1905, 87, 1620), in failing to give crystalline salts. It is oxidised by nitric acid at 100° to a *substance*, $C_{16}H_{14}O_5N_2(OBz)(OMe)_2 \cdot CO_2H$, m. p. 251° (cf. Brady, J.C.S., 1913, 103, 1827). *Aconine*-chasmanthum, $C_{21}H_{27}O_2N(OH)_2(OMe)_4$ (also +EtOH), m. p. 95°, $[\alpha]_D^{20}$ +4·0° [amorphous *hydrochloride*, m. p. 168—179° (decomp.); *tetra-acetyl* derivative, m. p. 213—214°, and its *hydrochloride*, m. p. 142—144°], is distinguished from indaconine by its solubility in ether. It is oxidised by nitric acid to oxalic acid and a *substance*, $C_4H_7O_8N$ (also $+H_2O$), m. p. 132°.

H. E. F Notton.

Constitution of oxyacanthine. II. F. von Bruchhausen and P. H. Gericke (Arch. Pharm., 1931, 269, 115—125).—The structure proposed by Kondo and Tomita (this vol., 242, 243) for dauricine is shown to be incorrect. The authors' previous views on the structure of oxyacanthine are confirmed by a new degradation of the methine base, $C_{40}H_{46}O_6N_2$ (A., 1930, 98, formula III). This is ozonised almost quantitatively in aqueous solution slightly acidified with sulphuric acid to the base (I) (1 mol.) and 2′-*methoxydiphenyl ether*-4 : 5′-*dialdehyde* (1 mol.), m. p. 72° [*disemicarbazone*, m. p. 228° (decomp.); *di-phenylhydrazone*, m. p. 218°; oily *oxime*], identified by oxidation to 2′-methoxydiphenyl ether-4 : 5′-dicarboxylic acid. The dialdehyde affords with malonic acid in pyridine in presence of piperidine 2′-*methoxydiphenyl ether*-4 : 5′-*diacrylic acid*, m. p. 283°, reduced by sodium amalgam and water to 2′-*methoxydiphenyl ether*-4 : 5′-(ββ)-*dipropionic acid*, m. p. 144°. The *base*, I, m. p. 76°, which may be 2 : 3 : 2′-trimethoxy-5 : 4′-bis-(β-dimethylaminoethyl)-diphenyl ether-6 : 5′-dialdehyde, the position of the methoxyl groups and the ether linking being uncertain, yields a *dimethiodide*, m. p. 259° (decomp.). The corresponding ammonium base when gently heated in a vacuum gives trimethylamine and *trimethoxydivinyldiphenyl ether-dialdehyde*, m. p. 140° (*disemicarbazone*, decomp. 250°), hydrogenated (palladised barium sulphate) to *trimethoxydiethyldiphenyl ether-dialdehyde*, m. p. 88—89° [*disemicarbazone*, m. p. 248° (decomp.); *monoazlactone*, m. p. 252°]. On the assumption that oxyacanthine is formed by the



condensation of two molecules of *N*-methylcoclaurine, it must have one of the above structures, the other being assigned to berbamine (cf. Kondo and Tomita, *loc. cit.*).

H. E. F. Notton.

Derivatives of *p*-arsanilic acid. I. *p*-Arsinosuccinanilic acid and related compounds. G. T. Morgan and E. Walton (J.C.S., 1931, 615—619).—Monosodium *p*-arsanilate (atoxyl) with excess of succinic anhydride gives p-*arsinosuccinanilic acid* (I), whereas with succinic acid in smaller proportions, *succinanilido*-pp′-*diarsinic acid* (*disodium* salt) is formed (also obtained by heating I with atoxyl in equimolecular proportion). I gives products of type II, $AsO_3H_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot [CH_2]_x \cdot CO \cdot NR_1R_2$ on warming with (*a*) aniline, *succinilide*- (II, $x=2$, $R_1=H$, $R_2=Ph$); (*b*) methylamine, *succinanilomethylamide*- (II, $x=2$, $R_1=H$, $R_2=Me$) (*monosodium* salt, $2H_2O$); (*c*) ethylamine, *succinanilethylamide*-p-*arsinic acid* (II, $x=2$, $R_1=H$, $R_2=Et$) (*monosodium* salt). On reduction with sulphur dioxide, I yields p-*dichloroarsinosuccinanilic acid* (crystallising in needles and prisms, both varieties m. p. 210—211°), which could not be converted into the acid chloride. When heated at 240°, I affords succinanil-*p*-arsinic acid, which regenerates I on addition of water. The crude anil, heated in a sealed tube, is converted by (*a*) anhydrous alcoholic ammonia into *succinanilamide*- (II, $x=2$, $R_1=R_2=H$) (*monoammonium* salt, $1H_2O$, *monosodium* salt, $1H_2O$); (*b*) alcoholic dimethylamine, into *succinanildimethylamide*- (II, $x=2$, $R_1=R_2=Me$) (*monosodium* salt; $1H_2O$); (*c*) piperidine, into *succinanilopiperidide*-p-*arsinic acid* (II, $x=2$, $R_1R_2=C_5H_{10}N$).

The monosodium salts of compounds of type II, in comparison with tryparsamide, show very low toxicities combined with therapeutic activity.

F. R. Shaw.

Azo-dyes derived from arsanilic acids. V. Deulofeu and F. R. Marín (Anal. Fís. Quím., 1931, 29, 65—73).—The following compounds have been prepared by diazotisation of the aminophenylarsinic acids and coupling with phenols in alkaline solution. From *p*-aminophenylarsinic acid: 2 : 4-*dihydroxyazobenzene*-4′-*arsinic acid* [*mono*- and *di-sodium* (+5·5H_2O) salts], 2 : 4 : 6-*trihydroxyazobenzene*-4′-*arsinic acid* [*disodium* salt (+4H_2O)], 2-*methyl*-4 : 6-*dihydroxyazobenzene*-4′-*arsinic acid* [*disodium* salt (+4H_2O)];

from 4-amino-3-methylarsinic acid: 2:4-*dihydroxy-2'-methylazobenzene-4'-arsinic acid*; from *o*-aminophenylarsinic acid: 4-*hydroxyazobenzene-2'-arsinic acid*, 2:4-*dihydroxyazobenzene-2'-arsinic acid*, and 2:4:6-*trihydroxyazobenzene-2'-arsinic acid*. The compounds are yellow to deep reddish-brown; the depth of colour increases with mol. wt. in each series in accordance with Nietzki's rule. R. K. CALLOW.

Arsinic acids of the fluorene series. G. T. MORGAN and (MISS) J. STEWART (J.C.S., 1931, 620—623).—2-Nitrofluorenone is reduced by a modified catalytic method (cf. Bennett and Noyes, A., 1930, 1291) successively to 2-amino-fluorenone, -fluorenol, and -fluorene. 2-Aminofluorene on diazotisation and conversion by the Bart reaction gives *fluorene-2-arsinic acid* (*monosodium* salt, $1H_2O$). *Fluorenone-2-arsinic acid* (*monosodium* salt, *disodium* salt, $6H_2O$, and *semicarbazone*), similarly prepared, on nitration in sulphuric acid, yields the 7-*nitro*-compound (*monosodium* salt, $1H_2O$). The nitro-derivative is reduced with ferrous hydroxide to 7-*aminofluorenone-2-arsinic acid* (*monosodium* salt, $3H_2O$); on acetylation this affords 7-*acetamido-* (*monosodium* salt, I) and, on boiling with chloroacetic acid in alkaline solution, 7-*glycine-* (somewhat unstable, *monosodium* salt), or with chloroacetamide, 7-*glycinamido-2-arsinic acid* (*monosodium* salt). 2-*Dichloroarsino-fluorene*, m. p. 109°, and -fluorenone, m. p. 142°, are also described. Of the foregoing I has proved to have the greatest trypanocidal activity. F. R. SHAW.

Oxidation of heterocyclic arsenious derivatives by iodine. G. A. RAZUBAIEV and V. S. MALINOVSKI (J. Russ. Phys. Chem. Soc., 1930, 62, 2173—2186).—A volumetric method for the determination of tervalent arsenic by oxidation with iodine in alcoholic solution is described. The use of sodium hydrogen carbonate to neutralise the hydriodic acid formed is recommended. The method is applicable to phenoxarsine oxide, triphenylarsine, and compounds of the type 10-R-9:10-dihydrophenarsazine. The product of oxidation of the latter is the corresponding dihydroxide if sodium hydroxide is used to neutralise the hydriodic acid formed, and the oxide if silver oxide is used. The following of these were prepared: R=Me, *dihydroxide*, m. p 201—215°, *oxide*, decomp. 256—257°; R=Et, *dihydroxide*, m. p. 141—143°, *oxide*, m. p. 239°; R=Pr, m. p. 81—82°, *dihydroxide*, m. p. 93°, *oxide*, m. p. 111—112°; R=iso*amyl*, m. p. 76—78°, *dihydroxide*, m. p. 95—96°, *oxide*, m. p. 101—102°; R=Ph, *oxide*, m. p. 280—300° (decomp.). E. B. UVAROV.

New water-soluble organomercury compounds. J. H. WALDO (J. Amer. Chem. Soc., 1931, 53, 992—996).—By the interaction of various organomercury halides (prepared by the usual Grignard method) with thio-acids in dilute alcoholic sodium hydroxide are obtained various new organomercury compounds which, with sodium hydrogen carbonate, form water-soluble salts with germicidal properties: $RHgX+SH{\cdot}R'{\cdot}CO_2H$ (or SO_3H)$=RHgS{\cdot}R'{\cdot}CO_2H+HX$. The values of their therapeutic indices (product of the toxicity and germicidal value relative to that of sodium ethylmercurithiosalicylate as unity) for *B. typhosus* and *Staph. aureus*, respectively, are given in parentheses. Thus are prepared: *methyl-*, m. p. 174° (0·533; 0·80); *ethyl-*, m. p. 111° (1; 1); iso*amyl-*, m. p. 78° (0·80; 0·90); *phenyl-*, m. p. 228·5° (decomp.) (0·10; 0·075); and *benzyl-*, m. p. 144·5° (decomp.), *-mercurithiosalicylic acid*: p-*ethylmercurithiolbenzoic acid*, not melting up to 250° (0·667; 0·50); α-*ethylmercurithiobutyric*, m. p. 76° (0·533; 0·40); p-*ethylmercurithiol-phenylacetic*, m. p. 116·7° (0·667; 1·0), and *-benzenesulphonic*, m. p. above 300° (0·167; 0·125), *acid*. Thus the alkarylmercuri-derivatives are less toxic than the aryl, and the salts of carboxylic acids less so than those of the sulphonic acids. The alkyl compounds are less stable than the alkaryl derivatives. All m. p. are corrected. J. W. BAKER.

Tertiary arylalkyl phosphines. II. I. K. JACKSON and W. J. JONES (J.C.S., 1931, 575—578).—The action of *p*-xylyldichlorophosphine on the required Grignard reagent results in: p-*xylyl-dimethylphosphine*, b. p. 106°/12 mm., d_4^{25} 0·9541 [*oxide*, m. p. 94—95°, *mercurichloride*, m. p. 225°; *methiodide*, m. p. 204° (*mercuri-iodide*, m. p. 152°; *chloroplatinate*, m. p. 236°; *tri-iodide*, m. p. 91°)]; *-diethylphosphine*, b. p. 157°/52 mm., d_4^{25} 0·9392 [*mercurichloride*, m. p. 184°; *methiodide*, m. p. 137° (*chloroplatinate*, m. p. 217°; *mercuri-iodide*, m. p. 105°; *tri-iodide*, m. p. 85°)]; *-di-n-propylphosphine*, b. p. 161°/25 mm., d_4^{25} 0·9281 [*mercurichloride*, m. p. 188°; *methiodide*, m. p. 105° (*chloroplatinate*, m. p. 141°; *mercuri-iodide*, m. p. 90°, *tri-iodide*, m. p. 76°)]; *-di-n-butylphosphine*, b. p. 171°/16 mm., d_4^{25} 0·9124 [*mercurichloride*, m. p. 179°; *methiodide*, m. p. 93° (*chloroplatinate*, m. p. 215°; *tri-iodide*, m. p. 70°]; *-diisobutylphosphine*, b. p. 184°/20 mm. (*mercurichloride*, m. p. 227°; *methiodide*, m. p. 120°); *-di-n-amylphosphine*, b. p. 214°/23 mm. (*mercurichloride*, m. p. 117°; *methylchloroplatinate*, m. p. 151°). All *p*-xylylphosphines give a coloration with carbon disulphide but, with the exception of the *inner anhydride* of p-*xylyldimethylhydroxyphosphinocarbithionic acid*, m. p. 76°, no solid compound can be isolated. F. R. SHAW.

Distibyls. I. Tetraphenyldistibine. Attempts to obtain tetraphenyldibismuthine. F. F. BLICKE, U. O. OAKDALE, and F. D. SMITH (J. Amer. Chem. Soc., 1931, 53, 1025—1029).—Tetraphenylstibyl oxide, prepared by slight modification of Schmidt's method (A., 1920, i, 900), is converted by acetic acid into the acetate, m. p. 133—135° (lit. m. p. 132°), converted by the appropriate hydrogen halide in acetic acid into the corresponding chloride, and *bromide*, m. p. 86°, the *iodide*, m. p. 68—70°, being obtained by the action of sodium iodide on the chloride in acetone solution. Experiments on the conversion of the iodide into the distibyl by shaking with bromobenzene and copper-bronze are described, but it is best converted into *tetraphenyldistibine*, m. p. 121—122° (in sealed tube, nitrogen-filled), by the action of sodium hypophosphite in aqueous alcohol in the absence of oxygen. Like the corresponding diarsine (A., 1929, 1090) it rapidly absorbs oxygen to form the peroxide $(SbPh_2{\cdot}O{\cdot})_2$ and reacts with iodine. Conditions for a greatly improved yield (84%) of triphenylbismuthine from magnesium phenyl bromide and bismuth trichloride are given, but similar attempts to convert diphenylbismuthyl iodide (Challenger and

Allpress, J.C.S., 1915, **107**, 19) into tetraphenyldibismuthine were unsuccessful. J. W. Baker.

Aromatic compounds of tin with halogen in the benzene nucleus. K. A. Kozeschkov and A. N. Nesmejanov (Ber., 1931, **64**, [*B*], 628—636; cf. A., 1930, 1603).—Mercury di-*p*-chlorophenyl is transformed by stannous chloride in boiling alcohol into mercury and *tin di-*p*-chlorophenyl dichloride*, m. p. 86·5°. *Tin di-*p*-chlorophenyl dibromide*, m. p. 73°, is analogously prepared, whereas the corresponding *di-iodide*, m. p. 46—47°, is derived from the dichloride and sodium iodide in boiling alcohol. The dichloride is transformed by aqueous potassium hydroxide into *tin di-*p*-chlorophenyl oxide* and by alcoholic potassium hydrogen sulphide into *tin di-*p*-chlorophenyl sulphide*, m. p. 179°; with stannic chloride at 150° the dichloride affords *tin* p-*chlorophenyl trichloride*, m. p. 39°, converted into p-*chlorophenylstannonic acid* and the *sulphide* $(C_6H_4Cl{\cdot}Sn)_2S_3$, which darkens at 295° after softening at 240°. The following *tin di-*p*-bromophenyl* compounds are prepared by analogous methods: *dichloride*, m. p. 103°; *dibromide*, m. p. 82°; *di-iodide*, m. p. 79—80°; *oxide*; *sulphide*, m. p. 228—229°. *Tin* p-*bromophenyl trichloride*, m. p. 64·5—65°, is converted into the corresponding *stannonic acid* and the *sulphide* $(C_6H_4Br{\cdot}Sn)_2S_3$. *Tin di-*p*-iodophenyl dichloride*, m. p. 147°, the corresponding *dibromide*, m. p. 102°, and *di-iodide*, m. p. 88·5°, are described. When treated with chlorine in cold chloroform the dichloride gives the *iodochloride* $(Cl_2,IC_6H_4)_2SnCl_2$, m. p. 82—82·5°. *Tin di-*p*-iodophenyl oxide* and *sulphide*, m. p. 248°, are described. *Tin* p-*iodophenyl trichloride*, m. p. 55—56°, yields the *iodochloride* $Cl_2,IC_6H_4{\cdot}SnCl_3$, gradual decomp. 50—70°. *Tin* p-*iodophenyl tribromide*, m. p. 80—80·5°, p-*iodophenylstannonic acid*, and the *sulphide* $(C_6H_4I{\cdot}Sn)_2S_3$ are described. H. Wren.

Protein structure and denaturation. C. Rimington (Nature, 1931, **127**, 440—441).—A discussion. L. S. Theobald.

Alkaline decomposition of serine. F. S. Daft and R. D. Coghill (J. Biol. Chem., 1931, **90**, 341—350).—Serine in hot alkaline solution gives ammonia, glycine, alanine, and oxalic and lactic acids. Pyruvic acid is an intermediate product. In the determination of arginine by the method of Van Slyke the decomposition of serine does not falsify the result, as the serine is effectively separated from arginine by the phosphotungstic acid precipitation, but errors may be introduced when the method suggested by Plimmer and Rosedale (A., 1926, 313) is followed. W. O. Kermack.

Tube for micro-determination of carbon and hydrogen according to Pregl. A. Verdino (Mikrochem., 1931, **9**, 123—125).—The apparatus described consists essentially of a tube 65 mm. long, having an external diameter of 30 mm. and an internal diameter of 11 mm. so that the combustion tube passes axially through it. The tube is filled with about 30 c.c. of decalin, which is kept steadily boiling. The advantage thus obtained is a constancy of temperature of the lead peroxide layer superior to that obtained by direct gas or electric heating. E. S. Hedges.

Ter Meulen–Heslinga method for determination of nitrogen, carbon, and hydrogen in organic material. E. P. Griffing and C. L. Alsberg (J. Amer. Chem. Soc., 1931, **53**, 1037—1039).—Several improvements in the technique of this method of analysis which allow accurate results to be obtained with 20—40 mg. of material are described. J. W. Baker.

Determination of nitrogen by a micro-Kjeldahl method. A. C. Andersen and B. N. Jensen (Z. anal. Chem., 1931, **83**, 114—120).—The method previously described for macro-determinations (A., 1926, 375) has been adapted to micro-analysis. A. R. Powell.

Detection of carbon disulphide. F. Feigl and K. Weisselberg (Z. anal. Chem., 1931, **83**, 93—104).—The sensitivity of various methods which have been proposed for the detection of carbon disulphide has been determined and two new very sensitive reactions are described. Of the known methods the xanthate–copper salt test detects 1 part of carbon disulphide in 90,000 parts of solution and the sodium azide–iodine test 1 part in 500,000 parts after waiting 10 min. Just as sensitive as the latter test is the instantaneous development of a characteristic brown to black colloidal suspension of lead sulphide when a drop of the carbon disulphide solution is treated with an alkaline solution of sodium plumbite and formaldehyde. An even more sensitive reaction comprises heating in a water-bath a closed test-tube containing the solution to be tested together with a few crystals of nickel acetate and of Hector's base; in the presence of carbon disulphide a rose colour or red precipitate is produced due to the formation of a complex nickel salt of the empirical formula $C_{30}H_{22}N_8S_6Ni$ (sensitivity 1 part of CS_2 in 2×10^6). A. R. Powell.

Determination of benzene in alcoholic solutions. G. Gróh and E. Faltin (Magyar Chem. Fol., 1930, **36**, 156—159; Chem. Zentr., 1931, i, 490).—The extinction coefficients of alcoholic solutions of benzene were determined; the Beer–Lambert law is valid. The limiting concentration of benzene for sufficiently accurate determination is about 0·01 g. per litre. A. A. Eldridge.

Colour reaction of aromatic amines. I. de Paolini (Atti R. Accad. Sci. Torino, 1930, **65**, 201—204; Chem. Zentr., 1931, i, 490—491).—The aromatic amine is added to a cold alcoholic suspension of benzoyl peroxide; a reddish-brown or violet colour is developed, the reaction being accelerated by heat. With benzylamine the reaction is: $3C_7H_7{\cdot}NH_2 + Bz_2O_2 \longrightarrow C_7H_7{\cdot}NHBz + CHPh{:}NH + OBz{\cdot}NH_3{\cdot}C_7H_7 + H_2O$. A. A. Eldridge.

Titrimetric determination of acetylsalicylic acid. A. Edwardsson (Svensk farm. Tidskr., 1929, **33**, 557—560; Chem. Zentr., 1930, ii, 1106—1107).—The procedure given in the Swedish pharmacopœia for the titrimetric determination of acetylsalicylic acid is confirmed. The detection of salicylic acid in this acid is also investigated. The colour reaction with ferric chloride is unsuitable, but Hoffmann's fluorescence test will detect the presence of 0·1% of salicylic acid in spite of a weak fluorescence of acetylsalicylic acid. L. S. Theobald.

Rapid volumetric determination of nicotine with silicotungstic acid. B. KASANSKY (Z. anal. Chem., 1931, **83**, 107—114).—The material (*e.g.*, 10 g. of tobacco) is made into a paste with 150 c.c. of water and 50 g. of sodium chloride, and after addition of 5 g. of magnesia or sodium hydroxide the nicotine is removed by steam distillation or extraction with a mixture of ether and light petroleum. An aliquot part of the distillate or extract is treated with 2 g. of ammonium chloride and titrated with a 2·5% solution of silicotungstic acid with vigorous shaking until no further turbidity is produced, when another drop of the acid is added. The reagent is standardised against a solution containing a known amount of nicotine, as the reaction does not appear to be stoicheiometric, more acid being required than corresponds with the formation of $2C_{10}H_{14}N_2,2H_2O,12WO_3,SiO_2,5H_2O$.

A. R. POWELL.

Determination of pyramidone by cyano-argentimetry. R. MACHTOU (J. Pharm. Chim., 1931, [viii], **13**, 329—333).—Pyramidone is quantitatively precipitated by an excess of aqueous mercuric chloride as a complex containing 2Hg per mol. of pyramidone. Mercury is determined in the original solution and in an aliquot part of the filtrate by addition of ammonia and potassium cyanide and titration with silver nitrate. Mercuric chloride does not precipitate " dioxypyramidone." It precipitates antipyrine, but not quantitatively.

H. E. F. NOTTON.

Sensitiveness of the thalleioquinine reaction. J. EISENBRAND (Arch. Pharm., 1931, **269**, 65—67).—The limit of sensitiveness given by Salomon (A., 1919, ii, 87; cf. Hart, J.S.C.I., 1921, **40**, 72) applies only when ammonia is added immediately after the bromine. When 0·0005% quinine sulphate solution (10 c.c.) is treated with one-tenth saturated bromine water and, after 10—15 sec., with excess of ammonia, a faint positive reaction is observed. The substance responsible for the reaction is formed by the action of hypobromous acid and is itself easily oxidised. Accordingly its formation is retarded by a decrease in p_H, whilst both changes are accelerated by an increase in p_H or in bromine-ion concentration, until at p_H 7 the intermediate compound can no longer be detected.

H. E. F. NOTTON.

Microchemical detection of alkaloids in plants. XV. Echinopsine. G. KLEIN and F. SCHUSTA (Oesterr. Bot. Z., **79**, 231—248; Chem. Zentr., 1930, ii, 3821).—Sensitive and characteristic micro-reactions with various iodo-salts were employed for the determination of echinopsine in various species of *Echinops*.

A. A. ELDRIDGE.

Microchemical detection of alkaloids in plants. G. KLEIN (Oesterr. Bot. Z., **78**, 67—70; Chem. Zentr., 1930, ii, 3821).—Polemical (cf. Mothes, Planta, 1928, **5**, 563).

A. A. ELDRIDGE.

Microchemical detection of alkaloids in plants. II. Nicotine. G. KEIN and E. HERNDLHOFER (Oesterr. Bot. Z., **76**, 222—228; Chem. Zentr., 1930, ii, 3821).—The gold chloride–sodium bromide reaction is suitable for the histochemical detection is nicotine; the sensitivity is 1 in 4×10^5. For determination the alkaloid is liberated by micro-distillation. Nicotine is present in all organs of *Nicotiana* plants in all stages of growth, and in fresh, dried, and fermented tobacco.

A. A. ELDRIDGE.

Determination of methylglyoxal, pyruvic acid, acetaldehyde, and lactic acid. E. SIMON and C. NEUBERG.—See this vol., 662.

Biochemistry.

Respiratory quotient of fish as a function of temperature. L. BAUDIN (Compt. rend., 1931, **192**, 637—639).—The oxygen intake and carbon dioxide output increase with rise of temperature. A minimum *R.Q.* is observed for *Carassius auratus* at 15°. Similar results are observed in *Cottus bubalis.*

C. C. N. VASS.

Resistance of *Eurytemora hirundoides*, Nordquist, to oxygen depletion. H. O. BULL (Nature, 1931, **127**, 406—407).—*E. hirundoides* can survive in brackish water, highly polluted, when the oxygen concentration is only 4 g. per 10^8 g., but total deprivation of oxygen can be suffered only for short periods.

L. S. THEOBALD.

Lack of inhibition of respiration of cells by hydrogen cyanide. O. WARBURG (Biochem. Z., 1931, **231**, 493—497).—The conclusions of Dixon and Elliott (A., 1929, 1197) concerning the supposed incompleteness of the inhibition of respiration by hydrogen cyanide are rejected on the ground that these authors worked with damaged cells. The views of other workers are also criticised.

W. MCCARTNEY.

Determination of blood-volume. Behaviour of colloidal substances in blood. B. MINZ (Z. klin. Med., 1930, **114**, 623—641; Chem. Zentr., 1931, i, 323).—No existing methods are sufficiently exact. Experiments designed to explore the use of colloidal silver for the determination show that the metal is detectable in blood after 24 hrs.; the concentration remains constant for 4—10 min., but the silver is quickly absorbed by organs. Silver–protein gave similar results. When a silver salt is added to blood *in vitro* it is found only in the plasma. Part of the colloidal silver in circulating blood passes into the erythrocytes; after 3 min. a large part of the colloidal silver is converted into a silver salt; this is more rapidly removed, as silver–protein, by organs.

A. A. ELDRIDGE.

Combination of the stroma-substance of red blood-corpuscles with thymol. LUTOWSKI (Schmerz, Narkose, Anæsth., 1930, **3**, 233—247; Chem. Zentr., 1930, ii, 3800).—Unchanged and defatted stromata differ markedly in their thymol-combining power. The curve supports the lipoid theory of narcosis, and not Warburg's adsorption process.

A. A. ELDRIDGE.

Colloid-osmotic pressure. XIII. Arterial and venous blood. E. KYLIN (Arch. exp. Path. Pharm.,

1931, **159**, 401—407).—The colloid-osmotic pressure of arterial blood 2—3 hrs. after a meal is higher and the protein content lower than the corresponding values for venous blood. In cardiac inefficiency and anæmia from loss of blood the pressure is lower for arterial blood. F. O. HOWITT.

Osmotic changes in some marine animals. R. MARGARIA (Proc. Roy. Soc., 1931, B, **107**, 606—624).—When living in diluted sea-water the osmotic pressure of the blood of crabs and dogfish falls in general to the level of that of the medium within the limits of dilution of one third to one half, whilst the blood of the conger and one species of crab is maintained at an osmotic pressure higher than that of the surrounding medium. The mechanism of the osmotic regulation is discussed. B. LEVIN.

Specific viscosity of native fibrinogen. W. STARLINGER and E. WINANDS (Z. ges. exp. Med., 1930, **71**, 389—394; Chem. Zentr., 1930 ii, 3722).—The viscosity of 1 g.-% fibrinogen in unchanged human blood-plasma, determined by measurement of the viscosity of the plasma before and after precipitation of fibrin, is 0·400—0·904 (average 0·568). A. A. ELDRIDGE.

Chemical constitution of serum-proteins. IV. A. FISCHER and A. BLANKENSTEIN (Biochem. Z., 1931, **231**, 404—411; cf. this vol., 247).—The proteins of two pathological sera have been separated by the authors' methods into their various fractions. In these sera the amount of the euglobulin which can be precipitated by sodium chloride is greater than the corresponding amount in normal sera. It has been found that the method used for determining the tryptophan content of the fractions does not give absolute values, but that satisfactory relative values can be obtained provided that the reaction of the solution used is kept constant. W. McCARTNEY.

Dialysis in the determination of serum-proteins. A. A. SCHMIDT and K. TULJTSCHINSKAJA (Biochem. Z., 1931, **232**, 323—334).—By precipitation with ammonium sulphate and subsequent dialysis the proteins in 1 c.c. of serum can be sharply separated into euglobulin, pseudoglobulin, and albumin fractions, and the amounts of these fractions can be deduced from nitrogen determinations. Very little denaturation of the proteins occurs during the process. W. McCARTNEY.

Globulin and albumin fractions of serum. III. Elementary composition of the various fractions of ox-serum and distribution of amide-, humin-, diamino-, monoamino-, and non-amino-nitrogen and of tryptophan and carbohydrate in them. B. LUSTIG and P. HAAS (Biochem. Z., 1931, **231**, 472—492; cf. this vol., 505).—The fractions were prepared as previously described, but were further purified by precipitation with acetone or alcohol and freed from lipins by extraction with ether. Great differences in the chemical composition of the fractions were revealed. Of the globulin fractions the euglobulins which are soluble in water and sodium chloride solutions have the lowest, the pseudoglobulins which are soluble in the same liquids the highest, carbon and hydrogen contents. The sulphur contents of the albumin fractions are approximately the same, but those of the globulins vary from 1·28 to 1·71%. The globulins soluble in sodium chloride solution have high methylimino-contents. The water-soluble pseudoglobulin has a high methoxyl content. As regards their contents of nitrogen in its various forms of combination and of tryptophan the albumin fractions do not differ much from each other, but the globulin fractions exhibit great differences. The albumin fractions have low carbohydrate contents. The globulin fractions which are soluble in sodium carbonate and hydroxide solutions contain from two to six times as much carbohydrate as do the other globulin fractions. Since all the fractions are hygroscopic, account must be taken of their water content when analytical determinations are made. W. McCARTNEY.

Influence of lipins on the separation of proteins by neutral salts. A. BOUTROUX (Compt. rend., 1931, **192**, 854—857).—Precipitation by sodium sulphate (cf. A., 1922, ii, 172) affords larger yields of protein from pneumonia serum than does acetone. After removal of the lipins, the yield of serum-albumin is approximately 3% less, whilst the intermediate concentrations of the globulin show similar divergences. A comparative photometric study of the opalescence produced in 0·075% serum-protein solutions shows that in whole serum the globulins commence to flocculate at 33% saturated ammonium sulphate solution and in lipin-free protein solution at 25% saturation; further, that the myxoproteins I and II and the globulin fractions obtained by treatment of serum with acetone have closely-related flocculation characteristics although in distinct groups. C. C. N. VASS.

Inter-relationship of cholesterol and protein fractions. W. N. NEKLUDOV (Biochem. Z., 1931, **232**, 50—57).—A portion of the cholesterol of normal horse and dog plasma is united with the globulin fraction and with a fraction of fibrinogen. A similar but less firm union is obtained with certain fractions of egg-albumin, and with the fraction precipitated from horse-serum by phosphotungstic acid after preliminary removal of albumin and globulin fractions. P. W. CLUTTERBUCK.

Determination of phosphatides in blood and tissues. A. CRUTO (Biochim. Terap. sperim., 1930, **17**, 242—248; Chem. Zentr., 1931, i, 118).—Blood or plasma (1 c.c.) is well mixed with 95% alcohol (10 c.c.); after a few min., benzene (20 c.c.) is added, well mixed, and 15—20 c.c. are then distilled off. To the cold residue is added anhydrous ether (10 c.c.), the mixture being kept for several hours with frequent shaking; the filtered solution and washings (anhydrous ether) are evaporated to dryness and the residue is heated for a few min. with sulphuric (1 c.c.) and nitric (2 c.c.) acids, with final evaporation to fuming after addition of 0·5 c.c. of nitric acid. The residue is dissolved in water, treated with magnesia mixture, and centrifuged; the determination is completed colorimetrically by Bell and Doisy's method. A. A. ELDRIDGE.

Blood-glycolysis. C. REID and B. NARAYANA (Biochem. J., 1931, **25**, 337—341).—Starvation decreases and the administration of food increases the rate of glycolysis in the blood of the dog. The factors

responsible for glycolysis in blood are present both in erythrocytes and serum. S. S. ZILVA.

Blood-sugar. K. P. JACOBSON (Biochem. Z., 1931, **231**, 498—499).—The view of Rona and Fabisch (this vol., 110) that the author's results confirm theirs is incorrect, and this is supported by the findings of other workers. W. MCCARTNEY.

Variations in blood-urea and -chlorine during venesection. A. DAUMAS and G. PAGES (Compt. rend. Soc. Biol., 1930, **103**, 1030—1031; Chem. Zentr., 1930, ii, 3590).—Variations during venesection (300—500 c.c. of blood) were not observed.
A. A. ELDRIDGE.

Diurnal variations in blood-urea and -chlorine. A. DAUMAS and G. PAGES (Compt. rend. Soc. Biol., 1930, **103**, 1031—1034; Chem. Zentr., 1930, ii, 3590).—Constant values are observed so long as food is not taken; a marked increase is observed after meals (cf. preceding abstract). A. A. ELDRIDGE.

Micro-determination of chloride in blood. J. A. F. KOK (Arch. Néerl. Physiol., 1931, **16**, 132—135).—The method of Kolthoff and Bak (cf. A., 1922, ii, 159) for the determination of chloride has been applied to blood. The proteins in blood hæmolysed by dilution with an equal volume of distilled water are precipitated with sulphosalicylic acid and to 8 c.c. of the filtrate 3 drops of a solution of sodium nitroprusside are added as indicator. The chloride is then titrated with a standard solution of mercuric nitrate until a turbidity just appears.
W. O. KERMACK.

Micro-determination of calcium in blood-serum. L. VELLUZ and R. DESCHASEAUX (Compt. rend. Soc. Biol., 1930, **104**, 977—978; Chem. Zentr., 1931, i, 324).—A procedure for the precipitation of calcium as oxalate is described; the precipitate is washed with a mixture of 95% alcohol (18 c.c.), ether (18 c.c.), and water (15 c.c.), then with equal parts of alcohol and ether, and finally with ether. Sulphuric acid and $N/150$-potassium permanganate are added with agitation; after 5 min. potassium iodide is added, and the iodine liberated is titrated with $0{\cdot}005N$-thiosulphate. The permanganate solution must be similarly titrated. The error is with serum 5%, with pure salt 3%. A. A. ELDRIDGE.

Determination of sodium in blood-serum. A. GRIGAUT and A. BOUTROUX (Compt. rend. Soc. Biol., 1930, **104**, 872—874; Chem. Zentr., 1931, i, 118).—The serum (1 c.c.) is deproteinised with 9 c.c. of a solution containing uranyl acetate (6 g.) and acetic acid (2 c.c.) in water (to 100 c.c.); 5 c.c. of the filtrate are treated with 15 c.c. of Kahane's reagent (uranyl acetate 32 g., magnesium acetate 100 g., acetic acid 20 c.c., 90% alcohol 500 c.c., water to 1000 c.c.), the precipitate being collected, washed with 90% alcohol, and dried at 100° for 30 min. The weight $\times 30$ is that of sodium in 1000 c.c. of serum. The titrimetric determination depends on the reduction of sexa- to quadri-valent uranium by means of copper and titration with permanganate. A. A. ELDRIDGE.

Use of Folin's method for determination of amino-nitrogen in 0·2 c.c. of blood. S. A. POVORINSKAJA (Biochem. Z., 1931, **232**, 69—71).—A method is described. P. W. CLUTTERBUCK.

Amount of ammonia and of its precursors in blood and muscle. E. FREUND and B. LUSTIG (Biochem. Z., 1931, **232**, 442—448).—Normal fresh blood, after being deproteinised in the cold, gives no ammonia reaction with Nessler's reagent, but by means of this reagent it can be shown that the precursors of the ammonia which is produced in blood and in muscle extracts are compounds containing carbamic acid and adenine nucleotide. These precursors give a green precipitate with the reagent, but if they are previously warmed with alkali they yield ammonia and hence give the usual brown precipitate. Although carbamates are decomposed by water they are stable, even in hot acid solutions, if deproteinised blood or muscle extracts are present.
W. MCCARTNEY.

Effect of physical factors on blood-catalase. II. Effect of some physico-therapeutic procedures. A. I. ALEXEEV and K. G. RUSSINOVA (Biochem. Z., 1931, **231**, 460—471).—Variations, caused by physical and physiological factors, in the activity of the blood-catalase of healthy and diseased men have been measured. Where the physical factors remain constant, the activity of the catalase likewise remains constant, other things being equal. Since the activity is considerably influenced by the temperature of the surrounding medium, this must be taken into account when determinations are made. In men who have taken electric, hot water, or warm water baths (the latter at 2·5 atm. pressure) the activity of the catalase is decreased. Baths in cold water, in mineral waters, or in air have no effect on the activity. Consumption of food and light muscular exercise likewise have no effect. W. MCCARTNEY.

Presence of proteolytic enzymes in serum. K. YOKOTA (Biochem. Z., 1931, **232**, 58—68).—Human serum is able to decompose animal fibrin to a small extent, but cannot attack human fibrin. Serum of carcinomatous and luetic patients is unable to attack normal human fibrin and shows no greater action on animal fibrin than does normal serum. Ligaturing the pancreatic duct in dogs often, but not always, leads to a small increase of serum-protease.
P. W. CLUTTERBUCK.

Oxidation of ethyl alcohol by blood. W. FLEISCHMANN and E. TREVANI (Biochem. Z., 1931, **232**, 123—127).—Ethyl alcohol is oxidised *in vitro* both by the red and the white corpuscles of the horse, but not by the serum, the oxidation being inhibited by $0{\cdot}005M$-hydrogen cyanide. The oxidation may be demonstrated using Warburg's charcoal model in presence of some aldehyde-fixing agent (calcium sulphite). P. W. CLUTTERBUCK.

Hydrogen-ion concentration of the alimentary tracts of the fowl, the cat, and the rabbit. A. R. MCLAUGHLIN (Science, 1931, **73**, 191—192).—The values, determined by means of the quinhydrone electrode, are recorded. L. S. THEOBALD.

Buffering power of central nervous tissue. M. MITOLO (Atti R. Accad. Lincei, 1930, [vi], **12**, 246—251).—The central nervous tissue of *Bufo*

vulgaris exhibits a marked buffering power. This power is probably due to acid–salt systems equilibrated near to the neutral point and of low dissociation constant, and not to proteins. T. H. POPE.

Occurrence of ergosterol in the human brain. I. H. PAGE and W. MENSCHICK (Biochem. Z., 1931, **231**, 446—459).—Spectroscopic and chemical examinations of material extracted from the brains indicate that the organ contains both cholesterol and ergosterol. The absolute amounts and the percentages of these substances vary according to the age of the brain. At the age of a little less than one year the absolute amount of ergosterol reaches its maximum and thereafter decreases and possibly even disappears. W. McCARTNEY.

Volumetric determination of fats and lipins by Bang's chromic acid oxidation method. H. STAUB (Biochem. Z., 1931, **232**, 128—145).—The reduction quotients of a series of fats, sterols, and lipins are obtained by Bang's method and compared with those of other authors, the effect of the various factors which change the reduction quotient, *e.g.*, the amount of the excess of dichromate, the rise in temperature on addition of sulphuric acid, etc., being examined. A convenient apparatus for carrying out determinations by Bang's method is described, the method extended to determinations on larger amounts of fat (0·5—10 mg.), and curves are given from which the amounts of fat and lipin corresponding with a known utilisation of dichromate may be read. Examples are given of the determination of fat and lipins in human, dog, and rabbit blood and in cat's liver. P. W. CLUTTERBUCK.

Fatty substance in the interstitial cells of the cock's testicle. J. BENOIT and A. WENSLAW (Compt. rend. Soc. Biol., 1929, **102**, 45—47; Chem. Zentr., 1931, i, 302).—The fatty deposit consists of cholesteryl esters covered with a thin film of phosphatides. A. A. ELDRIDGE.

Biology of the meal-worm (*Tenebrio molitor*). II. Tenebrioglycol, a wax-like material. F. N. SCHULZ and M. BECKER (Biochem. Z., 1931, **232**, 189—195).—The wax-like substance of the envelope of the meal-worm (this vol., 115) is shown to be a glycol, $C_{30}H_{62}O_2$, m. p. 116°, which cannot be acetylated or benzoylated but readily gives an anhydride, $C_{30}H_{60}O$, m. p. 85—86°, reconverted quantitatively into the glycol on hydrolysis with alcoholic alkali. P. W. CLUTTERBUCK.

Determination of glycogen in liver-tissue. A. CARRUTHERS (Chinese J. Physiol., 1931, **5**, 85—92).—The tissue is extracted with boiling water, the proteins are precipitated from the extract by trichloroacetic acid, and the glycogen present in the filtrate is precipitated by the addition of sufficient alcohol to make the concentration of the latter 70%. The precipitated glycogen is washed by centrifuging with alcohol and ether and hydrolysed with 2% hydrochloric acid. The reducing sugars are then determined. Evidence is presented that liver-tissue contains a carbohydrate insoluble in 70% alcohol, but destroyed by aqueous potassium hydroxide solution at 100°. This carbohydrate is not present if less than 1 min. elapses between the time of death and treatment of the liver with boiling water. W. O. KERMACK.

Determination of total sugar in liver-tissue. A. CARRUTHERS (Chinese J. Physiol., 1931, **5**, 93—102).—The liver-tissue is extracted with boiling water and the protein in the filtrate precipitated by trichloroacetic acid. The carbohydrates present are hydrolysed by boiling with 2% hydrochloric acid for 3 hrs. and the non-sugar reducing substances in the solution after neutralisation are precipitated by means of the mercuric sulphate reagent employed by West, Scharles, and Peterson (A., 1929, 714). After elimination of the mercury the reducing sugar is determined. W. O. KERMACK.

Animal sinistrin. F. MAY (Z. Biol., 1931, **91**, 215—220).—A method is described for separating sinistrin from glycogen in the carbohydrate from *Helix pomatia* by repeated precipitation with alcohol after enzymic hydrolysis of the glycogen. The product has $[\alpha]_D$ −13·55°, and inversion experiments show that it contains a polysaccharide of galactose (90·12%) and an unknown substance. A. COHEN.

Synthesis of glutathione in the adrenals. L. BINET, A. BLANCHETIERE, and A. ARNAUDET (Compt. rend. Soc. Biol., 1930, **104**, 56—57; Chem. Zentr., 1931, i, 303).—The glutathione content of the adrenal vein increases on perfusion with citrated blood only after addition of cystine and glutamic acid. A. A. ELDRIDGE.

Constituents of the epidermis with a thiol function. A. GIROUD and H. BULLIARD (Bull. Soc. Chim. biol., 1931, **13**, 138—140).—Extracts of the mucous cells of the "chestnut" of the horse give with the nitroprusside or the starch reaction 100—118 mg. per 100 g. glutathione in fresh tissues, whilst the hoof of the ox gives with the nitroprusside reaction 145 mg. and with the starch reaction 200 mg. per 100 g. Histological examination of these cells and determination of their fatty acid content suggest that prior to keratinisation there is an accumulation of sulphur in the tissues. Although the sulphur content of the mucous cells of the hoof of the ox is twice as large as that in the chestnut of the horse the S : P ratios are identical. C. C. N. VASS.

Tissue substances with a thiol function. A. GIROUD (Bull. Soc. Chim. biol., 1931, **13**, 141—142).—Micro-injection of tissues with sodium nitroprusside solution indicates the existence of a soluble (glutathione) and a fixed thiol linking in the cells. C. C. N. VASS.

Protein sulphuric acid ester from the spleen. A. EBEL (Biochem. Z., 1931, **231**, 306—308; cf. Mathis, this vol., 379).—A protein sulphuric acid ester has been isolated in purified form from the spleen of the ox. It is very soluble in water, but can be salted out from aqueous solution with ammonium sulphate. It contains neither tyrosine nor phenylalanine, but traces of tryptophan are present. All the sulphur (about 1·7%) in the ester is present in sulphuric acid radicals. W. McCARTNEY.

Coagulin of muscle. I. F. KRAUS and H. J. FUCHS (Z. ges. exp. Med., 1929, **64**, 583—593; Chem. Zentr., 1931, i, 308).—Muscle contains thermolabile

prothrombin, which coagulates plasma-fibrinogen similarly to, and has the same complement action on sensitised blood-corpuscles as, plasma-prothrombin.

A. A. ELDRIDGE.

Determination of lipins in thyroid gland powder. E. LABORDE and ENVER (Bull. Soc. Chim. biol., 1931, **13**, 148—149).—Powdered sheep's thyroid contains 1·4% of unsaponifiable matter, 5·66% of fatty acids, and 0·48% of cholesterol.

C. C. N. VASS.

Iodine content of the thyroid glands of the horse. H. COURTH (Biochem. Z., 1931, **232**, 310—322).—In horses, donkeys, and mules large variations are found in the weight and total and percentage of iodine of the thyroid glands. No relation exists between the weight of the glands and the amount of iodine which they contain, but the absolute amount of iodine usually increases with increase in the weight of the gland. Although the percentage of iodine in the glands is greatest soon after birth, the weight of the glands increases until the sixth year of age. As regards the percentage iodine contents of their thyroid glands horses of different breeds exhibit no differences. In geldings the absolute iodine content of the glands is greater than in stallions or mares.

W. McCARTNEY.

Tin in the animal organism. G. BERTRAND and V. CIUREA (Compt. rend., 1931, **192**, 780—782).—Tin may be determined in animal organs as follows. The dried material is heated for several days with a nitric acid–sulphuric acid mixture in a quartz vessel, the excess of acid removed by evaporation in a platinum dish, and the residue treated with hydrochloric acid. The solution is filtered from silica, and treated with hydrogen sulphide. The tin sulphide is then converted into, and weighed as, stannic acid. The organs of the cow, horse, and sheep contain 0·0005—0·004 g. per kg., with the exception of the skin (0·00948 g., 0·00853 g., and 0·00620 g. per kg., for the cow, horse, and sheep, respectively), and the tongue (0·01865 g., 0·02611 g. per kg., for the cow and sheep). B. LEVIN.

Preparation and analysis of representative samples from the bovine skeletal structure. W. M. NEAL and L. S. PALMER (J. Agric. Res., 1931, **42**, 107—113).—Longitudinal sections of bone are cut with a double-bladed hacksaw. Analytical data representative of the skeletal structure may be obtained by taking sections of the femur, humerus, and the sixth and eleventh ribs. A. G. POLLARD.

Staining of calcium. G. R. CAMERON (J. Path. Bact., 1930, **33**, 929—955).—Alizarin reacts readily with recently deposited calcium phosphate or carbonate, but may fail to stain older deposits. Hæmatoxylin does not stain calcium salts, although it may identify areas favourable to their deposition.

CHEMICAL ABSTRACTS.

Action of formaldehyde in histological fixation. K. ZEIGER (Z. wiss. Mikros., 1930, **47**, 273—293; Chem. Zentr., 1931, i, 322—323).—Sections of organs were stained with methylene-blue or crystal-ponceau after fixation with alcohol or formaldehyde. The protein colloids fixed by the latter become more acid than those fixed by alcohol. A. A. ELDRIDGE.

Determination of the alkali metals in sea-water and in the tissue fluids of some marine invertebrates. A. LEULIER and A. BERNARD (Bull. Soc. Chim. biol., 1931, **13**, 133—137).—The dry residue, ash, sodium content as determined by the uranium acetate method (cf. A., 1923, ii, 579), and the potassium content as determined by the cobaltinitrite method (the nitrite is oxidised by an excess of potassium permanganate) of Mediterranean sea-water and the body-fluids of *Holothuria tubulosa, Aplysia fasciata, Phallusia mamillata,* and *Pinna nobilis,* which give only traces of or no precipitates with trichloroacetic acid, are practically identical. In *Maia squinado, Carcinus mœnas, Octopus vulgaris,* and *Sepia officinalis,* the body-fluids of which contain varying amounts of protein, the sodium content is identical with that of the sea-water, but the potassium content is generally increased. C. C. N. VASS.

Intestinal secretion in insects. IV. Comparison of the p_H optima of the digestive enzymes from different groups of insects. O. SHINODA (Chikashige Anniv. Vol., 1930, 9—24).—The p_H of the intestinal secretions of various orders of insects are parallel with their systematic position. The p_H optima of proteases from the same orders of insects are in general parallel with the p_H of the intestinal juice, but the carbohydrates depend to a greater extent on the food habits of the insect. B. LEVIN.

Effect of ultra-violet irradiation of the skin on the secretion of gastric juice. F. DIEHL (Arch. exp. Path. Pharm., 1931, **159**, 367—371).—When human subjects were irradiated with ultra-violet light sufficiently intensely to cause the rapid development of an erythema there was a histamine-like effect on the secretion of gastric juice, but with less intense irradiation no noticeable stimulation of the gastric secretion ensued. This result supports the view that a histamine-like substance produced in the skin by irradiation is the cause of the erythema.

W. O. KERMACK.

Significance of the thiocyanogen content of gastric juice. G. LOCKEMANN and W. ULRICH (Deut. med. Woch., 1930, **56**, 1900—1902; Chem. Zentr., 1931, i, 478).—The thiocyanogen in presence of hydrogen ions has a bactericidal action.

A. A. ELDRIDGE.

Change of some physico-chemical properties of aqueous colloidal sericin solution of the cocoon during storing. H. KANEKO and M. MIYASAKA (Bull. Sericult. Japan, 1930, **3**, 4—5).—Slow denaturation of the sericin of the cocoon takes place during storage in a sealed vessel. The solubility, relative viscosity, refractive index, degree of turbidity, surface tension, and adsorptive capacity for dyes decrease, whilst the coagulation value towards platinic chloride and the rate of diffusion through 0·1% agar gel increase. These changes occur more quickly in the open atmosphere. Carbon dioxide and especially ammonia preserve the sericin. The solubility of sericin is increased by ammonia and decreased by carbon dioxide. E. S. HEDGES.

Occurrence of citric acid in the amniotic fluid. S. GENELL (Biochem. Z., 1931, **232**, 335—337).—Citric acid to the extent of, on the average, 0·005%

is a normal constituent of the amniotic fluid. Blood from the placenta probably contains less citric acid than does the fluid, and the acid is absent from the urine of new-born children. The citric acid of the fluid is probably secreted by the amniotic epithelium.

W. McCartney.

Colouring matter of milk. M. Lundborg (Biochem. Z., 1931, **231**, 274—289).—The yellow colouring matter of butter-fat is carotene. Methods of extracting the fat from milk and of determining the carotene content of the unsaponified and saponified fat are described and discussed. The most rapid and satisfactory method for the determination of carotene in milk is the author's modification, here described, of the method of Rose and Gottlieb.

W. McCartney.

Significance of liver-glycogen in liver function. I, II. T. Ikushima (Japan. J. Gastroenterol., 1930, 2, 213—219, 220—225).—A study of the rate of excretion of azorubin-*S* in the bile after injection into the blood; the pigment excretion function falls or rises when the liver-glycogen diminishes or increases, respectively.

Chemical Abstracts.

Excretion of halogen from the liver. I. Chlorine. Y. Maruno (Japan. J. Gastroenterol., 1930, 2, 231—238).—After intravenous injection of sodium chloride (10%; 5 c.c. per kg.) into rabbits the blood-chlorine increases, becoming normal in 2—3 hrs.; the bile-chlorine is maximal in 15—30 min. and is high after 23 hrs. Injury to the liver disturbs the excretion of chlorine.

Chemical Abstracts.

Formation of bilirubin. I. M. Ascoli and A. Fioretti. **II.** M. Ascoli and G. B. Malago (Bull. Atti Acad. Med. Roma, 1930, **54**, 6 pp., 6 pp.; Chem. Zentr., 1930, ii, 3596).—In nephrectomised dogs plasma-hæmoglobin is converted in the liver into bilirubin. Determinations of the quantity of bilirubin in various arteries and veins have been made. The liver is the chief source of bilirubin, although other places of formation exist.

A. A. Eldridge.

Fate of bilirubin introduced into the blood-vessels. I. S. Saiki (Japan. J. Gastroenterol., 1930, 2, 203—212).—When injected into the circulating blood of rabbits or dogs, bilirubin rapidly disappears from the plasma. It readily passes into the bile and urine.

Chemical Abstracts.

Absorption spectrum of bilirubin in chloroform, alcohol, and alkalis. L. Heilmeyer (Biochem. Z., 1931, **232**, 229—239).—Bilirubin in chloroform and alcohol possesses a well-defined absorption with a maximum at 450 mμ, the absorption falling away continuously to the ultra-violet. The absorption ratio at the maximum is $1{\cdot}054\times10^{-5}$. On keeping in light, the absorption decreases in the short-wave range and increases in the long-wave range. In alkaline solution, bilirubin shows a continuous absorption in the visible range, but the solution is too unstable to obtain a curve. The difference between the alkaline and neutral spectrum is not due to oxidative changes, but to the alkaline medium (salt formation ?).

P. W. Clutterbuck.

Cholesterol of protoplasm. VII. Ox-bile. G. Pfeiffer (Biochem. Z., 1931, **232**, 255—259; cf. this vol., 507).—The bile of young cattle contains oxycholesterol, the ratio of the amount of this to that of total cholesterol compounds present not differing much from the ratio found in liver. The ratio of oxycholesterol to precipitable cholesterol, however, is about 25% lower in the case of the bile than in that of the liver, possibly because the liver oxidises oxycholesterol to bile acids. The liver contains a larger percentage of cholesteryl esters than does the bile.

W. McCartney.

Urinary composition and acid–base equilibrium. I. S. M. Neuschlosz. **II.** S. M. Neuschlosz and J. Planas (Biochem. Z., 1931, **232**, 82—97, 98—105).—I. A method is given for determining the ratio of weak bases (ammonia, creatinine) to weak acids (organic acids, acid phosphate ion) in urine; in 100 normal human urines this base–acid quotient is a linear function of the p_H of the urine, and equals unity at p_H 5·7. The quotient also stands in direct relationship with the "buffer constant" calculated from the hydrogen-ion concentration of the urine and its concentration in primary and secondary phosphates.

II. The effect of slow intravenous injection of various acids (hydrochloric, sulphuric, phosphoric, lactic, and acetic), bases (ammonia and sodium hydroxide), and salts (ammonium and calcium chlorides, sodium hydrogen carbonate), 10 c.c. of 0·1*N* solution per kg. body-weight being used in hydrogen carbonate-free Ringer's solution at a rate of a 100 c.c. per hr., on the alkali reserve and the urinary composition in dogs is investigated. Hydrochloric and sulphuric acids cause a decrease of alkali reserve, which persists over 24 hrs., whilst the urinary acidity may increase, decrease, or remain unchanged. The base–acid quotient decreases in every case. With lactic and phosphoric acids, and also with ammonium and calcium chlorides, a decrease in alkali reserve is obtained, but this persists only a short time. The urine becomes more acid and the base–acid quotient increases considerably. Acetic acid causes a long-persisting decrease of alkali reserve, alkalisation of the urine, and a decrease of base–acid quotient. Sodium hydroxide and hydrogen carbonate cause a prolonged increase of alkali reserve, an alkaline urine, and a decrease of base–acid quotient. The action of ammonia depends on the initial alkali reserve. With low initial reserve, an increase of reserve occurs with ammonia, the urine becomes more acid, and the base–acid quotient increases. With high initial reserve, ammonia produces but little effect, the urine becomes more alkaline, and the base–acid quotient decreases.

P. W. Clutterbuck.

C : N-quotient. Determination of carbon. W. Biehler (Knoll's Mitt. fur Arzte, 1929, 3 pp.; Chem. Zentr., 1930, ii, 3611).—Urine (3—5 c.c.) is diluted with water (to 50 c.c.), and heated for 15 min. at 70° with potassium persulphate (10 g.) and mercuric nitrate (1 crystal); air free from carbon dioxide is passed through the combustion vessel, then through potassium antimonyl tartrate solution, and into a known quantity of barium hydroxide solution.

A. A. Eldridge.

Detection of lactose in urine. E. Freund and B. Lustig (Biochem. Z., 1931, **232**, 449—451).—The

method of Bauer (A., 1907, ii, 310) for the determination of mucic acid (derived from lactose) in urine gives satisfactory results as far as lactose orally administered is concerned. Certain constituents of urine, however (urea, ammonium salts), prevent the conversion of the small amounts of lactose present in urine nitric acid into mucic acid. A method is described by which these constituents may be removed and this lactose also determined.

W. McCartney.

Solubility of urinary uric acid. R. Ascoli (Biochim. Terap. sperim., 1929, **16**, 33—46; Chem. Zentr., 1931, i, 492—493).—Synthetic uric acid is soluble in alkaline or neutral urine, but at p_H 6·5—7 it is practically insoluble. When urine at p_H 5·5—6·5 is shaken with synthetic uric acid, natural uric acid separates. The solubility of synthetic uric acid in alkaline urine is closely related to the natural uric acid content. A. A. Eldridge.

Clinical colorimetry. IX. Urochrome. Analysis of urinary residual colouring matter. L. Heilmeyer and W. Otto (Z. ges. exp. Med., 1930, **74**, 490—513; Chem. Zentr., 1931, i, 324).—"Urochrome" is separated by saturation of urine with ammonium sulphate into two substances with different absorption spectra: *A*, 26—42%, sensitive towards oxygen, *B*, 50—74%. Lead acetate cannot be used for the separation of the colouring matters of normal urine. A. A. Eldridge.

Allergy and the acid-base equilibrium. F. Diehl and E. G. Schenck (Arch. exp. Path. Pharm., 1931, **159**, 372—382).—Modification of the acid-base equilibrium, *e.g.*, by administration of ammonium chloride, does not significantly affect the allergic skin reactions of human patients. W. O. Kermack.

Dialysability of proteins. A. F. Coca (J. Immunol., 1930, **19**, 405—410).—The dialysability of the excitants of atopic hypersensitiveness in egg-white is confirmed. Chemical Abstracts.

Goats' milk anæmia. Experiments with growing pigs. C. Kronacher, J. Kliesch, and W. Schaper (Z. Tierzücht., 1930, **14**, 231—294; Chem. Zentr., 1930, ii, 1093—1094).—Goats' milk anæmia is not due to avitaminosis, in particular, -*C*.

A. A. Eldridge.

Gastric acidity in diabetes mellitus. I. M. Rabinowitch, A. F. Fowler, and B. A. Watson (Arch. Int. Med., 1931, **47**, 384—390).—Of 100 cases of diabetes in which there were no digestive disorders, more than fifty had gastric juices in which the total acidity and free hydrochloric acid were below normal, and free hydrochloric acid was absent in 39 cases. Since the incidence of achlorhydria in non-diabetics is 20%, diabetes *per se* may be responsible for low gastric acidity. A. Cohen.

Biological diagnosis of gout. P. Escudero and A. Escudero (Semana Med., 1930, II, 1945—1954).—The method is based on measurement of the retention of purine substances.

Chemical Abstracts.

Congestive heart failure. VI. Effect of overwork and other factors on the potassium content of the cardiac muscle. J. A. Calhoun, G. E. Cullen, G. Clarke, and T. R. Harrison. **VII. Skeletal muscle.** J. A. Calhoun, G. E. Cullen, and T. R. Harrison (J. Clin. Invest., 1930, **9**, 393—403, 405—408).—VI. The potassium content of the right ventricle is diminished owing to overwork in pneumonia and massive collapse and in myocardial insufficiency.

VII. Overwork of the muscles of one leg of a dog led to loss of potassium. Chemical Abstracts.

High carbonuria in severe hepatic injury after administration of menthol. K. Voit and H. Wendt (Z. klin. Med., 1930, **114**, 432—438; Chem. Zentr., 1931, i, 307).—On administration of menthol normal urine contains an amount of carbon approximately corresponding with the anticipated quantity of mentholglycuronic acid; in hepatic disease much larger quantities are excreted. A. A. Eldridge.

Glyoxaline derivatives in the urine in liver disease. F. Kauffmann and R. Engel (Z. klin. Med., 1930, **114**, 405—431; Chem. Zentr., 1931, i, 304).—Glyoxaline derivatives are normal constituents of urine. The glyoxaline value" increases on a protein diet; it is related to the dietary histidine. It increases in water diuresis or on administration of histidine hydrochloride or glyoxalinelactic acid, and decreases slightly in hunger acidosis. High values are observed in hepatic disease; the cause is discussed.

A. A. Eldridge.

Intermediary protein and carbohydrate metabolism. I—III. J. Bloch (Z. ges. exp. Med., 1930, **74**, 439—448, 449—453, 454—457; Chem. Zentr., 1931, i, 307—308).—Galactosuria following administration of galactose in degenerative hepatic disease is markedly diminished by administration of glycine, alanine, or aspartic acid. In glycogen impoverishment the alanine or aspartic acid is partly employed in the production of sugar. A. A. Eldridge.

Distribution of bile-pigments in the organism. F. K. Gassmann (Z. klin. Med., 1930, **114**, 477—480; Chem. Zentr., 1931, i, 474).—In hepatic disease with icterus and in dogs with experimental icterus the pancreas and spleen are almost free from bile-pigments; the liver, skin, kidneys, adrenals, and lungs contained bilirubin. A. A. Eldridge.

Biochemical investigation of blood in cases of experimental disturbance of liver function. I. Liver function and carbohydrate metabolism. T. Sawada (Japan. J. Gastroenterol., 1930, **2**, 191—202).—Rabbits' blood-sugar at first increases and then becomes subnormal after liver injury by chloroform, carbon tetrachloride, or yellow phosphorus. *X*-Ray injury produced a rise in blood-sugar for 3 days; partial hepatectomy decreased it. Ligation of the common bile duct increased and then decreased the blood-sugar. Chemical Abstracts.

Blood-phosphorus in parathyroid- and thyroparathyroid-ectomised animals. C. I. Parhon and G. Werner (Compt. rend. Soc. Biol., 1930, **104**, 228—229; Chem. Zentr., 1931, i, 304).—The total, inorganic, and total organic phosphorus increase, whilst the ester-phosphorus falls. A. A. Eldridge.

Causative agent of a chicken tumour. J. B. Murphy, O. M. Helmer, A. Claude, and E. Sturm

(Science, 1931, **73**, 266—268).—Adsorption of the active agent by aluminium hydroxide leaves an extract more active than the original in spite of the removal of a large proportion of the agent by the hydroxide. Evidence of an inhibiting principle in the chicken tumour has been obtained, and the increased activity resulting after adsorption by aluminium hydroxide is explained by preferential adsorption of this principle. L. S. THEOBALD.

Western duck sickness produced experimentally. E. R. KALMBACH (Science, 1930, **72**, 658—660).—Duck sickness has been produced by the administration of a toxic material resulting from incubation of the tissues of ducks which have succumbed to the disease. L. S. THEOBALD.

Changes of serum-proteins in under-nutrition. S. M. LING (Chinese J. Physiol., 1931, **5**, 1—10).—In 24 human subjects on a diet poor in protein and showing marked œdema, the serum-albumin was below normal, the serum-globulin in most cases was within the normal limits, the basal metabolism was low, and there was a negative nitrogen balance. On an adequate diet, the œdema soon disappeared, the serum-albumin returned more slowly to the normal limits, the basal metabolism rose, and the nitrogen balance was positive. The low colloid osmotic pressure is probably the cause of the œdema which occurs on a diet poor in protein.

W. O. KERMACK.

Metabolism as related to chromosome structure and the duration of life. J. W. GOWEN (J. Gen. Physiol., 1931, **14**, 463—472).—The rates of production of carbon dioxide by *Drosophila* flies possessing different types of chromosome constitution have been measured. The types possessing balanced chromosomes, namely males and triploid females, have smaller rates than do those types possessing unbalanced chromosomes, namely males and sex-intergrades. The smaller rates of the former two types appear to be correlated with their longer average life. W. O. KERMACK.

Metabolism of tissue cultures. I. Measurement of respiration. II. Determination of weight of tissue cultures. Relation of increase of weight to increase of surface. R. MEIER (Biochem. Z., 1931, **231**, 247—252, 253—259).—I. A method of measuring the respiration of tissue cultures is described, a modified form of Carrel flask being used. The carbon dioxide produced is measured after respiration has ceased.

II. Since the measurement of the area of tissue cultures involves many errors, a method of determining their weight is used and the amounts of lactic acid produced by unit weight of various cultures have been determined. W. MCCARTNEY.

Standard metabolism of Australian aboriginals. C. S. HICKS, R. F. MATTERS, and M. L. MITCHELL (Austral. J. Exp. Biol., 1931, **8**, 69—82).

Metabolism of nerves on electric stimulation. H. WINTERSTEIN (Biochem. Z., 1931, **232**, 196—201). —A reply to Meyerhof and Schulze (this vol., 254) and to Gerard (Science, 1930, **72**, 196).

P. W. CLUTTERBUCK.

Increase in the p_H of the white and yolk of hens' eggs. P. F. SHARP and C. K. POWELL (Ind. Eng. Chem., 1931, **23**, 196—199).—The of the white rises from 7·6 to 9·3 during the first few days after laying, due largely to loss of carbon dioxide; this change takes place more rapidly at higher temperatures. Fertile eggs then fall to about 8·0, but infertile ones show no change unless kept at high temperatures. Hydrolysis of the protein takes place more rapidly the further is the p_H from its isoelectric point, and the loss of carbon dioxide may be prevented by increasing its amount in the air in which the eggs are stored, or by dipping the eggs in oil. The yolk shows a slower and smaller change than the white. T. MCLACHLAN.

Sugar, the fuel of life. F. FISCHLER (Arch. Pharm., 1931, **269**, 9—22).—A lecture.

H. E. F. NOTTON.

Influence of amino-acids on the glycogen mobilisation in the toad's liver through adrenaline. Y. TANIUCHI (Folia Pharm. Japon., 1930, **10**, No. 1, 64—99).—When perfused with adrenaline, glycine and tryptophan (1 in $2—4\times10^4$) have a weak, but histidine and cystine no, sugar-producing action. The sugar mobilisation of the adrenaline is strengthened, especially by histidine and cystine. The combined effect of two amino-acids is weaker than their separate action. The sugar mobilisation is not parallel to the concentration of the amino-acid or the combination with adrenaline. CHEMICAL ABSTRACTS.

Carbohydrate tolerance at high altitudes. G. FERRALORO (Arch. Sci. biol., 1929, **13**, 109—126; Chem. Zentr., 1930, ii, 3803).—In rarefied air and intense sunlight, hyperadrenalinæmia is accompanied by a rise in blood-sugar and an increase in dextrose tolerance. A. A. ELDRIDGE.

Tolerance of normal subjects to lævulose. Factors influencing the variations in rise in blood-sugar. N. JOLLIFFE (J. Clin. Invest., 1930, **9**, 363—380).—Oral ingestion of 30—50 g. of lævulose normally causes a rise in blood-sugar to 115 mg. per 100 c.c. (max.). A value above 95—110 appears to stimulate a sugar-storage mechanism, which rapidly lowers the blood-sugar. The rapidity of disappearance of the blood-sugar probably depends on the glycogen-forming ability of the sugar used.

CHEMICAL ABSTRACTS.

Metabolism of galactose. I. Use of galactose in tests of the function of the liver. H. SHAY, E. M. SCHLOSS, and M. A. BELL (Arch. Int. Med., 1931, **47**, 391—402).—Galactose is regarded as a suitable sugar for testing liver function, since (*a*) it is readily absorbed from the intestine, (*b*) its conversion into glycogen by the liver is relatively difficult, (*c*) it is not appreciably utilised by tissues other than the liver, and (*d*) its excretion is not influenced by endocrine activity. A. COHEN.

Effect of yeast on the chemical processes in the liver and muscle of exercising animals. I. C. PI-SUNER BAYO, G. LISS, and T. OSUKA. **II.** C. PI-SUNER BAYO and G. LISS (Anal. Fis. Quím., 1931, **29**, 193—199, 200—205).—I. Administration of 0·2 g. of dried yeast daily to well-exercised rats caused

an increase of the liver-glycogen and a smaller increase of the muscle-glycogen; the lactic and phosphoric acid content of both the liver and muscle also increased slightly.

II. The daily administration of 2 g. per kg. of dried yeast to dogs maintained in regular training for 48 days caused the liver-fat to increase to 6—8 times its normal value without influencing the liver-glycogen. In the case of dogs which, after resting for several days, were exercised for only 1 hr., the liver- and muscle-glycogen increased very greatly. It appears that the glycogen deposit, which attains a maximum after a few hours, is gradually converted into fat.

H. F. Gillbe.

Inhibition of glycolysis and accumulation of methylglyoxal. H. K. Barrenscheen, K. Braun, and M. Dreguss (Biochem. Z., 1931, **232**, 165—180). —Addition of iodoacetic and bromoacetic acids to fresh muscle, liver, or kidney pulp containing hexosediphosphate causes accumulation of methylglyoxal. Addition of pancreatic extract to muscle or yeast pulp treated with iodoacetic acid causes the formation of methylglyoxal from glycogen. Methylglyoxal may be detected in the musculature of animals poisoned with iodoacetic or bromoacetic acid. The organ pulp of animals so poisoned added to hexosediphosphate formed methylglyoxal, and in two of these experiments pyruvic acid also accumulated. Organ pulp of animals poisoned with insulin also formed methylglyoxal from added hexosediphosphate.

P. W. Clutterbuck.

Pyruvic acid as a food for *Drosophila melanogaster*. L. Nemeth (Biochem. Z., 1931, **231**, 385—392).—An agar medium containing pyruvic acid and yeast but free from sugars is a sufficient food for *Drosophila melanogaster*, since the fly thrives on this material and lays fertile eggs. If pyruvic acid is absent or is replaced by acetic, tartaric, formic, lactic, or succinic acid, the insects cannot live on the medium.

W. McCartney.

Passage of chemical substances from the mother to the fœtus at the end of gestation. E. Brandstrup (Bull. Soc. Chim. biol., 1931, **13**, 172—185).—In the rabbit during the last quarter of gestation dextrose, glycine, alanine, aspartic acid, glutamic acid, and urea diffuse slowly across the placenta, xylose and arabinose diffuse more rapidly, whilst there is no diffusion of sucrose or lactose. The chloride ion diffuses rapidly across the placenta.

In woman at the commencement of labour there is a slow diffusion of urea across the placenta, equilibrium being attained after some hours. C. C. N. Vass.

Ammonia content of, and production of ammonia in, muscle. Relation of these to change in function and condition. IX. Stage at which ammonia is produced during the chemical processes occurring in active muscle. W. Mozołowski, T. Mann, and C. Lutwak (Biochem. Z., 1931, **231**, 290—305).—The greater part of the ammonia produced in active frog muscle which has been poisoned with iodoacetic acid is formed when a state of fatigue has been reached, the creatinephosphoric acid being exhausted and rigor about to appear.

W. McCartney.

Pyrimidine base metabolism. A. Boivin (Compt. rend. Soc. Biol., 1930, **104**, 99—100; Chem. Zentr., 1931, i, 308).—Pyrimidine bases are absent from animal and from normal or pathological human urine. An analytical method is described.

A. A. Eldridge.

Biochemistry of sulphur. VIII. Rate of absorption of cystine from the gastrointestinal tract of the white rat. M. X. Sullivan and W. C. Hess (U.S. Publ. Health Rep. Suppl., 1931, No. 89, 1—16).—The rate of absorption of cystine administered as the sodium salt is approximately 50 mg. per 100 g. body-weight per hr. as determined by the Sullivan and Okuda iodometric methods, and 30 mg. per 100 g. body-weight per hr. by the Folin–Marenzi method (cf. A., 1929, 1093). Hydrolysates of amino-acids containing no cystine react positively as cystine in the Folin–Marenzi method, but are negative in the other two. The Okuda method shows that there is an accumulation of S·S compounds, calculated as glutathione, in the liver of rats fed with cystine compared with those of fasting rats or those fed with glycine and alanine. C. C. N. Vass.

Origin of creatine and creatinine in the animal organism. I—III. E. Abderhalden and S. Buadze (Z. ges. exp. Med., 1929, **65**, 1—26; **66**, 635—652; 1930, **69**, 561—576; Chem. Zentr., 1930, ii, 3803).—II. Kidney, brain, thyroid, thymus, pancreas, testicle, lung and spleen tissue can form creatine (creatinine) from nucleic acid or from guanine and adenine. In the liver, formation is masked by decomposition. The minced tissue loses its activity when boiled. Urea is not formed from allantoin; allantoin, in presence or absence of choline, gives no creatine. Negative results were obtained with carbonyldicarbamide and methylglyoxaline. In gout the urinary and blood-total creatinine is diminished.

III. Allantoin, uric acid, uracil, methylglyoxaline, and caffeine do not increase the excretion by the adult dog of total creatinine; increase results from ingestion of placenta powder or subcutaneous administration of menoformone. Administration of globin or hæmoglobin considerably increases the excretion of total creatine, with simultaneous increase in urinary uric acid and allantoin. Purine, creatine, and creatinine metabolisms thus appear closely related. Hydrolysed globin from which arginine and histidine were removed was ineffective; addition of histidine, but not of arginine, partly restored the activity. A. A. Eldridge.

Do allantoin and purines of the urine of mammals arise partly from the degradation of proteins? E. F. Terroine and G. Mourot (Bull. Soc. Chim. biol., 1931, **13**, 94—109).—When the mineral salts are decreased in the diet of pigs well supplied with proteins (caseinogen) a sharp increase occurs in the total nitrogen excretion and also in the excretion of allantoin and purines. These substances therefore arise in part from the degradation of proteins. W. O. Kermack.

Do protein reserves exist in frog's liver prior to hibernation? C. Gautier (Bull. Soc. Chim. biol., 1931, **13**, 142—147).—Average determinations show that whilst the total weight of frog's liver is

increased twofold prior to hibernation the protein content increases by almost a third.

C. C. N. VASS.

Specific dynamic action of protein. H. BORSOOK and H. M. WINEGARDEN (Proc. Nat. Acad. Sci., 1931, **17**, 75—91).—The specific dynamic action of protein is parallel to nitrogen excretion and in the well-nourished animal is the result of at least two processes, one of which is the work imposed on the kidney and the other is due to the metabolism other than excretion of nitrogen and of carbon. The increase in metabolism following the ingestion of protein or amino-acid shows a close correlation between the specific dynamic action of proteins and the increase, over the basal level of excretion, in the urinary nitrogen. Neither the experimental evidence nor consideration of energy relations supports the view that the specific dynamic action of protein is due to the conversion of deaminised fractions into dextrose.

E. S. HEDGES.

Partition of urinary nitrogen in endogenous nitrogen metabolism during growth. E. F. TERROINE, G. BOY, M. CHAMPAGNE, and G. MOUROT (Compt. rend., 1931, **192**, 634—636).—The total expenditure of nitrogen per kg. of body-weight diminishes considerably with growth. Whilst the urea, ammonia, amino-nitrogen, and allantoin decrease correspondingly, the amount of creatinine remains constant or increases slightly. In the pig, the urinary amino-nitrogen forms 15—20% of the nitrogen excreted as ammonia, urea, and amino-nitrogen.

C. C. N. VASS.

[Biological formation of] ketonic substances. O. STEPPUHN and A. TIMOFEIEVA (Z. ges. exp. Med., 1930, **74**, 467—481; Chem. Zentr., 1931, i, 307).—When the liver is impoverished in glycogen peripheral fat migrates to the liver; ketonic substances are formed and the degradation of protein is increased. The protein–carbohydrate metamorphosis is stimulated by the ketonic acids only under certain conditions.

A. A. ELDRIDGE.

Resorption of fat by desaturation of fatty acids. H. TANGL and N. BEREND (Biochem. Z., 1931, **232**, 181—188).—The desaturation of fatty acids is brought about by the action of bile, an action which is augmented by pancreatic juice, although the latter alone is inactive. The action is inhibited by heating and is therefore probably an enzymic process.

P. W. CLUTTERBUCK.

Effect of diet on the composition of adipose tissue. K. MOSSE and C. BRAHM (Jahrb. Kinderheilk., 1928, **122**, 151—167; Chem. Zentr., 1930, ii, 1093).—Experiments on piglings are described. Data relating the weight and the quantity of fat to the diet are recorded; the chemical characteristics of the fat remained practically constant. With a protein-rich diet, the protein, water, and ash of the adipose tissue were high; with a carbohydrate-rich diet the phosphorus content was high.

A. A. ELDRIDGE.

Growth studies with swine. J. H. LONGWELL, H. O. HENDERSON, and W. M. INSKO, jun. (W. Virginia Agric. Exp. Sta. Bull., 1930, No. 230, 24 pp.).—Butter and oleomargarine were equally effective as sources of vitamin-*D* for pigs. Lard and vegetable-oil margarine gave less satisfactory results.

A. G. POLLARD.

Influence of the consumption of fats and oils, meat, and bread on the growth of rats. W. A. LEIBOVITSCH-LIVSCHINA (Biochem. Z., 1931, **231**, 260—273).—The consumption of small amounts of cod-liver oil considerably stimulates the growth of rats, but large amounts have a toxic effect, causing loss of weight and early death. Correspondingly large amounts of olive oil have a similar, but not so pronounced, effect. Administration of small or medium amounts of olive, hemp-seed, and linseed oils to growing rats does not stimulate growth. Medium amounts of meat or of meat with bread produce the greatest increases in weight, especially in fasting rats which have previously received large amounts of cod-liver or olive oil. The effect of the consumption of meat lasts longer in fasting rats than in those which have not fasted.

W. MCCARTNEY.

Bread. II. Physiological action of whole-meal bread. I. ABELIN (Biochem. Z., 1931, **232**, 278—294; cf. A., 1930, 108).—Young rats fed exclusively on whole-meal bread which has been so baked as to avoid damage to certain valuable constituents grow and develop practically normally. If calcium lactate is added to such bread in order to compensate for the excess of phosphoric acid which it contains, the result is even more satisfactory. White and other breads, although alone insufficient and unsatisfactory as foods, are also improved, although to a smaller extent, by such addition of calcium salt.

W. MCCARTNEY.

Inadequacy of white wheat flour and fish meal for prolonged growth of pigs and its amelioration with yeast or stout. A. H. BLISSETT and J. GOLDING (Biochem. J., 1931, **25**, 349—357).—Daily additions of dried brewer's yeast to the inadequate diet of white wheat flour and fish meal made the ration satisfactory. Stout had a similar effect.

S. S. ZILVA.

Lipin metabolism. I. Metabolism in experimental fever of rabbits. H. HAMANO (Proc. Imp. Acad. Tokyo, 1931, **7**, 80—81).—In rabbits after piqure, the amount of fatty acids in the blood and blood-plasma decreases, reaching a minimum in 24 hrs., thereafter returning to normal. Cholesterol and lecithin in the whole blood and plasma increase at first, and then decrease to normal. The leucocytes increase during fever. The serum-protein and -lipase both decrease during the initial stage. The author concludes that there is a relation between the amount of blood-lipin and the body temperature.

B. LEVIN.

Cholesterol balance in chicks in the first two weeks after hatching. H. DAM (Biochem. Z., 1931, **232**, 269—273; cf. A., 1930, 951).—In chicks, during the first two weeks after hatching, both the total amount of cholesterol and the ratio of cholesteryl ester to total cholesterol decrease.

W. MCCARTNEY.

Mineral feeding [of animals]. Iodine, lime, and salt-licks. B. W. SIMPSON (New Zealand J. Agric., 1931, **42**, 18—23).—Plants from seed soaked

in potassium iodate solution and grown in soil treated with potassium iodate contained more iodine than control plants and, when fed to rabbits, improved their growth rates. Addition of lime to rations, either direct or in the form of salt-licks, did not cause enlargement of the thyroid in rabbits. Lime alone did not appreciably affect the gland size or rates of growth, but the salt-lick increased the rate of growth and reduced the size of the glands. Large glands of low iodine content were produced by feeding healthy rabbits with food grown in goitrous areas.

A. G. POLLARD.

Effect of age and nutrition on the calcium phosphate : calcium carbonate ratio in the bones of cattle. W. M. NEAL, L. S. PALMER, C. H. ECKLES, and T. W. GULLICKSON (J. Agric. Res., 1931, **42**, 115—121).—The ratio of residual calcium to residual phosphate (excluding calcium present as carbonate and phosphate as trimagnesium phosphate) of cattle bones approximates to the ratio in tricalcium phosphate, and is not affected by deficiency of calcium or phosphorus in the ration. The ratio of calcium phosphate to calcium carbonate in the bones of dairy cattle decreases with age and is affected by nutrition, decreasing if the ration is deficient in phosphorus and returning to normal with the subsequent use of phosphate supplements. High values may occur if the ration has a high phosphorus content. Calcium deficiency is probably without effect on the proportion of phosphorus in the whole skeleton. High-calcium rations do not influence the calcium : phosphorus ratio. A. G. POLLARD.

Physico-chemical theory of the action of substances on living matter. P. LASAREV (J. Chim. phys., 1931, **28**, 42—48).—On the assumptions that the effect of a substance on the function of a living cell is dependent on its concentration (C), and that the function of the cell (E) may be expressed in measurable quantities (*e.g.*, amount of liquid secreted etc.), formulæ are derived mathematically giving E in terms of C and the period of time (t in sec.) during which the effect of the substance is felt. In the case of the depressing effect of ether on chlorophyll assimilation (Bose), the difference between the normal oxygen content and the oxygen liberated in the presence of ether is given with great precision, compared with experimental values, by the expressions $108(1-e^{-0\cdot111t})$ and $121[1-1/(1+0\cdot017t)]$. The theory is also applied to the action on the nervous centres of substances introduced into the blood and, in the general case, into the stomach. J. GRANT.

Vital staining and permeability. II. E. GELLHORN (Protoplasma, 1931, **12**, 66—78).—The permeability of the surface layer of sea-urchin eggs to dyes is decreased by the presence of calcium salts and increased by sodium and magnesium salts, the effect of the latter being greater than that of salts of any univalent cation. The increased permeability caused by sodium or magnesium chlorides is diminished or entirely suppressed by the addition of calcium chloride. The antagonistic effect of barium or strontium chlorides is very slight in comparison with that of the calcium salt. Changes in permeability due to salt treatment do not prevent fertilisation or development of the eggs. A. G. POLLARD.

Effect of intravenous injection of dyes on blood-cholesterol. A. LESZLER (Z. ges. exp. Med., 1930, **71**, 477—479; Chem. Zentr., 1930, ii, 1092).—Intravenous injection of tetraiodophenolphthalein, trypaflavine, and indigo-carmine to patients suffering from different diseases resulted in a diminution in blood-cholesterol. L. S. THEOBALD.

Alcohol content of blood under various conditions. P. I. TUOVINEN (Skand. Arch. Physiol., 1930, **60**, 1—134; Chem. Zentr., 1931, i, 310).—The relation depends on the amount and nature of the stomach contents as well as on the concentration of the alcohol ingested. The sensation is proportional to the blood-alcohol value, and is perceived at 0·006—0·01%. A. A. ELDRIDGE.

Exhalation of alcohol in breath. G. LILJESTRAND and P. LINDE (Skand. Arch. Physiol., 1930, **60**, 273—298; Chem. Zentr., 1931, i, 310).—After ingestion of alcohol the alcohol contents of arterial and venous blood are practically identical. The alcohol content of expired air is a measure of that of the body-fluids. Variations and their physiological causes are considered. A. A. ELDRIDGE.

Action of chloroform and ether on the oxido-reductive properties of tissues. N. GAVRILESCO (Bull. Soc. Chim. biol., 1931, **13**, 47—60).—The reduced glutathione in the minced muscle of fish of several species diminishes very slowly on exposure to air. When the tissue is exposed to ether or chloroform vapour the rate of disappearance of reduced glutathione is even less rapid. Anæsthetisation of the fish before extraction of the muscle does not affect the quantity of reduced glutathione in the latter. Experiments on the rate of reduction of methylene-blue at p_H 7·4 by aqueous extracts of brain or by solutions of pure glutathione in presence or in absence of tissue residues show that the action of chloroform and ether is exercised on the tissue residues. W. O. KERMACK.

Reversible coagulation in living tissue. I. W. D. BANCROFT and J. E. RUTZLER, jun. (Proc. Nat. Acad. Sci., 1931, **17**, 105—111).—The physiological effect of ether, amytal, morphine, and histamine is to coagulate certain nerve-colloids, apparently the proteins. Anaphylactic shock is due to the coagulation of certain nerve-proteins, chiefly those of the sympathetic nerves. Sodium thiocyanate peptises proteins and should therefore alleviate or counteract disturbances due to coagulation of the nerve-proteins. Intravenous injections of solutions of sodium thiocyanate bring rabbits out of the unconsciousness due to ether, amytal, or morphine more rapidly than is normal. The treatment can also prevent death from strychnine or histamine and can prevent anaphylactic shock in rabbits previously sensitised by subcutaneous injection of an egg-white sol. E. S. HEDGES.

Influence of p_H on the activity of certain local anæsthetics as measured by the rabbit's cornea method. T. D. GERLOUGH (J. Pharm. Exp. Ther., 1931, **41**, 307—316).—The durations of the local

anæsthetic actions of solutions of procaine hydrochloride, procaine borate, and of butyn as measured by the rabbit's cornea method increase with increase of the p_H of the solution, whilst that of butesin picrate is apparently independent of p_H. The duration of anæsthesia produced by procaine hydrochloride or butyn was greater when the anæsthetic was dissolved in buffer solutions or at concentrations greater than 0·01*M*. The anæsthetic activity of buffered butyn solutions was not influenced by *N*/8-sodium chloride, *N*/8-potassium chloride, *N*/7-sodium sulphate, and *N*/5-magnesium sulphate.

W. O. KERMACK.

Effect of certain drugs on blood-sugar concentration. I. BURDI (Z. ges. exp. Med., 1930, **71**, 480—488; Chem. Zentr., 1930, ii, 1091—1092).—Administration of chloral hydrate, hedonal, and paraldehyde leads to an increase in blood-sugar which in the case of the first is counteracted by insulin. Sulphonal leads to hypoglycæmia and alcohol also lowers the blood-sugar. Veronal and trional produce no regular changes, and dionin is without significant effect. In dogs, morphine and heroin hydrochlorides increase the blood-sugar. L. S. THEOBALD.

Avertin detoxication by glycuronic acid. W. STARK (Schmerz, Narkose, Anæsth., 1930, **3**, 247—261; Chem. Zentr., 1930, ii, 3808).—Detoxication is conditioned by pairing with glycuronic acid. Moderate doses of thyroxine favour detoxication, whilst large doses increase the toxic action.

A. A. ELDRIDGE.

Irritative properties of various halogenated and unhalogenated oils and their compounds. L. A. CRANDALL, P. H. HOLINGER, and E. L. WALSH (J. Pharm. Exp. Ther., 1931, **41**, 347—354).—Forty-eight different halogenated and unhalogenated oils have been injected intrapleurally and intrapericardially into dogs. Of the natural oils suitable as bases for halogenation, olive oil and lard oil are the least irritating. Halogenation increases the irritative properties of an oil. Increased irritation is also caused by the presence of small quantities of free fatty acid. W. O. KERMACK.

Tolerance to benzene. N. V. LAZAREV, L. P. BRÜLLOVA, S. N. KREMNEVA, L. T. LARIONOV, M. P. LUBIMOVA, and D. J. STALSKAJA (Arch. exp. Path. Pharm., 1931, **159**, 345—358).—The effect of benzene on white mice is less marked in a fasting condition than after feeding only in as far as it brings about epileptoid convulsions. When the animals are repeatedly exposed to the effects of benzene a deterioration in their condition occurs followed by development of tolerance to the poison which exhibits itself in an increase in weight, and in the erythrocyte count as well as in the disappearance of abnormal forms of red blood-cells. In the first stage a lowering of resistance to infection is observed, but normal resistance returns during the acquirement of tolerance.

W. O. KERMACK.

Pharmacological action of certain phenol esters with special reference to the etiology of so-called ginger paralysis. M. I. SMITH, E. ELVOVE, and W. H. FRAZIER (U.S. Publ. Health Rep. Reprint No. 1419, 1930, 1—16).—*o*-Tolyl phosphate is much more toxic to the rabbit than phenol or the *p*-ester, or *o*-, *m*-, or *p*-cresol. Whereas the systemic action of phenol and the cresols is prompt, that of the *o*-ester is delayed. In the monkey, the toxicity of phenol and the cresols is of the same order as in the rabbit; the *p*-ester has the same pharmacological action as *p*-cresol, but the *o*-ester can produce a partial motor paralysis after 6—8 days. In the chicken the symptoms of the disease produced in man after taking adulterated fluid extract of Jamaica ginger are reproducible with remarkable uniformity; such symptoms were obtained only on administration of *o*-tolyl phosphate. It is probable that the lethal dose for man is about 1 g. of the *o*-ester per kg. body-weight, whilst 2 g. would cause a moderate motor paralysis. The difference in species susceptibility to the *o*-ester is attributed to differences of absorption from the alimentary canal. The fraction behaving pharmacologically like *o*-tolyl phosphate was obtained from the adulterated extract after removal of the alcohol, on distillation at 246—275°/50 mm.; it contained no free phenols and gave Melzer's benzaldehyde test. C. C. N. VASS.

Chemical constitution and biological action. II. T. SASAKI and H. UEDA (Biochem. Z., 1931, **232**, 260—268; cf. J. Biochem. Japan, 1930, **12**, 429).—3-Aminocarbostyryl is an amyostatic poison, but the 3 : 6-diamino-derivative has scarcely any such effect, whilst the 1- and 7-amino-derivatives as well as the ethyl ester of *p*-aminophenylalanine have none. Of five ethyl diaminobenzoates the 2 : 4-compound has the most powerful amyostatic action on mice, the 2 : 5-compound is half as powerful, and the 2 : 3-, 3 : 4-, and 3 : 5-compounds (equal) are again half as powerful as the 2 : 5-compound. In guinea-pigs, however, the 3 : 4- and 3 : 5-compounds are most powerful, the 2 : 4- and 2 : 5-compounds are much less active, and the 2 : 3-compound is least so. *o-Nitrobenzylidenehydantoin*, m. p. 300° (decomp.), from *o*-nitrobenzaldehyde and acetylhydantoin, gives 3-aminohydrocarbostyryl (*acetyl* derivative, m. p. 241—242°) when boiled with hydriodic acid and phosphorus. *6-Nitro-3-acetamidohydrocarbostyryl*, m. p. 289—290°, is reduced to the *hydrochloride*, m. p. above 300°, of the corresponding *diamino*-compound. The *ethyl* ester of *dl-p*-aminophenylalanine has m. p. 243—244°. The *hydrochloride*, m. p. 219—220°, of *ethyl* 2 : 3-*diaminobenzoate* is obtained by reduction of 2-nitro-3-acetamidobenzoic acid. The *hydrochloride* of *ethyl* 2 : 4-*diaminobenzoate* has m. p. 203—204°. The hydrochloride of ethyl 2 : 5-diaminobenzoate was also prepared by reduction of 5-nitroacetanthranilic acid. W. MCCARTNEY.

Influence of β-1-piperidylethyl acetyltropate ("navigan") on the blood-sugar mobilisation in the liver. K. TODA, Y. TANIUCHI, and M. NAKANO (Folia Pharm. Japon., 1930, **11**, No. 2, 15).—In perfusion experiments with toad livers navigan slightly increased the sugar content; when injected with adrenaline it depresses the sugar mobilisation of the latter. CHEMICAL ABSTRACTS.

Physostigmine-like action of certain synthetic urethanes. A. C. WHITE and E. STEDMAN (J. Pharm. Exp. Ther., 1931, **41**, 259—288).—The action

of miotine (methylurethane of α-m-hydroxyphenylethyldimethylamine) on the eye, intestine, uterus, bladder, bronchioles, heart, vessels, vagus, and response to acetylcholine, salivary glands, suprarenals, and voluntary muscle is similar to that of physostigmine. The methylurethanes of o-hydroxybenzyltrimethylammonium iodide, m-hydroxybenzyldimethylamine, and of p-hydroxybenzyldimethylamine behaved similarly. The toxicities of miotine and physostigmine are not significantly different, and the symptoms produced are identical, but the toxicities of the other three urethanes are considerably smaller. It is concluded that the actions of physostigmine and of miotine are exerted in large measure through the same mechanism, probably by inhibiting the action of the esterase responsible for hydrolysis of acetylcholine and thus preventing the destruction and thereby producing an accumulation of the latter in the tissues. W. O. KERMACK.

Chemotherapy of quinoline compounds. II. Action of certain quinoline compounds on *Paramecia*. U. BRAHMACHARI, T. BHATTACHARYYA, P. BRAHMACHARI, R. BANERJEA, and B. B. MAITY (J. Pharm. Exp. Ther., 1931, **41**, 255—257).—Besides the quinoline derivatives previously reported (A., 1930, 1316), 8-amino-4-phenylquinaldine hydrochloride has a toxic action on *Paramecia*. 6-Amino-4-phenylquinaldine hydrochloride as well as certain styryl- and anil-quinoline derivatives (cf. A., 1930, 1445) were not toxic to *Paramecia* at concentrations of 1 : 2000 or below. W. O. KERMACK.

Hyperthermia and hyperglycæmia with tetrahydro-β-naphthylamine. J. F. HEYMANS (Ar. Int. Pharm. Ther., 1929, **35**, 153—168; Chem. Zentr., 1931, i, 303).—Insulin diminishes tetrahydro-β-naphthylamine hyperglycæmia, and may even cause hypoglycæmia, without affecting the hyperthermia. The hyperthermia and hyperglycæmia are therefore independent; the former is observed in dogs after adrenal- and parathyroid-ectomy, and the latter is attributed to liberation of adrenaline.
A. A. ELDRIDGE.

Effect of certain diuretics on the concentration of blood-chlorides in dogs. H. L. HANSEN, L. S. FOSDICK, and C. A. DRAGSTEDT (J. Pharm. Exp. Ther., 1931, **41**, 325—331).—Neither in intact nor in nephrectomised dogs is there any significant change in the blood-chloride content prior to, during, or following the diuresis produced by diuretics such as euphyllin (theophylline-ethylenediamine) or by mercurials such as novasurol or salyrgan. The fall that occurs in the blood-chloride concentration of nephrectomised dogs when distilled water is injected into the peritoneal cavity was slightly but definitely less when either type of diuretic was simultaneously administered. W. O. KERMACK.

Accumulation of guanidine in the blood following acute liver injury by carbon tetrachloride, chloroform, arsenic, or phosphorus. J. T. CUTLER (J. Pharm. Exp. Ther., 1931, **41**, 337—345).—During the poisoning there is an increase in blood-guanidine and a fall in blood-sugar. There may be no general retention of nitrogenous substances, so that the increase in blood-creatinine is presumably due to liver and not to kidney damage. The increase in amino-acid nitrogen which occurs is also probably to be referred to the same cause. W. O. KERMACK.

Chronic morphine poisoning. I. Blood picture of morphinism. II. Sedimentation of the blood-corpuscles in the morphine addict and the addicted dog. M. SUO (Folia Pharm. Japon., 1930, **11**, No. 2, 127—143, 143—152).
CHEMICAL ABSTRACTS.

Relationship between vomiting, blood-sugar, and uric acid regulation centre. I. Influence of emetics on vomiting and blood-sugar. M. MUN (Folia Pharm. Japon., 1930, **11**, No. 1, 75—83).—The following emetics, injected intravenously into dogs, are in order of reduction of blood-sugar: emetine hydrochloride, antimonial wine, copper sulphate, erycon, *apo*morphine hydrochloride.
CHEMICAL ABSTRACTS.

Responses of sheep to *Zygadenus gramineus*. A. R. MCLAUGHLIN (Science, 1931, **73**, 135—136).—Intravenous injection of an extract of *Z. gramineus* is followed by respiratory inhibition. Caffeine dissolved in sodium benzoate and sodium chloride solution stimulates respiration affected by this extract.
L. S. THEOBALD.

Chinese antidiabetics. III. Effect on the blood-sugar of rabbits. P. MIN (Folia Pharm. Japon., 1930, **11**, No. 2, 181—187; cf. this vol., 510).—Alcoholic extracts of *Bupleurum falcatum, Lycium chinense, Fritillaria verticillata*, and *Anemarrhena asphodeloides* rapidly increase the blood-sugar; those of *Cannabis sativa, Pachyma coccus, Astragalus membranaceus, Morus bombycis, Atractylis ovata, Phellodendron amurense, Pueraria hirsuta*, and *Rehmannia lutea* first increase and then decrease it.
CHEMICAL ABSTRACTS.

***Leonurus sibericus*, L. II. Pharmacological study of leonurine.** S. KUBOTA and S. NAKASHIMA (Folia Pharm. Japon., 1930, **11**, No. 2, 159—167).
CHEMICAL ABSTRACTS.

Active principles of digitalis leaves. Y. KOBAYASHI (Proc. Imp. Acad. Tokyo, 1931, **7**, 76—79).—Various fractions obtained from the alcoholic extract of the leaves of digitalis by fractional precipitation with water, saturated sodium chloride, and ammonium sulphate solutions, ether, chloroform, and benzene showed a digitalis-like action. The glucoside which was most soluble in water had the least effect on the heart. B. LEVIN.

Effect of ions. IV. Influence of various ions on the toad's heart-beat. V. Influence of various ions on the excitability of strips of frog's heart muscle. S. HOMMA (Japan J. Med. Sci., III, 1930, **1**, 109—146, 147—156).—IV. Perfusion with Ringer solutions containing bromine and iodine ions increases the rate of beat of the isolated heart of the Japanese toad, whilst the lithium ion markedly decreases it. The sulphate ion has only a small effect, whilst the nitrate and thiocyanate ions are negatively chronotropic in concentrated solutions, positively chronotropic in dilute solutions. The use of rubber tubing must be avoided, since it is positively chronotropic. The potassium ion exerts

an antagonistic action on the lithium ion, 1 part of potassium ion to 18 parts of lithium ion neutralising the effect of the latter.

V. Bromine, iodine, and thiocyanate ions increase the excitability of strips of the ventricle in dilute solution, whilst they decrease it in more concentrated solutions. The sulphate ion increases it in nearly all concentrations used, whilst the nitrate ion acts in the opposite manner. B. LEVIN.

Toxicity of fresh and preserved mineral waters. J. GODONNÈCHE (Bull. Soc. Chim. biol., 1931, **13**, 41—46).—The toxicity of various natural waters has been examined by intraperitoneal injection into guinea-pigs. In general the toxicity is greater when the water is injected fresh from the spring, otherwise it has approximately the same effect as an artificial solution of the same composition.
W. O. KERMACK.

Vascular action of iodide ion. M. KOCHMANN (Arch. exp. Path. Pharm., 1931, **159**, 516—519).—Sodium iodide solutions of concentrations from 1 : 60 to 1 : 1000 have a vasodilator action on the frog.
F. O. HOWITT.

Influence of arsenic and antimony compounds on enzymic functions of the organism. VII. Buffering power of arsenates and arsenites. A. N. ADOVA and J. A. SMORODINCEV (Biochem. Z., 1931, **232**, 459—468).—The buffering power of 1% disodium arsenite solution is four times as great as that of 1% disodium arsenate solution. When sodium arsenate solution is diluted (1 : 1) the p_H is decreased. Moderate dilution of sodium arsenite solution increases the p_H, but great dilution (50-fold) decreases it. The buffering power of 1% sodium arsenite solution is equal to that of phosphate buffer and 6 times as great as that of citrate buffer. At a dilution of 0·033*N* the hydrogen-ion concentrations of solutions of sodium arsenate and sodium arsenite are equal, and when this is so the buffering power of the arsenite towards alkali is two thirds, and towards acid one third, of that of the arsenate. The buffering power of arsenic acid towards alkali is twice that of phosphate buffer and 12 times that of citrate buffer. Towards acid the buffering power of sodium arsenate solution is half that of phosphate buffer and one quarter of that of the latter towards alkali. Phosphate mixture has 6 times the buffering power towards alkali and 1·5 times that towards acid of citrate mixture. The detrimental effect produced by the sodium arsenate solutions used medically for injection is due to the disturbance in acid–base equilibrium. Such solutions should have the same p_H as have the blood and the fluids of the tissues. W. MCCARTNEY.

Radioactive indicator method for determining the solubility of acid lead arsenate in the alimentary tract of the silkworm. F. L. CAMPBELL and C. LUKENS (J. Econ. Entom., 1931, **24**, 88—94).—A solution of thorium-*B* in acetic acid mixed with lead arsenate was fed to silkworms and the subsequent distribution of lead examined by radioactive measurement. At least 25% of a lethal dose of acid lead arsenate passes into solution in the alimentary tract during the survival period. Basic lead acetate was less soluble. A. G. POLLARD.

Interaction of metallic containers and living organisms. II. J. SCHWAIBOLD and F. FISCHLER (Biochem. Z., 1931, **232**, 240—253).—The growth of young tadpoles (4—6 days after hatching) in vessels made of various materials, and the corrosion of the vessels, were examined. In glass and porcelain vessels growth was normal, aluminium, iron, and tin had little effect, but zinc inhibited growth considerably and copper proved very toxic in extremely small doses.
P. W. CLUTTERBUCK.

Treatment of mercury poisoning with [injected] sodium thiosulphate. J. C. G. PODESTA and R. E. TORVISO (Semana Méd., 1931, I, 19—24).
CHEMICAL ABSTRACTS.

Influence of irradiation on the behaviour of silver in the organism. I. Investigation with young rats. L. PINCUSSEN and W. ROMAN (Biochem. Z., 1931, **232**, 202—208).—Litters of young rats maintained at 20—40° were injected 4 hrs. to 2·5 days after birth with 0·2 c.c. of 0·5% silver sulphate solution. Half of each litter was irradiated with an Osram lamp or the mercury-vapour lamp and the other half used as controls. All the animals were then killed and the silver fractions (ionised, united with protein, metallic) were determined. The mean percentage recoveries of silver for the three fractions were for the unirradiated animals 54·08, 28·62, 17·31%, for the animals irradiated with the Osram lamp 27·33, 57·16, 15·51%, and for the animals irradiated with the mercury-vapour lamp 61·21, 25·02, 13·77%.
P. W. CLUTTERBUCK.

Fluctuation of blood-cholesterol, -calcium, and -sugar in blood of rabbits poisoned with thallium. S. KOYANAGI (Folia Pharm. Japon., 1930, **11**, No. 2, 202—213).—Repeated subcutaneous administration of thallium causes a rise in blood-cholesterol, -free cholesterol, and particularly -cholesteryl esters. Subcutaneous or intravenous administration of thallium causes a fall in blood-calcium. Intravenous administration causes hyperglycæmia, whilst subcutaneous administration causes either a rise, or a fall superseded by a rise, in blood-sugar.
CHEMICAL ABSTRACTS.

Curative action of plants and plant juices in sub-acute uranium poisoning. G. EISNER (Biochem. Z., 1931, **232**, 218—228).—Rabbits which on poisoning with small amounts of uranium nitrate die on an oats–water diet, remain alive on addition to the diet of turnip, fresh green food, cauliflower leaves, or the fresh press-juice thereof before or after heating and filtering or treating with alcohol.
P. W. CLUTTERBUCK.

Additive compound theory of enzyme action. B. WOOLF (Biochem. J., 1931, **25**, 342—348).—An enzyme is a definite chemical compound capable of forming an additive compound with all its substrates, the actual process of catalysis consisting of a series of tautomeric changes in this enzyme–substrate complex. S. S. ZILVA.

Manometric determination of catalase. A. FUJITA and T. KODAMA (Biochem. Z., 1931, **232**, 20—34).—A new method for the manometric determination of catalase is described. The catalase quotient ($Q_{cat.}$) is defined as the amount of oxygen

liberated in 30 min. at 38° by 1 mg. of substance (dry weight) from hydrogen peroxide, the result being regarded as valid only if less than 50% of the total peroxide is decomposed. The values for a large number of bacteria and tissues are tabulated.

P. W. CLUTTERBUCK.

Dextrose-oxidase. IV. Dextrose-oxidase from *Aspergillus niger*; its behaviour towards disaccharides, glycuronic acid, ethyl alcohol, methylene-blue, and monoiodoacetic acid. D. MÜLLER (Biochem. Z., 1931, **232**, 423—434; cf. A., 1929, 1489).—Neither lactose nor—if accompanying invertase is destroyed—sucrose is attacked by dextrose-oxidase. Maltose is directly attacked by an enzyme, *maltose-oxidase*, which accompanies dextrose-oxidase and is more thermolabile than the latter. The product of air-oxidation is a non-reducing substance. So far as at present known the only compounds of which the oxidation is catalysed by dextrose-oxidase are such as have six carbon atoms and the same configuration as dextrose as far as carbon atoms 1 and 6 are concerned. Hence glycuronic acid and ethyl alcohol are not attacked by dextrose-oxidase. The enzyme is less sensitive to the action of monoiodoacetic acid than is zymase. Of the known dehydrases only that of malic acid is separated along with dextrose-oxidase. The accelerated reduction of methylene-blue caused by material containing the enzyme is restricted or inhibited by dextrose, lævulose, gluconic acid, and certain other substances.

W. MCCARTNEY.

Amylosynthease. S. NISHIMURA (Biochem. Z., 1931, **232**, 156—164).—Higher dextrins are enzymically synthesised from "limit" dextrin (lowest achroodextrin) and shown to be much more readily saccharified than the latter by malt-amylase. The greater is the degree of polymerisation the more closely does the course of saccharification approximate to that of starch (cf. A., 1930, 1218, 1477, 1619).

P. W. CLUTTERBUCK.

Diastase from wheat. D. V. KARMARKAR and V. N. PATWARDHAN (J. Indian Inst. Sci., 1930, **13A**, 159—164).—The diastase from malted wheat is more active than that from barley malt prepared under the same conditions. The temperature and p_H optima are 49—58° and 4·6, respectively. The enzyme is inactivated when heated for 1 hr. at 160° in the dry state or in solution by 14 days' dialysis or by treatment with pepsin. Neither trypsin nor papain inactivates the enzyme. Neutral salts or amino-acids are without effect on the activity of the diastase.

F. E. DAY.

Action of ptyalin on starch. II. Effects of electrolytes. J. R. BROEZE (Biochem. Z., 1931, **231**, 365—384).—In the absence of electrolytes the velocity of reaction is very small; minute concentrations of these are sufficient to raise it greatly. The velocity is only slightly augmented when the valency of the cations rises. The increase of the velocity under the influence of univalent cations follows a lyotropic series: $CNS<NO_3<Cl,F$.

H. W. DUDLEY.

Starch. II. Limit of enzymic decomposition, and the amylase complement. III. Changes in rotatory power occurring in the enzymic decomposition of starch. R. WEIDENHAGEN and A. WOLF (Z. Ver. deut. Zucker-Ind., 1930, **80**, 866—876, 935—948; cf. A., 1930, 1168).—II. The authors failed to confirm the statements of Pringsheim and others (B., 1923, 858; 1924, 28, 843; A., 1926, 864) that yeast and peptic products of certain proteins contain an amylase complement which enables malt-amylase to saccharify the so-called stable dextrin with ease and thus to effect a complete conversion of starch into maltose. Stable dextrin prepared from starch by conversion with malt-amylase and subsequent fermentation was almost non-reducing, had $[\alpha]_D$ +167°, and appeared to be substantially a single substance. A product obtained similarly by means of pancreatic amylase had 16% of the reducing power of maltose and $[\alpha]_D$ +161°. Malt-amylase attacked the stable dextrin so slowly that about 224 times as much enzyme was required as for a starch saccharification at the same rate. Neither the rate of saccharification of the stable dextrin nor the limit of saccharification of starch, by malt-amylase, was affected by addition of yeast extract or peptic products from yeast-, egg-, or serum-albumin or gelatin, prepared as described by Pringsheim. The stable dextrin is not altered by heating with glycerol in accordance with Pringsheim's method of preparing trihexosan. The latter substance appears to be only a somewhat modified form of starch; it undergoes saccharification by amylase almost as readily as starch, to the extent of 40%, but when about 60% of sugar has been formed the residual matter is more resistant to saccharification than the stable dextrin.

III. In the conversion of starch and trihexosan by malt-amylase or pancreatic amylase, the mutarotation observed on addition of alkali at various stages confirmed Kuhn's statement that maltose is liberated in the α-form by pancreatic amylase and in the β-form by malt-amylase (A., 1925, i, 636). In starch conversions by either enzyme the amounts of maltose found iodometrically, up to 40%, agreed fairly well with those calculated from the change in rotation, corrected for mutarotation, but when 60—70% of sugar had been formed discrepancies were encountered indicating a fall in $[\alpha]_D$ of the unsaccharified residue to 160—170° or lower. Still more pronounced was the calculated fall in $[\alpha]_D$ of the residue from trihexosan after 40—50% of maltose had been formed.

J. H. LANE.

Hydrolysis of sucrose by aqueous extracts of mushrooms. R. WEIDENHAGEN (Z. Ver. deut. Zucker-Ind., 1930, **80**, 569—571).—The statement of Ivanov and others (A., 1930, 1067) that mushrooms contain maltase but no invertase conflicts with the author's view of the nature of these enzymes (A., 1928, 1157, 1281; 1929, 352, 722) and is not borne out by experiments now described, which showed rapid hydrolysis of sucrose and raffinose, but scarcely any action on maltose, melezitose, or melibiose. The inverting enzyme present was accordingly β-*h*-fructosidase.

J. H. LANE.

Fission of sucrose by α-glucosidase from yeast. R. WEIDENHAGEN (Z. Ver. deut. Zucker-Ind., 1930,

80, 374—383).—Sucrose is hydrolysed almost twice as rapidly as maltose by α-glucosidase (maltase). In both cases the unimolecular character of the reaction is masked by the retarding influence of α-dextrose. The enzyme was obtained from neutral yeast autolysate by adsorption on β-aluminium hydroxide, followed by elution with diammonium hydrogen phosphate solution after a preliminary elution with potassium dihydrogen phosphate solution to remove a small amount of adsorbed β-*h*-fructosidase. The latter enzyme also hydrolyses sucrose, but is most active at p_H 3·5—5, whilst the optimum reaction for α-glucosidase is p_H 6—7 and the limits of its activity are about p_H 5—8. The hydrolysis of sucrose by yeast is thus due, not to a single enzyme, invertase, but to one or both of the enzymes mentioned above. If α-glucosidase alone is present there is no inversion at p_H 4, whilst if both are present the activity at p_H 7 is more than 40% of that at p_H 4·5, since at p_H 7 β-*h*-fructosidase has 40% of its maximum activity. (Cf. A., 1929, 352.) J. H. LANE.

Specificity of the α-glucosidases. H. KARSTROM (Biochem. Z., 1931, 231, 399—403).—The α-glucosidase of *B. coli* which hydrolyses maltase is unable to hydrolyse either sucrose or melezitose and hence the views of Weidenhagen (A., 1928, 1157; 1930, 499) cannot be accepted. W. McCARTNEY.

Co-enzyme of lactic acid production in muscle. K. LOHMANN (Naturwiss., 1931, 19, 180).—The system adenylpyrophosphate + magnesium appears to be the co-enzyme in the process of lactic acid formation in muscle. B. LEVIN.

Analysis of bioluminescences of short duration, recorded with photo-electric cell and string galvanometer. E. N. HARVEY and P. A. SNELL (J. Gen. Physiol., 1931, 14, 529—545).—The rates of decay of the luminescence produced by mixing solutions containing luciferin and luciferase (from *Cypridina hilgendorgii*; cf. A., 1928, 814, 1051) in presence of an excess of oxygen have been followed by means of a photo-electric cell, the readings being made after amplification on a string galvanometer. For rapid flashes of luminescence the decay is logarithmic if the ratio of luciferin to luciferase is small; logarithmic plus an initial flash if this ratio is greater than 5, but the logarithmic law does not hold exactly when the ratio is very large. The velocity coefficient of rapid flashes of luminescence is approximately proportional to enzyme concentration, is independent of luciferin concentration, and varies approximately inversely as the square root of the total luciferin (luciferin plus oxyluciferin) concentration. For large total luciferin concentrations, the velocity coefficient is almost independent of the total luciferin. W. O. KERMACK.

Phosphatases. I. Kidney-phosphatase of various animals. II. Liver-phosphatase of these animals. III. Phosphatase content of kidneys and liver in experimental nephritis. IV. Optimal and decomposition temperatures of kidney-phosphatase. V. Glycerophosphatase of leucocytes. VI. Phosphatases in bile and in pancreatic juice. M. UMENO (Biochem. Z., 1931, 231, 317—323, 324—327, 328—333, 334—338, 339—345, 346—351).—I. The phosphatase contents of the kidneys of the following animals decrease in the order: hen, cat, dog, ox, toad, rabbit, guinea-pig. The cortex of the kidneys contains more phosphatase than does the medulla and the medulla contains more than do the papillæ.

II. Phosphatase from the liver is, in general, about half as active as that from the kidneys of the same animal and varies in its activity according to the species of animal from which it is obtained. The activity of the liver-phosphatases decreases in the order: hen, rabbit, dog, guinea-pig, toad.

III. In experimental nephritis in rabbits the phosphatase content of the liver is slightly reduced, whilst that of the kidneys is reduced to one half to two thirds of the normal amount.

IV. Phosphatase from the kidneys of cattle and dogs exhibits greatest activity at 42·5°. Below this temperature the activity decreases slowly and above it decreases rapidly, being completely destroyed at 60—65°.

V. Leucocytes from leucæmic (but not from normal) human blood and also those from rabbit's blood contain large amounts of phosphatase, but the enzyme is not present either in human or in rabbit erythrocytes.

VI. Bile contains considerable amounts of a glycerophosphatase. The enzyme is also present in pancreatic juice (which contains about half as much as does bile) and in considerable amounts in the mucous membrane of the stomach, duodenum, and small intestine as well as in the salivary glands. Liver, spleen, and pancreatic glands also contain glycerophosphatase. The amount of enzyme in the different organs is independent of that in their secretions. W. McCARTNEY.

Reversion of protein hydrolysis. A. SARLUY (Arch. Neerl. Physiol., 1931, 16, 136—144).—The conclusion of Wasteneys and Borsook (cf. A., 1929, 1197) that protein synthesis takes place when a protein hydrolysate is incubated and shaken with benzene, benzaldehyde, toluene, xylene, or benzoic acid is criticised. In the case of benzaldehyde Schiff's bases are probably formed. In the case of benzene, toluene, and xylene only adsorption on the emulsion takes place and no decrease in the number of carboxyl groups can be detected by the titration method of Willstatter and Waldschmidt-Leitz (A., 1922, ii, 169). W. O. KERMACK.

Action of pancreatin on collagen in the absence of neutral salts and buffers. I, II. A. KUNTZEL and O. DIETSCHE (Biochem. Z., 1931, 231, 423—434, 435—440).—I. Collagen is decomposed by pancreatin in the absence of neutral salts and buffers to an extent increasing very greatly as the degree of subdivision of the material is increased and, to a smaller extent, as its water content increases. In the early stages of the process the decomposition proceeds more rapidly than in the later stages and its extent likewise increases, although not proportionally, with rise of temperature, at least between 35° and 60°. Within certain limits the extent of decomposition is directly proportional to the amount of pancreatin used.

II. Provided that it is renewed every 12 hrs. pancreatin solution at 40° after 11 days decomposes collagen to the extent of 73% of its weight, and it is probable that the collagen could be completely decomposed and brought into solution if the treatment were sufficiently prolonged. The rate of decomposition increases during about the first 4 days and then gradually decreases. At above 55° the decomposition proceeds very rapidly in a different manner and probably leads eventually to complete decomposition and dissolution. W. McCartney.

Relation between the swelling and the proteolysis of collagen. F. Nauen (Biochem. Z., 1931, **231**, 441—445; cf. preceding abstract).—The proteolysis of collagen by pancreatin is greatly stimulated by salts of benzoic, salicylic, and *p*-hydroxybenzoic acids, the extent of the stimulation being proportional to the degree of swelling produced. These salts are much more effective than are the neutral salts used by Stiasny and Ackermann (A., 1923, ii, 301). That the phenomenon is a general one and that the extent of proteolysis depends on that of swelling is proved by the fact that collagen swollen in dilute hydrochloric acid is subsequently decomposed by pancreatin to an extent proportional to the amount of swelling caused.

W. McCartney.

Proteolytic enzymes. VII. Peptidases of green malt. M. Sato (Compt. rend. Trav. Lab. Carlsberg, 1931, **19**, No. 1, 1—26; cf. A., 1930, 93).—The affinity of the peptidase complex of malt for alanyl- and leucyl-glycine has been determined (cf. A., 1930, 642). The malt extracts used were prepared from fresh and dried malt by extraction with (*a*) glycerol, (*b*) water, and the dialysed solution therefrom. The extracts varied in their action on the peptides. At p_H 7·9, the velocity of hydrolysis of alanylglycine is practically independent of the substrate concentration, whilst that of leucylglycine increases rapidly with increasing substrate concentration. At p_H 8·5, the velocity of hydrolysis of leucylglycine first increases with increasing substrate concentration up to 0·1—0·2*M*, and thereafter decreases. It was found, however, that the addition of leucylglycine strongly inhibits the hydrolysis of alanylglycine. Fresh glycerol extracts of malt have a powerful action on leucylglycylglycyl-, leucylglycyl-, leucyl-, and alanyl-glycine, but attack alanylglycylglycine very little. The experiments support the conclusion that there are two or more distinct peptidases in malt. B. Levin.

Protein crystals possessing tryptic activity. J. H. Northrop and M. Kunitz (Science, 1931, **73**, 262—263).—A crystalline protein which can digest caseinogen and gelatin in neutral solution has been prepared from commercial preparations of trypsin.

L. S. Theobald.

Beer yeast. Conditions of its action on cystine. R. Fabre and H. Simonnet (Compt. rend., 1931, **192**, 852—854).—Colloidal silica, kaolin, and fuller's earth cause no diminution of the thiol compounds or the reduction of cystine in an aqueous extract of dried yeast. Ferric ions inhibit the reduction and "norit" charcoal removes the thiol derivatives and the reducing power of the solution.

C. C. N. Vass.

Effect of nickel and cobalt on the development of *Aspergillus niger*. M. Mokragnatz (Bull. Soc. Chim. biol., 1931, **13**, 61—71).—The presence of small quantities of nickel in the culture medium accelerates the growth of cultures of *A. niger*, the maximum effect being observed with concentrations of 1 in 15,000. Cobalt exercises a toxic action at concentrations of 1 in 250,000 or greater. Nickel is taken up from the medium by the mould, the ratio of the amount taken up to the concentration in the medium decreasing as the latter increases.

W. O. Kermack.

Biochemical action of boron. I. Influence of boric acid on cultures of *Mycodermes* and its probable role in the formation of the bloom of the grape. I. Voicu and M. Niculescu (Bull. Soc. Chim. biol., 1931, **13**, 150—171).—Boric acid up to 50 mg. per 100 c.c. for *Mycodermes* of wine, and up to 25 mg. per 100 c.c. for *Mycodermes* of medlar juice, promotes growth on Fernbach's medium containing 10—12% of dextrose. The toxicity of the free boric acid is increased and growth inhibited with smaller concentrations of dextrose (1·5%). Cultivation of the organism away from its natural medium diminishes the growth promotion and the toxic action of boric acid. C. C. N. Vass.

Reversibility of coupled reactions in biological systems and the second law of thermodynamics. D. Burk (J. Physical Chem., 1931, **35**, 432—455).—The extent to which the applicability of the second law of thermodynamics to life processes has received experimental support is indicated. The law is applicable to autotrophic reduction of carbon dioxide by hydrogen in the case of *Bacillus pycnoticus* (Ruhland, Jahrb. Wiss. Bot., 1924, **63**, 321), and the reversibility of this autotrophic reduction is practically complete when account is taken of the extraneous energy consumed in the metabolic processes of the organism. Other biological coupled reactions are described and summarised. L. S. Theobald.

Primitive form of *Anthomyces Reukaufii* and other inclusions introduced into amber by insects. J. Gruss (Woch. Brau., 1931, **48**, 63—68).—A number of micro-organisms associated with insect remains in amber are described and illustrated. The presence of microscopic crystals of pyrites is noted. F. E. Day.

Marine denitrifying organism. B. Lloyd (J. Bact., 1931, **21**, 89—96).—An organism (*B. costatus*) is capable of reducing nitrates under aerobic and anaerobic conditions. No ammonia is produced, reduction proceding by way of nitrite to free nitrogen.

A. G. Pollard.

Cellulose-fermenting organism (*Cl. cellulosolvens*, N. Sp.). P. B. Cowles and L. F. Rettger (J. Bact., 1931, **21**, 167—182).—The organism was isolated from horse fæces. Of numerous carbohydrates examined only cellulose, dextrin, arabinose, and xylose were decomposed by the organism. The products of decomposition of

cellulose were carbon dioxide, hydrogen, and organic acids. A. G. POLLARD.

Effect of temperature on the production of hydrogen sulphide by *Salmonella pullorum*. R. P. TITTSLER (J. Bact., 1931, **21**, 111—117).—Hydrogen sulphide production by *S. pullorum* ceases at temperatures above 37°, the optimum being 30°. Strains producing little or no hydrogen sulphide also produced little or no gas from carbohydrates.

A. G. POLLARD.

***B. coli* in water.** F. DIENERT and P. ETRILLARD (Ann. Inst. Pasteur, 1931, **46**, 277—290).—A discussion of the various methods of detecting *B. coli* in water. C. C. N. VASS.

Methylglyoxalylacetic acid. Its dismutation by *B. coli*. S. VEIBEL (Biochem. Z., 1931, **232**, 435—441; cf. Neuberg and Collatz, A., 1930, 1474).—Methylglyoxalylacetic acid can be almost quantitatively converted into almost pure *d*-α-hydroxyglutaric acid by the action of *B. coli*. The former acid yields a *bis*-p-*nitrophenylhydrazone*, m. p. 270—271°, and a *bis*-2 : 4-*dinitrophenylhydrazone* which forms a double *compound*, m. p. 252—253° (decomp.), with an equimolecular amount of pyridine and also a stable double *compound*, m. p. 245—246° (decomp.), with nitrobenzene. W. MCCARTNEY.

Acetic fermentation. I. Significance of cytochrome in the physiology of cell respiration. H. TAMIYA and K. TANAKA (Acta Phytochim., 1930, **5**, 167—211).—The formation of acetic acid by the fermentation of alcohol and acetaldehyde by *B. Pasteurianum* is followed. In agreement with the observations of Wieland and Bertho (A., 1929, 219, 1492) benzoquinone is found to be as good a hydrogen acceptor as oxygen; further, the rate of reaction is independent of the oxygen concentration within wide limits. The action of oxygen is strongly inhibited by carbon monoxide. The ratio of the affinities of oxygen and carbon monoxide to the enzyme is about 0·2—0·6/1. With fresh bacterial cultures the inhibiting effect of carbon monoxide is greatly lessened by light. The fermentation with benzoquinone is unaffected by carbon monoxide. The indophenol reaction of the acetic bacteria is inhibited by carbon monoxide and more in the dark than in light. Toluene inhibits the acetic fermentation with oxygen, but not with benzoquinone or methylene-blue; it also inhibits the indophenol reaction of acetic bacteria or yeast but not that of cytochrome-free extract of *Lactarius* oxidase. Shibata and Tamiya (A., 1930, 949) have shown that in presence of less than 0·01M concentration of benzoquinone the cytochrome of yeast remains strongly oxygenated. This is attributed to the greater diffusibility of the quinone, enabling it to combine with the activated hydrogen of the donator to the exclusion of the cytochrome-fixed oxygen. Toluene irreversibly denatures cytochrome, and carbon monoxide prevents its combination with oxygen; these two facts are sufficient to explain the results obtained. The experiments support the theory of Shibata and Tamiya that cytochrome acts as a "pressure regulator" for the oxygen and is identical with Warburg's respiration enzyme. F. E. DAY.

Physiological behaviour of the propionic acid group of bacteria. S. E. KENDALL and C. H. WERKMAN (Proc. Iowa Acad. Sci., 1929, **36**, 111).—Cultures of *Propionibacterium* are catalase-positive; carbohydrates, glucosides, and alcohols are attacked with production of propionic and acetic acids and carbon dioxide. CHEMICAL ABSTRACTS.

Production of propionic acid from pentoses by *Propionibacterium pentosaceum*. C. H. WERKMAN, R. M. HIXON, E. I. FULMER, and C. H. RAYBURN (Proc. Iowa Acad. Sci., 1929, **36**, 111—112).—In a medium of p_H 7·1 containing potassium monohydrogen phosphate 1 g., dried yeast 10 g., calcium carbonate 5 g., pentose 15 g., and water 750 c.c., xylose or arabinose affords propionic and acetic acids. A small quantity of a substance, probably succinic acid and probably derived from protein, is also formed. Glycerol affords only propionic acid in significant quantity. CHEMICAL ABSTRACTS.

Concentration of antipneumococcic and antimeningococcic horse sera. K. GOODNER (J. Immunol., 1930, **19**, 473—484).—During immunisation the amount of a euglobulin, of low solubility, in horse serum is increased. The antibody of the immune serum is associated with this protein.

CHEMICAL ABSTRACTS.

Advantages and disadvantages of the buffered diluent for diphtheria toxin. W. E. BUNNEY and B. WHITE (J. Immunol., 1931, **20**, 61—70).

CHEMICAL ABSTRACTS.

New diluent for diphtheria toxin in the Shick test. W. E. BUNNEY (J. Immunol., 1931, **20**, 71—84). CHEMICAL ABSTRACTS.

Stability towards heat of diphtheria toxin. K. ANDO and H. NISHIMURA (J. Immunol., 1930, **19**, 465—471).—Thermal stability is greatest in presence of acid. CHEMICAL ABSTRACTS.

Action of formaldehyde on diphtheria toxin. W. E. BUNNEY (J. Immunol., 1931, **20**, 47—59).—Toxoid formation appears to be due to the action of a compound resulting from interaction between formaldehyde and the amino-group of an amino-acid. A method of preparation consists in concentrating low-grade toxins and diluting in a solution of glutamic acid containing formaldehyde.

CHEMICAL ABSTRACTS.

Toxic properties of tuberculoproteins and polysaccharides. F. R. SABIN, F. R. MILLER, C. A. DOAN, and B. K. WISEMAN (J. Exp. Med., 1931, **53**, 57—80).—The temperature reaction in tuberculous or normal guinea-pigs and rabbits is elicited by the tuberculoprotein. Both proteins and polysaccharides cause a change in the white blood-cells.

CHEMICAL ABSTRACTS.

Sorption of bacteriophage by living and dead susceptible bacteria. I. Equilibrium conditions. A. P. KRUEGER (J. Gen. Physiol., 1931, **14**, 493—516).—The distribution of bacteriophage between a broth medium and cells of susceptible *S. aureus* suspended throughout the latter may conform to either of two types. With live resting bacteria, the bacteriophage is distributed in the same manner as is any substance soluble in both phases of a two-

phase system, *i.e.*, it follows the equation $C_b/C_a=K$, where C_b is the extracellular and C_a the intracellular concentration of the bacteriophage. The equilibrium is perfectly reversible. With heat-killed bacteria the distribution follows the adsorption law $a=kC^{1/n}$, where a is the amount adsorbed per unit weight of bacteria, C the concentration in the medium at equilibrium, $1/n=0{\cdot}80$, and K is a constant. The reaction in this case is not reversible. Experiments on the kinetics of the removal of bacteriophage from solution by living and by dead cells failed to reveal any significant difference in the velocities in the two cases. W. O. KERMACK.

Cryptotoxic properties of halogenated hydroxybenzoic acids. H. VINCENT and L. VELLUZ (Compt. rend., 1931, **192**, 648—651; cf. A., 1928, 674).—Halogenation of salicylic acid increases its neutralising effect against bacterial toxins, the order being iodine>bromine>chlorine. Sodium 3 : 5-di-iodosalicylate has a cryptotoxic power 100 times as great as that of the sodium salicylate. In the *p*-hydroxybenzoic acid series only the 3 : 5-dibromo-isomeride shows a marked increase in cryptotoxic power. Halogenation does not increase the cryptotoxic power of *m*-hydroxybenzoic acid. C. C. N. VASS.

Germicidal efficiency of sodium hydroxide, sodium carbonate, and trisodium phosphate. F. W. TILLEY and J. M. SCHAFFER (J. Agric. Res., 1931, **42**, 93—106).—Sodium hydroxide solutions were relatively highly toxic to a number of pathogenic organisms even in the presence of organic matter. Sodium carbonate or phosphate or slaked lime alone showed no notable germicidal properties, but each increased the efficiency of sodium hydroxide. The activity of such mixed solutions was considerably increased by heat. Additions of sodium carbonate and phosphate increased the germicidal action of soap solutions. Solutions containing 2% of sodium hydroxide and 10% of calcium hydroxide failed to kill *Mycobacterium tuberculosis* after 2 hrs. A. G. POLLARD.

Chemistry of disinfection. W. D. BANCROFT and G. H. RICHTER (J. Physical Chem., 1931, **35**, 511—530).—Antisepsis is mainly a state of narcosis which depends on the reversible coagulation of the colloids of the cell. Disinfection results from irreversible coagulation of these colloids. Adsorption of the drug precedes coagulation. L. S. THEOBALD.

Influence of adrenaline on the lipins of blood and organs. I. H. PAGE, L. PASTERNAK, and [in part] M. L. BURT (Biochem. Z., 1931, **232**, 295—309; cf. this vol., 528).—Subcutaneous administration to rabbits produces decreases in the phosphatide, cholesterol, fatty acid, and total fat contents of their blood-serum, in the phosphatide, fatty acid, and total fat contents of their kidneys, and in the phosphatide and cholesterol contents of their hearts. In the brains and hearts the degree of unsaturation of the fats is slightly decreased. An increase produced in the cholesterol content of the brains is accompanied by a decrease in the phosphatide content of these organs. The fatty acid, cholesterol, and total fat contents of the livers are increased by adrenaline administration. In rabbits suffering from lipæmia the effects of adrenaline administration may be masked by those due to the disease. The action of adrenaline on the serum is similar to but less pronounced than that of insulin, although the ways in which the two substances act are different. Except as regards the increase in cholesterol content of the brains and the slight decrease in fatty acid content of the kidneys there is no other similarity between the effects caused by the two hormones. W. MCCARTNEY.

Influence of the oxytocic and pressor hormones of the posterior pituitary lobe on basal metabolism. I. I. NITZESCU and I. GAVRILA (Compt. rend. Soc. Biol., 1929, **102**, 184—186; Chem. Zentr., 1931, i, 303).—The increase after injection of pitressin, 6·8—14·5%, is greater than after that of pituitrin; oxytocin has practically no effect. A. A. ELDRIDGE.

Effect of pitressin and pitocin on human blood-sugar. I. GAVRILA and G. MIHAILEANU (Compt. rend. Soc. Biol., 1930, **104**, 601—602; Chem. Zentr., 1930, ii, 3798—3799).—Subcutaneous injection of pitressin, but not that of pitocin, causes hyperglycæmia. A. A. ELDRIDGE.

Effect of pitressin and pitocin on glycæmia and blood-inorganic phosphorus. I. I. NITZESCU and G. BENETATO (Compt. rend. Soc. Biol., 1930, **103**, 1359—1362; Chem. Zentr., 1930, ii, 3798).—Subcutaneous or intravenous injection of pitressin into rabbits causes hyper-glycæmia and -phosphatæmia; intravenous injection of pitocin causes hyperglycæmia, but has no effect on the blood-phosphorus. A. A. ELDRIDGE.

Effect of pitocin and pitressin on the blood-calcium and -phosphorus. C. I. URECHIA, I. GROZE, and RETEZEANU (Compt. rend. Soc. Biol., 1930, **103**, 1363—1364; Chem. Zentr., 1930, ii, 3798).—Injection of pitocin increased the blood-phosphorus in half of the cases examined; the blood-calcium was unchanged. Pitressin depressed the blood-calcium, but did not affect the blood-phosphorus. A. A. ELDRIDGE.

Action of vagotonin on blood-sugar. T. BRIEU, G. FUCHS, D. SANTENOISE, and M. VIDACOVITCH (Compt. rend. Soc. Biol., 1930, **104**, 768—770; Chem. Zentr., 1931, i, 103).—The hypoglycæmic effect of vagotonin is not due to the presence of insulin; the curves differ. Vagotonin has no hypoglycæmic action on dogs after vagotomy or injection of atropine. A. A. ELDRIDGE.

Vagotonin and liver-glycogen. D. SANTENOISE, H. VERDIER, and M. VIDACOVITCH (Compt. rend. Soc. Biol., 1930, **104**, 770—772; Chem. Zentr., 1931, i, 103—104).—A close relation exists between the function of the vagus and the ability of the liver to store glycogen. A. A. ELDRIDGE.

Action [on blood] of extracts of salivary glands. C. I. URECHIA, CIOCANELLI, and RETEZEANU (Compt. rend. Soc. Biol., 1930, **104**, 595—598; Chem. Zentr., 1930, ii, 3800).—Extracts of the submaxillary and parotid glands depressed the blood-sugar and -cholesterol, but did not markedly affect the -calcium or -phosphorus. A. A. ELDRIDGE.

Standardisation of male sexual hormone on the basis of its anti-feminin action. L. LENDLE (Arch. exp. Path. Pharm., 1931, **159**, 463—487).—The injection of testicular extract into female rats inhibits the normal œstrus cycle. This action depends on an inhibition of ovulation and not on a direct antagonism of ovarian and male sexual hormones. Its application to a method of standardisation of testicular extracts is discussed. Extracts of posterior lobe of pituitary synergise the ovarian hormone, the combined action not being inhibited by simultaneous injection of testicular extract. F. O. HOWITT.

Determination of potency of male sexual hormone by its effect on the seminal vesicles of rodents. H. E. VOSS and S. LOEWE (Arch. exp. Path. Pharm., 1931, **159**, 532—544).—The seminal vesicles of castrated rats and mice following injection of testicular extracts show macroscopically an increase in the length-breadth index and in weight, and microscopically a formation of secretory cells and increased activity of the epithelial cells. Evidence of the latter precedes the macroscopic changes and the histo-cytological method is preferred for the evaluation of testicular extract potency. F. O. HOWITT.

Purification of the male hormone by high-vacuum distillation. E. DINGEMANSE, J. FREUD, S. KOBER, E. LAQUEUR, and A. P. W. MUNCH (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 1206—1209).—At 0·001 mm. and 80° the male hormone does not distil, but at 90° it is found in the distillate. This is suggested as a possible method for separating the male and female hormones. O. J. WALKER.

Mol. wt. of insulin. T. SVEDBERG (Nature, 1931, **127**, 438—439).—Sedimentation of insulin in centrifugal fields of $10^5 g$ at 20° between 3·5 and 12·3 shows it to be stable between p_H 3·5 and 7·0. The sedimentation constant is $3{\cdot}47\times10^{-13}$. Dissociation into low-molecular products occurs when the stability range is exceeded, but this dissociation is reversible if the material is not too acid or too alkaline. The sedimentation equilibrium at p_H 6·7—6·8 gives a mol. wt. of 35,100. Crystalline insulin is homogeneous with regard to mol. wt. and appears to be a well-defined protein of the egg-albumin class. L. S. THEOBALD.

Insulin and liver-glycogen. D. SANTENOISE, H. VERDIER, and M. VIDACOVITCH (Compt. rend. Soc. Biol., 1930, **104**, 773—774; Chem. Zentr., 1931, i, 104).—Insulin has only a mobilising action, and vagotonin a fixing action, on liver-glycogen. Earlier contradictory results are due to the use of insulin containing vagotonin. A. A. ELDRIDGE.

Resistance of insulin to the action of various bacteria. A. A. SCHMIDT and K. TULJTSCHINSKAJA (Biochem. Z., 1931, **231**, 352—364).—The activity of insulin is not destroyed by the action of *B. coli communis*, *Staphylococcus aureus*, *Streptococcus hæmolyticus*, or of some of the anaerobic bacteria of the fæces of the dog. Such fæces, however, contain putrefactive bacteria which destroy insulin. It seems that only those bacteria which contain proteolytic enzymes can destroy insulin and hence that the latter is a protein-like substance. W. MCCARTNEY.

Effect of external secretion of the pancreas on insulin secretion. E. ZUNZ and J. LA BARRE (Compt. rend. Soc. Biol., 1930, **104**, 790—792; Chem. Zentr., 1931, i, 104).—Increase, by means of hydrochloric acid, in the external pancreatic secretion of the dog is accompanied by an increased production of insulin. A. A. ELDRIDGE.

Initial insulin hyperglycæmia. D. IONESCO, I. COSMULESCO, and M. TOMESCO (Compt. rend. Soc. Biol., 1929, **102**, 167—169, 170—172; Chem. Zentr., 1931, i, 304).—Transitory hyperglycæmia after injection of insulin into the rabbit, dog, or man is observed after 1 min. and is maximal at 5—13 min. Experiments on the injection into dogs of insulin together with adrenaline, ergotamine, pilocarpine, and atropine are described. A. A. ELDRIDGE.

Existence of a pancreatic hormone which reduces the blood-pressure. P. GLEY and N. KISTHINIOS (Wien. klin. Woch., 1930, **43**, 1530—1536; Chem. Zentr., 1931, i, 476).—The reduction of blood-pressure shown by many insulin preparations is attributed to a substance which is not identical with histamine. The increase in blood-pressure caused by adrenaline is counteracted by such a preparation (angioxyl). A. A. ELDRIDGE.

Effect of cod-liver oil on the calcium metabolism of young chicks. A. D. HOLMES and M. G. PIGOTT (Ind. Eng. Chem., 1931, **23**, 190—196).—To raise poultry by artificial methods and at the same time to obtain more rapid growth a proper balance of the Ca : P ratio and of vitamins must be maintained. Optimum conditions prevail if the diet has a maximum Ca : P ratio of 1·5 : 1; when this is increased rickets develop, and at a level of 5 : 1 dosage with cod-liver oil causes no alleviation of the symptoms. T. MCLACHLAN.

Fluorescence of cod-liver oil. C. A. MOREHOUSE (Proc. Iowa Acad. Sci., 1929, **36**, 297).—A bright band extending from 546 to 436 mμ was observed; the same band was given by solutions of cod-liver oil or cholesterol in alcohol. CHEMICAL ABSTRACTS.

Conductivity of cod-liver oil. L. W. BUTLER (Proc. Iowa Acad. Sci., 1929, **36**, 299—300).—The conductivity diminishes as the temperature falls from 50° to −4°; the form of the curves, but not the value, is the same for oils of different origin or under different conditions. Exposure to air causes a slight fall, followed by a considerable rise, in conductivity; decomposition of vitamin-*A* by air at 90° largely diminishes the conductivity. The oil is not photoelectric on irradiation with ultra-violet light. The specific resistance of the oil varies from 10^{10} to 10^{13} ohms per cm. CHEMICAL ABSTRACTS.

Quantitative relationship between vitamin-*A* in maize and the number of genes for yellow pigmentation. P. C. MANGELSDORF and G. S. FRAPS (Science, 1931, **73**, 241—242).—A white-seeded variety of maize forms vitamin-*A* in its seeds when the gene for yellow pigmentation is introduced. Each gene for yellow pigmentation induces the formation of approximately 2·5 units of vitamin-*A* per g. of seed, and is responsible, either directly or indirectly,

for the formation of the vitamin with the intermediate production of carotenoid pigments. A direct chemical reaction between the gene and some substance present in the endosperm of maize is indicated.

L. S. THEOBALD.

Fat-soluble vitamin requirements of the chick. I. Vitamin-*A* and -*D* content of fish meal and meat meal. W. D. MCFARLANE, W. R. GRAHAM, jun., and F. RICHARDSON (Biochem. J., 1931, **25**, 358—366).—A sample of white fish meal when fed at a level of 15% in a diet composed of marmite and white rice contained sufficient vitamin-*A* and -*D* to promote normal growth of chicks until 8 weeks old. A sample of meat meal contained little or no vitamin-*A* or -*D*. More than 1% of cod-liver oil is required to rear chicks in the laboratory to 8 weeks. Some factor other than vitamin-*D*, calcium, or inorganic phosphorus of the diet of the chick profoundly affects the concentration of inorganic phosphorus in the blood-serum of chicks during the first 8 weeks of growth.

S. S. ZILVA.

Comparison between irradiation of diet and supplemental irradiation of animals [rats] in vitamin-*A* and -*D* deficiency. F. E. CHIDESTER, A. G. EATON, and N. K. SPEICHER (Science, 1931, **73**, 190—191).—The daily addition of 0·01 mg. of irradiated ergosterol to a diet free from vitamin-*A* and low in vitamin-*D* stimulated the growth of rats, which had been depleted, for three weeks, after which death soon took place. Daily irradiation with a carbon arc lamp further stimulated growth for a short time but not to the extent previously observed when iron iodide was included in the diet. Relatively short exposures to ultra-violet radiation combined with irradiated ergosterol feeding did not induce marked hypervitaminosis. L. S. THEOBALD.

Mode of action of vitamin-*D*. Hypervitaminosis-*D*. Influence of the calcium phosphate intake. L. J. HARRIS and J. R. M. INNES (Biochem. J., 1931, **25**, 367—390).—An increase in the calcium phosphate allowance to rats causes an increased severity of hypervitaminosis. By reducing the calcium phosphate sufficiently, a level of vitamin-*D* excess which is otherwise toxic becomes innocuous. Doses which are just on the border-line of toxicity for a synthetic, salt-rich diet may be partly harmless for bread and milk diets. When, however, slightly larger excesses of vitamin-*D* are given the difference becomes less noticeable and with still larger excesses the difference vanishes. The addition of calcium and phosphate salts to bread and milk diets renders them indistinguishable from synthetic diets in the production of hypervitaminosis with excess of vitamin-*D*. A given overdose of irradiated ergosterol, just sufficient to cause rapid loss of weight with diets rich in calcium and deficient in phosphate, becomes less toxic when calcium is balanced by phosphorus and relatively harmless when the calcium is omitted and the phosphorus remains high. Similar results are obtained when the dose is increased or when heavier rats are employed. At least eight times as much irradiated ergosterol is needed to cause loss of weight on a diet high in phosphorus and calcium-free as with a diet with a normal calcium content. The nature of the hypervitaminosis thus produced differs, however, from the usual condition and resembles the condition produced by the administration of a calcium-free diet without any vitamin excess, but with a more extensive loss of mineral substance from the spongiosa. On a diet deficient in both calcium and phosphorus similar results are obtained. There is a formation of calcium deposits in the soft tissues when there is an abundance of calcium salts in the diet. With insufficient excess of vitamin-*D* no calcium deposits are formed. With a very large excess the animal usually dies before the deposits are formed. Large doses of vitamin-*D* with normal diets stimulate osteogenesis and a densely calcified overgrowth appears at the growing end of the bone, in contrast with rickets, whilst in the advanced degrees of hypervitaminosis resorption is extensive and the cortex of the shaft and other "compact" bone becomes spongy. Vitamin-*D* excess also gives rise to a remarkable overgrowth of cement in the growing animal. In hypervitaminosis produced on diets rich in calcium with moderate overdoses of vitamin-*D* there is an increased net absorption of calcium and phosphorus from the gut, whilst with calcium-deficient diets and with larger excesses of the vitamin there is a withdrawal of these elements from the bone-shaft. S. S. ZILVA.

Calcifying action of irradiated ergosterol on guinea-pigs infected with tuberculosis. A. POLICARD, PAUPERT-RAVAULT, and P. BARRAL (Compt. rend. Soc. Biol., 1930, **104**, 633—635; Chem. Zentr., 1930, ii, 1094).—Infected guinea-pigs were treated with "vigantol" before and after infection. Daily doses of 13 mg. of ergosterol from the 18th day after infection produced calcification in all organs, normal or diseased. Smaller doses had a negligible effect.

L. S. THEOBALD.

Pharmacological classification of irradiated ergosterol. H. HANDOVSKY (Arch. exp. Path. Pharm., 1931, **159**, 383—386).—The administration of large doses of irradiated ergosterol to animals brings about changes in metabolism similar to those produced by saponin and in particular increases the rate at which oxidation proceeds in the cells of the liver as shown by experiments on tissue sections by the method of Warburg. W. O. KERMACK.

Distribution of vitamin-*B* and its components in the peanut. F. W. SHERWOOD and J. O. HALVERSON (J. Elisha Mitchell Sci. Soc., 1930, **46**, 14).—Whole raw peanuts are fairly rich in vitamin-B_1 but not in -B_2; the red skins are especially rich.

CHEMICAL ABSTRACTS.

Differentiation of the so-called antipellagric factor, vitamin-B_2. B. SURE, M. E. SMITH, and M. C. KIK (Science, 1931, **73**, 242—243).—It is concluded that vitamin-B_2 is composed of two dietary essentials, deficiency of the one producing in the rat symptoms like those of pellagra and of the other, a decline in growth. It is suggested that the former be denoted by the letter *F* and the latter by *G*.

L. S. THEOBALD.

Content of thiol compounds in striated muscle, liver, and blood of normal and underfed rats, and of those deprived of vitamin-*B*. L. RANDOIN and R. FABRE (Compt. rend., 1931, **192**, 815—818).—

The striated muscle of normal rats contains on the average, per 100 g. of fresh tissue, 0·020 g. of thiol compounds, the liver 0·172 g., and the blood 0·025 g. With rats which have been deprived of vitamin-*B*, the muscles contain a smaller amount of substances of the glutathione type (*G*) (average 0·0157 g.), whilst an increase is observed in the amount of other reducing substances (*G'*). The same applies to the liver (average 0·1217 g.). In the blood, the amount of *G* remains approximately the same, but the amount of *G'* is greatly increased. The variations from the average are within fairly wide limits. Malnutrition causes variations in the ratio of *G* to *G'* similar to those caused by deprivation of vitamin-*B*.

B. LEVIN.

Accumulation of ternary substances in the blood during avitaminosis-*B*. J. ROCHE (Bull. Soc. Chim. biol., 1931, **13**, 186—196).—During the initial stages of fasting the C/N ratio in the deproteinised blood of pigeons is normal (approx. 4), but with the onset of hypothermia both this ratio and the dextrose content decrease. On a polished rice diet, the C/N ratio increases with the continuation of the diet, but falls towards the normal value when yeast is added to the diet. A slight degree of hyperglycæmia is induced in avitaminosis-*B* which disappears on fasting.

C. C. N. VASS.

Formation of compounds in some cultivated plants. K. SJOBERG (Svensk Kem. Tidskr., 1931, **43**, 57—69).—Analyses of a number of commonly cultivated plants (principally flax, clover, cress, oats, carrot, and beet) have been made at intervals during the whole period of growth with a view of ascertaining the rate of production of the various components (starch, sugar, pentoses, ash, etc.), together with the total increase in weight.

H. F. HARWOOD.

Forcing of plants. A. NIETHAMMER (Biochem. Z., 1931, **232**, 146—155).—The effect of freezing and drying elder twigs is examined. The amount of reducing sugar is increased by frost, whilst dryness causes only a transient increase. The sugar content of elder twigs shows considerable variations during the year. The sugar maximum does not, but the plasmolysability of the parenchymatous cells does correspond with the opening of the buds.

P. W. CLUTTERBUCK.

Photosynthesis in various vine species. H. SCHANDERL (Pflanzenbau, 1930, **3**, 529—560; Chem. Zentr., 1931, i, 298).—Assimilation takes place with *Vitis riparia* in diffused light, but with *V. vinifera* only in direct sunlight. Methods of determination of carbon dioxide assimilation, and the significance of the results in German vine culture, are discussed.

A. A. ELDRIDGE.

Use of Beijerinck's indigo-white method in quantitative assimilation experiments [with plants]. M. MATSUBARA (Planta [Z. wiss. Biol.], 1931, **12**, 670—685).—Oxygen produced during photosynthesis in plants is determined colorimetrically by means of reduced indigo-carmine; 0·001% of oxygen may be detected.

A. G. POLLARD.

Nitrogen metabolism in higher plants. III. K. MOTHES (Planta [Z. wiss. Biol.], 1931, **12**, 686—731; cf. A., 1928, 93).—The translocation of nitrogen in plants under varying conditions is examined. The age of leaves and the water content of the tissues are important factors controlling the translocation of nitrogen within the plant and the extent to which protein synthesis or decomposition occurs in the tissues. Water deficiency is associated with protein decomposition and reduced carbon dioxide production in older leaves, and with protein synthesis and enhanced respiration in younger leaves. Inter-relationships between these functions are discussed. Exhalation of nitrogen in any form was not observed.

A. G. POLLARD.

Effect of increasing quantities of nitrogen on plant yield. H. EICHLER (Pflanzenbau, 1930, **3**, 494—528; Chem. Zentr., 1931, i, 298).—Curves for yield of root, grain, and straw with increasing quantities of nitrogen are independent; the optima are 0·7—0·9, 1·8—2·0, and 2·4 g. of nitrogen (in pot experiments with sodium or ammonium nitrate or ammonium sulphate) respectively.

A. A. ELDRIDGE.

Nodule bacteria and leguminous plants. IX. Utilisation of different nitrogenous substances and of the nodule nitrogen by leguminous plants. A. I. VIRTANEN and S. VON HAUSEN (Biochem. Z., 1931, **232**, 1—14).—Growth of red clover in a sterile medium is best with amino-acids (hydrolysed caseinogen) as the source of nitrogen, is much less with ammonium sulphate, and still less with potassium nitrate, whilst growth of white clover is best with ammonium sulphate, poorer with potassium nitrate, and feeblest with amino-acids (cf. A., 1928, 558).

P. W. CLUTTERBUCK.

Carbohydrate metabolism of *Stipa pulchra*. A. W. SAMPSON and E. C. MCCARTY (Hilgardia, 1930, **5**, 61—100).—Analyses of the total carbohydrates, polysaccharides, sucrose, and reducing sugars in the stem bases, roots, and herbage of *S. pulchra* in varying stages of growth are recorded. An accumulation of carbohydrates in the stem bases corresponds with a low or declining rate of growth and is most marked as maturity is approached. Removal of the herbage by cutting or grazing at any time prior to maturity is followed by regenerative growth and a decreased carbohydrate accumulation. Cutting during the early stages of growth does not affect the final yield nor prevent the maximum accumulation of carbohydrate characteristic of maturity. Between the period of flowering and maturity, cutting or grazing prevents the maximum carbohydrate accumulation and tends to prolong the vegetative period. A decreased carbohydrate accumulation at the end of the annual growth cycle may lead to a reduced crop in the subsequent year.

A. G. POLLARD.

Relation between physiological phenomena in plants and the colouring matters appearing in different organs. II. Relation between activity of assimilation and formation of anthocyanin in *Abutilon avicennæ*. H. KOSAKA (J. Dept. Agric. Kyushu, 1931, **3**, 29—45).—The production of anthocyanin pigments in the stems and leaf stalks of *A. avicennæ* runs parallel with the accumulation of food stores in the cells. It varies with the rate at which the foodstuffs are synthesised as shown

by experiments in which this rate was decreased by plucking off the leaf blades or by covering the latter with black paper. The reduction in the synthetic activity of the plant was associated with a reduction in the rate of formation of the pigments. The rate of formation of the pigments varies inversely with the rate at which the food stores are used up.

W. O. KERMACK.

Phæophorbide-*b*-iron. O. WARBURG (Ber., 1931, **64**, [*B*], 682—683).—Iron powder, sodium chloride, and glacial acetic acid are heated in a current of carbon dioxide and phæophorbide *b* is added to the cooled and filtered solution. After being heated on the water-bath the *iron* salt is filtered and crystallised from propionic acid containing hydrochloric acid. After dehydration, it has the composition $(Et\cdot CO)C_{35}H_{33}O_6N_4FeCl$. H. WREN.

Protoplasmic substances with a thiol function. A. GIROUD (Protoplasma, 1931, **12**, 23—41).—Plant cells contain two types of thiol substances, an insoluble protein type which is observed by the customary histological reaction, and glutathione. Both forms are present in the reduced condition in living cells and are not produced by secondary reduction processes accompanying intracellular changes. Failure to demonstrate, in certain cases, the thiol grouping in living cells by the nitroprusside test is due to the impermeability of the cell wall to the reagent.

A. G. POLLARD.

Biochemical studies on the bamboo. VI. Carbohydrates and organic acids of bamboo shoots. Y. SASAOKA (Chikashige Anniv. Vol., 1930, 175—181).—In addition to the substances mentioned previously (A., 1927, 599), oxalic, tartaric, citric, and lactic acids were isolated from the juice expressed from fresh bamboo shoots. B. LEVIN.

Organic acids of wheat plants. E. K. NELSON and H. HASSELBRING (J. Amer. Chem. Soc., 1931, **53**, 1040—1043).—The non-volatile organic acids in green wheat-plants have been determined by extraction with boiling water, precipitation as lead salts with lead acetate, conversion into their esters, fractionation of these, and identification as their hydrazides. The proportions of such acids, calculated on the green plant, are: malonic 0·005, aconitic 0·040, malic 0·06, citric 0·018%, and a trace of oxalic, whilst 0·02% of oxalic acid remains in the residue from the original extraction. J. W. BAKER.

Glucosides of the *Gramineæ*. Importance of the lævulosans. A. CUGNAC (Bull. Soc. Chim. biol., 1931, **13**, 125—132).—Lævulosans are the characteristic glucosides of European *Gramineæ* and form up to 20% of the fresh tissue. The *Gramineæ* of warmer countries contain sucrosans. The lævulosans occur in the stems and accumulate in the roots, particularly before flowering. Graminin, $[\alpha]_D$ −43°, is more soluble than phlerin, $[\alpha]_D$ −49°; both, unlike tricitin, $[\alpha]_D$ −48·5°, are completely hydrolysed by yeast or its autolysate or dilute mineral acids. On the basis of the reaction $C_6H_{10}O_5+H_2O=C_6H_{12}O_6$ the hydrolysis is incomplete and the specific rotation is less than that of pure lævulose, hence for these lævulosans the equation is only an approximation.

C. C. N. VASS.

Microchemical detection of glucoside. A. NIETHAMMER (Mikrochem., 1931, **9**, 136—142).—The extraction of æsculin, rhinanthin, syringin, saponarin, digitonin, and salicin from vegetable tissues has been effected by sublimation and the properties of the products are described. The sublimation process and precipitation by means of 20% potassium bromide solution saturated with bromine are useful methods for the microchemical detection of glucosides in plants. E. S. HEDGES.

Occurrence of methyl mercaptan in the leaves of *Lasianthus lævigatus*, Bl., *L. lucidus*, Bl., *L. purpureus*, Bl., *L. stercorarius*, Bl., and *L. bracteolatus*, Miq. D. R. KOOLHAAS (Biochem. Z., 1931, **230**, 446—450).—The methyl mercaptan is separated by steam-distillation of the freshly plucked leaves and determined by precipitation as the mercuric salt. The amount of mercaptan per 1000 g. of leaves varies from 1·351 g. with *L. purpureus* to none with *L. lævigatus*. P. W. CLUTTERBUCK.

Tobacco. IV. Analysis of tobacco smoke. N. J. GAVRILOV and A. V. KOPERINA (Biochem. Z., 1931, **231**, 25—32; cf. A., 1930, 824).—A method and apparatus by means of which all the smoke from a given quantity of smouldering tobacco can be passed into 0·1*N*-sulphuric acid of which the total nitrogen, ammoniacal nitrogen, and nicotine-nitrogen contents can then be determined are described. The deviations in parallel experiments with the same tobacco do not exceed 3—4%. Within certain limits the results obtained are not affected by the rate at which the tobacco is burned nor by its moisture content.

W. MCCARTNEY.

Distribution of nitrogen in plant extracts that contain a high proportion of nitrate-nitrogen. A. C. CHIBNALL and E. J. MILLER (J. Biol. Chem., 1931, **90**, 189—196).—Analysis is given of an extract from rye-grass (*Lolium perenne*) obtained from a sewage farm. The extract contained abnormally large concentrations of nitrate-nitrogen. It was fractionated according to the method of Vickery and Pucher, but the "other amide-nitrogen" contained in the fractions did not account for the total present in the original extract. It is highly probable that the results are therefore vitiated by the effect of nitrate on amide-nitrogen determinations (see this vol., 537). It also appears from the "apparent amide-nitrogen" content of the various fractions that the easily oxidisable substance detected but not isolated by Vickery and Pucher in tobacco leaf is a nitrogen-containing compound. W. O. KERMACK.

Amino-acids of glutenin. M. DAMODARAN (Biochem. J., 1931, **25**, 190—199).—The hydrolysis products of glutenin have been fractionated by means of their copper salts. The yields of most of the monoamino-acids are higher than those previously recorded. S. S. ZILVA.

Proteins. II. Uniformity of the protein fraction extracted from orange-seed meal by salt solutions. F. SAUNDERS (J. Amer. Chem. Soc., 1931, **53**, 696—700).—Extraction of the oil-free, ground seeds with *N*-solutions of alkali halides gives extracts containing the same amount of nitrogen in

each case. The protein extracted is probably the same in each case. H. BURTON.

Aluminium content of plants. G. BERTRAND and G. LEVY (Compt. rend., 1931, **192**, 525—529; cf. McCollum and others, and Kahlenberg and Closs, A., 1930, 492).—Data are presented for the aluminium content (determined gravimetrically as phosphate) of several species of edible roots and leaves, showing the variation with age. Leaves contain most aluminium, those of spinach, rhubarb, and radish having 96—104, 166, and 157—280 mg. per kg. dry wt., respectively. A. COHEN.

Detection and intensity of mitogenetic radiation. A. GURWITSCH (Biochem. Z., 1931, **230**, 505).—A reply to Schreiber and Friedrich (this vol., 125). P. W. CLUTTERBUCK.

Elongation of roots of Georgia collards as affected by sodium luminal. T. W. PRATT (Plant Physiol., 1930, **5**, 587—597).—The rate of growth of the roots of Georgia collards was retarded by solutions of sodium luminal (0·1—1·0%), the effect being immediate and reaching a maximum within 15 min. of treatment. The extent of the retardation was closely related to the concentration of the sodium luminal solution. Washing with distilled water partly removed the depressive effect. A. G. POLLARD.

Colloidal zirconium hydroxide as a deproteinising agent. J. ERDOS and J. SURU (Biochem. Z., 1931, **231**, 6—12).—When zirconium tetrachloride is evaporated to dryness several times with anhydrous acetic acid and the product digested for some hours with water the salt is quantitatively converted into the hydroxide $Zr(OH)_4$. A colloidal solution of the purified hydroxide is an excellent deproteinising agent, since the substance is non-toxic and harmless to the materials with which it is used. Any excess of the hydroxide is easily removed from deproteinised solutions by heating or by altering the reaction of the medium. W. McCARTNEY.

Spectrographic determination of aluminium in biological ash. D. TOURTELLOTTE and O. S. RASK (Ind. Eng. Chem. [Anal.], 1931, **3**, 97—102).—The volatility of the aluminium compound used and the nature of the combined anion or of other salts present simultaneously are without influence on the spectrographic determination of aluminium. The error of the determination at concentrations from 0·5 to 1000 in 10^6 is $\pm 25\%$. The arc and condensed spark methods are equally satisfactory in most cases, but for certain kinds of biological ash, especially if free carbon is present, the arc method appears to be the more sensitive. H. F. GILLBE.

Detection of lead in organic tissues. W. GERLACH and W. GERLACH (Naturwiss., 1931, **19**, 111).—The mode of procedure described previously (cf. this vol., 328) has been applied to the detection of lead in the gums. The spectrograms give definite indications of the presence of lead in circumstances in which the histological method is untrustworthy. J. W. SMITH.

Detection of small amounts of lead and mercury in the organism. H. BÜLL (Biochem. Z., 1931, **230**, 299—303).—Methods are given for blood, urine, and fæces. Lead usually occurs in the fæces when present in the urine, but could not be detected in blood even when present in both urine and fæces. P. W. CLUTTERBUCK.

Determination of ferric and ferrous ions and of iron in organic combination in biological material. L. PINCUSSEN and W. ROMAN (Biochem. Z., 1931, **231**, 54—58).—To separate the ionised iron from that which is in organic combination a suitable amount of material, after being ground with sand in an ice-cold mortar, is thoroughly mixed and kept for 3 hrs. with frequent stirring with 20% sulphuric acid from which air is excluded by means of a layer of paraffin oil. When the mixture is then centrifuged the organically combined iron remains in the deposit, whilst the ionised iron is in solution. In the solution the ferric iron is determined by titration with titanous chloride solution, using potassium thiocyanate as indicator; the ferrous iron is then oxidised with nitric acid, excess of which is subsequently removed by evaporation to dryness, the residue is dissolved in dilute sulphuric acid and titrated as before with titanous chloride solution. The amount of ferrous iron is then obtained by difference. The organic matter in the deposit is destroyed with nitric acid and hydrogen peroxide and the iron which is present in the residue after the removal of the excess of nitric acid is dissolved in dilute sulphuric acid and titrated with titanous chloride solution. Where required throughout the process suitable measures must be taken to prevent oxidation of dissolved substances. A micro-burette for use with titanous chloride solutions is described. W. McCARTNEY.

Spectrophotometric micro-determination of phosphorus [in organic material]. T. TEORELL (Biochem. Z., 1931, **230**, 1—9).—The colorimetric method of Fiske and Subbarow (A., 1926, 443) is modified, the blue colour being determined spectrophotometrically. A single phosphorus standard is necessary and 0·01—0·05 mg. of phosphorus may be determined with an error of $\pm 2\%$. F. O. HOWITT.

Determination of methylglyoxal, pyruvic acid, and acetaldehyde alone or in mixtures. Determination of lactic acid in the presence of these substances and in biological material. E. SIMON and C. NEUBERG (Biochem. Z., 1931, **232**, 479—484).—Methylglyoxal, pyruvic acid, and acetaldehyde (but not lactic acid) in dilute acid solutions (1·0—0·1%) are quantitatively precipitated by excess of acid solution of 2 : 4-dinitrophenylhydrazine hydrochloride. The hydrazones are separated quantitatively by removing that of pyruvic acid by means of sodium carbonate and dissolving that of acetaldehyde from the residue in 94% alcohol, in which the methylglyoxal compound is insoluble. The process can likewise be applied to the determination of trioses if they are first converted by distillation with 20% sulphuric acid into methylglyoxal. W. McCARTNEY.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JUNE, 1931.

General, Physical, and Inorganic Chemistry.

Stellar hydrogen lines and their relation to the Stark effect. C. T. Elvey and O. Struve (Astrophys. J., 1930, **72**, 277—300).—Observations of the wings of the hydrogen lines in early type stars.

L. S. Theobald.

Stark effect in molecular hydrogen in the range 4100—4700 A. J. K. L. MacDonald (Proc. Roy. Soc., 1931, **A**, **131**, 146—154; cf. A., 1929, 616).—Certain complex structures reported by Kiuti as components of a single line (A., 1926, 103) are resolved into separate lines. Displacements of line components are measured and the observations discussed from a theoretical point of view.

L. L. Bircumshaw.

Spectra of the helium glow discharge. H. McN. Cowan, W. L. Brown, and K. G. Emeléus (Nature, 1931, **127**, 593).—The distribution of intensity in the arc spectrum of He I obtained in an investigation of the cold cathode glow discharge in helium with probe wires is described.

L. S. Theobald.

New ultra-violet spectrum of helium. J. J. Hopfield (Astrophys. J., 1930, **72**, 133—145).—The resonance series of helium in the ultra-violet has been extended to ten members, and lines in orders as high as the fifth have been measured. Intense continuous spectra of molecular origin have been found between 500 and 1125 A., and this is the only strong continuous spectrum in the region 500—900 Å. Two distinct species of helium molecules are postulated to explain the results. The first absorption spectra to be obtained between 500 and 900 Å. are recorded for O_2 and H_2.

L. S. Theobald.

Combined electric and magnetic fields on the helium spectrum. II. J. S. Foster (Proc. Roy. Soc., 1931, **A**, **131**, 133—146; cf. A., 1929, 364).—A study has been made of the effect of simultaneous electric and magnetic fields applied in either parallel or perpendicular directions on the helium spectrum.

L. L. Bircumshaw.

Temperature determination from band spectra. I. Vibrational energy distribution and vibrational transition probabilities in the cyanogen $^2\Sigma-^2\Sigma$ band system. L. S. Ornstein and H. Brinkman (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 33—41).—The intensity distribution in the cyanogen $^2\Sigma-^2\Sigma$ band system has been determined by measurements of the maximum intensities of the band heads. A distribution temperature for the vibrational levels exists and is the same as for the rotational levels.

J. W. Smith.

Intensity relationships in the alkali doublets. E. Fermi (Nuovo Cim., 1930, **7**, 201—207; Chem. Zentr., 1930, ii, 2352—2353).—A recomputation gives results in accord with experimental values.

A. A. Eldridge.

Zeeman effect in silicon and band spectra of alkaline-earth fluorides. (Miss) E. von Mathes (Z. Physik, 1931, **68**, 493—504).—The Zeeman effect in the $3p^3P_{0,1,2}-4D^3P_{0,1,2}$ lines near 2510 Å., and in the lines at 2881 and 3905 Å. of silicon, were measured, and were found to agree with Fowler's electronic level system for neutral silicon. The Zeeman effect in calcium, barium, and strontium fluorides was also measured and compared with theory.

A. B. D. Cassie.

Interpretation of certain $^2\Delta$, Π^2 bands of silicon hydride. R. S. Mulliken (Physical Rev., 1931, [ii], **37**, 733—735).—Theoretical. It is shown that the bands found by Jackson (cf. A., 1930, 388) have a regular $^2\Pi$ state and are thus closely analogous to the λ 4300 bands of CH.

N. M. Bligh.

Intensities in stellar spectra of a triplet of Si III. O. Struve and C. T. Elvey (Astrophys. J., 1930, **72**, 267—276).—The ratios of total adsorptions of the Si III triplet at 4553, 4568, and 4575 Å. in stellar spectra depend on the form of the absorption coefficient.

L. S. Theobald.

Resonance spectrum of sulphur vapour. J. Fridrichson (Compt. rend., 1931, **192**, 737—739; cf. Swings, A., 1930, 650, 829).—The resonance spectrum of sulphur vapour has been observed to 6000 Å., and three sets of four doublets excited by the 3132, 3126, and 2968 mercury lines, and of a series of four quadruplets excited by the 3132 Å. line, have been measured.

C. A. Silberrad.

Absorption lines of sulphur (S III and S II) in stellar spectra. F. E. Roach (Astrophys. J., 1930, **72**, 191—198).—Stellar lines due to the S III ion have been identified. Six newly-measured lines are attributed to the S II ion.

L. S. Theobald.

Resonance multiplets and the moment of inertia of diatomic sulphur molecules. P. Swings (Bull. Acad. roy. Belg., 1931, [v], **17**, 420—424).—The moment of inertia of the diatomic sulphur molecule is 7×10^{-39} c.g.s.u. Fine structures observed in the resonance radiation of S_2 are classified as rotation doublets.

C. W. Gibby.

Titanium comparison spectrum as a photometric scale. P. C. Keenan (Astrophys. J., 1931, **73**, 118—123).—The relative intensities of 18 lines in

the titanium comparison spectrum have been determined in order to provide photometric calibration for early stellar spectrograms. L. S. THEOBALD.

Resonance radiation from manganese vapour. J. FRIDRICHSON (Z. Physik, 1931, **68**, 550—553; cf. A., 1930, 1227).—Radiation from copper and silver arcs, and also white light excite the resonance triplet at 4032 Å. A. B. D. CASSIE.

Anomalous doublet structure of the 4^2F terms of copper. S. SAMBURSKY (Naturwiss., 1931, **19**, 309—310).—It appears that the 4^2F term is inverted. Similar behaviour has been evidenced in the spark spectrum of zinc. A. J. MEE.

New band system of copper hydride. P. C. MAHANTI (Nature, 1931, **127**, 557).—A six-headed band system has been found in the region 2900—2200 Å. The bands are double-headed and the structure consists of six main branches and three satellites. L. S. THEOBALD.

Spectrum of selenium. I. Se IV and Se V. K. R. RAO and J. S. BADAMI (Proc. Roy. Soc., 1931, **A, 131**, 154—169).—The spectrum of selenium has been investigated from 7000 to 650 Å., using suitably strong discharges through capillary tubes containing selenium vapour. Photographs have also been taken of the vacuum spark spectrum of selenium in the region 1400—400 Å. The doublet system of trebly-ionised selenium has been identified, and a term scheme is proposed. The ionisation potential is about 42·72 volts. The four iso-electronic spectra Ga I, Ge II, As III, and Se IV are compared. A few singlet and intercombination lines have been added to the triplet system of Se V found by Sawyer and Humphreys (A., 1928, 1296). The approximate ionisation potential is 72·8 volts. L. L. BIRCUMSHAW.

Spectrum of singly-ionised antimony. D. G. DHAVALE (Proc. Roy. Soc., 1931, **A, 131**, 109—121).—New measurements of the first spark spectrum of antimony have been made over the range 8500—3000 Å. The classification of the lines again illustrates the use of the arithmetic progression law (cf. Saha and Kichlu, A., 1928, 209) and the method of horizontal comparison (Saha and Mazumdar, A., 1928, 1296). The ionisation potential of Sb^+ is estimated to be about 18·8 volts. L. L. BIRCUMSHAW.

Temperature classification of the stronger lines of niobium, with preliminary notes on their hyperfine structure. A. S. KING (Astrophys. J., 1931, **73**, 13—25).—The electric furnace spectra at 2500—2900° have been compared with the arc and spark spectra. Approximately 200 lines appear in the furnace spectrum, but many neutral and all ionised lines required higher excitation. About 40% of the 646 lines tabulated show hyperfine structure. L. S. THEOBALD.

Evidence for the presence of rhenium from the Fraunhofer lines in the solar spectrum. H. SCHOBER (Naturwiss., 1931, **19**, 310).—Of 60 strong lines in the rhenium spectrum 24 appear to coincide with Fraunhofer lines, there being correspondence as regards intensity. A. J. MEE.

Fine structure in the mercury singlet terms. S. TOLANSKY (Nature, 1931, **127**, 595).—A correction. L. S. THEOBALD.

Relative intensities of mercury lines under different conditions of excitation. M. J. E. GOLAY (Physical Rev., 1931, [ii], **37**, 821—829; cf. Houston, A., 1929, 480).—Using a Cooper-Hewitt arc and a mercury-filled tube the relative intensities of the lines of the $2s-2$ triplet were measured. The variations, their interpretation, and the mechanisms of emission are discussed. N. M. BLIGH.

Molecular spectra of mercury, zinc, cadmium, magnesium, and thallium. H. HAMADA (Nature, 1931, **127**, 555).—The band system emitted from diatomic molecules of mercury, cadmium, zinc, and magnesium vapours has two broad maxima and one flat minimum of intensity. The calculated energy of dissociation of the molecules Zn_2, Cd_2, and Hg_2 are 0·29, 0·24, and $\geq$0·07 volt, respectively. Symmetrical and asymmetrical bands accompanying the lines in the spectrum of thallium are probably due to thallium molecules. L. S. THEOBALD.

Structure of excitation functions for mercury lines. K. SIEBERTZ (Z. Physik, 1931, **68**, 505—521).—An improved apparatus for measurement of optical excitation functions is described; electron velocities can be varied by as little as 0·2 volt, and this reveals several maxima in curves showing optical intensity at any electron velocity. A. B. D. CASSIE.

Isotope effect in the hyperfine structure of thallium. H. SCHÜLER and J. E. KEYSTON (Naturwiss., 1931, **19**, 320—321).—The intensity relationships in the hyperfine structure of the Tl I and Tl II lines may be quantitatively interpreted in terms of a new isotope effect. If the isotopes are assumed to have at. wts. of 203 and 205 and to be present in the proportion necessary to yield the normal at. wt. of the element, the calculated number, positions, and intensities of the components accord fully with those determined experimentally. The relative displacement of the isotope terms is especially large for the $6s^26p^2P_{\circ,}$ term of Tl I and the $6s7p^1P_1$ term of Tl II. H. F. GILLBE.

Band spectrum of bismuth hydride. A. HEIMER and E. HULTHÉN (Nature, 1931, **127**, 557).—A band spectrum in the region of the bismuth line 4722 Å. has been observed. The bands consist of single P and R branches with well-resolved lines. L. S. THEOBALD.

Hyperfine structure separations. S. GOUDSMIT (Physical Rev., 1931, [ii], **37**, 663—681).—Theoretical. Using Slater's method of the invariance of energy sums (cf. A., 1930, 126) expressions are derived for the hyperfine structure separations of the levels of complicated electron configurations in different types of coupling. N. M. BLIGH.

Synchronous film drum for recording periodic spectra. D. C. STOCKBARGER and C. G. SELIG (Rev. Sci. Instr., 1931, [ii], **2**, 211—216).—The construction of a drum film holder to replace the plate holder of a quartz spectrograph for the photography of the periodic spectra of alternating-current arcs is described. It is driven by a synchronous motor

operating on the same current supply as the discharge tube. C. W. GIBBY.

Hyperfine structure as a test of a linear wave equation in the two-body problem. D. R. INGLIS (Physical Rev., 1931, [ii], **37**, 795—799).—Mathematical. The relativistic treatment of a nucleus and an electron gives rise to doubtful terms not agreeing with hyperfine structure measurements.

N. M. BLIGH.

Transmission of light by thin films of metal. S. RAMASWAMY (Proc. Roy. Soc., 1931, **A**, **131**, 307—320).

Theoretical formula for the absorption jump. V. POSEJPAL (Compt. rend., 1931, **192**, 879—881; cf. this vol., 13).—A formula is given for the absorption jump, defined as the ratio where τ_1, τ_2 are the true absorption coefficients for the frequencies $\nu_\kappa+\varepsilon$ and $\nu_\kappa-\varepsilon$ for the limit $\varepsilon=0$, ν_κ being the critical K absorption frequency. is calculated for all elements; the values agree satisfactorily with the experimental results available.

C. A. SILBERRAD.

Scattering of X-rays by mercury vapour. Y. H. WOO (Nature, 1931, **127**, 556—557).—Theoretical. L. S. THEOBALD.

Dependence of X-ray absorption spectra on chemical and physical state. J. D. HANAWALT (Physical Rev., 1931, [ii], **37**, 715—726).—The X-ray absorption spectra of arsenic, selenium, bromine, zinc, mercury, xenon, and krypton, and some of their compounds were photographed for the solid and vapour states, and the effect of the chemical and physical state of the absorbing atom on the secondary structure lying to the short wave-length side of the main absorption edge was investigated. The four last-named monatomic vapours showed no secondary structure farther from the main edge than the ionisation potential of the atom; polyatomic vapours usually have a secondary structure similar to that for the solid state. The secondary absorption of solid sodium bromate shows an additional structure not observed for a solution. The view that completed electron shells of atoms in the solid state indicate the absence of secondary absorption edges is not supported. N. M. BLIGH.

The "Ray" modification of the frequency of X-rays. J. H. VAN DER TUUK (Naturwiss., 1931, **19**, 308).—A repetition of Ray's experiment of passing copper $K\alpha_2$ rays through carbon, nitrogen, and oxygen is described. The author was unable to find the modified lines on the long-wave-length side reported by Ray. A. J. MEE.

Energy distribution in continuous X-ray spectra. K. K. AGLINTZEV (J. Appl. Chem. Russia, 1929, **6**, No. 2, 38—46). CHEMICAL ABSTRACTS.

X-Ray nondiagram lines. G. B. DEODHAR (Proc. Roy. Soc., 1931, **A**, **131**, 476—493).—In the K and L series non-diagram lines, pairs have been detected which show approximately constant $\sqrt{\nu}/R$ differences. The components of these pairs appear to arise from transitions in multiply-ionised atoms which are characterised by the same initial and final total quantum numbers, but have different screening constants. In spite of the constancy of the $\Delta\sqrt{\nu}/R$ values, all the pairs do not show the required linear variation of $\Delta\nu/R$ with atomic number. These pairs also show some analogy with the usual screening doublets. L. L. BIRCUMSHAW.

Electron reflexion in $\alpha\beta$-dichloroethane. E. BERGMANN and L. ENGEL (Physikal. Z., 1931, **32**, 263—264).—Contrary to the conclusion of Wierl that electron reflexion in $\alpha\beta$-dichloroethane indicates that this substance consists of a mixture of *cis*- and *trans*-modifications, reconsideration of the mechanism of the reflexion leads to a structure in agreement with those obtained from X-ray analysis and organic chemistry. W. GOOD.

Electron diffraction and molecular structure. R. WIERL (Ann. Physik, 1931, **8**, [v], 521—564; A., 1931, 13).—The theory of diffraction of X-rays by a single molecule is applied to the case of diffraction of electrons by the molecules of a gas. From the electron diffraction pattern obtained by passing a beam of high-speed electrons through a gaseous stream the characteristic form and atomic distances of the molecule of the substance are evaluated. Experimental details of the method and results for 20 substances are given. W. GOOD.

[Mean free path of electrons in gases.] V. A. BAILEY (Phil. Mag., 1931, [vii], **11**, 1052—1057).—Remarks on publications by Ramsauer and by Franck and Jordan.

Influence of radiative forces on the scattering of electrons. N. F. MOTT (Proc. Camb. Phil. Soc., 1931, **27**, 255—267).

Ionisation of mercury vapour by electron impact. P. T. SMITH (Physical Rev., 1931, [ii], **37**, 808—814; cf. Jones, A., 1927, 708; Bleakney, A., 1930, 391).—By using an apparatus previously described (cf. this vol., 10), the total number of positive charges per electron impact in mercury was determined as a function of the energy of the impacting electrons up to 750 volts. The maximum efficiency 19·4 occurs at about 85 volts (cf Lawrence, A., 1927, 85; Hughes, A., 1930, 1230). N. M. BLIGH.

Quantum mechanics of crystals. E. L. HILL (Physical Rev., 1931, [ii], **37**, 785—794; cf. Morse, A., 1930, 976).—Mathematical. The reflexion of a beam of electrons from a type of one-dimensional lattice containing any number of unit cells is investigated; the more complex case approximating to actual crystals is considered briefly. N. M. BLIGH.

Capture of electrons from mercury atoms by positive ions of helium. C. F. POWELL and A. M. TYNDALL (Nature, 1931, **127**, 592—593; cf. A., 1930, 1336).—Measurements of the mobilities of ions in helium containing a small amount of mercury vapour ($1:3\times10^4$) show electron exchange from mercury to helium, and provide a method for the determination of mobility of positive ions in gaseous helium.

L. S. THEOBALD.

Concentration of bundles of slow electrons. I. RANZI (Nuovo Cim., 1930, **7**, 254—259; Chem. Zentr., 1930, ii, 2350—2351).

Crystal photographs of electron waves by a focussing method. S. von Friesen (Naturwiss., 1931, **19**, 361).—A qualitative attempt to photograph the diffraction of electrons from a thin layer of zinc oxide by means of an arrangement similar to that used by Bohlin and Seeman for X-rays is discussed.

W. R. Angus.

"Internal" degrees of freedom of an electron. V. Fock (Z. Physik, 1931, **28**, 522—534).—Mathematical. A. B. D. Cassie.

Quantum mechanics of atomic collisions. L. Goldstein (Compt. rend., 1931, **192**, 1022—1024).—A calculation of the probability of excitement of discrete or continuous atomic levels by collision with neutral atoms or rapid positive ions.

C. A. Silberrad.

Metrical theory and its relation to the charge and masses of the electron and proton. H. T. Flint (Proc. Roy. Soc., 1931, A, **131**, 170—177).—The principles of conservation of momentum and energy applied to two masses show that the four-dimensional momentum is conserved. A five-dimensional continuum is investigated, and it is shown that the corresponding five-dimensional quantities are also conserved. On this theory it is deduced that matter can be destroyed by the union of an electron and a proton when the two particles possess equal and opposite fifth momentum components.

L. L. Bircumshaw.

Superposition of electron charges in molecules and α-particles. W. H. Rodebush (J. Amer. Chem. Soc., 1931, **53**, 1611—1612).—Theoretical. The "residual affinity" postulated to explain such compounds as B_2H_6 may be due to the overlapping of charge, without the exchange phenomenon.

J. G. A. Griffiths.

Possibility of separating neon into its isotopic components by rectification. W. H. Keesom and H. van Dijk (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 42—50).—Attempts have been made to separate the isotopic components of neon by rectification at —248·4°, just above the triple point. Light and heavier fractions were obtained of densities 0·00089830 and 0·00090211, corresponding with at. wts. of 20·14 and 20·23, respectively. The fact that the lighter isotope is more volatile than the heavier indicates to a large degree of probability that the solid state possesses zero point energy. J. W. Smith.

Constitution of rhenium. F. W. Aston (Nature, 1931, **127**, 591).—Rhenium consists of two isotopes 185 and 187, with estimated relative abundance 1·62 : 1, and packing fraction -1 ± 2, giving an at. wt. 186·22±0·07, in good agreement with Honigschmid's value of 186·31. The strongest isotope is isobaric with the weakest of osmium.

L. S. Theobald.

At. wt. of krypton. H. E. Watson (Nature, 1931, **127**, 631).—Comparison of the densities of krypton and oxygen gives a provisional value of 83·62 for the at. wt., a result which supports Aston's value of 83·77 instead of the accepted 82·9.

L. S. Theobald.

Isotopes. G. Fournier (Compt. rend., 1931, **192**, 940—941; cf. A., 1929, 863; 1930, 269).—Several of the predicted isotopes, C^{13}, N^{15}, O^{17}, Cr^{50}, Ge^{73}, Mo^{98}, and Mo^{100}, have been discovered, and a further list of probable, but hitherto undiscovered, isotopes is given. The existence of N^{16} (cf. Naude, A., 1930, 1232) is doubtful in this classification. C. A. Silberrad.

β-Transformation. B. M. Sen (Nature, 1931, **127**, 523).—The probability of a β-ray escaping from the nucleus is discussed. L. S. Theobald.

Activation of matter by resistance cells. G. Reboul (Compt. rend., 1931, **192**, 926—928; cf. A., 1930, 976).—The activation previously described is traced to articles of furniture, on which radioactive dust had been deposited accidentally in the course of other experiments. Experiments repeated after removal of these articles are described.

C. A. Silberrad.

Upper limit of energy in the spectrum of radium-*E*. F. R. Terroux (Proc. Roy. Soc., 1931, A, **131**, 90—99).—The cloud expansion method has been used to determine the general form of the upper region of the radium-E spectrum and the upper limit of velocity. No trace of an end-point is found at 5000 $H\rho$ (cf. Madgwick, A., 1927, 1120) and there is evidence of particles emitted with an energy of the order of 3,000,000 electron volts ($H\rho$ 12,000). The number of particles observed decreases very gradually with increasing $H\rho$. It is estimated that about 4% of the total number of particles emitted are above 5000$H\rho$, and about 1·5% above 7000$H\rho$, and that the average energy per disintegration is 473,000 volts (probable error 20%). The general shape of the distribution curve indicates that the β-particles are emitted from the nuclei according to a Maxwellian law.

L. L. Bircumshaw.

Valve methods of recording single α-particles in the presence of powerful ionising radiations. C. E. Wynn-Williams and F. A. B. Ward (Proc. Roy. Soc., 1931, A, **131**, 391—409; cf. Ward, Wynn-Williams, and Cave, A., 1930, 7).—The Greinacher method cannot be employed in experiments involving the counting of comparatively few α- or H-particles in the presence of disturbances caused by powerful β- or γ-radiation, or by large groups of α-particles which it is not desired to count. These difficulties may be avoided by the use of an apparatus which is described in detail, by means of which problems connected with long- and short-range α-particles emitted by various radioactive bodies and artificial disintegration phenomena may be investigated.

L. L. Bircumshaw.

Ionised gases and Coulomb's law. T. V. Ionescu (Compt. rend., 1931, **192**, 928—930).—Regarding the relative displacement of positive ions and electrons caused in a gas by an electric field as producing an elastic force, and applying Poisson's equation, the period of vibration of the electron is deduced. C. A. Silberrad.

Origin of cosmic radiation. (Sir) J. H. Jeans (Nature, 1931, **127**, 594).—Agreement of the absorptions calculated for the annihilation of 1 and 4 protons and their accompanying electrons with Regener's observed values suggests that the most penetrating constituent of cosmic radiation originates in the annihilation of an α-particle and its two neutralising

electrons and the next, softer constituent in the annihilation of one proton and an electron. These two constituents alone appear to form the fundamental radiation; other constituents are softer or degraded forms. L. S. THEOBALD.

Values of e, h, e/m, and M_P/m. W. N. BOND Nature, 1931, **127**, 557).—Re-calculated values are $e\times10^{10}$, $4{\cdot}779_4\pm0{\cdot}001_1$; $h\times10^{27}$, $6{\cdot}558_6\pm0{\cdot}003_1$; $(e/m)\times10^{-7}$, $1{\cdot}769_0\pm0{\cdot}0004_6$; M_P/m, $1846{\cdot}5_7\pm0{\cdot}4_8$; and $hc/2\pi e^2$—$137{\cdot}01_7\pm0{\cdot}05_9$. L. S. THEOBALD.

Interpretation of the density matrix in the many-electron problem. P. A. M. DIRAC (Proc. Camb. Phil. Soc., 1931, 27, 240—243).

Absorption of light by synthetic blue spinels. K. SCHLOSSMACHER (Z. Krist., 1930, **74**, 41—48; Chem. Zentr., 1930, ii, 1039—1040).—Measurements of the transmitting powers of synthetic blue spinels show that the colouring matter is different from that of the natural products (cf. A., 1930, 1267). L. S. THEOBALD.

"Line" absorption of crystalline chrome alums. H. SAUER (Ann. Physik, 1931, [v], **9**, 92).—A correction to a previous paper (A., 1928, 1305). A. J. MEE.

Vibration spectra of some simple carbon compounds containing the carbon-chlorine linking. I. Raman spectra. W. WEST and (MISS) M. FARNSWORTH (Trans. Faraday Soc., 1931, **27**, 145—160).—The Raman spectra of a number of saturated and unsaturated monochlorinated straight-chain hydrocarbons in the liquid state have been examined. In all cases one or more strong lines, corresponding with molecular frequencies of 600—700 cm.$^{-1}$, and a less intense line at 300—400 cm.$^{-1}$, have been observed; they are ascribed to the C·Cl linking, as they do not appear in the Raman spectra of the corresponding alcohols. The corresponding characteristic frequencies of related compounds are polarised to about the same extent, and several examples have been found of depolarisation ratios greater than unity; for the intense line at 1450 cm.$^{-1}$ it is frequently very high, attaining a value of about 2 in the case of *iso*propyl chloride. A high-frequency value for a given linking, if it can be interpreted as representing a high value of the force constant for the vibration, appears to be associated with a lack of chemical reactivity, at least in reactions which involve principally the rupture of the linking.

2-Chloropropylene may be readily prepared by rapidly boiling β-dichloropropane with an amyl-alcoholic solution of metallic potassium at atmospheric pressure. H. F. GILLBE.

Absorption spectra of saturated chlorides of multivalent elements. A. K. DUTTA and M. N. SAHA (Nature, 1931, **127**, 625—626).—As is the case with sodium chloride, the tetrachlorides of carbon, silicon, titanium, and tin show continuous absorption beginning at a long wave-length limit and extending towards the ultra-violet. The relation $Nh\nu=Q/4$ holds, where Q is the heat of formation of the chloride and ν is the frequency at which absorption begins. L. S. THEOBALD.

Some properties of cuprous oxide. B. GUDDEN and G. MONCH (Naturwiss., 1931, **19**, 361).—With freshly prepared cuprous oxide at 20°, irrespective of its conductivity, the optical absorption centre is at 639±2 mμ. Linear and completely reversible displacement of 0·17 mμ per degree towards longer wave-lengths results from raising the temperature. It is concluded that the absorption of cuprous oxide in the visible has no connexion with its electrical conductivity (cf. Auwers, this vol., 409). W. R. ANGUS.

Ultra-violet absorption spectrum of various kinds of quartz. G. O. WILD (Zentr. Min. Geol., 1930, **A**, 428—431; Chem. Zentr., 1931, i, 745).—Various kinds of quartz have been arranged in order of transparency to ultra-violet rays. The colour of smoky topaz may be due to the separation of silicon. The only other possible pigments are sodium or lithium compounds. A. A. ELDRIDGE.

Infra-red absorption bands in hydrogen sulphide. H. H. NIELSEN and E. F. BARKER (Physical Rev., 1931, [ii], **37**, 727—732).—Using a prism grating spectrometer for an investigation of the region 1—10 μ, bands showing fine structure were found at 2·6 and 3·7 μ; wave-numbers and intensities of the lines in the bands are tabulated. Bands previously reported (cf. Rollefsen, A., 1929, 1215) were found to be due to impurities. The 2·6 μ band consisted of P, R, and Q branches, the latter broadening unsymmetrically; the 3·7 μ band consisted of only one branch. A qualitative interpretation of the structure, based on the classical quantum mechanics of an asymmetric rotator (cf. Witmer, A., 1926, 1192) is given. N. M. BLIGH.

Absorption bands of gaseous hydrogen cyanide in the near infra-red. R. M. BADGER and J. L. BINDER (Physical Rev., 1931, [ii], 37, 800—807).—The absorption spectrum was photographed in the region λ 7000—9200; weak bands were found at λ 7912 and λ 8563, the former apparently a harmonic of a fundamental band at 3·04 μ. The bands have P and R, but no Q branches; wave-lengths and frequencies of the lines of each band are tabulated. The normal molecule is linear. Hydrogen cyanide is discussed in regard to its fundamental oscillations of frequencies 3290, 2090, and 710 cm.$^{-1}$, and to its dissociation energy and products. Evidence indicates a normal molecule HCN, built up of a normal hydrogen atom and a normal CN radical. Gaseous cyanogen showed no absorption bands. N. M. BLIGH.

Arrangement for studying the Raman effect. H. HULUBEI and (MLLE.) Y. CAUCHOIS (Compt. rend., 1931, **192**, 935—937).—A mercury-vapour lamp is placed at the focus of a parabolic reflector directed upwards towards another reflector in the shape of a truncated cone (apex upwards) with sides inclined at 45°. This reflects the light perpendicularly on to a tube, blackened at the bottom and upper part of the sides, containing the substance under examination, and placed vertically in the axis of the cone. The diffused light is viewed by means of a mirror inclined at 45° placed vertically above the tube. C. A. SILBERRAD.

Raman effect and chemical linkings in certain organic liquids. L. E. HOWLETT (Canad. J. Res., 1931, **4**, 79—91).—The general theory of the

Raman effect is briefly reviewed. An expression is derived for the fundamental frequencies of three masses connected by elastic forces in a straight line. With the aid of the expression an attempt is made to associate certain frequencies with definite linkings and structures from the results of an experimental study of the Raman effect in ethylene glycol and five derivatives, four nitriles, and benzyl alcohol. The values of the stretching forces of single, double, and triple linkings are deduced with the aid of the assumptions that the frequency 300 mm.$^{-1}$ arises from longitudinal vibrations of the C·H linking and that double and triple linkings have stretching forces twice and three times respectively that of a single linking. W. Good.

Raman effect in hydroxyl ions. L. A. Woodward (Physikal. Z., 1931, **32**, 261—262).—The Raman effect in concentrated solutions of sodium and potassium hydroxide has been investigated. In both cases the same frequency, $\Delta\nu=3615\pm25$ cm.$^{-1}$, was found and is attributed to the hydroxyl ion.

W. Good.

Raman effect and association. E. H. L. Meyer (Physikal. Z., 1931, **32**, 293—295).—Although Raman spectra have been made of many liquid mixtures, no case of association has been reported and only displacements due to the individual liquids are exhibited. The influence of molar concentration on molecular polarisation of mixtures is discussed. In a mixture of carbon tetrachloride and ethyl alcohol molecular polarisation of the ethyl alcohol is a maximum at a concentration of 35%. Manifestation of association in the Raman effect would be expected in a similar way. It has been found in mixtures of ethyl and methyl alcohol with carbon tetrachloride that no new lines are present. Solutions of copper sulphate in water give no indication of hydrate formation. Solutions of copper sulphate in ammonia show a new band due to $Cu(NH_3)_4SO_4$. Raman displacements are given for definite chemical linkings only; linkings between associated molecules are transitory and association displacements are not to be expected. Experiments on mixtures of different concentrations of the two dipolar substances, methyl alcohol and water, showed that variation in the concentration influenced the intensity and altered the displacement due to methyl alcohol by about 5 Å. towards shorter wave-lengths.

W. R. Angus.

Raman effect in calcite and aragonite. S. Bhagavantam (Z. Krist., 1931, **77**, 43—48).—The following Raman frequencies have been determined: calcite 158·7, 241·7, 283·8, 717·3, 1087·4, 1439·6; aragonite 94, 158·4, 209·0, 271·3, 708·1, 1087·0 cm.$^{-1}$ Frequencies less than 708 are attributed to lattice oscillations, those above to atomic. 1087·0 is the inactive frequency of the carbonate ion.

C. A. Silberrad.

Polarisation of the Raman spectrum of water. C. Ramaswamy (Nature, 1931, **127**, 558).—The three Raman bands excited by the same incident lines are differently polarised: the degree of polarisation apparently increases with an increase in intensity of the band. L. S. Theobald.

Raman spectra of crystals. F. Rasetti (Nature, 1931, **127**, 626—627).—Fluorite gives a Raman shift of 321·5—1 cm.$^{-1}$, corresponding with an infra-red wave-length of 31·1 μ, and a group of lines with a large frequency shift (7255·8—7297·6 cm.$^{-1}$). Calcite gives a similar group, frequency shift 7270·3—7455·5 cm.$^{-1}$, and in each case the new lines are comparatively weak in intensity. Similar lines in ice, quartz, rock salt, gypsum, anhydrite, aragonite, and barite could not be found. The Raman spectrum of rock-salt is weak and consists of a continuous band from 165 to 365 cm.$^{-1}$, with a fairly sharp line at 235 cm.$^{-1}$, which does not coincide with the infra-red reflexion maximum at 52·5 μ. L. S. Theobald.

Anomaly in the polarisation of Raman radiation. W. Hanle (Naturwiss., 1931, **19**, 375).—Some Raman lines of several compounds are found to be circularly polarised in the reverse direction to the circularly polarised exciting light.

W. R. Angus.

Rotational Raman spectrum of carbon dioxide. W. V. Houston and C. M. Lewis (Proc. Nat. Acad. Sci., 1931, **17**, 229—231).—The rotation band excited by the lines 2536 and 2534 Å. is composed of equidistant lines showing only one moment of inertia: $7·02\times10^{-39}$ g. cm.^{2} C. W. Gibby.

Structure of Raman bands in liquids. A. Kastler (Compt. rend., 1931, **192**, 1032—1034).—Doublets and triplets in Raman spectra of liquids, near $\nu=3400$ in water (cf. Gerlach, A., 1930, 1091) or $\nu=3210$—3300—3380 cm.$^{-1}$ in liquid ammonia (cf. A., 1930, 14) correspond with lines of the corresponding gas in the infra-red. It is suggested that quantised rotations occur in liquids, and that certain Raman doublets and triplets are of the types *PR* and *PQR*. The changes in the Raman spectra of water caused by salts (cf. Gerlach, *loc. cit.*) would then be due to the hindrance caused to this rotation by the attachment of molecules of water to the ions.

C. A. Silberrad.

Dependence of Raman scattering on frequency. J. Rekveld (Z. Physik, 1931, **68**, 543—549).—Intensity measurements with methyl alcohol show that Raman radiation increases more rapidly than the fourth power of the frequency as an electronic absorption band is approached. Simple resonance theory gives an expression for Raman scattering, and from this the frequency of the electronic absorption band can be calculated; the calculated value for methyl alcohol was 2280 Å., and compares favourably with Henri's value 2200 Å. Henri ascribes this to the C·H linking, and the Raman line was also due to this linking; the method should therefore prove useful in ascribing electronic frequencies to particular linkings.

A. B. D. Cassie.

Influence of temperature on the Raman spectrum of quartz. (Miss) M. J. Ney (Z. Physik, 1931, **68**, 554—558).—Photometric curves were obtained of light scattered by quartz crystals at 18° and 500°. At 500° Raman lines became diffuse, and were displaced towards the exciting line; changes in intensity depended on individual lines, and anti-Stokes lines became relatively more intense. A. B. D. Cassie.

Resonance fluorescence. V. Weisskopf (Ann. Physik, 1931, [v], **9**, 23—66).—Theoretical.

A. J. Mee.

Dipole moment and Kerr effect. E. H. L. Meyer and G. Otterbein (Physikal. Z., 1931, **32**, 290—293).—The Kerr effect in dipolar media is discussed. Measurements made with chlorobenzenes indicate that the Kerr constants decrease in the order *o*-dichlorobenzene, chlorobenzene, *m*-, *p*-dichlorobenzene. This is the order deduced theoretically.

J. W. Smith.

Dipole moments of benzyl and benzylidene chloride and benzotrichloride. A. Parts (Z. physikal. Chem., 1931. **B**, **12**, 323—326).—The dipole moments of these substances in benzene solution at 20° are, respectively, 1·85, 2·05, and $2{\cdot}15\times10^{-18}$. Comparison with the corresponding derivatives of methane indicates that displacement of a hydrogen atom by the phenyl group hinders the spreading of the valency linkings of the central carbon atom. F. L. Usher.

Dipole moments of primary, secondary, and tertiary aliphatic halogen derivatives. A. Parts (Z. physikal. Chem., 1931, **B**, **12**, 312—322; cf. A., 1930, 667).—The dipole moments of halogen derivatives of propane and of pentane have been measured at 20° in benzene solution. A table of values is given. As in the butane derivatives, the tertiary compounds possess the highest, and the primary the lowest, dipole moments. F. L. Usher.

Electric moment and molecular structure. III. Double and triple linkings and polarity in aromatic hydrocarbons. C. P. Smyth and R. W. Dornte (J. Amer. Chem. Soc., 1931, **53**, 1296—1304; cf. A., 1929, 1128).—The dielectric constants and densities of benzene or heptane solutions of the hydrocarbons at temperatures between 10° and 70°, and the molar refractions have been determined. The following electric moments have been evaluated: CPh_3Me, $0{\cdot}4\times10^{-18}$ e.s.u.; $CHPh{:}CH_2$, CHPh.CHPh, and $CPh_2{:}CPh_2$, 0·0; $CPh_2{:}CH_2$, 0·5; $CPh_2{:}CHPh$, 0·6; CPh:CH, 0·83; and CPh·CPh, 1·12. There is thus no evidence of polarity inherent in the ethylene linking itself. The large moments of the substituted acetylenes and the variations with temperature are attributed to the existence of tautomeric equilibria involving unsymmetrical forms containing bivalent carbon, as suggested by Nef. J. G. A. Griffiths.

Dielectric constant of hydrogen chloride from 85° to 165° Abs. R. M. Cone, G. H. Denison, and J. D. Kemp (J. Amer. Chem. Soc., 1931, **53**, 1278—1282).—Dielectric constants, *D*, and polarisabilities are tabulated. At the transition temperature, 98·4° Abs. (Giauque and Wiebe, A., 1928, 228), *D* changes isothermally from 3 to 10. This behaviour accords with Pauling's theory of the rotation of molecules in crystals (A., 1930, 1357).

J. G. A. Griffiths.

Dielectric properties of antimony pentachloride and phosphorus pentachloride. J. H. Simons and G. Jessop (J. Amer. Chem. Soc., 1931, **53**, 1263—1266).—The dielectric constant and density of molten antimony pentachloride and its carbon tetrachloride solutions have been determined between 2·5° and 47°. Similar data for carbon tetrachloride solutions of phosphorus pentachloride are recorded. The dielectric constant and conductivity of molten phosphorus pentachloride are less than those of the crystals. It is concluded that the chlorides have very small or zero dipole moments and therefore have a symmetrical structure with a shell of 10 electrons round the central atom. J. G. A. Griffiths.

Refractometric investigations. XV. Measurement of refraction of isotropic and anisotropic crystals with the crystal-interference refractometer. P. Wulff (Z. Krist., 1931, **77**, 61—83).—A detailed account of the apparatus and method of using it. C. A. Silberrad.

Refractometric investigations. XVI. Refractometric measurements of crystals. P. Wulff and A. Heigl (Z. Krist., 1931, **77**, 84—121; cf. Fajans and Joos, A., 1924, ii, 372; Haase, A., 1928, 694).—To examine the relations between the molecular refraction as deduced from the refractive indices and that deduced additively from the values obtained for the gaseous ions (cf. Fajans, A., 1928, 1320; Geffcken Kohner, A., 1929, 258; Geffcken, *ibid.*, 1233) the following determinations have been made at 25°. For anisotropic crystals, $n=\sqrt[3]{n_\epsilon n_\omega^2}$ or $\sqrt[3]{n_\alpha n_\beta n_\gamma}$): potassium fluoride, *d* 2·505, *n* 1·3629, R_L 5·16; potassium chloride, *d* 1·969, n_D 1·4897 (at 18° 1·4904), R_L 10·83; rubidium chloride, *d* 2·803, n_D 1·4937, R_L 12·55; cæsium chloride, *d* 3·988, n_D 1·6397, R_L 15·20; strontium fluoride, *d* 4·286, n_D 1·442, R_L 7·76; barium fluoride, *d* 4·893, n_D 1·474, R_L 10·08; calcium chloride, *d* 2·15, n_D (max.) 1·542, (min.) 1·531, R_L 16·1; strontium chloride, *d* 3·085. n_D 1·6499. R_L 18·74; $SrCl_2,2H_2O$, *d* 2·671, n_α 1·5942, n_β 1·5948, n_γ 1·6172, 24·99; $SrCl_2,6H_2O$, *d* 1·9663, n_ω 1·5356, n_ϵ 1·4856, R_L 41·14; barium chloride, *d* 3·917, n_α 1·730, n_β 1·736, n_γ 1·742, R_L 21·36; $BaCl_2,2H_2O$, *d* 3·096, n_α 1·629, n_β 1·642, n_γ 1·658, R_L 28·54; sodium perchlorate, *d* 2·499, n_α 1·4606, n_β 1·4617, n_γ 1·4731, R_L 13·58; potassium perchlorate, *d* 2·530, n_α 1·4717, n_β 1·4724, n_γ 1·4760, R_L 15·37; ammonium perchlorate, *d* 1·952, n_α 1·4824, n_β 1·4828, n_γ 1·4868, R_L 17·22; barium perchlorate trihydrate, *d* 2·911, n_ω 1·5330, n_ϵ 1·5323, R_L 41·60; potassium sulphate, d^{20} 2·665, n^{20} 1·4933, n_β 1·4946, n_γ 1·4973, R_L 19·07. Comparison of calculated and experimental results shows that as regards alkali and alkaline-earth fluorides and chlorides previous conclusions are confirmed, but that the ammonium ion in the form of the perchlorate stable at the ordinary temperature shows a refractometric behaviour markedly different from that of the other alkali ions, and from itself in its halides, but resembles that in its sulphate. C. A. Silberrad.

Anomalous dispersion in band spectra. E. Segrè (Nuovo Cim., 1930, **7**, 144—147; Chem. Zentr., 1930, ii, 2352).—The anomalous dispersion of the absorption bands in iodine vapour has been investigated, and the dependence of the refractive index on the exciting frequency established.

L. S. Theobald.

Influence of temperature on the electric birefringence of organic liquids. A. Kürten (Physikal. Z., 1931, **32**, 251—252).—An experimental arrangement is described with which the Kerr effect in organic liquids and its variation with temperature have been quantitatively investigated. Results for chlorobenzene and carbon disulphide are given.

W. Good.

Influence of temperature on molecular polarisation. L. Meyer (Physikal. Z., 1931, **32**, 260—261).—The suggestion of Sanger (cf. this vol., 147) that the deviation of the molecular polarisation of αβ-dichloroethane in hexane solution at low temperatures from linear dependency on the reciprocal of the temperature is due to association effects is shown to be improbable. W. Good.

Magnetic rotation of the plane of polarisation. Example of anomalous dispersion. J. Verhaeghe (Natuurwetensch. Tijds., 1931, **13**, 173—178).—Optical data are given for cinammaldehyde. The wave-length-rotation curve has a point of inflexion at about 6300 Å., and at higher wave-lengths the Verdet constant diminishes at an abnormal rate. H. F. Gillbe.

Change of susceptibility of paramagnetic salts under the influence of light. D. M. Bose and P. K. Raha (Nature, 1931, **127**, 520—521).—In agreement with the views of Bose (A., 1927, 805), diminutions of the paramagnetic susceptibilities of solutions of chromic, ferric, and nickel chlorides and copper sulphate on exposure to light of suitable wave-length have been qualitatively observed. L. S. Theobald.

Stereochemistry of crystal compounds. V. Dependence of structure type of crystalline compounds of types AB and AB_2 on lattice energy. P. Niggli (Z. Krist., 1931, **77**, 140—145).—Previous results are discussed (cf. Pauling, A., 1927, 399; A., 1929, 122; Unsold, A., 1927, 919; Hylleraas, A., 1930, 1234) and the dependence of the type of structure of such compounds on the ionic distances, d_A, d_B, d_{AB}, and the co-ordination numbers of A and B is demonstrated. The conclusions are illustrated by the series zinc blende ⟶ rock salt ⟶ cæsium chloride, and cuprite ⟶ anatase ⟶ fluorite. C. A. Silberrad.

Isomorphism and chemical homology. P. C. Ray (Nature, 1931, **127**, 631).—Concerning Lange's claim for priority (cf. this vol., 182). L. S. Theobald.

Ionic theory of organic reactions. I. C. Prévost and A. Kirrmann (Bull. Soc. chim., 1931, [iv], **49**, 194—243).—It is suggested that all the reactions of organic chemistry are ionic. The activated molecule is identified with the ion. F. J. Wilkins.

Nature of the chemical linking. Application of results obtained from quantum mechanics and from a theory of paramagnetic susceptibility to structure of molecules. L. Pauling (J. Amer. Chem. Soc., 1931, **53**, 1367—1400; cf. A., 1928, 690).—By means of the quantum mechanics a series of rules is formulated for the electron-pair linking. These afford information of the relative strengths of linkings formed by different atoms, the angles between the linkings, the presence or absence of free rotation about the axes of the linkings, the relation between the quantum numbers of electrons involved, and the number and spatial arrangement of the linkings. The angle between the hydrogen–oxygen linkings in water is 90—109·5°; other cases are discussed. One *d* with *s* and *p* eigenfunctions afford four strong linkings in one plane directed towards the corners of a square. This applies to bivalent nickel, palladium, and platinum. With two *d* eigenfunctions, six strong linkings directed towards the corners of an octahedron are produced. Other cases are examined.

Except for rare-earth ions, the magnetic moment of a molecule or complex ion is given by $\mu_s=2\sqrt{S(S+1)}$, where $2S$ is the number of unpaired electrons. Thus it is possible to determine from magnetic data which type of linking is involved. This has been investigated for a large number of compounds. J. G. A. Griffiths.

Structure of ferric thiocyanate and the thiocyanate test for iron. H. I. Schlesinger and H. B. Van Valkenburgh (J. Amer. Chem. Soc., 1931, **53**, 1212—1216; cf. Rosenheim and Cohn, A., 1901, i, 455).—Since the absorption spectra of aqueous solutions of sodium and ammonium ferrithiocyanates, the ethereal extracts, anhydrous ethereal ferric thiocyanate, and the aqueous solution (the red colour of which migrates to the anode during electrolysis) are almost identical, it is concluded that the colour is due to the ion $Fe(CNS)_6'''$. Confirming this, the mol. wt. of ferric thiocyanate in benzene and ether is found to correspond with the formula $Fe[Fe(CNS)_6]$ and it is concluded that this compound is extracted by ether from aqueous solutions. The decrease of colour caused by ammonium chloride is attributed to the formation of a hexachloroferric ion. J. G. A. Griffiths.

Energy diagram of sodium chloride. P. J. van Rysselberge (J. Physical Chem., 1931, **35**, 1054—1060).—The structure of compounds of the sodium chloride type is discussed. Curves relating the interaction energy of sodium and chlorine ions and atoms in the gaseous state and in solution with the distance between the nuclei of the two constituents are drawn, and the resulting energy diagram is discussed. L. S. Theobald.

Parachor of tervalent iodine. N. V. Sidgwick and E. D. P. Barkworth (J.C.S., 1931, 807—809).—In order to investigate the effect of an increase of valency the parachor of iodosobenzene propionate was determined, using chlorobenzene as solvent; it showed a parachor defect of 17·3 units. N. M. Bligh.

***X*-Ray studies of motions of molecules in dielectrics under electric stress.** R. D. Bennett (J. Franklin Inst., 1931, **211**, 481—487).—A paraffin was found by *X*-ray analysis to consist chiefly of $C_{27}H_{56}$. Under electric stress it solidified, the diffraction halo being typical of a powdered crystal aggregate. J. Lewkowitsch.

***X*-Ray emission spectrum and chemical combination. Experiments with secondary rays.** A. Faessler (Naturwiss., 1931, **19**, 307—308).—The fluorescence spectrum of sulphur, free and combined, was studied. Results differ considerably from those obtained when primary *X*-rays alone are used. A doublet $K\alpha$ is obtained from sulphur in sulphates with the wave-lengths of the lines slightly shorter than for free sulphur. A. J. Mee.

Scattering of unpolarised *X*-rays. G. E. M. Jauncey and G. G. Harvey (Physical Rev., 1931,

[ii], **37**, 698—711).—The relative scattering of unpolarised *X*-rays by paraffin at three angles was measured and compared with theoretical values calculated by formulæ due to Dirac, Compton, and Jauncey and to Klein and Nishina (cf. A., 1929, 373).
N. M. Bligh.

Appearance of extra lines in *X*-ray diffraction patterns of mixtures and absence of some lines peculiar to the components of the mixtures. R. W. Drier (Physical Rev., 1931, [ii], **37**, 712—714) —Abnormalities in *X*-ray spectra of mechanical mixtures of the minerals rutile (TiO_2) and barite ($BaSO_4$), and of Cu–Zn, Cu–Ag, Cu–NaCl, and Cu–Ni are described, and some explanations are considered.
N. M. Bligh.

Oscillating crystal and the causes of its action. E. Habann (Ann. Physik, 1931, [v], **9**, 1—22).—The oscillating crystal is improved, and the causes of its falling characteristic are investigated. Its action depends on adsorption of air. A. J. Mee.

Crystal structure of the compounds formed in the system Sb–Cd. M. Chikashige and T. Yamamoto (Chikashige Anniv. Vol., 1930, 195—199). —The compound SbCd exists in two modifications which have identical space lattices belonging to the hexagonal system; *a* is 4·42 Å. and the axial ratio is 0·78. The " compound " Sb_2Cd_3 is a eutectic mixture of β-SbCd and cadmium. H. F. Gillbe.

Lattice constant of ammonium hexafluoaluminate. L. Pauling (Z. Krist., 1930, **74**, 104—105; Chem. Zentr., 1930, ii, 1033).—Menzer's value (A., 1930, 1351), *a* 8·904, is correct.
L. S. Theobald.

***X*-Ray examination of crystal structure of violet phosphorus.** A. V. Frost (J. Russ. Phys. Chem. Soc., 1930, **62**, 2235—2241).—The crystal structure of violet phosphorus obtained by crystallisation from lead or bismuth is different from that obtained by slow crystallisation of molten red phosphorus heated at 580°. Both forms belong to the monoclinic system. R. Truszkowski.

Lattice constant of niobium. M. C. Neuburger (Z. anorg. Chem., 1931, **197**, 219—223).—Niobium possesses a cubic body-centred lattice of the tungsten type, with *a* 3·303±0·002 Å., $d_{calc.}$ 8·56, in agreement with the observed density and with Meisel's value (A., 1930, 983). Olhausen's value of *a* (4·19 Å.) is that of an aluminium–niobium mixed crystal (A., 1926, 228). H. F. Gillbe.

Crystal structure of anhydrous sodium sulphate. M. Z. Colby (Z. Krist., 1931, **77**, 49—60).—The unit cell has *a* 5·812, *b* 12·30, *c* 9·82 Å., and contains 8 mols. The space-group is V_h^{24}, thus differing from that of the other alkali sulphates (cf. Goeder, A., 1928, 223; Taylor, A., 1929, 243).
C. A. Silberrad.

***X*-Ray examination of iron tetracarbonyl.** R. Brill (Z. Krist., 1931, **77**, 36—42).—Crystallographic and *X*-ray examination of iron tetracarbonyl shows it to crystallise in the prismatic class of the monoclinic system; space-group C_{2h}^{6}. The unit cell has *a* 13·00, *b*—*c* 11·41 Å., 85° 35·1′, and contains 4 mols. of $Fe_3(CO)_{12}$, thus confirming Hieber's formula (cf. A., 1930, 1008). The constitution is probably $Fe[(CO)_3Fe(CO)_4]_2$. C. A. Silberrad.

Structure of solid hydrogen sulphide and selenide at the temperature of liquid air. L. Vegard (Z. Krist., 1931, **77**, 23—35; cf. this vol., 150).—The *X*-ray examination of hydrogen sulphide and selenide at the temperature of liquid air has been repeated with an improved apparatus, and the following revised results have been obtained. Space-group T_h^{6}; unit cell (hydrogen sulphide) *a* 5·79 Å., $d_{calc.}$ 1·16; (selenide) *a* 6·05 Å., $d_{calc.}$ 2·39. With certain assumptions the atomic radii of sulphur and selenium are respectively 2·05 and 2·14 Å., of hydrogen in the sulphide 0·77, in the selenide 0·71 Å.
C. A. Silberrad.

Crystal structure of mercuric bromide. H. J. Verweel and J. M. Bijvoet (Z. Krist., 1931, **77**, 122—139).—Mercuric bromide, which is isomorphous with yellow mercuric iodide, belongs to the pyramidal class of the rhombic system; space-group C_{2v}^{12}. The unit cell has *a* 4·67, *b* 6·85, *c* 12·45 Å., and contains 4 mols. C. A. Silberrad.

Lattice constant of cuprous oxide. M. C. Neuburger (Z. Krist., 1931, **77**, 169—170).—The lattice constant of cuprous oxide has been redetermined, using a specially pure sample, as 4·252±0·002 Å. C. A. Silberrad.

Crystal structure of hexahydrated strontium iodide, calcium chloride, and calcium bromide. Z. Herrmann (Z. anorg. Chem., 1931, **197**, 212—218).—Strontium iodide has *a* 8·51, *c* 4·29; calcium chloride *a* 7·86, *c* 3·905; calcium bromide *a* 7·97, *c* 3·97 Å.; the ortho-hexagonal unit cells contain 2 mols.; space-group C_{3i}. H. F. Gillbe.

Relation between crystalline structure and magnetic properties of the ferrites. H. Forestier (Compt. rend., 1931, **192**, 842—854).—Powder photographs of the ferrites of (*a*) iron (magnetite), (*b*) nickel, (*c*) strontium, (*d*) barium, (*e*) lead, (*f*) cadmium, and (*g*) calcium show that these compounds fall into three classes corresponding with their magnetic characteristics: I, (*a*) and (*b*), spinel structure, strongly ferromagnetic; II, (*c*), (*d*), and (*e*) apparently hexagonal, low coefficient of magnetisation; and III, (*f*) and (*g*), in two forms, (i) moderately ferromagnetic, (*f*) probably hexagonal, (*g*) not cubic, and (ii) paramagnetic, (*f*) cubic, *a* 8·45 Å., (*g*) tetragonal. If R_M is the atomic radius of the bivalent constituent and R_O that of oxygen (cf. Goldschmidt, A., 1929, 747) the ratios R_M/R_O of the three classes are respectively for I$\ngtr$0·62, for II $>$0·62$<$0·96, and for III $\nless$0·96. C. A. Silberrad.

Structure of apophyllite. W. H. Taylor and S. Naray-Szabo (Z. Krist., 1931, **77**, 146—158).—Contrary to the results of Gossner and Kraus (cf. A., 1929, 1036) the unit cell has *a* 9·00, *c* 15·8 Å., and contains 2 mols. of composition $KF,Ca_4Si_8O_{20},8H_2O$; space-group D_{4h}^{6}. The water is probably constitutional and present as hydroxyl ions.
C. A. Silberrad.

Boleite, pseudoboleite, and cumengite. B. Gossner (Z. Krist., 1930, **75**, 365—367; Chem. Zentr., 1930, ii, 3530).—Boleite has *d* 5·05—5·06. The lattice

constants previously reported for cumengite (A., 1930, 1352) have been confirmed (cf. Friedel, this vol., 331; Hocart, Z. Krist., 1930, 74, 20). A. A. ELDRIDGE.

Barytocalcite and its structural relationships to other substances. B. GOSSNER and F. MUSSGNUG (Zentr. Min., 1930, 321—328; Chem. Zentr., 1930, ii, 2362).—Barytocalcite has *a* 8·15, *b* 5·22, *c* 6·58 Å., β 106° 8′, *d* 3·689, with 2 mols. of $BaCO_3,CaCO_3$ per unit cell. Given an arrangement of atoms similar to that in calcite the space-group is C_2^3, but half the CO_3 groups in barytocalcite are rotated nearly 180° about a trigonal axis. L. S. THEOBALD.

Artificial coloration of crystals of carbamide oxalate and nitrate. P. GAUBERT (Compt. rend., 1931, 192, 965—967).—Addition of various dyes to a solution of carbamide oxalate or nitrate modifies the crystal form. All such crystals are much larger than the uncoloured crystals, and the strong birefringence (α 1·3887, β 1·6078, γ—α 0·2278) makes a suitably coloured crystal of one form an excellent polariser. The coloured crystals of the nitrate are solid solutions, but mixed crystals are obtainable. All the coloured crystals fluoresce in ultra-violet light, according to salt and dye. C. A. SILBERRAD.

Space-group of 2 : 4 : 6-tribromobenzonitrile. M. A. BREDIG (Z. Krist., 1930, 74, 56—61; Chem. Zentr., 1930, ii, 1034).—The space-group C_{2h}^2 is in agreement with Weiszenberg's views. L. S. THEOBALD.

Crystallographic examination of hydrocinchonidine dihydrobromide, $C_{19}H_{24}ON_2,2HBr,2H_2O$. F. SPAENHAUER (Z. Krist., 1931, 77, 159—163).—The crystals are monoclinic sphenoidal, $a:b:c=1·1022:1:1·1086$, β 100° 37′; optically negative, γ 1·718, β 1·67, birefringence strong, γ—α 0·158. C. A. SILBERRAD.

***X*-Ray diffraction by organic solutions.** A. W. MEYER (Proc. Iowa Acad. Sci., 1929, 36, 303—304).—The shift and width of the diffraction peak for varying concentrations were observed for butyl alcohol and 1 : 2-dimethyl*cyclo*hexane, and for ethyl alcohol and *cyclo*hexane. There was no evidence of a double peak. The molecules of both constituents form a single type of group; the spacing is determined by the proportion of the constituents present. CHEMICAL ABSTRACTS.

Molecular structure of benzene, *cyclo*hexane, and their derivatives. G. W. STEWART (Proc. Iowa Acad. Sci., 1929, 36, 305—306).—Benzene, toluene, *o*-, *m*-, and *p*-xylene, mesitylene, ethylbenzene, *iso*propylbenzene, *cyclo*hexane, methyl*cyclo*hexane, *m*-2-xylenol, *o*-, *m*-, and *p*-toluidine, and *o*-, *m*-, and *p*-tolyl methyl ether have been examined by the *X*-ray diffraction ionisation method. The benzene and *cyclo*hexane rings are flat, the thickness being 4·70 and 5·10 Å., respectively. The diameter in a plane perpendicular to the thickness is approx. 6 Å., indicating the general correctness of the ring conception. The thicknesses of the benzene and *cyclo*hexane rings depend on the relative positions of the substituents. CHEMICAL ABSTRACTS.

Crystallography of three salts of thiolmethanetrisulphonic acid. P. TERPSTRA (Natuurwetensch. Tijds., 1931, 13, 153—158).—Full crystallographic data are given for dihydrated potassium, ammonium, and thallous thiolmethanetrisulphonates (cf. A., 1930, 1556). All three form triclinic pinacoidal crystals: the potassium salt exhibits extreme variations of habit. H. F. GILLBE.

***X*-Ray investigation of cellulose derivatives. IX. *X*-Ray diagram of cellulose trinitrate. The stabilising process.** C. TROGUS and K. HESS (Z. physikal. Chem., 1931, B, 12, 268—278; cf. A., 1930, 750).—Differences in the lattice constants of cellulose (ramie) trinitrate obtained under fixed conditions of nitration have been investigated by examining the material at different stages in the preparation. A reproducible value of the fibre period, viz., 25·5±0·1 Å., is obtained when the nitrated fibre is stabilised after washing, by boiling with water or with 50% acetic acid or ethyl or methyl alcohol. F. L. USHER.

Structure of nitrated cellulose. II. *X*-Ray examination of nitroramie. F. D. MILES and J. CRAIK.—See B., 1931, 92.

Formation of thin films of organic substances and orientation phenomena accompanying them. J. J. TRILLAT and A. NOWAKOWSKI (Ann. Physique, 1931, [x], 15, 455—488).—The tangential drop method was used to investigate the structure of thin films of organic substances, including fatty acids, saturated dibasic acids, paraffins, and triglycerides. The films in contact with water and in contact with the molten substance were investigated. *X*-Ray spectra gave the conditions necessary for the formation of the films. The form and polarity of the molecules exert a great influence on the orientation. The structure of the films was compared with the surface structure of solid films obtained by slow cooling of the liquid drop. The formation of films in contact with water made slightly alkaline or acid was also investigated. A. J. MEE.

Chemical applications of crystal measurements. P. TERPSTRA (Chem. Weekblad, 1931, 28, 275—277). H. F. GILLBE.

Theory of linear crystallisation velocity of supercooled liquids and supercooled solid modifications. M. VOLMER and M. MARDER (Z. physikal. Chem., 1931, 154, 97—112).—The mean specific heat of solid glycerol over the temperature range 6—11° is 0·389 and the molecular heat of fusion 4414 g.-cal. The rate of crystallisation of the supercooled liquid has been measured for various degrees of supercooling. If the velocity of crystallisation is considered as being determined by the difference in the rates at which molecules pass from the liquid to the solid phase and in the reverse direction and also by the rate at which new lattice planes are formed (cf. A., 1926, 676), the relationship between the rate of crystallisation and the degree of supercooling is in accordance with the experimental results. R. CUTHILL.

Hall effect for nickel, iron, and copper in weak magnetic fields. Correction. E. BOSSA (Atti R. Accad. Lincei, 1930, [vi], 12, 582; cf. A., 1930, 844).—Corrected readings of the deviations previously reported are given. F. G. TRYHORN.

Hall effect with extended electrodes. E. Persico and F. Scandone (Nuovo Cim., 1930, **7**, 208—224; Chem. Zentr., 1930, ii, 2356).—The effect of the extension of the primary electrode and the position of the secondary on the magnitude of the Hall effect is treated theoretically. L. S. Theobald.

Possible anomalies in resistance at low temperatures. S. Choubine (Compt. rend., 1931, **192**, 1020—1022).—Theoretical. Anomalies in resistance at low temperatures of metals with an even number of conductivity electrons are discussed with reference to Brillouin's results (cf. this vol., 139), and superconductivity is shown to be associated with large interatomic distances. C. A. Silberrad.

Electrical properties of thin layers of metals prepared by thermal projection and cathodic sputtering. II. F. Joliot (Ann. Physique, 1931, [x], **15**, 437—454; cf. A., 1930, 531).—The electrical properties of films prepared by thermal vaporisation and cathodic sputtering are compared. The results show that the films formed by the two methods have the same crystalline structure. A. J. Mee.

New magneto-optic effect: rotatory power along the optic axis of a uniaxial crystal in the neighbourhood of absorption bands caused by a magnetic field normal to that axis. J. Becquerel and L. Matout (Compt. rend., 1931, **192**, 937—939).—With xenotime, tysonite, or ruby, cut normally to the optic axis, and a transverse magnetic field, at the temperature of liquid nitrogen there is produced circular birefringence, which in xenotime is about 45° per mm. in a field of 20,000 gauss. This rotatory power is essentially a function of the orientation of the incident vibration, and is independent of the direction of the magnetic field. The rotatory dispersion in the neighbourhood of the various bands, or of the same band for different orientations of the polariser, varies. C. A. Silberrad.

Magnetic susceptibilities of metals [cold drawn] at low temperatures. A. Kussmann and H. J. Seemann (Naturwiss., 1931, **19**, 309).—Experiments were made on the paramagnetism of aluminium and some nickel–copper–zinc alloys. A. J. Mee.

Magnetic disturbance of the superconducting state of alloys. W. J. de Haas and J. Voogd (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 56—62; cf. A., 1929, 652, 1135).—The magnetic disturbance of the superconductivity in solid solutions of 35% Bi in lead, 40% Tl in lead, 15% Hg in lead, and of the eutectic gold–bismuth mixture have been investigated. The highest field not disturbing the superconductivity was 21,150 gauss, observed for the solid solution of 35% Bi in lead at 1·88° Abs. J. W. Smith.

Effect of internal stress on the magnetic susceptibility of metals. W. Gerlach (Nature, 1931, **127**, 556).—Honda and Shimizu's result (this vol., 154) can be explained by the view that a part of the metal becomes amorphous under high pressure. L. S. Theobald.

Magnetic states of platinum. (Mlle.) P. Collet and G. Foex (Compt. rend., 1931, **192**, 930—932).—Four samples of platinum, all apparently pure, and having in fields of 6000—7000 gauss the same magnetic moment (8 magnetons) at temperatures above 50°, show, with one exception, different moments at lower temperatures. Reheating and fusion had no effect on the magnetic state. C. A. Silberrad.

Relation between ferromagnetism and conductivity. K. Gosh (Z. Physik, 1931, **68**, 566—572).—Properly prepared magnetite passes under suitable conditions into hæmatite, which can be transformed into the usual paramagnetic form. Experiments on the relation of the magnetic condition and electrical conductivity of different forms of Fe_3O_4 indicate that in ferromagnetic bodies conductive electrons are divided into two classes, one associated with electrical conductivity alone, and the other associated with both conductivity and ferromagnetism. A. B. D. Cassie.

Magnetic properties of matter in strong magnetic fields. I. The balance and its properties. II. Measurement of magnetisation. P. Kapitza (Proc. Roy. Soc., 1931, A, **131**, 224—243, 243—273).—I. The application of intense magnetic fields has been extended to the study of magnetic susceptibility and magnetostriction. A balance by means of which forces of a few grams can be measured in a time of the order of 0·01 sec. is described.

II. The experimental arrangements and results of measurements of the magnetisation of iron, nickel, some ferrous alloys, gadolinium sulphate, manganese, and bismuth are described. The laws of magnetisation as given by modern theories and verified in fields up to 30 kilogauss apply also in a region of fields up to ten times as great. In the case of bismuth, the magnetisation is measured for different crystal orientations at the ordinary temperature and the temperature of liquid nitrogen, and found to be proportional to the magnetic field. The dependence of the magnetic susceptibility on the temperature is estimated for different crystal orientations. L. L. Bircumshaw.

Physical properties of magnesium single crystals. E. Goens and E. Schmid (Naturwiss., 1931, **19**, 376—377).—Pure magnesium single crystals in the form of rods were prepared and the crystallographic orientation was determined by *X*-rays. The results are compared with previous investigations on magnesium, zinc, and cadmium single crystals. W. R. Angus.

Degradation of metallic crystals by etching. M. Straumanis (Z. Krist., 1930, **75**, 430—448; Chem. Zentr., 1931, i, 437).—Experiments with single crystals of zinc are recorded. A. A. Eldridge.

Transformation of metallic phases. II. Allotropy of pure metals. U. Dehlinger (Z. Physik, 1931, **68**, 535—542).—Transition of cerium, cobalt, and thallium from hexagonal to face-centred cubic systems is consistent with an increase in electron entropy in passing to a more symmetrical form (cf. A., 1930, 1360); in iron the first transition is from cubic-centred to face-centred cubic systems, which again increases the electron entropy. A. B. D. Cassie.

Modulus of elasticity, temperature, and m. p. W. WIDDER (Physikal. Z., 1931, **32**, 349—351).—Recent results for various metals are collected and shown not to agree with the previous hypothesis that the change in the modulus of elasticity with temperature is a linear function of the temperature.

A. J. MEE.

Metallic state. J. D. BERNAL (Metall-Wirt., 1930, 9, 983—987; Chem. Zentr., 1931, i, 891).—The physico-chemical constitution of the metals and their compounds is examined from a consideration of crystal structure and quantum mechanics.

A. A. ELDRIDGE.

Electric resistivity of silicon. C. BEDEL (Compt. rend., 1931, **192**, 802—804).—The resistivities of silicon containing 0·1, 1·4, and 8·5% Fe are 0·267, 0·069, and 0·035 ohm per cm., respectively.

C. A. SILBERRAD.

Change in resistance of graphite, thorium, titanium, and titanium-zirconium between 20·4° and 1·1° Abs. W. J. DE HAAS and P. M. VAN ALPHEN (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 70—74).—The resistances of single crystals of graphite, thorium, titanium, and a titanium-zirconium mixed crystal have been investigated at low temperatures. The resistance of a graphite crystal in a direction perpendicular to the principal axis changes very little in the helium region. Thorium keeps its normal resistance down to 1·9° Abs., when the resistance begins to fall, becoming zero at 1·4° Abs. The vanishing range is very large for a single crystal: titanium between 1·88° and 1·63° Abs. and titanium-zirconium between 1·63° and 1·12°. J. W. SMITH.

Measurements of the electrical resistance of pure indium, thallium, and gallium at low temperatures and of the magnetic disturbance of the superconductivity of thallium. W. J. DE HAAS and J. VOOGD (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 51—55).—The electrical resistances of wires of indium, thallium, and gallium have been measured at temperatures down to their superconductivity temperatures. A longitudinal magnetic field of greater than a critical value destroys the superconductivity. The observations are compared with those on mercury (A., 1928, 695). J. W. SMITH.

Sonic studies of physical properties of liquids. II. Velocity of sound in solutions of alkali halides and their compressibilities. E. B. FREYER (J. Amer. Chem. Soc., 1931, **53**, 1313—1320; cf. A., 1929, 637).—The data refer to sodium and potassium chlorides, bromides, and iodides at concentrations between 1 and 45% in water between 15° and 60°. Adiabatic and isothermal compressibilities of the solutions at 20° are recorded. The effect of increasing concentration on the velocity of sound depends on the predominance of the effect of decreasing adiabatic compressibility or of increasing density; minimal velocities are observed at certain concentrations of the iodides. The results are discussed in relation to the aggregation of the solvent and the hydration of ions. J. G. A. GRIFFITHS.

Velocity of sound in substances in the solid and liquid state. II. O. STIERSTADT (Physikal. Z., 1931, **32**, 346—348).—The sudden increase in the velocity of sound in a metal at the m. p. is investigated on thermodynamic grounds, the velocity being regarded as related to the energy content of the metal.

A. J. MEE.

Dimensional analysis applied to the thermal conductivity of liquids. J. F. D. SMITH (Ind. Eng. Chem., 1931, **23**, 416—419).—Mathematical. An equation is developed, in which thermal conductivity, compressibility, thermal expansion, viscosity, specific heat, density, the mol. wt., and the gas constant are involved. E. S. HEDGES.

Thermal conductivity of tin at low temperature. W. J. DE HAAS, S. AYOAMA, and H. BREMMER (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 75—77).—The thermal conductivity of pure tin has been measured between 12·5° and 97° Abs. The results are similar to those of Grüneisen and Goens for other metals (A., 1927, 1017). J. W. SMITH.

Exact measurement of the specific heat of osmium and rhodium between 0° and 1625°. F. M. JAEGER and E. ROSENBOHM (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 85—99).—The specific heat of pure osmium at temperatures between 0° and 1500° is given by $c_p=0·030986+0·000004721t$ and the atomic heat by $C_p=5·9152+0·0009019t$. The value of $3R$ g.-cal. for C_p seems to be exceeded at 100°. The density at 18° is 21·6 (calculated 22·7) and the m. p. about 2500°. Between 0° and 1300° the specific heat of rhodium is represented by $c_p=0·05893+0·01066\times10^{-3}t+0·027744\times10^{-6}t^2-0·017642\times10^{-9}t^3$; at higher temperatures by $c_p=0·054008+0·0584608\times10^{-3}t-0·086973\times10^{-6}t^2+0·078256\times10^{-9}t^3-0·0244072\times10^{-12}t^4$. The latter formula is unsuitable for temperatures below about 420°. The c_p-t curve shows a steep maximum at between 1200° and 1400°. No similar discontinuities could be observed, however, in the temperature coefficients of the magnetic susceptibility, electrical resistance, or in the thermo-electric force against platinum. The values of c_v and C_v for rhodium are also calculated for temperatures between 0° and 1300°. J. W. SMITH.

Specific heat of methane. P. C. LUDOLPH (Physical Rev., 1931, [ii], **37**, 830—831).—Calculations of c_v for a symmetrical tetrahedral and for a symmetrical pyramidal form of the methane molecule give results disagreeing with experiment. The temperature–c_v curve on the tetrahedral assumption shows the better agreement. N. M. BLIGH.

Chemical constant of chlorine vapour and the entropy of crystalline chlorine. T. E. STERN (Proc. Roy. Soc., 1931, **A**, **131**, 339—354).—Mathematical. Chlorine is considered to consist, at atmospheric temperature, of three types of molecules, $Cl^{35}Cl^{35}$, $Cl^{35}Cl^{37}$, and $Cl^{37}Cl^{37}$. Using the Einstein–Bose statistics, the relative numbers of the different types of molecules present in the ordinary gas are calculated, and by an analysis applicable not only to chlorine but also to other diatomic homopolar gases which consist of two or more isotopes, the vapour pressure of chlorine crystals is determined and hence the chemical constant. This is found to be 1·35, in good agreement with the value obtained by Eucken,

$1{\cdot}51 \pm 0{\cdot}16$ (A., 1925, ii, 98). By means of statistical mechanics the entropy of crystalline chlorine at 0° Abs. is calculated. L. L. BIRCUMSHAW.

Prediction of critical temperatures and heats of vaporisation. K. M. WATSON (Ind. Eng. Chem., 1931, **23**, 360—364).—The critical temperature of a liquid can be calculated from the formula $T_e/T_c = 0{\cdot}283(M/d_s)^{0{\cdot}18}$, where T_e is the absolute b. p. of the liquid, T_c the absolute critical temperature, M the mol. wt., and d_s the density at the b. p. The equation is applicable only to non-polar liquids and the error in its use is in general less than 2%. A graphical method has been developed for determining the latent heat of vaporisation of a non-polar liquid at any desired temperature or pressure without experimental determinations, using the critical temperature and the b. p. The errors involved are less than 5%, except for relatively small values of latent heats. If one experimental value is available and the critical temperature is known, the latent heat of vaporisation of a liquid, either polar or non-polar, may be determined at any desired temperature. E. S. HEDGES.

Thermodynamic properties of dichlorodifluoromethane, a new refrigerant. I. Equation of state of superheated vapour. R. M. BUFFINGTON and W. K. GILKEY (Ind. Eng. Chem., 1931, **23**, 254—256).—The constants of a Beattie–Bridgeman equation of state for superheated dichlorodifluoromethane vapour (cf. A., 1929, 252) have been determined from measurements of isometrics between volumes of 1·4 and 4·2 litres per mol. The equation is : $(V^2 - A/V^2)$, where $A = 23{\cdot}7(1 - 0{\cdot}305/V)$ and $B = 0{\cdot}59(1 - 0{\cdot}622/V)$, the units being atm., ° Abs., and litres per mol. The equation fits the observed data with an average error of 0·5%. W. J. WRIGHT.

Thermodynamic properties of dichlorodifluoromethane, a new refrigerant. II. Vapour pressure. W. K. GILKEY, F. W. GERARD, and M. E. BIXLER (Ind. Eng. Chem., 1931, **23**, 364—366). —The vapour pressures of dichlorodifluoromethane have been measured between −70° and 111·5° by a static method and are in accordance with the equation $\log_{10} p = 31{\cdot}6315 - 1816{\cdot}5/T - 10{\cdot}859 \log_{10} T + 0{\cdot}007175T$. The calculated normal b. p. is −29·8° and the Trouton and Hildebrand constants are, respectively, 20·0 and 27·1. A table of calculated vapour pressures at 10° intervals is given.
E. S. HEDGES.

Thermodynamic properties of dichlorodifluoromethane, a new refrigerant. III. Critical constants and orthobaric densities. F. R. BICHOWSKI and W. K. GILKEY (Ind. Eng. Chem., 1931, **23**, 366—367).—The orthobaric densities of dichlorodifluoromethane have been measured up to the critical temperature and the critical constants have been determined ; the saturated vapour densities below 50° have been calculated from the vapour-pressure equation and the equation of state and above 50° by dew-point determinations. Liquid densities from −40° to 50° have been determined by a dilatometric method and above 50° by the use of small glass floats ; d^0 is 1·3946 and the coefficient of expansion is 0·00233. The critical temperature, pressure, and density are, respectively, 111·5°, 39·56 atm., and 0·555 g. per c.c. The ratio of the absolute b. p. to the critical temperature is 0·632 and the constants a and b of van der Waals' equation are, respectively, 0·02116 and 0·00445. E. S. HEDGES.

Van der Waals' forces in gases. J. C. SLATER and J. G. KIRKWOOD (Physical Rev., 1931, [ii], **37**, 682—697).—Mathematical. Van der Waals' potential of two atoms at large separation is calculated for hydrogen and helium by wave mechanics, and leads to values of the polarisability of the molecule and mutual energy of two atoms in satisfactory agreement with existing data (cf. Hasse, this vol., 14 ; Eisenschitz, A., 1930, 525). N. M. BLIGH.

Equation of state of helium. J. G. KIRKWOOD and F. G. KEYES (Physical Rev., 1931, [ii], **37**, 832—840).—The statistical theory of the equation of state is reviewed briefly. Using a recent expression for the interatomic energy (cf. this vol., 410) the second virial coefficient of helium is calculated. Some properties of helium are computed therefrom. N. M. BLIGH.

Quantum statistics and the entropy of solid bodies at absolute zero. I. Discussion of experimental data on zero point entropy. II. Formulæ for entropy of solid bodies according to Fermi statistics. III. Multiplicity of lowest energy states. H. LUDLOFF (Z. Physik, 1931, **68**, 433—445, 446—459, 460—492).—I. Theoretical. Entropy near absolute zero is determined by remaining energy states of the atoms and their statistical weights, or degree of degeneracy. When interatomic forces are small, rotational and spatial degeneracy occur ; as these forces increase, rotational and finally spatial degeneracy disappear. Corresponding entropies are calculated and compared with experimental data.

II. Entropies are recalculated, using Fermi statistics.

III. Atoms in symmetrical fields, such as occur within crystals, have, in addition to spatial degeneracy, a degeneracy depending on the degree of symmetry of the crystal. This general problem is discussed, and the results are applied to calculations of entropy. A. B. D. CASSIE.

Entropy and free energy of methane. H. H. STORCH (J. Amer. Chem. Soc., 1931, **53**, 1266—1269). —The entropy at 25° computed from recent specific heat data (Clusius, A., 1929, 635) is 43·39. The following free energy equation for methane is derived : $\Delta F = -15{,}313 - 10{\cdot}54T \log T - 4{\cdot}36 \times 10^{-3}T^2 - 0{\cdot}11 \times 10^{-6}T^3 - 47{\cdot}6T$. The entropy computed from equilibria (Randall and others, B., 1929, 82 ; 1930, 49) and specific heat data (Eucken and Lüde, A., 1929, 1372) has the values 42·16 and 45·24.
J. G. A. GRIFFITHS.

Density of carbon dioxide. D. LEB. COOPER and O. MAASS (Canad. J. Res., 1931, **4**, 283—296).— By the method previously described (A., 1930, 1244), the density at five temperatures between −30° and 77°, and over a pressure range of 76—25 cm., has been determined. Extrapolation of these curves to zero pressure gives a mean value of $44{\cdot}004 \pm 0{\cdot}003$ for the mol. wt. of carbon dioxide, from which the at. wt. of carbon is found to be $12{\cdot}004 \pm 0{\cdot}003$. B. LEVIN.

Application of Bernoulli's formula to the expansion of gases. DRZEWIWCKI (Compt. rend., 1931, **192**, 1024—1026).—Bernoulli's formula is applied to deduce the formula for the velocity of a gas discharging from a vessel. C. A. SILBERRAD.

Spectrochemistry of solutions of boric acid in glycerol. M. MORELLI (Atti R. Accad. Lincei, 1930, [vi], **12**, 451—456).—The refractive indices, for the D, α, β, and γ lines, of glycerol solutions of boric acid (1—20%), at 20°, have been determined. The refractivity of the acid decreases with increase in concentration, but is greater than for aqueous solutions. Expansion occurs when boric acid is dissolved in glycerol. F. G. TRYHORN.

Viscosity of the binary system $Na_2B_4O_7$–B_2O_3 in the fused state. M. N. VOLAROVITSCH and D. M. TOLSTOI (Bull. Acad. Sci. U.S.S.R., 1930, 897—906).—The viscosity–composition curves for this system at temperatures between 650° and 750° show maxima corresponding with the compounds, $Na_2O,3B_2O_3$ and $Na_2O,4B_2O_3$ (cf. Ponomarev, A., 1915, ii, 449). T. H. POPE.

Dynamic azeotropism. V. (MLLE.) G. SCHOULS (Bull. Acad. roy. Belg., 1931, [v], **17**, 369—378; cf. this vol., 566).—Mathematical. When the pressure of an isothermal azeotropic system passes through a maximum or a minimum, the temperature corresponds with a minimum or a maximum in the isobaric diagram for this value of the pressure. C. W. GIBBY.

Freezing of solutions as a method of investigation in pure chemistry. V. Freezing of mixtures of antipodes of the malic and tartaric acid series. J. TIMMERMANS and (MLLE.) M. J. HEUSE (Bull. Soc. chim. Belg., 1931, **40**, 105—128).—An attempt has been made to ascertain the relative configurations of the acids from the f.-p. curves of mixtures assuming that two optically active substances with similar configurations will tend to form mixed crystals or a eutectic, whilst substances with dissimilar configurations will probably form a compound (A., 1930, 1121). R. CUTHILL.

Magnetic susceptibility of binary systems of organic liquids. (MISS) V. C. G. TREW and J. F. SPENCER (Proc. Roy. Soc., 1931, **A**, **131**, 209—224; cf. John and Spencer, A., 1927, 1016).—Measurements have been made for the mixtures: benzene–ethylene dichloride, carbon tetrachloride–ethyl acetate, benzene–ethyl acetate, benzene–carbon tetrachloride, pyridine–water, acetone–chloroform, acetone-bromoform, ethyl ether–chloroform, acetone–trichloroethylene, and ethyl ether–bromoform. The first two pairs obey the mixture law; the third and fourth show small deviations, whilst the remainder deviate markedly. Since the magnetic susceptibility is very sensitive to small changes in the physical and chemical state, large deviations are obtained when chemical changes occur in the mixtures. L. L. BIRCUMSHAW.

Alloys of the transitional elements. A. WESTGREN (Metall-Wirt., 1930, **9**, 919—923; Chem. Zentr., 1931, i, 677).—A discussion of the structure of the alloys in relation to the properties of the elements. A. A. ELDRIDGE.

X-Ray investigation of lead–bismuth and tin–bismuth alloys. D. SOLOMON and W. M. JONES (Phil. Mag., 1931, [vii], **11**, 1090—1103; cf. A., 1930, 1359; this vol., 33).—Although the crystal structures of antimony and bismuth are similar, their respective alloys with lead and with tin show marked differences. Solid solutions are formed at the lead end of the lead–bismuth system, whilst antimony is practically insoluble in lead. No compounds or solid solutions are formed from tin and bismuth. Measurements are recorded. F. L. USHER.

Eutectoid transformation of aluminium bronze. III. X-Ray analysis. IV. X-Ray analysis at high temperature. I. OBINATA (Mem. Ryojun Coll. Eng., 1931, **3**, 285—294, 295—298).—III. Powder diagrams for the saturated solid solutions of the α and δ phases of the aluminium–copper system show that the α possesses a face-centred cubic lattice and the δ a cubic lattice, each with 52 atoms in the unit cell. Annealed and quenched alloys containing 16% Al give identical lines. Quenched alloys containing 12·5% Al consist essentially of the β' phase, with a small quantity of the β phase: the former has a hexagonal lattice, a 11·13, c 6·342 Å., and the latter has a body-centred cubic super-lattice, a 5·835 Å. The transformation $\beta \longrightarrow \beta'$ is retarded by quenching to a low temperature or by adding a small quantity of manganese; for tempered alloys containing 12·5% Al the transformation takes place between 400° and 450°, and the transformation $\beta' \longrightarrow \alpha+\delta$ is nearly complete at 500°.

IV. Powder diagrams of an alloy containing 12·38% Al show that the alloy consists solely of the β phase at 650°. H. F. GILLBE.

Constitution of high-purity aluminium–titanium alloys. W. L. FINK, K. R. VAN HORN, and P. M. BUDGE (Amer. Inst. Min. Met. Eng., Tech. Pub., 1931, No. 393, 18 pp.).—Aluminium-rich alloys contain crystals of $TiAl_3$ having a 5·424, c 8·574 Å. In the determination of the liquidus accurate results were obtained by determining the solubility of $TiAl_3$ in aluminium by chemical analysis of the supernatant mass. The constitutional diagram for the alloys is given. CHEMICAL ABSTRACTS.

Molecular constitution of the η and H solid alloys and of the corresponding liquid solutions of the copper–tin series examined thermodynamically. F. H. JEFFERY (Trans. Faraday Soc., 1931, **27**, 188—190).—Resistance–temperature measurements show that at 691—767° Abs. the liquid phase consists of a mixture of molecules of the compound Cu_4Sn and monatomic tin, and that the solid (η) phase is the pure compound Cu_3Sn. For alloys consisting of H+liquid at 507—586° Abs. the constitution of the liquid phase is the same, whilst the solid phase is a mixture of the compound Cu_3Sn and monatomic tin. H. F. GILLBE.

M. p. in the system tungsten–rhenium. K. BECKER and K. MOERS (Metall.-Wirt., 1930, **9**, 1063—1066; Chem. Zentr., 1931, i, 750).—The system forms a compound W_2Re_3, m. p. 3280° Abs., which forms eutectics at 50 and 67 at.-% Re, and 3165° and 3095° Abs. Rhenium has m. p. 3440°±50° Abs. (Agte and others, this vol., 448). The absorption coefficient of

rhenium, or of its alloys with tungsten, at the m. p. is $A_\lambda=0\cdot42$ for $\lambda=0\cdot65\ \mu$. A. A. ELDRIDGE.

System water-chloroform. C. W. GIBBY and J. HALL (J.C.S., 1931, 691—693).—The solubility–temperature curve for water in chloroform, determined from —25° to 54° by observation of the clearing temperature of mixtures of known composition, consists of two linear portions which intersect at 0°. Chancel and Parmentier's report (A., 1885, 363) of the formation of a hydrate of chloroform could not be confirmed. H. F. GILLBE.

Mutual solubility of ethylene glycol and esters. G. E. MUCHIN and A. A. MUCHINA (Ukraine Chem. J., 1930, 5 [Sci.], 251—253).—The critical solution temperatures for mixtures of ethylene glycol with methyl and ethyl acetates and the corresponding benzoates are, respectively, 26·8°, 57·0°, 109·5°, and 137·0°. In the case of propyl esters no definite critical temperature could be obtained, partial replacement of propyl alcohol by glycol taking place. R. TRUSZKOWSKI.

Partial pressures of vapours of volatile liquids in the presence of inert gases. W. G. BEARE, G. A. McVICAR, and J. B. FERGUSON (J. Physical Chem., 1931, 35, 1068—1073).—The partial pressures of methyl and ethyl alcohols, acetone, and ether have been determined at 25° and 40°, 40·02°, 30°, and 20°, respectively, in the presence of dry air and dry carbon dioxide. The differences between the partial pressures and the vapour pressures are usually less than 1 mm. The large discrepancies previously reported (cf. Campbell, A., 1915, ii, 516) are not confirmed. L. S. THEOBALD.

Solubility of potassium iodide in water to 240°. F. C. KRACEK (J. Physical Chem., 1931, 35, 947—949).—Values given by the synthetic method between 78° and 236·4° are recorded. The most probable values between 0° and 120° are selected. L. S. THEOBALD.

[Solubility of] iodine. J. LANZA (Anal. Fis. Quim., 1931, 29, 221—234).—Aqueous iodine solutions exhibit marked supersaturation phenomena; a solution saturated at 37° when cooled to 17° does not reach equilibrium within 8 days. The true solubility between 10° and 75° has been determined; there is a maximum at about 60°. The results obtained by working always with solutions of increasing temperature are considerably lower than those given in the literature. The solubility of potassium iodide in water is increased by addition of iodine, and a solution cannot be saturated simultaneously with respect to both substances. The ratio iodine : iodide, in presence of an excess of water, falls from 0·96 at 17° to 0·79 at 60°; at 75° it rises again to 0·90. The solubility of iodine in a given solution of iodide is a maximum at about 60°. H. F. GILLBE.

Metastability of matter and its significance for calorimetric standards. I. E. COHEN and H. GOEDHART (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 1—14).—Exact solubility measurements indicate that salicylic acid at the ordinary temperature exists in two modifications, and that the metastable form is capable of existence for considerable periods. This accounts for the wide discrepancies between the solubility data as obtained by different experimenters. Owing to the metastability the material used as a calorimetric standard may be an undefined mixture, and the heat of combustion will depend on the previous history of the specimen. It is modified by grinding, heating, or by the presence of moisture. Consequently the accepted value for the heat of combustion of salicylic acid should not be taken as a calorimetric standard. J. W. SMITH.

Solubility of mixtures. W. HALLER (Kolloid-Z., 1931, 55, 6—9).—For both heterogeneous phase mixtures and gel mixtures it is shown that the solubility should depend on the proportion of solid phase present. The author's theory does not explain all aspects of the solid-phase rule and it would seem that convex and S-shaped curves are due to the operation of colloid chemical factors, such as adsorption and swelling. E. S. HEDGES.

Effect of ammonium formate on the solubility of cupric formate in formic acid. A. W. DAVIDSON and V. HOLM (J. Amer. Chem. Soc., 1931, 53, 1350—1357).—The f.-p. curves for solutions of cupric formate in pure formic acid and in mixtures containing 10—44 mols.-% of ammonium formate have been determined. The solubility of cupric formate increases with the concentration of ammonium formate, and at high values the solid phase is $2Cu(CHO_2)_2,3CH_2O_2$. Variations of colour with temperature are observed similar to those in the corresponding acetate system (cf. this vol., 683). J. G. A. GRIFFITHS.

Solubilities of lanthanum oxalate and lanthanum hydroxide in water. Mobility of lanthanum ion at 25°. I. M. KOLTHOFF and (MISS) R. ELMQUIST (J. Amer. Chem. Soc., 1931, 53, 1217—1225).—The equivalent conductivity, Λ, of lanthanum chloride at 25° is given by $\Lambda=152\cdot8-475\sqrt{c}$, where $c=0$—0·001. The p_H of the 0·1M solution is 6·2. The mobility of the lanthanum ion is 77. The solubility of lanthanum oxalate, determined volumetrically and colorimetrically, is 2·08 mg. of anhydrous salt per litre. The conductivity method affords much lower values, probably owing to formation of complex ions. The solubility of lanthanum oxide and the aged hydrous oxide is 0·7 mg. of La_2O_3 per litre at 25°.

0·1—2 Mg. of lanthanum (as sulphate) per litre can be determined colorimetrically by adding 1 c.c. of acetate buffer (2N-ammonium acetate and 2N-acetic acid) and 0·4 c.c. of 0·1% sodium alizarinate to 10 c.c. of the solution. The violet colour is compared with standards similarly prepared. J. G. A. GRIFFITHS.

Conditions of growth of crystals of sparingly soluble substances. I. KURBATOV (Z. Krist., 1931, 77, 164—168).—From a consideration of the solubility product it is deduced that large crystals of sparingly soluble substances, *e.g.*, barium sulphate, are probably produced in nature from supersaturated solutions containing the necessary ions in non-equivalent amounts. C. A. SILBERRAD.

Adsorption of hydrogen on charcoal. F. E. T. KINGMAN (Nature, 1931, 127, 742).—" Norite " charcoal adsorbs hydrogen at temperatures above the ordinary, but below 200° the rate is still immeasurably slow. L. S. THEOBALD.

Nature of sorption of hydrogen by platinum metals, and tenacity with which the gas is retained. E. MULLER and K. SCHWABE (Z. physikal. Chem., 1931, 154, 143—166; cf. A., 1929, 639).—When palladium has taken up hydrogen under a pressure of 1 atm. and is then subjected to a very low pressure the hydrogen is removed again. Under similar conditions, ruthenium, rhodium, osmium, and iridium retain practically the whole of the hydrogen, and platinum gives up only a part. It is considered that such cases of the fixation of hydrogen by metals involve both atomic sorption and molecular sorption. In either type of sorption the force is maximal when the metal is in the form of single isolated atoms, and minimal when the hydrogen is within the metal lattice; with increase in the degree of dispersity of the metal the hydrogen is held more and more firmly. Atomic sorption results in chemical activation of the sorbed gas and is independent of the gas pressure; in the case of platinum atomic sorption occurs only on the metal surface. The hydrogen fixed by molecular sorption, however, is located within the metal lattice and is held more loosely, so that the amount sorbed varies with the pressure. All the platinum metals have the power of atomic sorption, but at the ordinary temperature molecular sorption occurs only with platinum and palladium. R. CUTHILL.

Ortho-para-hydrogen conversion at surfaces. H. S. TAYLOR and A. SHERMAN (J. Amer. Chem. Soc., 1931, 53, 1614—1615; cf. Bonhoeffer and Harteck, A., 1929, 982)—At liquid air temperatures equilibrium is established as readily with very active nickel (10% Ni on kieselguhr) as with charcoal. On zinc–chromium oxide or zinc oxide surfaces conversion occurs over the temperature range (above 0°) in which the hydrogen undergoes "activated" adsorption (cf. Taylor, this vol., 421). J. G. A. GRIFFITHS.

Reaction between carbon and oxygen at low pressures and at the ordinary temperature. H. I. BULL, M. H. HALL, and W. E. GARNER (J.C.S., 1931, 837—847).—The maxima on the differential heat of adsorption–surface concentration curves for the adsorption of oxygen on carbon previously reported (cf. A., 1926, 1091) are due to experimental error. The results of Marshall and Bramston-Cook (A., 1929, 999) have now been confirmed. The rate of adsorption of oxygen, at low pressures, on a partly saturated carbon surface is a linear function of the pressure. Subsequent slow changes in the adsorbed layer are due either to diffusion into the interior of the adsorbent or to a slow chemical reaction. H. F. GILLBE.

Determination of particle size of powdered adsorbents. I. F. KRCZIL (Kolloid-Z., 1931, 55, 25—30).—By means of a sedimentation method the particle sizes of five kinds of carbon and six kinds of silica have been measured and the percentage distribution of particle size is represented graphically. Bone charcoal occupies a special position in having the largest percentage of particles between 0·03 and 0·002 mm. The results for the silica adsorbents show a relatively high percentage of particles smaller than 0·001 mm. E. S. HEDGES.

Dependence of activity of methylene-blue on particle size of active carbons. F. KRCZIL (Kolloid-Z., 1931, 55, 30—32).—The adsorption of methylene-blue by poorly adsorbent forms of carbon is increased very greatly by fine subdivision, but the effect for an active form of carbon is small. E. S. HEDGES.

Adsorption of aromatic acids on charcoal. I. Influence of solubility, association, and orientation in the boundary layer. Adsorption affinity and specific adsorption. G. BERGER (Rec. trav. chim., 1931, 50, 377—406).—The adsorption of benzoic, toluic, chloro-, bromo-, and nitro-benzoic acids, of the three dimethylbenzoic acids, and of 2:6-dibromobenzoic acid dissolved in acetone and in benzene has been studied at 19°±1°, using charcoal as adsorbent. The solubilities of all these acids in the above-mentioned solvents at 20° have also been determined. The values of the constants α and $1/n$ in the isotherm expression $a=\alpha c^{1/n}$ differ widely, both for different acids in the same solvent, and for the same acid in different solvents. The values of $\alpha L^{1/n}$ (L=solubility of adsorbed substance in the solvent), which should be constant according to Lundelius (A., 1920, ii, 358), also fluctuate considerably. The most satisfactory method of comparing the adsorption of the various acids is to calculate the adsorption affinity in accordance with Polanyi's theory and to plot this expression against the amount of substance adsorbed. The resulting affinity curves for a given substance in two different solvents should coincide, but this is in general not the case. The divergences, however, are shown to be due to two causes, viz., association of the molecules of the solute and, chiefly, the orientation of the adsorbed molecules in the boundary layer. The work involved in the orientation is made up of two parts, one of which depends on changes in the attractive forces between adsorbent and adsorbed substance, and the other on changes in the intermolecular forces within the adsorbed layer. The total effect of orientation can be determined approximately from the affinity curves and agrees qualitatively with the orientation effects to be expected from a consideration of the polar properties of the two phases at the boundary and of the adsorbed molecules. The assumption of a "specific" adsorption affinity which is independent of the nature of the solvent is fundamentally unsound. O. J. WALKER.

Adsorption of tetraethylammonium iodide from various solvents by carbon. J. K. SYRKIN and M. I. POLIAKOV (Kolloid-Z., 1931, 55, 33—36).—The adsorption by carbon of tetraethylammonium iodide dissolved in water or in methyl alcohol is in accordance with the formulæ of Freundlich and of Langmuir. The adsorption falls in the series water > methyl alcohol > ethyl alcohol, which are in increasing order of molecular polarisation. In acetone, benzaldehyde, anisaldehyde, propionitrile, and nitrobenzene the adsorbability is parallel with the surface tension of the solvent. Adsorption from aqueous solutions is diminished by the addition of alcohol. E. S. HEDGES.

Absorption of water vapour by cotton cellulose. R. H. PICKARD (J. Amer. Chem. Soc., 1931, 53, 1610—

1611).—Polemical. The technical importance of the discrepancies between the data of Pidgeon and Maass (A., 1930, 684) and those of earlier workers is emphasised. J. G. A. GRIFFITHS.

Adsorption of substances by fuller's earth. H. J. PHELPS (Proc. Roy. Soc., 1931, A, **131**, 17—29).—The adsorption of organic acids and bases by fuller's earth has been studied in relation to the p_H of the solution. The results indicate adsorption of non-ionised molecules and also of cations which displace calcium ions from the surface. No adsorption of propionic or hexoic acid occurs at any p_H. Oxalic acid is adsorbed when $p_H>1\cdot5$, the adsorption rising to a maximum at p_H 4 and then gradually decreasing. The results with *n*-butylamine and *n*-propylamine are very similar; in each case the adsorption rises from zero in strongly acid solution to p_H 4·5, remains constant to p_H 8, rises rapidly from p_H 9·5 to a maximum at p_H 11, after which a rapid fall occurs. Over the range p_H 4·5—8 an amount of calcium is displaced which is equivalent to the base adsorbed, whilst in more alkaline solutions the calcium displaced falls to zero. In strongly alkaline solutions the adsorption of bases by fuller's earth is therefore a true polar process, but for solutions more acid than p_H 8 adsorption proceeds by the displacement of calcium ions. The adsorption of *n*-butylamine by aluminium silicate gel yields further evidence in support of this view; the adsorption rises from zero at p_H 7 to a maximum at p_H 11, followed by a rapid fall in more alkaline solutions. The fact that the gel does not adsorb oxalic acid at any p_H supports the view that the adsorption of this acid by fuller's earth proceeds by the formation of insoluble calcium oxalate at the surface. L. L. BIRCUMSHAW.

Absorption of dye by granules of a hydrosol. A. BOUTARIC and M. DOLADILHE (Compt. rend., 1931, **192**, 1098—1099; cf. this vol., 19).—The fixation of a dye by granules of a hydrosol is determined by comparing the absorption of the dye in the hydrosol with that of the same amount of dye dissolved in an equal volume of water. Only that portion of the dye which is not fixed on the granules has any absorbing power. This method is applied to experiments on diamine-blue and arsenious sulphide sol (both negative), and Victoria-blue and ferric oxide sol (both positive). Particles of colouring matter affix themselves to granules of a colloid only if the signs are different. C. A. SILBERRAD.

Influence of adsorption on organic colloids. M. PIETTRE (Compt. rend., 1931, **192**, 894—897; cf. A., 1930, 235).—The increase in the p_H of 0 01*N*-hydrochloric acid produced by serum-albumin is attributed to adsorption of hydrochloric acid; this is confirmed by the behaviour towards indicators of serum-albumin solutions to which hydrochloric acid or sodium hydroxide has been added. The adsorption is masked in presence of strong acids. C. A. SILBERRAD.

Effect of addition of salts on the surface tension of sodium taurocholate solutions. M. SHIONO (J. Biochem., Japan, 1930, **12**, 317—339).—At higher concentrations the degree of lowering of the surface tension depends on the hydration, and at lower concentrations on the nature of the cations. The minimum surface tensions of solutions of sodium, calcium, and copper taurocholates differ. CHEMICAL ABSTRACTS.

Soap solutions. IX. Surface tension of aqueous solutions of binary mixtures of soaps having extremely different molecular weights. J. MIKUMO (J. Soc. Chem. Ind. Japan, 1931, **34**, 115—116B; cf. A., 1930, 1518).—The surface tensions of solutions of binary mixtures of sodium soaps of the saturated C_5 to C_{12} fatty acids with sodium erucate have been measured at 40°. The C_{22} soap is almost entirely responsible for the surface tension. Addition of the lower soaps does not improve the surface activity of solutions of the highest soaps, and may even produce a coagulating effect. E. LEWKOWITSCH.

Capillarity. XV. Capillary rise in disperse systems. K. SCHULTZE (Kolloid-Z., 1931, **55**, 9—25).—The capillary rise of liquids in coarsely disperse solid systems such as sand and glass powder is examined in the light of Schultze's views of simple capillary behaviour (A., 1929, 645). When the solid particles are irregular in form, both the capillary rise and the water capacity are greater than when the particles are spherical. Coating spherical glass particles with paraffin causes a greater reduction in water capacity than in capillary rise, whilst with irregular particles no appreciable difference in capillary rise was observed. E. S. HEDGES.

Method for rendering wetting visible. W. HALLER (Kolloid-Z., 1931, **55**, 1—3).—The technique described is suitable for determining the relative wetting of a glass surface by two immiscible liquids. A glass tube containing the liquid is immersed in a plane-parallel glass trough which contains a mixture of benzyl benzoate and xylene of such a composition that the refractive index of the mixture is exactly the same as that of the glass tube. The contents of the tube may then be observed or photographed in diffused, transmitted light. Thin liquid films, which normally escape observation, are rendered visible by this means. E. S. HEDGES.

Ultramicroscopic structure of unimicellar, iridescent films of albumin and other substances. C. SPIERER (Kolloid-Z., 1931, **55**, 36—41).—Ultramicroscopic observations on very thin films of albumin, gelatin, caoutchouc, oil of turpentine, olive oil, and xylene afford evidence of stratified structure of the films of soap and of albumin and of a micellar structure of the other films. Oil films on water consist of emulsions in the form of a single layer of droplets. The observations contradict the view that many oil films on water consist of a continuous, unimolecular layer and much of the work based on this conception is said to have been wrongly interpreted. E. S. HEDGES.

Surface chemistry of hydrates. I. Aged hydrous alumina. V. R. DAMERELL (J. Physical Chem., 1931, **35**, 1061—1067).—Hydrous aluminium oxide after ageing at the ordinary temperature under water containing small amounts of ammonia forms with water a compound which is probably a trihydrate. When exposed to partly-dehydrated sodium carbonate mono- or hepta-hydrate, this compound adsorbs water

in proportion to its surface, but over phosphorus pentoxide chemically combined water is lost. The different water contents of ground and unground hydrargillite observed by Simon and Fischer are probably due to an increase in surface and not to local heating during grinding. A similar difference has been observed in precipitates of different particle size which have not been ground.

L. S. THEOBALD.

Mechanism of p_H changes in liquid cells containing a diaphragm on continued passage of the current. M. CHANOZ (Compt. rend. Soc. Biol., 1930, **104**, 998—1000; Chem. Zentr., 1931, i, 583).—Aqueous solutions of copper sulphate exhibit the changes anticipated from a consideration of the permeability of the diaphragm to anions or cations, respectively. A. A. ELDRIDGE.

Osmosis in systems which contain liquids with constant composition. II. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 78—84; cf. A., 1930, 992).—Mathematical. J. W. SMITH.

Vapour-pressure method for measurement of osmotic pressure. W. D. TREADWELL [with A. WEISZ] (Helv. Chim. Acta, 1931, **14**, 609—614).—The difficulty of preparing accurately isotonic solutions of different substances is discussed. A method is described for comparing the vapour pressure of a solution with that of a standard, wherein one arm of a glass balance, weighing about 0·8 g., carries one drop of the solution and the other one drop of the standard solution. The rate of distillation, and therefore the difference of vapour pressure, is determined by observation of a beam of light reflected from a mirror attached to the balance beam. H. F. GILLBE.

Measurement of dielectric constants of aqueous solutions of electrolytes. O. MILICKA and A. SLAMA (Ann. Physik, 1931, **8**, [v], 663—701).—The Fürth static "ellipsoid method," which is shown to be free from inaccuracy through polarisation effects and heat convection currents, has been applied extensively to the measurement of the dielectric constants of aqueous solutions of salts, acids, and bases of different concentrations. The dielectric constant is found to be independent of the frequency in the range 277—2212 sec.$^{-1}$ and of the applied voltage between 0 and 30 volts. A modified ballistic method is described which possesses greater accuracy and enables measurements of the dielectric constants of liquids to be made up to conductivities of at least $10^{-2}\Omega^{-1}$ cm.$^{-1}$ The results for 11 salts, 5 acids, and 3 bases are given. The dielectric constant at small concentrations decreases with increasing concentration, passes through a minimum, and then increases with increasing concentration at greater concentrations. In some cases a point of inflexion or a second minimum occurs. At very large concentrations the dielectric constant approaches a saturation value which is in general higher than the dielectric constant of water. The initial decrease is explained by the formation of the "atmospheres" of water molecules around the ions, the appearance of a point of inflexion, or more than one minimum by the formation of complexes. It is suggested that at increasing high frequencies the position of the minimum is displaced towards higher concentrations, the initial sharp fall in the dielectric constant becoming at the same time flatter. W. GOOD.

Apparent volumes and refractions of dissolved electrolytes. W. GEFFCKEN (Naturwiss., 1931, **19**, 321—322).—Previous experimental results (A., 1929, 1233) show that $\phi_c=\phi_0+kc^{\frac{1}{2}}$, where ϕ_c is the apparent volume of a dissolved electrolyte at molar concentration c, and k, which is always positive, is constant for the alkali metal (except lithium) halides at concentrations up to the saturation point. The magnitude of k increases in the order Li, Na, (K, Rb, Cs), and I, Br, Cl, F. At low concentrations (0·01M) the relationship between ϕ_c and c is valid for sodium bromide, but with the alkali metal sulphates and carbonates there is a systematic deviation.

H. F. GILLBE.

Behaviour of electrolytes in mixed solvents. III. Molecular refractivities and partial molar volumes of lithium chloride in water–ethyl alcohol solutions. J. A. V. BUTLER and A. D. LEES (Proc. Roy. Soc., 1931, **A, 131**, 382—390).—The molecular refractivity, R, of lithium chloride is found to be constant in each solvent over the range of concentrations studied. There is little change in the value of R until the molar fraction of alcohol exceeds 0·2, after which it decreases steadily as the proportion of alcohol is increased. It is supposed that the ions are surrounded almost entirely by water molecules until the molar fraction of alcohol reaches 0·2. The partial molar volume of lithium chloride is much smaller in 100% alcohol than in water and increases rapidly with the concentration. Its variation with the composition of the solvent is similar to that of the refractivity. L. L. BIRCUMSHAW.

Solvent action. I. Influence of polar solvents on the rotatory power of *l*-menthyl methyl naphthalate. H. G. RULE and A. MCLEAN (J.C.S., 1931, 674—691).—The mol. rotation of *l*-menthyl methyl naphthalate varies from −219° in nitrobenzene solution to −788° in decalin. The rotation falls with increase of the polarity of the solvent, and for solvents of similar type an approximately smooth curve is obtained by plotting dipole moment against rotatory power. Measurements with homologous and isomeric solvents having approximately the same moment demonstrate the screening of the influence of the dipole by the larger groups. A non-polar solvent such as *p*-dichlorobenzene produces as large a depression of the rotation as the *o*-isomeride, probably because the distance between the dipoles permits them to function individually; this view is confirmed by the fact that the depression produced by *p*-dichlorobenzene is approximately twice that produced by chlorobenzene. The depression observed in associated solvents increases greatly if the associated molecules are dissociated by addition of a non-polar solvent, and the process of dissociation may thus be studied polarimetrically. The dissociation curves obtained resemble those deduced by Debye. The sensitivity of the rotatory power of the solute towards different solvents is probably due to the influence of the dipoles on the internal field of the solute. It is not a result

of variations of the electrostatic forces operating between the peri-groups. H. F. GILLBE.

Effect of pressures up to 17,000 atm. on colloidal suspensions. R. WILSON and T. C. POULTER (Proc. Iowa Acad. Sci., 1929, 36, 295—296).—Colloidal ferric hydroxide is precipitated in 30 min. at 100 atm., and immediately at 300 atm. Colloidal sulphur or silver is scarcely affected below 9000 atm., but is rapidly and completely precipitated at 17,000 atm. Prussian blue is completely precipitated at about 2000 atm., and red colloidal gold by pressures above that level. Molybdenum blue exhibits colour change from blue to green at pressures of 2000—9000 atm., but is not completely precipitated by higher pressures. CHEMICAL ABSTRACTS.

Viscosity and rigidity in suspensions of fine particles. I. Aqueous suspensions. C. M. McDOWELL and F. L. USHER (Proc. Roy. Soc., 1931, A, 131, 409—427).—Measurements of the viscosity and rigidity of cupric ferrocyanide and cadmium sulphide sols show that cupric ferrocyanide sols possess a viscosity which differs only slightly from that of water, but on the addition of an electrolyte the value increases with decreasing rate of shear. This phenomenon requires a definite time to appear, the time being the longer the more dilute is the suspension with regard to either electrolyte or copper ferrocyanide; the variation is more marked in the more concentrated sols, where small additions of electrolyte produce a large increase in viscosity at low rates of shear. It was found that some sols of both copper ferrocyanide and cadmium sulphide with electrolyte addition possess true rigidity—*i.e.*, they support, apparently permanently, small stresses without yielding. These sols also showed a linear relation between stress and strain, and therefore behave as perfectly elastic bodies under the experimental conditions. Two other methods of detecting rigidity in suspensions are described. The origin of the above effects is discussed. L. L. BIRCUMSHAW.

Dielectric polarisation and structure of colloids. N. MARINESCO (J. Chim. phys., 1931, 28, 51—91).—Methods for measuring the dielectric constant of colloidal solutions are described and the hydrophilic constants of colloids are calculated (cf. A., 1930, 156). The hydrophilic constant of a colloid is defined as the number of g. of water dielectrically adsorbed by 1 g. of the dry substance and the following values are recorded: hæmoglobin 2·7, starch 0·5, gum arabic 0·026, gelatin 0·013—0·570, egg-albumin 1·54, serum-albumin 0·11. The hydrophilic constant of gelatin varies considerably with the hydrogen-ion concentration of the solution and has a minimum value at the isoelectric point. For hæmoglobin, the most hydrophilic of the substances investigated, the micellar radius is $43·5 \times 10^{-8}$ cm., whilst the radius of the kernel is $26·5 \times 10^{-8}$ cm. Attention is directed to the large difference between the constants of egg- and serum-albumins. The data lead to 11,300 for the mol. wt. of gelatin in very dilute solution, a value in agreement with those obtained by other methods, although the mol. wt. increases greatly with increasing concentration. The dielectric constants of solutions of agar and of pepsin vary greatly with the concentration. The method has been used to follow the course of lactic acid fermentation; the time curve obtained is peculiar, having two minima and a maximum. The physical structure of the water bound to the hydrophilic colloid is discussed and it is concluded that the kernel of the micelle is surrounded by a sheath of water dielectrically saturated with ice VI. E. S. HEDGES.

Determination of emulsion type. B. VAN DER BURG (Chem. Weekblad, 1931, 28, 251).—A description of the changes of appearance under the microscope of the droplets in an emulsion, as the focussing is altered, when their refractive index is greater or less than that of the continuous phase. H. F. GILLBE.

Viscosity of emulsions. II. J. O. SIBREE (Trans. Faraday Soc., 1931, 27, 161—176).—The two assumptions on which Hatschek's equation (A., 1911, ii, 98) is based have been confirmed by direct measurements of particle size and viscosity (cf. A., 1930, 290). The viscosity of an emulsion decreases with increasing velocity gradient, and becomes independent of this above a certain critical value. This constant value of the viscosity confirms Hatschek's equation if the volume ratio, ϕ, is multiplied by the factor 1·3; the precise significance of this "volume factor," which is practically constant for all the emulsions studied and varies only slightly with concentration, is obscure.

H. F. GILLBE.

Hydrophilic colloid models. D. TALMUD and S. SUCHOVOLSKAJA (Kolloid-Z., 1931, 55, 48—64).—Three-phase emulsions consisting of benzene, water, and pulverised calcium carbonate or calcium sulphate, with or without the addition of some oleic acid, are regarded as types of hydrophilic colloids, the chief difference being in the degree of dispersion. There is no essential difference between three- and two-phase emulsions, the conditions of stability of the former being determined mainly by the nature and degree of dispersion of the solid adsorption layer. The addition of a surface-active substance, such as oleic acid, causes a phase reversal. The discontinuous phase in these systems is composed of the liquid which least readily wets the solid. Three-phase emulsions stabilised by hydrophilic powders serve as models of hydrophobic colloids, whilst those stabilised by hydrophobic powders are models of lyophilic colloids, where the particles are solvated by a non-aqueous liquid. Such emulsions gelatinise by "setting" of the adsorption layer. Quantitative measurements on swelling pressure, gelation, and syneresis in these model systems are described. Gelation was found to occur only when the three-phase emulsion contains oleic acid between certain limiting concentrations, in agreement with the observed maximum of solidity of an oleic acid adsorption layer at a benzene–water interface, which exists in the same concentration region. By syneresis reversal of the emulsion occurs, with a diminution of stability; the cause is traced to charging of the powder with similarly-charged ions. The solvation of lyophilic micelles is not related to the charge, but to the presence of polar groups, and has a maximum value. For a given polar group the solidity of the adsorption layer increases with the length of the non-polar part of the molecule. Syneresis

is regarded as the reverse of gelation and is due to the micelles losing the power to orient the solvent molecules, the polar groups being transformed into hydrophobic groups. E. S. Hedges.

Possible transformations in turbid media. A. Boutaric (Bull. Soc. chim., 1931, [iv], **49**, 389—397).—A theoretical consideration of the changes which may occur in the absorption of light by a colloidal solution when the dimensions of the disperse particles are subject to alteration. J. Grant.

Complex coacervation. V. Relative displacements in the electric field of liquid inclusions in complex coacervate droplets. H. G. B. de Jong and A. J. W. Kaas (Biochem. Z., 1931, **232**, 338—345).—A small, finely-divided amount of an organic fluid, either immiscible or partly miscible with water, is taken up in a coacervate drop. Only in the case of such inclusions is a relative displacement in an electric field observed; this displacement ends when the included droplets protrude from the coacervate drop in varying degree. The direction in which the displacement occurs depends on the cataphoretic charge of the complete coacervate drop. H. W. Dudley.

Relation between charge and stability of colloidal gold. G. M. Nabar and B. N. Desai (Nature, 1931, **127**, 666).—By dialysing a Zsigmondy gold sol it was found that the stability towards potassium chloride and the charge increase to a maximum and then decrease. L. S. Theobald.

Stability of elementary foam. D. Talmud and S. Suchovolskaja (Z. physikal. Chem., 1931, **154**, 277—308).—Measurements have been made of the stability of single air bubbles (about 1·5 mm. diameter) escaping through various types of water–air surfaces. When the water surface is covered with a film of an insoluble capillary-active substance, *e.g.*, palmitic, stearic, and oleic acids, cetyl alcohol, ethyl oleate, there is a sharp maximum in the stability of the bubble at a definite thickness of the film. The addition of electrolytes to the water does not alter the thickness of the film at which the maximum stability of the bubble occurs, so that a bubble which is stabilised by insoluble capillary-active substances is lyophilic towards electrolytes. Bubbles escaping through solutions of capillary-active substances, such as heptoic and octoic acids and aniline, are also lyophilic, but in solutions of electrolytes the stability of the bubble increases regularly with the concentration of electrolyte. When evaporation is prevented in the case of the solutions of capillary-active substances the stability curves obtained resemble those obtained with the films of insoluble active substances. A theory to explain the results is presented. O. J. Walker.

Thermo-senescence effect exhibited by gold sols at elevated temperatures, and ageing at the ordinary temperature. E. Jones and W. C. M. Lewis (J. Physical Chem., 1931, **35**, 1168—1173; cf. Butler, A., 1930, 414).—The effect of prolonged dialysis on the thermo-senescence of gold sols has been investigated. Thermo-senescence, with its fall in the value of β, the Smoluchowski coefficient, has been observed in all cases (2—70 days' dialysis). An ageing effect which increases β occurs when dialysis is prolonged more than 5 days at the ordinary temperature. Thermo-senescence cannot be attributed to further removal of impurities, but is best explained by a contraction of sol particles. No sol is in a suitable condition for examination until it has been dialysed for 4—5 days and then heated for 3 hrs. at approximately 80°. L. S. Theobald.

Coagulation of colloids from the point of view of Smoluchowski's theory. I. Coagulation of antimony sulphide sol. S. S. Joshi and S. M. Prabhu (J. Indian Chem. Soc., 1931, **8**, 11—17).—Measurements of the rate of coagulation of antimony sulphide sol by $0·1N$-sulphuric acid at 33° have been made in order to test Smoluchowski's equation. The bimolecular constant k decreases with the time, and the constant β also diminishes during coagulation. The influence of temperature on the percentage coagulation in a given time has been studied, and here also there are differences between theory and observation, which tend, however, to disappear if the viscosity of the colloid instead of that of water is used in the calculation. O. J. Walker.

***X*-Ray investigation of the coagulation of colloidal gold.** P. Scherrer and H. Staub (Z. physikal. Chem., 1931, **154**, 309—321).—In the coagulation of a highly-dispersed gold sol the primary particles of the hydrosol first unite to form larger secondary particles in which there is no regular arrangement of the primary units, the size of the latter being unaltered. The crystallisation of the primary particles to larger crystals occurs when the coagulated sol is intensively dried at the ordinary temperature or kept in an electrolyte solution. The rate of this crystallisation depends on the nature and previous treatment of the sol from which the coagulate is obtained, and is considerably increased by rise of temperature. Protective colloids, however, if added immediately after the coagulation process, prevent the crystallisation to larger crystals almost entirely. O. J. Walker.

Coagulation of colloids by electrolytes. VIII. Ion exchange and cataphoretic potential. A. J. Rabinovitsch and E. B. Fodimann (Z. physikal. Chem., 1931, **154**, 255—276; cf. A., 1930, 33).—The coagulation of arsenious sulphide sols by various electrolytes has been studied by measurements of conductivity and of the cataphoretic migration velocity, which gives a measure of ζ, the electrokinetic potential. With increasing concentration of added electrolyte (c), the ζ–c curves show at first a rapid, logarithmic decrease and then a slower, linear one, the change occurring at the concentration at which the conductometric curves also become linear, *i.e.*, when the exchange adsorption and displacement of hydrogen ions by metallic cations cease. Potassium chloride, when added to acidified arsenious sulphide sols, behaves abnormally and produces an initial increase in the velocity of cataphoresis (cf. Kruyt and Willigen, A., 1928, 18). If no displacement of hydrogen ions occurs, *e.g.*, when strychnine nitrate is added to the sulphide sols, or especially in the case of mastic sols, the ζ–c curve decreases very slowly and linearly. O. J. Walker.

Theory of swelling of gels. E. L. LEDERER (Kolloid-Z., 1931, **55**, 41—47).—Curves representing the drying of gypsum and lead shot are compared with those for aqueous solutions of gelatin and of soap, alcoholic soap solutions, and solutions of caoutchouc in toluene. The conclusion is reached that the dispersion medium is bound in two ways, partly by adsorption through the oriented fields of force of the molecular aggregates, and partly locked in the hollow spaces. E. S. HEDGES.

Theory of gelation [of pectins]. V. KURBATOV (Kolloid-Z., 1931, **55**, 70—72).—A note on the work of Glückmann (cf. following abstract). The addition of an organic substance affects the gelation of pectins probably by repressing the ionic dissociation of water and preventing incipient hydrolysis. E. S. HEDGES.

Production of pectin jellies. S. GLÜCKMANN (Kolloid-Z., 1931, **55**, 64—69).—The viscosity of solutions of pectin from lemon peel has been measured in presence of alcohols, acetone, glycerol, sucrose, and other organic substances. The relative viscosity of the aqueous pectin solution containing the organic substance is equal to the relative viscosity of the aqueous pectin solution multiplied by the relative viscosity of the aqueous solution of the organic substance. This relation is independent of the temperature and the concentration. The gelation of pectin is influenced by the addition of organic substances, the effect increasing in the order multivalent alcohols $<$ univalent alcohols $<$ ketones $<$ sucrose. In each homologous series the effect increases with the size of the molecule. This order is that of decreasing association, and the effect of the organic substance is probably to diminish the degree of association of water. A relation between gelation and association of the dispersion medium is indicated and the mechanism of the gelation of pectins is discussed in the light of Kurbatov's theory of crystal-polyamphions (Protoplasma, 1930, **9**, 37). E. S. HEDGES.

Coherent expanded aerogels and jellies. S. S. KISTLER (Nature, 1931, **127**, 741).—The liquid in a gel has been replaced by a gas without significant shrinkage by replacing the liquid with alcohol or ether, heating above the critical temperature, and allowing the vapour to escape. Aerogels of silica, alumina, nickel tartrate, stannic and tungstic oxides, gelatin, agar, cellulose, cellulose nitrate, and egg-albumin have been thus prepared. Silica aerogel (*d* 0·1—0·02) is opalescent, transparent, and has a glassy fracture. L. S. THEOBALD.

Combination curves, hydrogen-ion regulating power, and dissociation constants of gelatin. E. B. R. PRIDEAUX (Proc. Roy. Soc., 1931, B, **108**, --4—232).—From the electrometric titration curve of gelatin in 0·1% concentration on the alkaline side of the isoelectric point, and from the data of previous workers, the dissociation constants of the protein as acid and as base have been calculated both on the Zwitterion theory and on the older theory. On assumption that the isoelectric point of gelatin is at p_H 4·7, the Zwitterion theory leads to pK_A 4·05, pK_{B_1} 8·85, 4·05, and the older theory to pK_B 10·15, pK_{A_1} 5·35, pK_{A_2} 10·15. If the isoelectric point is taken to be at 5·0, the corresponding figures are pK_A 4·3, pK_{B_1} 8·6, pK_{B_2} 4·4, and pK_B 9·9, pK_{A_1} 5·6, pK_{A_2} 9·8. W. O. KERMACK.

The p_H stability region of insoluble proteins. J. B. SPEAKMAN and M. C. HIRST (Nature, 1931, **127**, 665—666).—Measurements of the force required to stretch fibres by 30% in solutions of different p_H show that insoluble proteins have a wide stability region which includes the isoelectric point. Wool keratin is completely stable from p_H 4 to 7, at least. The effects of formic, hydrochloric, and sulphuric acids on the resistance of wool to stretching are described, and the results are interpreted according to the theory of Astbury and Woods (this vol., 752). L. S. THEOBALD.

Law of degradation of solutions of rubber. P. BARY and E. FLEURENT (Compt. rend., 1931, **192**, 946—948; cf. B., 1927, 586).—The viscosity of solutions of rubber (η, defined as the ratio of the viscosity of the solution to that of the pure solvent) is related to the time of heating, t, by the equation $(\eta-1)(t+\theta)=A$, where θ and A are constants, the latter depending on the solvent and temperature. Putting $T=t+\theta$ and defining $1/(\eta-1)$ as the "degradation," D, this reduces to $T=AD$. From experimental determinations of A it is calculated that 2% solutions in benzene, toluene, and xylene, heated at 80°, 93·5°, and 138—140°, respectively, would take 35,400, 587·8, and 181·5 hrs. for their viscosities to be reduced to 10% above that of the solvent, *i.e.*, until $D=10$. C. A. SILBERRAD.

Graphical representation of homogeneous chemical equilibria. I. Systems with three kinds of molecules. K. POSTHUMUS (Rec. trav. chim., 1931, **50**, 513—521).—Mathematical. O. J. WALKER.

Dissociation constants of nitrogen tetroxide and nitrogen trioxide. F. H. VERHOEK and F. DANIELS (J. Amer. Chem. Soc., 1931, **53**, 1250—1263; cf. this vol., 553).—By means of an all-glass apparatus, the dissociation constant of nitrogen tetroxide is found to be $K_{p(\text{atm.})}=0{\cdot}1426-0{\cdot}7588\times C_{N_2O_4}$ at 25°, $0{\cdot}3183-1{\cdot}591C_{N_2O_4}$ at 35°, and $0{\cdot}6706-3{\cdot}382C_{N_2O_4}$ at 45°, where $C_{N_2O_4}=5-30\times10^{-3}$ g.-mol. of N_2O_4 per litre, assuming no dissociation. The equilibrium is not affected by oxygen, carbon dioxide, or adsorption on the walls. The admixture of nitrogen tetroxide with nitric oxide results in a decrease of pressure from which the equilibrium constant $K_{N_2O_3}=P_{NO}\times P_{NO_2}/P_{N_2O_3}$ is computed to be $2{\cdot}105-45{\cdot}63C$ at 25°, $3{\cdot}673-78{\cdot}11C$ at 35°, and $6{\cdot}88-196{\cdot}4C$ at 45°, where $C=6-15\times10^{-3}$ g.-mol. per litre of N_2O_3, assuming no dissociation. The reactions proceed according to the equations $N_2O_4 \rightleftharpoons 2NO_2$ and $N_2O_3 \rightleftharpoons NO+NO_2$. The influence of pressure on the equilibrium constants is attributed to deviations from the simple gas laws. Free energy and entropy changes and heats of reaction are evaluated. J. G. A. GRIFFITHS.

Solutions of salts in pure acetic acid. IV. Cupric acetate and ammonium cupric acetate. A. W. DAVIDSON and E. GRISWOLD (J. Amer. Chem. Soc., 1931, **53**, 1341—1349).—F.-p. data show that the solid phase $Cu(OAc)_2,HOAc$ undergoes transition, probably to $Cu(OAc)_2$, above 50°. F.-p. data between

28° and 54° for the ternary system cupric acetate–acetic acid containing 8—24 mols.-% of ammonium acetate are recorded. The solubility of cupric acetate at constant temperature increases with the concentration of ammonium acetate as long as solvated cupric acetate is the stable phase, but decreases when the *compound* $Cu(OAc)_2,4NH_4OAc,4HOAc$ separates. This ternary system, unlike that of cupric acetate–potassium acetate–acetic acid, changes reversibly from greenish-blue to deep violet-blue at higher temperatures, possibly due to the formation of copper–ammonia complex ions. The analogy between the system and cupric hydroxide in concentrated aqueous solutions of alkalis is discussed.

J. G. A. GRIFFITHS.

Potentiometric study of pyocyanine. E. FRIEDHEIM and L. MICHAELIS (J. Biol. Chem., 1931, **91**, 355—368).—Pyocyanine, a methylated oxyphenazine (cf. Wrede and Strack, A., 1929, 580), has been titrated by the methods of Michaelis and Eagle (A., 1930, 1142). Above p_H 6 it behaves as a reversible dye of quinonoid structure, accepting two hydrogen atoms and changing from blue to the colourless leuco-dye. Below p_H 6 the two hydrogen atoms are accepted one by one, corresponding with colour changes from red to green and from green to colourless. In strongly alkaline solutions the oxidised dye undergoes irreversible destructive oxidation. Doubt is cast on the bimolecular structure suggested by Wrede and Strack.

F. O. HOWITT.

Decomposition of monobarium phosphate in solution. R. PALLU (Compt. rend., 1931, **192**, 942—944).—Conductivity and p_H determinations of mixtures in varying proportions of solutions, both $0·248N$, of barium hydroxide and phosphoric acid show that the first hydrogen ion is neutralised at p_H 3. Viard's results (cf. A., 1899, ii, 26) as regards decomposition of monobarium phosphate by water are confirmed. No change occurs at 0°, but the rate increases as the temperature rises. Conductivity curves show breaks at 21°, 50°, and 85° in solutions of compositions indicated by the ratios P_2O_5/BaO of 1·14, 1·35, and 1·59, respectively, which figures indicate the minimum acidity necessary to prevent decomposition of the monophosphate at these temperatures; when in defect the diphosphate, $BaHPO_4$, is deposited as the sole solid phase.

C. A. SILBERRAD.

Physico-chemical properties of solutions of dibismuthyl monosodium citrate in ethylene glycol. W. F. VON OETTINGEN (J. Amer. Pharm. Assoc., 1931, **20**, 345—349).—Comparative observations on solutions of dibismuthyl monosodium citrate in water and ethylene glycol indicate that the compound is less dissociated in ethylene glycol. Solutions in the latter solvent have the properties of hypertonic solutions and the bismuth diffuses more rapidly therefrom than from aqueous solutions. The bismuth salt does not form a compound with ethylene glycol.

E. H. SHARPLES.

Rôle of water in chemical processes in concentrated solutions of electrolytes. M. BOBTELSKI (Z. anorg. Chem., 1931, **197**, 161—166).—Theoretical.

H. F. GILLBE.

Role of the solvent in electrolytic dissociation of salts. F. K. V. KOCH (Phil. Mag., 1931, [vii], **11**, 1122—1129; cf. this vol., 312).—Theoretical. The concept of " salt solution tension " (ratio of the free energies of transference of the ions from a vacuum to the pure solvent to those of their transference from a vacuum to the salt) is employed to express the distribution of ions between a salt and the solvent. The causes leading to different types of symmetrical and unsymmetrical dissociation are specified. In an ideal case the dissociation constant (K) of a salt may be expressed by the formula $\log K = a + b/\varepsilon$, a and b being isothermal constants and ε the dielectric constant. Specific forces of solvation are dominant factors both in the dissociation and the solubility of salts.

F. L. USHER.

Is there an intermediate horizontal portion between two eutectic points in the fusion curves of binary systems ? R. KREMANN (Z. physikal. Chem., 1931, **154**, 136—142).—Polemical against Pushin and Rikovski (this vol., 159).

R. CUTHILL.

System $CuCl-Cl_2$. (MLLE.) A. E. KORVEZEE (Rec. trav. chim., 1931, **50**, 505—512).—The dissociation pressures for the reaction $2CuCl_2 \rightleftharpoons 2CuCl + Cl_2$ have been measured between 360° and 500°. The slopes of the P–T curves at the quadruple point 379° are discussed.

O. J. WALKER.

Higher aliphatic compounds. I. Systems ethyl palmitate–ethyl stearate and hexadecyl alcohol–octadecyl alcohol. J. C. SMITH (J.C.S., 1931, 802—807).—Ethyl palmitate and ethyl stearate are dimorphous, the m. p. being 19·40° and 24·18°, and 30·92° and 33·4°, respectively. The forms with the lower m. p. yield a continuous series of mixed crystals, with neither maximum nor minimum. The following m. p. have been determined to within 0·04° : hexadecyl alcohol 49·27°, octadecyl alcohol 57·95°, palmitic acid 62·66°, stearic acid 69·41°. Hexadecyl and octadecyl alcohols form a continuous series of mixed crystals, with a minimum at 48·5° and 86 mols.-% hexadecyl alcohol.

H. F. GILLBE.

System cobalt chloride–cobalt nitrate–water. V. CUVELIER (Natuurwetensch. Tijds., 1931, **13**, 75—77).—The isotherms at 20° have been determined; no compound exists in the solution at this temperature.

H. F. GILLBE.

System $KCNS-Hg(CNS)_2-H_2O$. C. W. MASON and W. D. FORGENG (J. Physical Chem., 1931, **35**, 1123—1132).—At the ordinary temperature the double salts $KHg(CNS)_3$ and $K_2Hg(CNS)_4$ are formed. Neither salt is stable in contact with a saturated solution having the same molecular ratio of potassium thiocyanate to mercuric thiocyanate as the solid. The ternary diagram for 25° is given together with methods for the preparation of the salt $K_2Hg(CNS)_4$ for use in micro-analysis.

L. S. THEOBALD.

Ternary systems hexamethylenetetramine–magnesium chloride–water and hexamethylenetetramine–calcium chloride–water. V. EVRARD (Natuurwetensch. Tijds., 1931, **13**, 105—112).—The 25° isotherms of the systems have been determined. Addition of 0·2% $MgCl_2$ to a saturated solution of hexamethylenetetramine or of 2·3% of hexamethyl-

enetetramine to a saturated magnesium chloride solution causes the precipitation of a compound $2(CH_2)_6N_4,MgCl_2,10H_2O$, which forms well-defined, non-hygroscopic crystals. With calcium chloride two compounds are formed, viz., $2(CH_2)_6N_4,CaCl_2,10H_2O$ and $(CH_2)_6N_4,CaCl_2,6H_2O$. The former may be prepared by evaporation of a solution containing 2 mols. of hexamethylenetetramine and 1 mol. of calcium chloride, and resembles the analogous magnesium compound. The latter may be obtained in the pure state only from a solution containing an excess of calcium chloride, a suitable molar ratio being 6 : 1; it is slightly hygroscopic and is decomposed by water.
H. F. GILLBE.

Reciprocal salt pair $MgSO_4+2KNO_3 \rightleftharpoons Mg(NO_3)_2+K_2SO_4$. III. A. BENRATH and A. SICHELSCHMIDT (Z. anorg. Chem., 1931, **197**, 113—128).—The 75° isotherms of the ternary systems $Mg(NO_3)_2-KNO_3-H_2O$ and $MgSO_4-K_2SO_4-H_2O$ have been determined and the results, in combination with earlier work (A., 1930, 163, 702), have been employed to calculate the polythermal equilibrium diagram for the reciprocal salt pair between 0° and 100°. There are 14 triple and 8 quadruple points. H. F. GILLBE.

Reaction equilibrium in the cation-exchange of permutits. P. VAGELER (Z. Pflanz. Düng., 1931, **20A**, 111—113).—Reply to criticisms of Beling (this vol., 163). A. G. POLLARD.

Affinity. III. T. DE DONDER (Bull. Acad. roy. Belg., 1931, [v], **17**, 298—314; cf. A., 1930, 853).—A mathematical treatment of systems containing an infinite number of constituents. C. W. GIBBY.

Heat of formation of hydriodic acid and of chlorine monoxide. P. GUNTHER and K. WEKUA (Z. physikal. Chem., 1931, **154**, 193—206).—From the heat of the reaction $2HI+Cl_2=2HCl+I_2$ (27,966$\pm$50 g.-cal. per mol. HI) the heat of formation of hydriodic acid from solid iodine and gaseous hydrogen is found to be -5970 ± 50 g.-cal. per mol., using Thomsen's value for the heat of formation of hydrogen chloride. The heat of formation of chlorine monoxide derived from data for the explosive decomposition is $-25{,}100+100$ g.-cal. per mol.
O. J. WALKER.

Heats of formation of hydrates of silica. P. A. THIESSEN and O. KOERNER (Z. anorg. Chem., 1931, **197**, 307—312).—The heats of formation of the hydrates of silica, as calculated from vapour-pressure data, range from 1·2 to 1·5 kg.-cal. per mol., the stability diminishing as the degree of hydration increases. R. CUTHILL.

Determination of the heat of formation of silicates from their oxides. R. NACKEN (Zement, 1930, **19**, 818—825; Chem. Zentr., 1931, i, 1075).—A lecture. A. A. ELDRIDGE.

Heat effect of absorption of oxides of nitrogen trioxide, peroxide, and oxide by sulphuric acid. D. A. KARTASCHEV and A. N. ZEITLIN (Ukraine Chem. J., 1930, **5**, [Sci.], 257—266).—The heats of absorption of nitrogen trioxide and of nitrogen peroxide in sulphuric acid (*d* 1·7) are 271·2 and 124·12 g.-cal. per g. of oxide, respectively.
R. TRUSZKOWSKI.

Modified equation for heats of dilution of strong electrolytes. O. GATTY (Phil. Mag., 1931, [vii], **11**, 1082—1089).—Theoretical. The factor containing the temperature coefficient of the dielectric constant in Bjerrum's equation for the heat of dilution of electrolytes should be increased by a term based on the free energy function. The correction thus introduced is unimportant for water, but may be considerable for some solvents (*e.g.*, 42% for nitromethane). F. L. USHER.

The α-parameter of the Debye–Hückel theory. E. LANGE and H. STREECK (Naturwiss., 1931, **19**, 359—360; cf. this vol., 309).—Integral heats of dilution are discussed in relation to the Debye–Hückel theory and to osmotic and activity coefficients. Values of α vary in the same way as the radii of the unhydrated ions. W. R. ANGUS.

Transference numbers of potassium chloride. New determinations by the Hittorf method and comparison with results obtained by the moving boundary method [at 25°]. D. A. MACINNES and M. DOLE (J. Amer. Chem. Soc., 1931, **53**, 1357—1364).—The discrepancy between existing data determined by the Hittorf and the moving boundary methods has been investigated. Convection in the Washburn type of Hittorf apparatus (A., 1908, ii, 805) is eliminated by appropriate bends and taps of a type facilitating circulation of thermostat water round the bore. Vibration is minimised and the electrolyte must be oxygen-free. The cation transference number, T_K, at concentrations between 0·02 and 0·5N is $0{\cdot}4895\pm2\times10^{-4}$ in close agreement with unpublished data from the moving boundary method; at higher concentrations, T_K decreases.
J. G. A. GRIFFITHS.

Transference and transport potentials in metallic solutions. K. SCHWARZ (Z. physikal. Chem., 1931, **154**, 245—254).—The transport number n' of cadmium in cadmium amalgams has been determined (i) by measuring the *E.M.F.* of cells of the type Pt|Hg|Cd-amalgam|Pt and Pt|dil. Cd-amalgam (c_1)|conc. Cd-amalgam (c_2)|Pt at 25° and 35°, and (ii) by direct measurement of the changes in the cadmium concentration of the anode and cathode compartments in the electrolysis of dilute cadmium amalgams at 25°. In the first case the *E.M.F.* is given thermodynamically by $E-nRT(c_2-c_1)/aF$, where $a=\lambda_{Hg}/\lambda_{Cd}$, the ratio of the atomic conductivities of the two metals. Taking $a=0{\cdot}25$, the value of the transport constant n can be calculated, and hence n' from the relationship $n'=n\nu_1/(\nu_1+a\nu_2)$, where ν_1 and ν_2 are the mol. fractions of the cadmium and mercury, respectively. In the second case the small change in the cadmium concentration of the two electrode compartments is obtained from the *E.M.F.* of the cell Pt|anode amalgam|aqueous cadmium sulphate|cathode amalgam|Pt. If N is the number of faradays carried by 1 mol. of Cd then $n'-1/N$. For a 2% Cd amalgam $n'=2{\cdot}03$ and $2{\cdot}08\times10^{-5}$ by methods (i) and (ii), respectively, for a 1% amalgam $n'=1{\cdot}08$ and $1{\cdot}02\times10^{-5}$. O. J. WALKER.

Conductivity of electrolytes. B. BRENDEL (Physikal. Z., 1931, **32**, 327—336).—The resistance to high-frequency currents of twelve electrolytes has

been found by a new method. The results are in good agreement with theory. A. J. MEE.

Determination of the conductivity of poorly conducting liquids with the aid of the thermionic valve. L. W. JANSSEN (Chem. Weekblad, 1931, 28, 242—246).—The difficulties of such measurements are indicated and the development of methods employing the thermionic valve is described. Details are given of an oscillatory circuit and of an amplifying circuit for use with telephones. As only a very small current is necessary, heating effects and polarisation in the cell are reduced to a minimum. H. F. GILLBE.

Measurement of conductance of electrolytes. IV. Validity of Ohm's law for electrolytes. G. JONES and G. M. BOLLINGER (J. Amer. Chem. Soc., 1931, **53**, 1207—1212).—When heating, polarisation, inductance, and capacitance effects are avoided (cf. this vol., 433), there is no variation of real resistance of electrolytes with applied voltage (0·0001—1·4 volts per cm.) and frequency (500—4000 cycles per sec.). Ohm's law is therefore valid for electrolytes under the conditions of the Kohlrausch method for determining conductivity (cf. Wien, A., 1929, 33; Joos, *ibid.*, 20). J. G. A. GRIFFITHS.

Relation between electrical conductivity of strong electrolytes and potential. H. FALKENHAGEN (Physikal. Z., 1931, **32**, 353—365).—Theoretical. The complete Wien curve of electrical conductivity against field strength is theoretically explained. A. J. MEE.

Inner friction of strong electrolytes in very dilute solution. H. FALKENHAGEN (Physikal. Z., 1931, **32**, 365—369).—Theoretical. A. J. MEE.

Dissociation of salts in nitrobenzene. W. F. K. WYNNE-JONES (J.C.S., 1931, 795—801).—The conductivities of nitrobenzene solutions of dipropylamine and piperidine picrates and perchlorates and of diphenylguanidine picrate have been measured over a range of concentrations. The salts behave as weak electrolytes, the ionisation constants ranging from about 10^{-3} to 10^{-5}. It is suggested that the hydrogen atom attached to the central nitrogen atom is linked by a co-valency to the anion, and that ionisation is aided by preliminary solvation of the substituted ammonium ion. This view is confirmed by Walden's determinations of the mobilities of similar ions in hydroxylic and non-hydroxylic solvents. The results are discussed in relation to the conductimetric method of comparing the strengths of acids and to the use of substituted ammonium salts in buffer solutions. H. F. GILLBE.

Basicity of periodic acid. N. RAE (J.C.S., 1931, 876—877).—The conductimetric titration curve shows periodic acid to be dibasic. H. F. GILLBE.

Conductivity of alkali glutelinate. T. HAYASHI (Mem. Coll. Agric. Kyoto, 1931, **11**, 37—50).—The alkali salts of rice-glutelin have been prepared and the conductivity has been determined in alkaline solution. The limiting equivalent conductivities of sodium and potassium glutelinates are 110 and 130, respectively, at 18°, from which the mobility of the glutelinate ion is equal to 65·4—66·5. Alkali caseinate is approximately neutral, whilst alkali glutelinate is invariably alkaline in reaction. P. G. MARSHALL.

Measurement of potential of high-resistance cells with the aid of a thermionic valve. L. W. JANSSEN (Chem. Weekblad, 1931, **28**, 218—222).—The theory and practice of the use of the thermionic valve in the measurement of potentials is described with particular reference to cells of very high resistance. A circuit suitable for null-point measurements and the necessary precautions are indicated. Photoelectric emission, under the influence of external radiation, from the metal deposited on the inner wall of the valve during evacuation is a possible source of disturbance. H. F. GILLBE.

Normal potential of calcium. F. L. E. SHIBATA (J. Sci. Hiroshima Univ., 1931, **1**, 147—157).—*E.M.F.* measurements have been made with the cell Ca amalgam|$Ca(OH)_2$,aq.,HgO|Hg, with various concentrations of amalgam and of solution, and with the cell Ca|CaI_2 in pyridine|Ca amalgam. The potential of a 0·025% calcium amalgam towards a solution of the ions at unit activity is 1·914 volts at 15°, and the normal potential of the metal is 2·810 volts at 15°. H. F. GILLBE.

Observations on scraped metal electrodes and their relationship to the absolute zero of potential. K. BENNEWITZ and I. BIGALKE (Z. physikal. Chem., 1931, **154**, 113—135).—The behaviour of a silver electrode fitted with a scraper and immersed in a solution of silver nitrate (A., 1926, 1212) has been further examined with an improved apparatus, giving completely reproducible results. The current which flows between the scraped electrode and an ordinary silver electrode in the same solution during the scraping process changes in direction when the potential of the scraped electrode is $+0·605\pm0·01$ volt, referred to the hydrogen electrode. From measurements of the influence of temperature on the effect of scraping, however, it appears that the point at which the current reverses does not correspond with zero phase boundary potential. Substances which react with silver nitrate alter the electrode potential at which reversal takes place, but potassium nitrate has no effect. The results indicate that at the phase boundary there are one or more electric double layers in addition to the one constituting the surface charge on the electrode. R. CUTHILL.

Electrode potentials of silver halide electrodes against mixed halide solutions. J. TANIDA (J. Biochem., Japan, 1930, **12**, 411—418).—The potential of the silver halide electrode immersed in a solution containing halide ions is determined mainly by the activity of the halogen ions of greatest mol. wt. Silver, or silver chloride, bromide, or iodide electrodes give the same potential. CHEMICAL ABSTRACTS.

Polarographic studies with the dropping mercury cathode. XVIII. Soap solutions. E. VARASOVA (Coll. Czech. Chem. Comm., 1931, **3**, 216—222).—The waves on the current–voltage curves due to the alkali metals are proportional to the concentration, and the alkalinity of a soap solution may be determined by polarographic titration. The presence of iron is clearly demonstrated, and there is a wave

at about −0·6 volt, due to the presence of an unsaturated compound which appears to accompany oleic and, probably, linoleic acid. At cathode potentials greater than the electrocapillary zero the current maxima due to the reduction of oxygen adsorbed at the mercury–solution interface are suppressed strongly, and in a characteristic manner, as a result of interfacial adsorption of the soap micelles.

H. F. Gillbe.

Electrochemical and spectral investigation of nickel chloride solutions. I. M. Pavlík (Coll. Czech. Chem. Comm., 1931, **3**, 223—237).—The nature and degree of solvation of the nickelous ion has been investigated polarographically. The deposition potential of the metal falls from −1·01 volt in 0·001*N*-nickelous chloride solution to −0·417 volt in 5*N*-solution, and reversible deposition at the dropping mercury cathode at the ordinary temperature occurs only in presence of dehydrating chlorides, such as those of calcium or lithium, at concentrations greater than 6·4*N*. The deposition potential in such solutions is more positive by about 0·3 volt than in solutions containing only nickel chloride at the same concentration. The hydrogen-ion concentration influences the deposition, although to only a very small extent, by removing the products of hydrolysis; in presence of 6·4*N*-hydrochloric acid the deposition potential is depressed by about 0·3 volt as a result of dehydration. The primary deposition of nickel does not influence the hydrogen overvoltage. The irreversible deposition on nickel from dilute solutions is ascribed to the slow dehydration of the ions, whilst the reversible deposition from concentrated chloride solutions involves the removal of the chloride ions from complexes of the type $[NiCl_n]^{(n-2)'}$.

H. F. Gillbe.

Oxidation–reduction potentials. III. Mercuric–mercurous electrode. S. Popov, J. A. Riddick, V. I. Wirth, and L. D. Ough (J. Amer. Chem. Soc., 1931, **53**, 1195—1206; cf. Carter and Robinson, A., 1927, 209).—From the *E.M.F.* of the cell $Pt|H_2,HClO_4|HClO_4,Hg(ClO_4)_2,Hg_2(ClO_4)_2|Pt$, the standard oxidation–reduction potential of the mercuric–mercurous electrode is computed to be 0·9050 volt at 25°. With increasing concentration of perchloric acid, the potential passes through a minimum (0·9008 in 0·2*M*-acid). The activity coefficients of perchloric and hydrochloric acids are equal, within experimental error, at concentrations less than 0·4*M*.

J. G. A. Griffiths.

Oxidation–reduction potentials. (*a*) Ferric–ferrous, (*b*) mercuric–mercurous, (*c*) manganese dioxide electrode. S. Popov, A. H. Kunz, J. A. Riddick, and W. W. Becker (Proc. Iowa Acad. Sci., 1929, **36**, 263—264).—*E.M.F.* measurements were made with the cells $Pt,H_2|HCl|HCl+FeCl_3+FeCl_2,Pt$ and $Pt,H_2|HClO_4|HClO_4+Hg(ClO_4)_2+Hg_2(ClO_4)_2,Pt$. Attempts to measure the potentials of the MnO_4'–$H^\cdot$–MnO_2 and MnO_2–$H^\cdot$–$Mn^{\cdot\cdot}$ electrodes failed owing to secondary reactions and irreversibility.

Chemical Abstracts.

Determination of oxidation–reduction potentials from equilibrium data. S. Popov, V. B. Fleharty, and E. L. Hanson (Proc Iowa Acad. Sci., 1929, **36**, 265).—Results from equilibrium data are more trustworthy than those from *E.M.F.* data. The potential of the ferric–ferrous electrode was calculated from the equilibrium constant of the reaction $2Fe(ClO_4)_3+2Hg \rightleftharpoons 2Fe(ClO_4)_2+Hg_2(ClO_4)_2$.

Chemical Abstracts.

Oxidation–reduction potentials of sulphydryl compounds. E. K. Fischer (J. Biol. Chem., 1930, **89**, 753—763).—An electrometric study of thioglycollic acid, monothioethylene glycol, and α-hydroxy-β-thiolpropionic acid was made. It is suggested that the observed potentials depend not only on the hydrogen-ion concentration and the concentration of the reduced form, but also on the concentration of some intermediate oxidised form.

G. F. Marrian.

Rosinduline as oxidation–reduction indicator. L. Michaelis (J. Biol. Chem., 1931, **91**, 369—372).—Rosinduline ("Colour Index" No. 830) is recommended as an indicator for oxidation–reduction potential in a very negative potential range. Values for its normal potential at 30° referred to the normal hydrogen electrode are given.

F. O. Howitt.

Potentiometric studies on complex iron systems. L. Michaelis and E. Friedheim (J. Biol. Chem., 1931, **91**, 343—353).—Reduction-oxidation potentials were determined in solutions containing a small concentration of iron (0·001 g.-atom per litre) and a very high concentration (about 0·1*M*) of the complex-forming anion (pyrophosphate, malonate, salicylate, acetate, oxalate, ferrocyanide, and succinate) in order that only complexes containing one iron ion should be present. The normal potential range of such systems may lie within very wide limits, from +0·7 to −0·25 volt, according to the anion. Dependence of the potential on the p_H is very small for ferrocyanide, oxalate, and pyrophosphate, but is very great for acetate, salicylate, and malonate. In the iron complexes with oxalate, malonate, and succinate, the stabilities and the potential range of the complexes are widely different and related to the five-, six-, and seven-membered ring structures, respectively.

F. O. Howitt.

***E.M.F.* at moving electrodes and the electrokinetic potential of the metals.** S. Procopiu (Z. physikal. Chem., 1931, **154**, 322—331).—By moving one of the electrodes of a galvanic cell an *E.M.F.* (*e*) is produced which has the same order of magnitude and sign as the electrokinetic potential obtained by cataphoresis measurements. With pure water *e* is negative for platinum, mercury, silver, and copper, and positive for nickel, lead, aluminium, iron, and zinc, *i.e.*, opposite in sign to that of the corresponding stationary potential. The values of *e* are the same in acid solutions as in water. In the case of copper and zinc in solutions of their salts or of the potassium salts of various anions *e* varies with the concentration and passes through a minimum or maximum, or may even change in sign, and in general behaves like the electrokinetic potential.

O. J. Walker.

Conditions of silver chromate in gelatin hydrolysed and electrodialysed to different extents. G. M. Nabar and B. N. Desai (Nature, 1931, **127**, 628—629).—Measurements of the contact potential of silver in a mixture of 0·01*N*-silver nitrate,

0·01N-potassium chromate, and 3% gelatin have been made in order to ascertain the condition of silver chromate in gelatin hydrolysed by heating, and electrodialysed to different extents. As soon as a precipitate appears, the contact potential decreases gradually to a limiting value. The results indicate that (i) more than 95% of the silver chromate remains in the ionic condition in the gel, (ii) the inhibition of the growth of crystallisation centres by gelatin increases with increasing hydrolysis and electrodialysis and with a fall in p_H, and (iii) the solubility of the chromate in unhydrolysed gelatin is not increased by a fall in p_H, but increases with hydrolysis. In a mixture of silver nitrate and potassium chloride reacting in gelatin most of the silver chloride exists in a condition other than ionic.

L. S. THEOBALD.

Statistical treatment of reaction velocity data. II. Least-squares treatment of the unimolecular expression $Y=L(1-e^{-Kt})$. L. J. REED and E. J. THERIAULT (J. Physical Chem., 1931, 35, 950—971; cf. this vol., 571).—A statistical treatment applicable to unimolecular data is developed. The method is applied to Pennycuick's data on the inversion of sucrose (A., 1926, 249), which are shown to conform to an equation of the unimolecular type. The velocity coefficients obtained by Daniels and Johnston (A., 1921, ii, 249) for the decomposition of nitrogen pentoxide are recalculated. The least-squares procedure should be employed whenever a velocity coefficient is to be determined within an error of 5%.

L. S. THEOBALD.

Application of the diffusion equation to the theory of chain reactions. V. BURSIAN and V. SOROKIN (Z. physikal. Chem., 1931, B, 12, 247—267).—Mathematical. Expressions for the final steady velocity of a chain reaction in vessels with plane parallel walls, and in spherical and cylindrical vessels, are deduced.

F. L. USHER.

Simple gas reactions. H. EYRING and M. PÓLANYI (Z. physikal. Chem., 1931, B, 12, 279—311; cf. London, A., 1929, 1397).—Theoretical. Three reactions involving the participation of a hydrogen atom, viz., $H+H_2 \longrightarrow H_2+H$, $H+HBr \longrightarrow H_2+Br$, and $H+Br_2 \longrightarrow HBr+Br$, are considered from the point of view of energy paths, the energy of the system being represented as a function of interatomic distances. When the influence of the outer pair of atoms, the Coulomb effect, and the "zero" energy are taken into consideration, an expression for the energy of activation can be deduced from optical data. The value obtained in this way for the conversion of para- into ortho-hydrogen is in approximate agreement with the measured value.

F. L. USHER.

Ionisation in gaseous explosions. W. A. KIRKBY (J.C.S., 1931, 878—885).—The progress of the flame through an explosive mixture of gases and the conductivity of the gases have been studied simultaneously. At the moment the flame reaches the electrodes the gas is non-conducting. Conductivity is observed only in the gas through which the flame has passed. Further, this conductivity decreases at the same rate as the intensity of the re-illumination due to "after-burning" diminishes. It is suggested therefore that the luminescence observed in the "after-burning" is due to the recombination of ions formed thermally in the primary explosion.

F. J. WILKINS.

Role of adsorbed gases in initiating reaction chains. Combination of hydrogen and oxygen. H. N. ALYEA (J. Amer. Chem. Soc., 1931, 53, 1324—1336).—Independence of reaction phenomena and surface is not necessarily a proof of homogeneity. Previous results (cf. A., 1930, 1255, 1528; Hinshelwood, Semenov, and others) are interpreted as follows. The adsorption of hydrogen by glass increases greatly above 450°; the gas is therefore adsorbed in a highly activated form (cf. Taylor, this vol., 421) which is the origin of the reaction chains which extend into the gas phase in the quiet hydrogen–oxygen reaction at 500°. This reaction is sensitive to surface. With decrease of pressure, the hydrogen is gradually desorbed and the quiet combination becomes slower; at the upper explosion limit, further decrease of pressure permits oxygen to reach the surface, from which it can now remove excess of hydrogen. This phenomenon is independent of surface. Hydroxyl is then assumed to be produced so rapidly at the surface that the resulting chains lead to explosion.

Desorption of carbon disulphide or carbon monoxide may similarly account for explosion limits in the reactions with oxygen. Phenomena in the oxidation of hydrocarbons (Pease, A., 1929, 905) are interpreted.

J. G. A. GRIFFITHS.

Ignition of dried mixtures of carbon monoxide and oxygen on silica. V. E. COSSLETT and W. E. GARNER (Trans. Faraday Soc., 1931, 27, 176—188).—The ignition pressure, velocity of the stationary reaction, and the percentage combustion in dry mixtures of carbon monoxide and oxygen when admitted to an evacuated silica vessel at 610° have been determined, and the influence of various gases has been studied. The stationary reaction takes place partly in the gas phase and partly on the silica surface, and an equation for its velocity has been derived; its order varies between zero and three, being smallest on the most active surfaces. The ease of ignition is increased by argon or excess of oxygen, and decreased by carbon dioxide, nitrogen, or excess of carbon monoxide. The difference in the behaviour of an excess of the reactants indicates that the reaction chains are initiated by activation of oxygen, and that although their number is thus dependent on the oxygen concentration, their length is increased mainly by an increase of the carbon monoxide concentration. The mechanism suggested for the chain reaction is in accordance with the results of experiments on the chilling of flames in narrow cylindrical bombs.

H. F. GILLBE.

Explosion of ammonia–air and ammonia–oxygen mixtures, especially at high initial pressures. H. H. FRANCK and G. DÖRING (Z. angew. Chem., 1931, 44, 273—277).—Partial combustion occurs on sparking at 1 atm. a mixture of air with 17·8% of ammonia, and an almost complete reaction takes place if 19·5% of ammonia is present. The limit for the complete propagation of the flame varies somewhat with the method of ignition, and is

lowered (to about 16% ammonia) with increase of the amount of energy dissipated. With ammonia–oxygen mixtures a similar limit occurs, although at a rather lower ammonia content, viz., 13·5%, and, unlike the limit in ammonia–air mixtures, which is independent of the pressure, it falls with increase of pressure, being at 10·0% of ammonia at 20 atm. pressure. Mixtures of potassium chlorate and carbon, which are very effective for the ignition of the mixtures containing oxygen, behave abnormally towards the air mixtures, and induce rapid combustion only at an ammonia content greater than 20·6%.

H. F. GILLBE.

Explosions of hydrogen sulphide–oxygen mixtures. H. W. THOMPSON (Nature, 1931, **127**, 629).—The temperature of ignition of hydrogen sulphide–oxygen mixtures varies with the diameter of the ignition vessel. Under certain conditions explosion is never complete and is always preceded by an induction period of some seconds or minutes. Successive explosions have been observed with the same mixture, each being preceded by a lengthening induction period. The rise in temperature following an explosion is never greater than 1°.

L. S. THEOBALD.

Transmission of detonation. P. LAFFITTE and M. PATRY (Compt. rend., 1931, **192**, 948—951).—Two tubes, A and B, A slightly wider than B, containing explosive, are placed within a long wider tube at a distance d apart. The detonation of A causes that of B when the front of the luminous and shock waves reaches B provided that d is less than the distance, D, at which these waves begin to separate (cf. B., 1931, 224, 566). With dynamite No. 1, tetryl, or picric acid (the same explosive in A and B) the maximum value of d is always less than D, this maximum occurring with a high density of loading in A and a low density in B. If the explosive in B is well-dried mercury fulminate, d may exceed $2D$, detonation being caused at the greater distances by the arrival of the hot gases, and at smaller ($>D$) by the shock wave.

C. A. SILBERRAD.

Explosions of mixtures of acetylene and electrolytic gas. W. A. BONE, R. P. FRASER, and F. LAKE (Proc. Roy. Soc., 1931, **A**, **131**, 1—17; cf. Bone, Fraser, and Winter, A., 1927, 424).—A study has been made of "open-" and "closed-tube" explosions of a series of $xC_2H_2/(100-x)(2H_2+O_2)$ mixtures, x being successively increased from 0 to 65. Flame photographs are reproduced and analysed in detail. The effects of increasing additions of acetylene on the initial flame speeds, the duration of luminosity, and the carbon deposition are discussed. Evidence concerning the chemical features of the combustion is afforded by the analytical data obtained from the "closed-tube" explosions. The observation originally made by Bone and Drugman (J.C.S., 1906, **89**, 669), that in the explosion of a $C_2H_2+O_2+2H_2$ mixture the combustion conforms to the equation $C_2H_2+O_2+2H_2-2CO+3H_2$, is confirmed. Dilution of such a mixture with argon has no effect on the result, but a corresponding dilution with nitrogen causes visible carbon separation and steam formation. It is further found that in the combustion of $xC_2H_2/(100-x)(2H_2+O_2)$ mixtures, where x exceeds some small value below 8, (a) the acetylene is preferentially burnt in the flame front to carbon monoxide and hydrogen, (b) any excess of oxygen is distributed between the carbon monoxide and hydrogen in the medium behind it, and (c) only when acetylene is originally present in excess of the $C_2H_2+O_2+2H_2$ proportion does any of it either escape combustion or deposit carbon. Comparative "closed-tube" explosions made with moist $xC_2H_2/(100-x)(2CO+O_2)$ mixtures yielded very similar results.

L. L. BIRCUMSHAW.

Effect of an electric field on flames and their propagation. B. LEWIS (J. Amer. Chem. Soc., 1931, **53**, 1304—1313; cf. Guenault and Wheeler, this vol., 313).—Data for mixtures of air with Pittsburgh natural gas, methane, ethane, propane, butane, *iso*butane, ethylene, propylene, butylene, acetylene, and carbon monoxide are recorded. The rate of flow of the gas mixture is adjusted so that the stationary flame burns between two fine wire gauze electrodes by which the electric field is applied in the direction of the moving gas. In all cases, the flame is drawn towards the negative electrode, *i.e.*, in the direction of positive-ion flow, and thus the propagation of the flame is accelerated or retarded according to the direction of the field. With appropriate strength and direction of the latter, the flames can be extinguished. The importance of positive ions in the maintenance of flames is emphasised, and the apparent discrepancy between the results of Thornton (A., 1930, 708) and Malinovski and Lavrov (*ibid.*, 424) is explained.

J. G. A. GRIFFITHS.

Explosions in closed cylinders. IV. Correlation of flame movement and pressure development in methane–air explosions. W. A. KIRKBY and R. V. WHEELER (J.C.S., 1931, 847—853).—Vibratory and non-vibratory explosions of methane and air have been studied under conditions which permitted both the pressure and the movement of the flame to be measured simultaneously. In non-vibratory explosions change in the rate of flame movement is immediately reflected in the rate of development of pressure. In all cases the maximum pressure is attained after the flame front has reached the far end of the cylinder. Vibratory explosions differ in that the maximum pressure is reached at the moment the flame front reaches the end of the cylinder. The vibrations appear to be those of a longitudinal stationary wave maintained in the column of gases behind the flame front. The evidence shows that the frequency of the vibrations is constant, the normal increase in frequency which would accompany the rise in temperature of the gas, owing to the explosion, being compensated for by the increasing length of the column of gases in resonance. The conductivity of the gas during a vibratory explosion has been measured and found to be periodic; the frequency of the fluctuations of the current is very nearly the same as that of the striations behind the wave front. It is concluded that the luminescent bands of the striations represent a recombination of ions.

F. J. WILKINS.

Equilibria and temperature of combustion of hydrocarbons. P. MONTAGNE (Compt. rend., 1931,

192, 882—884; cf. this vol., 564; Ribaud, A., 1930, 418).—The course of the combustion of heptane in oxygen at 100 atm. is indicated by a series of curves showing for varying proportions of oxygen the temperature attained and the amounts of atomic and molecular hydrogen, hydroxyl, water, and carbon mon- and di-oxides formed. C. A. SILBERRAD.

Behaviour of antiknocks. A. EGERTON and L. M. PIDGEON (Nature, 1931, 127, 591).—Lead tetraethyl has a strong inhibiting effect on the combustion of a mixture of pentane and oxygen at 265° only when some oxygen is admitted to the combustion chamber before the lead tetraethyl and the mixed gases. Lead must thus be first oxidised before it becomes an inhibitor. L. S. THEOBALD.

Kinetics of reactions in solution. I. Comparison of the decomposition of chlorine monoxide in the gaseous state and in carbon tetrachloride solution. II. Decomposition of trinitrobenzoic acid in various solvents. E. A. MOELWYN-HUGHES and C. N. HINSHELWOOD (Proc. Roy. Soc., 1931, A, 131, 177—186, 186—198).—I. It has been suggested that bimolecular reactions are slower in solution than in the gaseous phase, whilst unimolecular reactions are uninfluenced by the presence of a solvent. The decomposition of chlorine monoxide in carbon tetrachloride solution at various temperatures is not unimolecular but probably bimolecular, proceeds at the same rate, possesses the same temperature coefficient, and apparently takes place by the same mechanism as the gaseous reaction. The rate of decomposition was studied in small tubes of 10 c.c. capacity with the volume of the gas phase reduced to about 0·5 c.c. The influence of the latter volume was found to be small. Small quantities of chlorine peroxide considerably increase the reaction rate, whilst small quantities of water reduce it. From the temperature coefficient the average value of the heat of activation for the range 25—75% decomposition is calculated to be 20,300 g.-cal. The value for the gas reaction in the range 20—80% is 21,000 g.-cal.

II. The decomposition of trinitrobenzoic acid in water, anisole, nitrobenzene, acetophenone, and toluene has been studied at temperatures ranging from 60° to 139·6°, and unimolecular velocity coefficients have been determined. By plotting $\log_e k$ against $1/t$, $\log_e Z$ (where Z is the collision number) and E, the heat of activation, have been calculated. Both these quantities vary considerably with change of solvent. The values of E in pure, dry acetophenone, water, and pure, dry nitrobenzene are 25,500, 30,000, and 35,000 g.-cal., respectively. The rate of reaction in water is only slightly influenced by either hydrochloric acid or sodium hydroxide. The velocity of decomposition and the heat of activation are dependent on the purity of the solvent, particularly in the case of nitrobenzene, careful purification of which causes k to decrease about 7000-fold. The rate of reaction is at all temperatures several hundred times greater in water than in toluene. The mechanism of the catalytic effects observed is discussed. L. L. BIRCUMSHAW.

Decomposition of halides by chromic and sulphuric acid mixtures in concentrated solutions of electrolytes. M. BOBTELSKI and R. ROSOVSKAJA-ROSSIENSKAJA (Z. anorg. Chem., 1931, 197, 147—160).—In solutions in which the ratio $H_2O : H_2SO_4$ is greater than 8 the reaction between hydrobromic and chromic acids is bimolecular and its velocity changes rapidly with change of the sulphuric acid concentration; in solutions containing a greater proportion of sulphuric acid the reaction is unimolecular, being independent of the chromic acid concentration, and its velocity is but little influenced by the sulphuric acid concentration. The two types of reaction merge more gradually at higher temperatures (40°) than at 0°. It is assumed that in the absence of free water molecules an unstable intermediate compound is formed between the chromic and hydrobromic acids, and that the decomposition of this compound is not influenced by water; at low sulphuric acid concentrations there is a catalytic stage in the reaction involving the production of quinquevalent chromium, which is concerned with the bromine ion rather than with a complex formed between the two reactants. The oxidation of chlorides by a mixture of sulphuric and chromic acids is complex, and varies with the nature of the cation. In magnesium chloride solutions of various concentrations the quantity of chlorine liberated rises to a constant value within 30—60 min.; this quantity is directly proportional to the chloride concentration and is increased by raising the sulphuric acid concentration, but is independent of the concentration of chromic acid. An unstable complex appears to be formed between the chromic acid and the chloride at the beginning of the reaction, but despite the great excess of the components its formation does not continue after the initial stage. The influence of magnesium chloride on the oxidation of the bromine ion has been studied. H. F. GILLBE.

Reactions between oxalic acid, iodine, and the iodate and iodide ions. I. Outline of kinetics. E. ABEL (Z. physikal. Chem., 1931, 154, 167—182).—The reaction between oxalic acid and iodic acid in aqueous solution, formally represented by the equation $5CO_2H{\cdot}CO_2H+2HIO_3=I_2+10CO_2+6H_2O$, really consists of the consecutive reactions $CO_2H{\cdot}CO_2H+I_2=2CO_2+2HI$ and $HIO_3+5HI=3I_2+3H_2O$ (cf. A., 1928, 1194), each of which is a complex reaction. In the former reaction the iodine reacts both directly, as shown, and indirectly as hypoiodous acid formed by hydrolysis, $I_2+H_2O=HI+HIO$, $HIO+CO_2H{\cdot}CO_2H=2CO_2+HI+H_2O$; in either case the acid reacts as undissociated molecules, as oxalate ions, and as hydrogen oxalate ions. The above reaction mechanism accounts quantitatively for the autocatalytic action of the iodine. R. CUTHILL.

Chemical kinetics in mixed solvents. G. E. MUCHIN, I. N. DRUSHININ, and A. I. KOMLEV (Ukrain. Chem. J., 1930, 5, [Sci.], 243—250).—The velocity of the reaction between $0{\cdot}25M$-pyridine and allyl bromide has been measured at 45° in mixtures of ether and chloroform and of ether and nitrobenzene, and between dimethylaniline and allyl bromide in ether and chloroform mixture. In all cases the value of K is less than the sum of those found for each solvent separately. R. TRUSZKOWSKI.

Phenolic decomposition of mixed ethers. II. Effect of substitution. Rate constant. D. M. Birosel (J. Amer. Chem. Soc., 1931, **53**, 1408—1412; cf. A., 1930, 907).—The hydrolysis of phenol ethers by hydrogen bromide in aqueous acetic acid is a unimolecular reaction, the following mean values of $k\times10^{-3}$ being observed at 100°: *p*-nitrophenetole, 1·23; *p*-bromo-, 15·58; *p*-chloro-, 15·4; 2 : 4-dibromo-, 7·82; and 2 : 4 : 6-tribromo-phenetole, 2·3; *p*-tolyl ethyl ether, 4·9. 2 : 4 : 6-Trinitrophenetole is completely decomposed under these conditions.

H. A. Piggott.

Velocity of corrosion from the electrochemical point of view. U. R. Evans, L. C. Bannister, and S. C. Britton (Proc. Roy. Soc., 1931, **A**, **131**, 355—375).—By tapping the electric currents flowing between the anodic and cathodic portions of a corroding metal it is shown that the currents measured are equivalent to the corrosion produced. This is true (*a*) when the anodic and cathodic areas consist of different metals and (*b*) when the whole specimen consists of one metal, the anodic and cathodic areas being determined by differences in oxygen concentration. Electrolytic iron, mild steel, electrolytic zinc, copper, and aluminium were studied and the problem of corrosion velocity becomes that of the electrochemical factors which determine the strength of the current. The influence of polarisation on the cathodic and anodic potentials is discussed and certain precautions necessary in interpreting the experimental results are indicated. The polarisation which limits the corrosion rate occurs at the cathodic area and is due to limitations in the rate of oxygen supply. Cathodic polarisation curves under controlled conditions of oxygen supply have been studied for several metals. If corrosion starts at a weak point in the invisible film on the surface of a metal, the area undergoing attack extends or contracts until the cathodic current density on the unattacked part is equal to the "protective value" and the current under these conditions will define the rate of corrosion. The protective value is the current density which will cause incipient attack on a weak point within an area to lead to the precipitation of rust so close to the surface as to seal the defect.

L. L. Bircumshaw.

Theory of metallic corrosion in the light of quantitative measurements. IV. G. D. Bengough, A. R. Lee, and F. Wormwell (Proc. Roy. Soc., 1931, **A**, **131**, 494—517).—By means of the experimental methods described in previous papers, supplemented by micrographic work and some potential measurements, an investigation has been made of the effect of the depth of immersion on the corrosion of zinc in potassium chloride solutions. Curves show the effect of concentration of potassium chloride and sulphate solutions on the initial rate of corrosion of zinc in tranquil conditions. To discover whether the corrosion rates are characteristic of the metal under test, the effect of faster and slower rates oxygen supply has been examined. Some of the factors which influence the distribution of corrosion over the metallic surface are discussed. The distribution cannot be adequately accounted for by differences in oxygen concentration, as postulated by the "differential aeration" theory. A modified view of the mechanism is suggested.

L. L. Bircumshaw.

Cysteine and glutathione as anticatalysts in oxidations with molecular oxygen. A. Schoberl (Ber., 1931, **64**, [*B*], 546—561).—In the presence of cupric acetate, leucomethylene-blue rapidly absorbs between 0·5 and 1 mol. of oxygen per mol. of leuco-compound. The intervention of hydrogen peroxide is therefore indicated and the reaction is represented by the scheme: MH_2(leucomethylene-blue)$+2(AcO)_2Cu \longrightarrow M+2AcOCu+2AcOH$; $2AcOCu+2AcOH+O{:}O \longrightarrow 2(AcO)_2Cu+OH{\cdot}OH$; $MH_2+O.O$ —— $M+HO{\cdot}OH$. Confirmation of this view is found in the observation that less oxygen is consumed in the presence of a ferrous salt (which activates the hydrogen peroxide) than in the "normal" experiment. Addition of thiol derivatives (cysteine and its hydrochloride, glutathione) restricts the rate of absorption of oxygen in the initial stages, but this effect passes as the thiol becomes oxidised to the disulphide. As expected, cystine has only feeble anticatalytic action. The inhibiting action of the thiols is attributed to the formation of complex copper compounds whereby a lowering of the copper-ion concentration is produced. This view is supported by the observation that hydrocyanic acid has a similar anticatalytic effect, but the behaviour of cystine which also yields a copper complex is not immediately explicable.

H. Wren.

Oxidation of carbohydrates and fats by air in presence of yellow phosphorus. S. N. Chakravarti and N. R. Dhar (J. Physical Chem., 1931, **35**, 1114—1122).—Potassium stearate, oleate, palmitate, and oxalate, as well as carbohydrates, are oxidised by the passage of a current of air at the ordinary temperature in diffused sunlight and the oxidation is increased by the presence of solid or vaporised phosphorus. Starch undergoes this slow oxidation to the greatest extent amongst the carbohydrates. Sulphur is oxidised to sulphurous and sulphuric acids by bubbling air through a mixture of finely-divided sulphur and phosphorus under water at the ordinary temperature.

L. S. Theobald.

Transformation of parahydrogen on platinum. Relation between catalysis and accommodation. K. F. Bonhoeffer and A. Farkas (Z. physikal. Chem., 1931, B, **12**, 231—246).—The rate of transformation of parahydrogen in contact with a platinum wire maintained at known temperatures has been studied at pressures between 30 and 760 mm. The change is accelerated by rise of temperature and retarded by increasing pressure. The platinum can be activated by short contact with oxygen, and can then effect at the ordinary temperature the same percentage change as is brought about in the same time at 170° by the non-activated surface. Hydrogen sulphide or toluene vapour acts as a poison. Platinum thus poisoned loses heat to the surrounding gas more slowly than does the clean or activated metal. The change is considered to be due to adsorption and desorption of the gas molecules. At high temperatures the reaction at a clean or an activated surface is accompanied by a large increase in the coefficient of

accommodation, whereas a poisoned surface behaves normally in this respect. F. L. USHER.

Reactions of hydrogen and oxygen on platinum wires at low temperatures and pressures. H. G. TANNER and G. B. TAYLOR (J. Amer. Chem. Soc., 1931, **53**, 1289—1296).—The catalysis of the reaction between hydrogen and oxygen at total pressures less than 100 bars by macro- and crypto-crystalline platinum wires at temperatures below 400° is variable even under carefully-controlled conditions. More oxygen disappears than corresponds with the formation of water, and this is attributed to the production of hydrogen peroxide. The addition of either constituent to electrolytic gas accelerates the reaction. The velocity varies with the difference of temperature between the wire and the wall of the containing vessel; *e.g.*, when both are heated at 200° no reaction occurs, but if the vessel is immersed in liquid air and the filament is momentarily heated at 100°, reaction ensues and persists with a smaller velocity when the filament is at the ordinary temperature. This wall-temperature effect is not apparent in other reactions investigated. By "flashing" the wire at 900° in a vacuum, hydrogen, or oxygen, the metal is temporarily highly activated and then catalyses the hydrogen–oxygen reaction at temperatures as low as −120°, the walls being at −180°. Sintering has little effect on the activity of platinum wires.

J. G. A. GRIFFITHS.

Kinetics of decomposition of nitric oxide in the presence of platinum. J. ZAWADZKI and T. BADZYNSKI (Rocz. Chem., 1931, **11**, 158—168).—The activity of a platinum catalyst in the above reaction increases at first rapidly and then slowly attains a steady value. The velocity of reaction using an "immature" catalyst is given by $dx/dt=k_1(a-x)/x$, and during the second stage of gradual increase in activity by $dx/dt=k_2(a-x)/(1+\quad)$, where b is the coefficient of adsorption of oxygen. The increase in activity is due to progressive diminution in the value of b. R. TRUSZKOWSKI.

Influence of poisons on reactions in heterogeneous systems. K. JABŁCZYNSKI and J. MACZKOWSKA (Rocz. Chem., 1931, **11**, 139—153, and Z. anorg. Chem., 1931, **197**, 292—300).—The velocity of dissolution of marble in hydrochloric acid is reduced by a maximum of 32% by 0·002N-potassium cyanide, and of 12% by 0·005N-arsenious acid. In the case of magnesium the velocity is reduced by 11% by 0·002N-cyanide and by 0·005N-arsenic, and by 22% by 0·01N-hydrogen sulphide. For zinc the maximal retardation, due to 0·01N-cyanide, is 67%, whilst 0·005N-arsenic accelerates reaction by about 30%, 0·004N-hydrogen sulphide by 17%, and 0·003N-iodine by 77%; formaldehyde is without effect.

R. TRUSZKOWSKI.

Influence of moisture on the reaction between sulphur and silver. J. W. SMITH (J.C.S., 1931, 860—863).—The reaction between sulphur and silver can be completely inhibited even at 150° by removing the moisture from the system. Calcium chloride drying causes a partial inhibition. F. J. WILKINS.

Reactivity of solid thiosulphates with iodine. I. H. CARLSOHN and F. WERNER (Z. anorg. Chem., 1931, **197**, 167—181).—With the object of investigating the influence of water of crystallisation on chemical reactivity, the reaction between a benzene solution of iodine and solid thiosulphates of the alkali and alkaline-earth metals of various degrees of hydration has been studied. In all cases the reactivity falls, nearly always in stages, with decrease of the degree of hydration of the salt, and becomes practically zero for all the anhydrous and monohydrated salts investigated. The discontinuity of the reactivity curves indicates that the distance between the ions in the lattice is constant for any given degree of hydration and that water does not exert any catalytic influence. The quantity of iodine which reacts within a constant time is observed to diminish by a constant amount (or multiple thereof) if the various thiosulphates be arranged in order of decreasing reactivity; it thus appears that the lattice energy diminishes by a constant amount at each successive dehydration.

H. F. GILLBE.

Oxide hydrates and active oxides. XXXVIII. Zinc oxide as catalyst of the decomposition of methyl alcohol. G. F. HUTTIG and I. FEHER (Z. anorg. Chem., 1931, **197**, 129—146).—The activity of a catalyst in a reaction involving the decomposition of a single substance in the vapour phase is defined in terms of the quantity of reactant decomposed in unit time; the "normal catalytic activity" ϕ is the value of this quantity under specified conditions relating to the form of apparatus, the absolute quantity of catalyst, the depth of the layer through which the vapour passes, and the rate of flow of the vapour. Study of the catalytic decomposition of methyl alcohol by zinc oxide under a variety of conditions shows ϕ to be a strictly reproducible quantity, independent of the quantity, packing density, and form of the catalyst, the duration of the reaction, the velocity of flow, the total pressure, and the presence of admixed inert gases. Rise of temperature or increase of the carbon dioxide content of the gas causes an increase of ϕ, whilst increase of the water vapour concentration causes a decrease. H. F. GILLBE.

Catalytic inhibition of decomposition of magnesium peroxide. A. M. KATZ (Ukrain. Chem. J., 1930, **5**, [Sci.], 255—256).—The rate of spontaneous decomposition of magnesium peroxide is retarded by luminal, hexamethylenetetramine, caffeine, citric acid, anthracene, or brucine, but not by benzine, benzene, quinine sulphate, magnesia, lime, potassium persulphate, boric acid, or by ammonium chloride and cobaltous nitrate. R. TRUSZKOWSKI.

Active alumina catalyst. E. V. ALEXEEVSKI and I. G. PREIS.—See B., 1931, 487.

Active platinum catalyst. E. V. ALEXEEVSKI and I. D. MAKAROV.—See B., 1931, 495.

Active palladium catalyst. E. V. ALEXEEVSKI, A. P. MUSAKIN, and I. D. MAKAROV.—See B., 1931, 495.

Decomposition of carbon monoxide at iron and iron oxides. P. RISCHBIETH (Z. physikal. Chem. Unterr., 1931, **44**, 22—24; Chem. Zentr., 1931, i, 1057).—A simple apparatus for demonstration of

the reaction $2CO \rightleftharpoons C+CO_2$ at the surface of limonite is described. A. A. ELDRIDGE.

Decomposition of diethyl ether in contact with platinum and tungsten. H. A. TAYLOR and M. SCHWARTZ (J. Physical Chem., 1931, **35**, 1044—1053).—The decomposition of ethyl ether in contact with platinum and tungsten wires has been investigated at filament temperatures between 846° and 968°, and 915° and 973°, respectively, for different pressures by the method previously described (A., 1930, 44). In both cases the constant values obtained for 25, 50, and 75% decomposition establish the unimolecular nature of the reaction, and the steady fall in the value of k with time is explained by the assumption that two unimolecular reactions occur simultaneously. The energies of activation with both platinum and tungsten are in good agreement. The decomposition is identical with the ordinary homogeneous reaction; the presence of the filament provides the necessary stationary concentration of active molecules. L. S. THEOBALD.

Oxidation of methane to carbon monoxide and hydrogen. K. YOSHIKAWA (Bull. Chem. Soc. Japan, 1931, 6, 106—110).—Investigation of the reaction of mixtures of methane with oxygen or air at 800—1000° in presence of various catalysts has shown that nickel with silica or thoria as promoter brings about the reaction $2CH_4+O_2=2CO+4H_4$ almost quantitatively, R. CUTHILL.

Oxidation of methyl alcohol with air over iron, molybdenum, and iron-molybdenum oxides. H. ADKINS and W. R. PETERSON (J. Amer. Chem. Soc., 1931, **53**, 1512—1520).—A mixture of iron and molybdenum oxides in equimolecular proportions is a very active catalyst for the oxidation of methyl alcohol to formaldehyde. Its activity increases during the first few hrs. of use, and then remains constant indefinitely; at this stage it gives a conversion of approx. 90% at the optimum temperature of about 373°. It is relatively inactive for the further oxidation of formaldehyde. Iron oxide causes oxidation mainly to oxides of carbon; molybdenum oxide, on the other hand, catalyses formation of formaldehyde exclusively, but has a much lower activity, the maximum conversion (57·8%) falling to a steady value of 33·5% in the course of a few hrs. H. A. PIGGOTT.

Rate of hydrogenation of acetoacetic ester, dehydracetic acid, benzene, phenol, and aniline over nickel at pressures from 27 to 350 atm. H. ADKINS, H. I. CRAMER, and R. CONNOR (J. Amer. Chem. Soc., 1931, **53**, 1402—1405; cf. this vol., 46).—At 150° ethyl acetoacetate is reduced by hydrogen and nickel at 30 atm., but the rate of reduction is considerably increased by increase in pressure, particularly in the range 120—350 atm. Dehydracetic acid is reduced at 195—200° with the relative velocities 1 : 2 : 4 at 108, 149, and 323 atm., respectively. Both benzene and phenol are readily reduced at 120° and 30—150 atm., and the rate of reduction is not greater at higher pressures. Aniline is not readily hydrogenated at 175° and 34 atm.; the rate of reduction increases steadily to 190 atm., further increase of pressure producing relatively little effect. Neither aniline nor phenol was completely reduced under the conditions chosen. H. A. PIGGOTT.

Formation of ferrite in the rusting of iron. C. CARIUS (Z. anorg. Chem., 1931, **197**, 254—256; cf. Krause and Tulecki, this vol., 324).—On electrolysis of a 0·2N-solution of sodium chloride of p_H 3·5 and saturated with air, using a platinum cathode and an iron anode, ferrous ferrite, $Fe(FeO_2)_2$, is formed. R. CUTHILL.

Electrodeposition of silver-cadmium alloys. C. G. FINK amd B. G. GEROPOSTOLOV.—See B., 1931, 496.

Electrodeposition of gold from alkaline cyanide solutions. E. T. DUNSTAN.—See B., 1931, 445.

Figures due to distribution of active deposit on electrodes. S. ROSENBLUM and M. VALLADARES (Compt. rend., 1931, **192**, 939—940).—Regular polygonal plates were placed horizontally above a cylindrical vessel containing air ionised by radiothorium within it. The plate was then raised to a potential of 15—1200 volts, and after 10—30 min. applied to a photographic plate for 1—2 min. On development flower-like images were obtained, independent of amount and sign of the charge, the number of "petals" corresponding with the number of sides of the polygon. The figures are probably due to movements of the active atoms near the electrode. C. A. SILBERRAD.

Chemical action of the electric discharge. IV. Maximum concentration of endothermic compounds at high temperatures; ozone and nitric oxide. E. BRINER and B. SUSZ (Helv. Chim. Acta, 1931, **14**, 594—609).—By application of the Nernst theorem the equations necessary for calculation of the equilibrium concentration of ozone at various temperatures from the heat of dissociation of the oxygen molecule have been derived. Thermal production of ozone is negligible at all temperatures; the maximum concentration (0·0000276%) occurs at 3750° Abs. Similar equations applied to the reaction between nitrogen (1 mol.) and oxygen (1 mol.) show that the maximum concentration at 1 atm. pressure (13·6%) occurs at 4000° Abs., when the gas contains 0·17% of nitrogen atoms and 20·8% of oxygen atoms; at 0·01 atm. pressure the maximum concentration (7·37%) occurs at 3200° Abs., whilst in air the maximum is 10·9%, at 4000° Abs. The formation of nitric oxide at these temperatures is due in part to electrical action. The temperature of maximum concentration of both ozone and nitric oxide lies considerably below that at which ionisation becomes appreciable. H. F. GILLBE.

Decomposition of hydrocarbons in the positive-ray tube. H. R. STEWART and A. R. OLSON (J. Amer. Chem. Soc., 1931, **53**, 1236—1244).—From results with a special tube it is concluded that the decomposition is due to primary dissociation by ionising electrons rather than to thermal decomposition at the hot cathode or to secondary reactions between ions and neutral molecules. Data for hydrocarbons at $1—10\times10^{-2}$ mm. show that butane does not afford $C_3H_8^+$, $C_2H_6^+$, or CH_4^+, whilst propane does not

afford $C_2H_6^+$ or CH_4^+, but other C_3H_x and C_2H_- ions are produced together with CH_3^+. Selective absorption of hydrocarbon ions is observed (cf. Kallmann and Rosen, A., 1930, 16). Identification of products of other hydrocarbon reactions by positive-ray methods may lead to ambiguous results owing to decomposition in the tube (cf. Olsen and Meyers, A., 1928, 150). J. G. A. GRIFFITHS.

Coloration of glasses and related materials by β- and γ-rays. J. HOFFMAN.—See B., 1931, 490.

Effect of irradiation on Liesegang rings. J. CLUZET and T. KOFMAN (Compt. rend. Soc. Biol., 1930, **104**, 1001—1003; Chem. Zentr., 1931, i, 583).—The formation of Liesegang rings from silver nitrate, dichromate, and gelatin is unaffected by visible light, *X*-rays, or radium rays, but is retarded by ultraviolet light. A. A. ELDRIDGE.

Correlation of certain photochemical reactions and wave-length of light. I. F. C. HYMAS (J.S.C.I., 1931, **50**, 81—83T).—The response of certain photochemical reactions to light of different wave-lengths has been studied by a spectrographic method, involving the exposure of tubes of the reaction mixture in the focal plane of a quartz spectrograph. The reactions employed are: (i) the decomposition of oxalic acid when catalysed by uranyl salts (Anderson and Robinson, A., 1925, ii, 415), and (ii) the decomposition of potassium iodide (A., 1929, 1152). The spectral energy distribution of the light source has been determined by thermopile and galvanometer and corresponding corrections have been applied to the results. Under practical conditions, using a mercury arc, the potassium iodide–starch test appears to respond almost exclusively to rays between 240 mμ and 300 mμ. The decomposition of oxalic acid catalysed by uranyl sulphate has a much wider response, covering the whole of the ultra-violet region from 220 mμ upwards and including that portion of the visible spectrum below 500 mμ. The maximum effect is obtained at about 330 mμ. There appears to be a subsidiary peak in the response curve at about 260 mμ. When these curves are corrected on the basis of equal energy distribution, it becomes evident that the photochemical effect increases with decrease of wave-length.

Action of ultra-violet light on alkyl iodides. G. EMSCHWILLER (Compt. rend., 1931, **192**, 799—802).—Ultra-violet light liberates methane and a condensation product, $(CH_2)_n$, of high mol. wt. from methyl iodide, ethylene and ethane from ethyl iodide, but no butane (cf. A., 1924, i, 929), propylene and propane from *n*- and *iso*-propyl iodides, butylenes and butanes from *n*-, *sec*.-, and *iso*-butyl iodides, but from *tert*.-butyl iodide propylene, ethylene, propane, and ethane. The quantities of saturated and unsaturated hydrocarbon are approximately equal. The reactions are explained by the equations: $C_nH_{2n+1}I+$light$=C_nH_{2n}+H'I'$ (1), and $C_nH_{2n+1}I+H'I'=C_nH_{2n+2}+I_2$ (2), the H′ and I′ in (1) being eliminated either separately or combined. One hydrogen atom has therefore apparently a function differing from that of the others. Ultra-violet light has no action on the dry vapour of an alkyl iodide in absence of oxygen; in presence thereof, together with iodine, gaseous methyl iodide yields as principal product formaldehyde, and gaseous ethyl iodide yields acetaldehyde, thus confirming the formation of the C_nH_{2n} groups. Results with *n*- and *iso*-propyl iodides are more complex, but some acetone is formed from *iso*propyl iodide (cf. A., 1930, 554, 717). C. A. SILBERRAD.

Daily course of photosynthesis on the shores of the Black Sea. S. P. KOSTYTSCHEV (Bull. Acad. Sci. U.S.S.R., 1930, 611—630).—The daily course of photosynthesis in this district is extremely irregular. With the exception of the bamboo, all the plants investigated prove sensitive to the sudden temperature changes which occur and on hot days assimilate carbon dioxide only during the forenoon; in some cases the leaves work only for 2 or 3 hrs. per day. The influence of heat is confirmed by experiments with shaded and unshaded leaves. T. H. POPE.

Daily course of photosynthesis during continuous sunshine in polar regions. S. P. KOSTYTSCHEV, E. N. BAZYRINA, and V. A. TSCHECNOKOV (Bull. Acad. Sci. U.S.S.R., 1930, 599—610).—The results of tests made on five different plant species in the polar circle during the summer solstice show that photosynthesis continues during the whole 24 hrs. of the day, the curve showing a maximum at about midday and a minimum at about midnight. Neither a sudden change in the energy of photosynthesis nor generation of carbon dioxide was observed; the stomata remain open during the whole day. The continuous production of organic matter results in a high daily yield, this being probably the cause of the short period of vegetation shown by many plants in northern regions. T. H. POPE.

Formation of a histamine-like substance from histidine by ultra-violet irradiation, and significance of the process in light erythema. F. ELLINGER (Strahlenther., 1930, **38**, 521—542; Chem. Zentr., 1931, i, 1128).—Irradiation of histidine affords a substance giving the biological reactions of histamine; at the same time a yellow substance, the presence of which prevents further formation of active material after 2 hrs.' irradiation, is produced. Ultra-violet irradiation of solid histidine also produces histamine. Irradiation of serum probably leads to a similar change. A mechanism of light erythema is proposed. A. A. ELDRIDGE.

Solar irradiation and vitamin-*D*. A. VAN WIJK, E. H. REERINK, and W. MORIKOFER (Strahlenther., 1930, **39**, 80—92; Chem. Zentr., 1931, i, 1126).—The absorption spectrum of a solution of ergosterol irradiated in sealed quartz vessels by sunlight with exclusion of the ultra-violet radiation of the sky differs from that of material exposed to sunlight or quartz lamp irradiation. The ratio of the vitamin-decomposing to -generating power is for the mercury lamp and the sun of the order 0·137 to 0·34. A. A. ELDRIDGE.

Electro-condensation of acetylene by β-rays. W. MUND and J. C. JUNGERS (Bull. Soc. chim. Belg., 1931, **40**, 158—176).—When acetylene polymerises under the influence of β-rays from radium, each pair of ions produced brings about the union of 26 mols. of

acetylene. A general theory of radiochemical reactions is described and shown to be capable of accounting for this result. R. CUTHILL.

Sodium silver thiosulphates. E. CARRIÈRE and RAULET (Compt. rend., 1931, 192, 746—748; cf. this vol. **443**; Lumière, A., 1907, ii, 866; Baines, A., 1930, 175).—By dissolving freshly-precipitated silver chloride in varying proportions of concentrated solution of sodium thiosulphate, besides the known $NaAgS_2O_3$ and $Na_4Ag_2(S_2O_3)_3$, there is obtained by using excess of solution and evaporating over sulphuric acid the complex $Na_2Ag(S\ O$ $2H_2O$, very soluble in water and losing $2H_2O$ at 115 .

C. A. SILBERRAD.

Metals and alloys. I. Salt-like compounds and intermetallic phases of sodium in liquid ammonia. E. ZINTL, J. GOUBEAU, and W. DULLENKOPF. **II. Polyplumbides, polystannides, and their transition to metallic phases.** E. ZINTL and A. HARDER (Z. physikal. Chem., 1931, **154**, 1—46, 47—91).—I. The reactions in liquid ammonia of sodium with sulphur, selenium, tellurium, arsenic, antimony, bismuth, tin, lead, thallium, zinc, cadmium, mercury, copper, silver, and gold have been investigated. Whereas the elements belonging to groups 1—3 of the periodic table form insoluble alloys with atomic lattices, the other elements give rise to soluble substances, which are shown by the behaviour of their solutions on electrolysis to be "polyanionic" salts, similar in constitution to polysulphides and polyhalides. These salts are present in solution, however, as ammines.

II. By extraction of suitable alloys of sodium and tin and sodium and lead with liquid ammonia, ammonosols of the ammines of sodium enneaplumbide, Na_4Pb_9, and sodium enneastannide, Na_4Sn_9, may be prepared, and on evaporation of the solutions, the solid amorphous ammines remain. The binary alloys which result from the removal of the ammonia from the solid ammines have atomic lattices and are identical with the compounds of the same composition which separate from molten mixtures of the two components. R. CUTHILL.

Preparation of potassium nitrate and alumina by double decomposition of potassium chloride and aluminium nitrate. I. System $3KCl+Al(NO_3)_3 \rightleftharpoons 3KNO_3+AlCl_3$. II. Treatment of clay with nitric acid. H. TANAKA.—See B., 1931, 487.

Action of potassium oxalate on copper ferrocyanide. M. KOHN (Z. anorg. Chem., 1931, **197**, 287—288).—Copper ferrocyanide dissolves in excess of a solution of potassium oxalate on warming, $Cu_2Fe(CN)_6+2K_2C_2O_4=2CuC_2O_4+K_4Fe(CN)_6$, but is reprecipitated by hydrochloric acid. R. CUTHILL.

Copper quadrantoxide. M. J. MURRAY (J. Physical Chem., 1931, **35**, 1011—1024).—Mainly a discussion. The oxide Cu_4O does not form a stable solid phase at the ordinary temperature.

L. S. THEOBALD.

Silver ferrites. I. Silver ferrites from ortho- and meta-ferric hydroxide. A. KRAUSE and K. PILAWSKI (Z. anorg. Chem., 1931, **197**, 301—306: cf. this vol., 324).—The *silver ferrites* $AgFeO_2$ and $Ag_3H(FeO_2)_4$ have been prepared from metaferric hydroxide and orthoferric hydroxide, respectively. From the composition of the latter salt it appears that the hydrogen atoms of the hydroxyl groups of the ortho-hydroxide are not all replaceable by metals. The meta-hydroxide and γ-FeOOH are apparently identical, but α-FeOOH has no acid properties.

R. CUTHILL.

Calcium oxalate from calcium cyanamide. G. BARSKY and G. H. BUCHANAN (J. Amer. Chem. Soc., 1931, **53**, 1270—1276; cf. A., 1930, 301).—Calcium oxalate, together with formate and carbonate, is produced approximately in accordance with the equation $2CaCN_2+Ca(CN)_2-10H_2O \longrightarrow 6NH_3+2CaC_2O_4+Ca(OH)_2$ when mixtures of calcium cyanamide and cyanide are autoclaved with water. The velocity of the reaction at 50° is increased by depressing the p_H from 11·5 to 9·0. The yield of oxalate is increased by adding the cyanamide in stages.

J. G. A. GRIFFITHS.

Polysulphides of barium and calcium. P. L. ROBINSON and W. E. SCOTT (J.C.S., 1931, 693—709).—The polysulphides of barium have been studied by investigating thermally a part of the barium–sulphur system and by examining the crystals obtained from solutions of sulphur in barium hydrosulphide. The thermal study indicates that the di- and tri-sulphides are very unstable at their m. p., which are 925° and 554°, respectively. Solutions of sulphur in barium hydrosulphide yield barium tetrasulphide monohydrate if the concentration is high and barium trisulphide trihydrate and barium hydrosulphide at moderate concentrations. Dilute solutions give crystals of $Ba(SH)(OH),5H_2O$. Calcium polysulphides have been prepared using anhydrous alcohol as a solvent, but it has not been possible to isolate the individual compounds. F. J. WILKINS.

Autoxidation of zinc. A. S. COCOSINSCHI (Z. anorg. Chem., 1931, **197**, 270—272).—The basic carbonate formed by the autoxidation of zinc in contact with water containing air is variable in composition. Autoxidation of pure zinc does not occur in absence of carbon dioxide, but zinc containing small amounts of other metals is oxidised by oxygen formed by the action of the impure metal on the water, even if access of air is prevented.

R. CUTHILL.

Compounds of mercuric and potassium iodides. (MLLE.) M. PERNOT (Ann. Chim., 1931, [x], **15**, 5—84).—Chiefly an account of work already published (see A., 1928, 20; 1929, 400, 1145). The system mercuric iodide–potassium iodide–ethyl alcohol has been studied at 34°: only one *compound*, HgI_2,KI,C_2H_6O, exists. The salt which crystallises in presence of a small quantity of water is HgI_2,KI,H_2O, and the same compound is obtained from acetone solutions containing more than 3% of water. H. F. GILLBE.

Mercuric iodosulphates. M. PAIC (Compt. rend., 1931, **192**, 951—953).—By heating at 100° mercuric iodide with 10 pts. of sulphuric acid containing 20% SO_3, iodine and sulphur trioxide are evolved and a crystalline product shown by X-ray

analysis to consist of a mixture of mercuric sulphate and the iodosulphate $HgSO_4,HgI_2$ is obtained. By the interaction of mercuric iodide and a saturated solution of mercuric sulphate in dilute sulphuric acid (best containing 40% H_2SO_4) white felted crystals of $3HgO,2SO_3,HgI_2$ are gradually formed. No other of Ditte's compounds (cf. A., 1905, ii, 391) could be obtained. The same basic iodosulphate can be prepared by pounding together equivalent amounts of mercuric iodide and the basic sulphate $3HgO,2SO_3,2H_2O$. It is also the chief product of the interaction of mercuric sulphate, iodine, and water (cf. Bruckner, A., 1907, ii, 772), some mercuric iodate being simultaneously formed. C. A. Silberrad.

Phosphorescent substances. III. Boric acid. N. F. Shirov (Ukrain. Chem. J., 1930, 5, [Sci.], 267—274).—Orthoboric acid yields a series of luminescent products when heated at 170° with fluorescein, the colour of the luminescence varying from violet with 0·0001% of fluorescein to bluish-green (0·001%), green (0·005%), and yellowish-green (0·01%). The product retains its properties indefinitely if protected from moisture. The colour of the luminescence using triphenylmethane in place of fluorescein is yellow, with phthalic anhydride greenish-blue, and with benzoic or salicylic acid green. The above observations can be applied to the detection of small quantities of boric acid. Two drops of 0·001% fluorescein solution are added to 1 c.c. of the solution under examination, placed in a small black porcelain vessel, and the solution is evaporated to dryness. The residue is heated at 170°, rapidly cooled, and illuminated by a 50-watt lamp. Luminescence can then be observed if the solution contains 0·002% of boric acid. R. Truszkowski.

Basic aluminium chloride. W. D. Treadwell [with O. T. Lien] (Helv. Chim. Acta, 1931, 14, 473—481).—A clear solution is obtained when 1 at. of aluminium is dissolved in 1 mol. of hydrochloric acid. If a greater excess of metal is employed the ratio OH : Cl in the precipitate which forms varies considerably, but tends towards values greater than 5. Potentiometric titration of the clear solution shows that in the precipitate obtained on addition of sodium hydroxide solution the ratio Cl : Al is 1 : 2. In the original solution the aluminium appears to exists in the form of chlorine-free ions such as $AlOH^{\cdot\cdot}$ or $Al(OH)_2^{\cdot}$, which in presence of hydroxyl and chloride ions yield $AlO_2,AlCl,OH$; on further addition of alkali this yields $AlO_2,Al(OH)_2$. The formation of this compound is completed at about p_H 9—9·5. If more aluminium is used than is required for the production of $Al(OH)_2^{\cdot}$ colloidal hydrates are formed, of which the composition varies with the temperature and period of heating; these substances react with alkali in the same manner as do the ions. H. F. Gillbe.

Oxidation of carbon monoxide in mixtures with air in presence of various metallic oxides. H. A. J. Pieters (Chem. Weekblad, 1931, 28, 250—251).—By passage of a 3% carbon monoxide–air mixture over manganese dioxide or cupric oxide formation of carbon dioxide is first observed at 80° or 200°, respectively; with cobalt dioxide and silver oxide oxidation occurs even at 20°, the monoxide, in the latter case, being completely oxidised to dioxide. A mixture of 50% manganese dioxide, 30% cupric oxide, 15% cobalt dioxide, and 5% silver oxide readily and completely oxidises the carbon monoxide to dioxide at the ordinary temperature; the mixture adsorbs a considerable quantity of carbon dioxide, which may be removed by heating the catalyst at 130°. H. F. Gillbe.

Constitution of the cyanogen halides. III. Reactions of cyanogen bromide. E. V. Zappi and S. Elorza (Bull. Soc. chim., 1931, [iv], 49, 397—399).—Silver nitrate gives a bromide reaction with 3% aqueous or alcoholic cyanogen bromide, the Prussian-blue test for cyanides being negative unless the concentration exceeds 3%. In 3% chloroform or ether solutions the former test is negative and the latter positive. These and other reactions indicate the existence of a carbylamine and nitrilic form of cyanogen bromide in the respective cases, and confirm the conclusion that the bromide is intermediate in constitution between the bromides of chlorine and iodine (cf. A., 1930, 1027, 1171). J. Grant.

Lower silicic acids. Losner (Chem.-Ztg., 1931, 55, 277—279).—Certain discrepancies in the analysis of various natural silicates indicate that oxidation of some constituent other than iron, manganese, or chromium takes place during the determination. Since the existence of a lower oxide of aluminium is unlikely, it appears that one or more lower oxides of silicon are present in the minerals, the probable formulæ being $Si_{10}O_{16}$, $Si_{12}O_{20}$, or $Si_{10}O_{18}$. Gossner's explanation (Z. angew. Chem., 1929, 42, 175) of similar discrepancies as being due to the presence of ferrosilicon is regarded as improbable, since this material is formed only at high temperatures, and the silicates, since they contain in many cases water of crystallisation, must have been produced from aqueous solutions. H. F. Gillbe.

Zirconium. II. Zirconium oxalate and diphenyl dinitrogen zirconium. III. Reaction between ammonia and methyl-alcoholic solutions of zirconium sulphate. H. S. Gable (J. Amer. Chem. Soc., 1931, 53, 1276—1278, 1612—1614).—II. Methyl-alcoholic oxalic acid precipitates normal *zirconium oxalate* from a methyl-alcoholic solution of zirconium tetrachloride. The metal is precipitated quantitatively as the compound $(PhN)_2Zr$ from the latter solution by aniline (cf. Jefferson, A., 1902, ii, 534). The effects of solvents on the compounds are tabulated. The oxalate is soluble in water.

III. When less than 3 min. old, solutions of zirconium sulphate afford with ammonia a white precipitate which, unlike zirconium hydroxide, is soluble in excess of reagent or in water. Older (5 min.) methyl-alcoholic solutions or fresh (5 sec.) aqueous solutions yield zirconium hydroxide. It is suggested that an unstable compound is formed between methyl alcohol and zirconium sulphate and that ammonia enters this compound, forming a complex with zirconium in the anion. J. G. A. Griffiths.

Nitrogen trifluoride. O. Ruff [with W. Menzel, Hecht, E. Hanke, L. Staub, H. Wallauer, and E. Ascher] (Z. anorg. Chem., 1931, 197, 273—286).—The chemical properties of nitrogen trifluoride have

been further investigated, and previous measurements of physical properties (A., 1928, 854) confirmed. Over the range 138—153° Abs. the density, d, of the liquid can be represented by the equation $d = 2{\cdot}162 - 0{\cdot}004316T$, where T is the temperature. The toxic properties of the gas are due to its inhibiting the oxidising action of the hæmoglobin of the blood. To determine the gas, it may be caused to react with hot hydriodic acid, $NF_3+7HI=NH_4I+3I_2+3HF$, the iodine formed being titrated, or with sodium, $2NF_3+6Na=N_2+6NaF$. R. CUTHILL.

Ammines of tervalent molybdenum. A. ROSENHEIM, G. ABEL, and R. LEVY (Z. anorg. Chem., 1931, **197**, 189—211).—By the action of pyridine on anhydrous ammonium or potassium molybdenum hexathiocyanate at the b. p. and extraction of the product with hot dilute acetic acid a solution is obtained from which yellow needles of *dipyridinotetrathiocyanatomolybdic acid*, $H[Mo(C_5H_5N)_2(SCN)_4],6H_2O$ separate (*dihydrate*). The residue of the extraction is the *pyridinium* salt ($2H_2O$), whilst if ethyl acetate is used for the extraction, the *salt* $(C_5H_5N)_2H[Mo(C_5H_5N)_2(SCN)_4]$ is obtained and the residue appears to contain the *compound* $[Mo(C_5H_5N)_3(SCN)_3]$, which, however, has not been isolated in a state of purity. The alkali metal salts cannot be prepared by direct neutralisation, as the acid readily hydrolyses, but by the action of a solution of ammonium or potassium acetate on an ethyl acetate solution of the pyridinium salt additive compounds of the type $(C_5H_5N)_2H[Mo(C_5H_5N)_2(SCN)_4]ROAc$ are obtained. Other *derivatives* of this type which have been prepared are $[(CH_2)_6N_4]H[Mo(C_5H_5N)_2(SCN)_4]$; $(CN_3H_5)_2H[Mo(C_5H_5N)_2(SCN)_4],H_2O$; $Tl_2OH[Mo(C_5H_5N)_2(SCN)_4]$; $HgCl[Mo(C_5H_5N)_2(SCN)_4]$; $CdOAc[Mo(C_5H_5N)_2(SCN)_4]$; $[Cd(NH_3)_4]OH[Mo(C_5H_5N)_2(SCN)_4]$; $[Cu(NH_3)_4]OH[Mo(C_5H_5N)_2(SCN)_4]$; $ZnOH[Mo(C_5H_5N)_2(SCN)_4]$. By heating a pyridine solution of molybdenum tribromide at 120°, acidifying, and recrystallising the product from chloroform, the *compound* $[Mo(C_5H_5N)_3Br_3]$ is obtained; for the preparation of the analogous *trichloro*-compound the solution must be heated under pressure at 270°. If the trichloro-compound is heated with anhydrous ethylamine at 100° *triethylaminetrichloromolybdenum* is formed. By the action of anhydrous ammonia under pressure on molybdenum trichloride at the ordinary temperature or on tripyridinotrichloromolybdenum at 45—50° the *compound* $[Mo(NH_3)_4Cl_2]Cl,2H_2O$ or $[Mo(NH_3)_4(H_2O)_2]Cl_3$ is produced, and by treatment of this substance with hydrochloric acid red needles of the *compound* $(NH_4)_3[MoCl_6]$ are formed. Methylamine, at a slightly higher temperature, yields a *compound* which cannot be readily purified but has probably the formula $[Mo(NH_2Me)_2Cl_2]OH$, together with red crystals of a *compound*, $(NH_3Me)_4MoCl_7$; ethylamine reacts still less readily to form the *compounds* $[Mo(NH_2Et)_2Cl_2]OH$ or $[Mo(NH_2Et)_2Cl_2]_2O$ and $(NH_2Et)_3[MoCl_6]$. By heating tripyridinotrichloromolybdenum with methylamine at 100° a *tetrammine*, $[Mo(NH_2Me)_4Cl_2]Cl,0{\cdot}5H_2O$, is formed; the corresponding *dichromate*, *thiocyanate*, and *chloroplatinate*, and the analogous *chromium* compound, have also been prepared. H. F. GILLBE.

Physico-chemical studies of complex acids. V. Precipitation of tungstates. H. T. S. BRITTON and W. L. GERMAN (J.C.S., 1931, 709—717).—The reactions between aqueous solutions of sodium tungstate, metatungstate, and paratungstate and various metallic salts have been investigated electrometrically and analytically. Metathesis resulting in the precipitation of corresponding tungstates of the metals does not take place. The precipitates which are formed begin to appear at the p_H values at which their respective hydroxides are precipitated. Moreover, all the precipitates are essentially basic in nature. F. J. WILKINS.

Precipitation of polonium and some of its complex derivatives. II. Determination of two valencies of polonium by formation of complex derivatives isomorphous with those of other metals. M. GUILLOT (J. Chim. phys., 1931, **28**, 92—129).—The preparation and properties of some complex dithiocarbamates of cobalt, nickel, bismuth, and copper are described and compared with those of polonium. These are stable compounds, non-electrolytes, insoluble in water, but soluble in chloroform. In these compounds, which are isomorphous with the corresponding compounds of tervalent cobalt, polonium appears to be tervalent, having the co-ordination number 6. Since in the formation of these complexes, however, the valency of other metals was observed to change (*e.g.*, cupric salts give cuprous complexes), it is not safe to conclude that the original solution contained tervalent polonium. Polonium appears to be tervalent in the *compound* $[PoCl_6](NH_4)_3,H_2O$, which is isomorphous with the corresponding compound of iridium, and also in the oxalate. The *compound* $[PoCl_6](NH_4)_2$ is isomorphous with the corresponding complex salts of tellurium, lead, tin, and platinum, and the polonium is considered to be quadrivalent. Polonium appears to be quadrivalent also in the hydroxide, to which is ascribed the formula $O=Po(OH)_2$. The conditions of transition between tervalent and quadrivalent polonium have been examined and it is concluded that the valency oscillates between 3 and 4, depending on the nature of the reagent added. No evidence has been found of the existence of compounds in which polonium has a valency lower than 3; on the other hand, it seems probable that polonium can assume a higher valency than 4, but the evidence goes to show that the higher valency is not 6 or 8. E. S. HEDGES.

Working up iodine residues. J. J. HAUSMA (Chem. Weekblad, 1931, **28**, 183—184; cf. van Voorst, this vol., 448).—In the recovery of iodine by precipitation as cuprous iodide and subsequent oxidation and distillation, heavy losses occur. It is better to treat the cuprous salt with iron in presence of water and then to add potassium carbonate for recovery as potassium iodide; several kg. can be thus treated at one time. Full directions for recovery of the pure iodide are given. S. I. LEVY.

Physical and chemical properties of rhenium. G. Heyne (Z. anorg. Chem., 1931, **197**, 224).—A reference to the work of Geilmann and Weibke (this vol., 328; cf. Agte and others, *ibid.*, 448).

H. F. Gillbe.

Ammoniates of the salts of oxy-acids. M. A. Rakuzin (Bull. Soc. chim., 1931, [iv], **49**, 363—366).—The chemical properties and methods of preparation of $MnSO_4,4NH_3$ (brown), $ZnSO_4,5NH_3$ (white), $CuSO_4,5NH_3$ (blue), $NiSO_4,6NH_3$, $CoSO_4,6NH_3$ (reddish-white), $CdSO_4,6NH_3$ (white), $AgNO_3,6NH_3$, and $Ag_2SO_4,2NH_3$ are described. All were prepared by the action of ammonia on the corresponding salt (magnesium sulphate, sodium and barium nitrates, potassium dichromate, and copper phosphate gave negative results) and all lose ammonia in warm air and are decomposed by water into the metal oxide or hydroxide. Except in the cases of silver and cadmium the hydrates and the ammoniates are analogous.

J. Grant.

Experimental confirmation of the film theory of the corrosion of iron. V. A. Kistiakovski and I. V. Krotov (Bull. Acad. Sci. U.S.S.R., 1930, 715—716).—Photomicrographs of polished iron surfaces exposed to iodine vapour show the gradual spreading of the corrosion from the original nuclei (crystallisation centres of the scale) in crystallised formations, both continuous and dendritic, and support the film theory of corrosion. In air, the corrosion probably proceeds in three stages: the formation, under the action of oxygen, of amorphous scale, probably of colloidal structure; thickening of the scale and its conversion into a pseudo-amorphous form, consisting of crystallites, and development of definite crystals of oxide of iron.

T. H. Pope.

Action of normal tartrates on Prussian-blue. M. Kohn (Z. anorg. Chem., 1931, **197**, 289—291).—Prussian-blue dissolves on warming in concentrated solutions of normal tartrates, with formation of a green solution, $Fe_4[Fe(CN)_6]_3+6K_2C_4H_4O_6=3K_4Fe(CN)_6+2Fe_2(C_4H_4O_6)_3$, but is reprecipitated on addition of hydrochloric acid.

R. Cuthill.

Stereochemistry of the platinous salts. IV. A. A. Grunberg (Helv. Chim. Acta, 1931, **14**, 455—472).—By treating a solution of Peyrone's salt $[Pt(NH_3)_2Cl_2]$ with silver nitrate solution, and heating the filtered solution with an excess of oxalic acid, the compound $Pt(NH_3)_2C_2O_4$ separates quantitatively as white, sparingly soluble crystals; its structure is $\left|\begin{matrix}NH_3 \\ NH_3\end{matrix}Pt\begin{matrix}OOC \\ OOC\end{matrix}\right|$ If Reiset's salt is treated similarly the product is a *trans*-dioxalate of the structure $\left|\begin{matrix}NH_3 \\ HC_2O_4\end{matrix}Pt\begin{matrix}C_2O_4H \\ NH_3\end{matrix}\right|$, which in solution yields hydrogen ions but no oxalate ions; the first dissociation constant, assuming the compound to function as a monobasic acid, is $6{\cdot}3\times10^{-4}$. These results confirm conclusively Werner's view that Peyrone's salt possesses the *cis* and Reiset's the *trans* structure. Glycine reacts with Peyrone's salt to give the *compound* $Pt(NH_3)_2C_2H_5O_2NCl$: the *chloroplatinite* also has been prepared. Reiset's compound reacts less readily with glycine, the product being the *compound* $Pt(NH_3)_2C_2H_5O_2N,2HCl$; the corresponding *hydrobromide* and *hydriodide* form yellow and green crystals, respectively. The hydrochloride does not form a tetrammine when treated with ammonia solution, and is not decomposed by formaldehyde; the glycine molecules are therefore attached to the platinum atom by the auxiliary valencies of the nitrogen atoms.

H. F. Gillbe.

Applications of Wood's light. L. Colombier (Ann. Falsif., 1931, **24**, 89—96).—The fluorescence of various substances has been studied in ultra-violet light especially with regard to p_H. It is not possible to determine the of a solution by fluorescence indicators, but some substances, especially umbelliferone, can be used in titrations to indicate neutrality. The fluorescent properties of this substance also enable its formation from malic acid and resorcinol to serve as specific tests for these substances, and an analogous test is possible for citric acid after oxidising with permanganate. Specific reactions are also given for β-naphthol and orcinol.

E. B. Hughes.

Capillary analysis. G. Badt (Arch. Pharm., 1931, **269**, 145—157).—In order to avoid gross errors in the quantitative study of the capillary rise of solutions in filter-paper, evaporation is prevented by placing the strips between glass or celluloid plates which are separated by the smallest possible gap from the reservoir. The strips are not allowed to dry before being analysed. Under these conditions the concentration of solute in the paper diminishes in passing from the lower to the upper end for acids, bases, and salts. Acids are adsorbed by paper, the hydrogen ion displacing metallic ions from the fibre. The adsorbed hydrogen ions retain their activity towards indicators. Caffeine, morphine hydrochloride, and codeine phosphate are not materially adsorbed by paper, but there is marked adsorption of the colouring matter and glucosides from Infusum digitalis. The thalleioquinine test may be advantageously carried out on filter-paper.

H. E. F. Notton.

Recommended specifications for analytical reagent chemicals. W. D. Collins and collaborators (Ind. Eng. Chem. [Anal.], 1931, **3**, 221—224).—The requirements and tests recommended by the American Chemical Society's Committee on Analytical Reagents are given for perchloric acid (60%), cadmium chloride ($CdCl_2,2{\cdot}5H_2O$), chromium trioxide, lead chromate, lead nitrate, magnesium oxide, mercuric chloride, mercurous chloride, sodium nitroferricyanide, and uranium nitrate. Some corrections are made to previously published specifications for phosphoric acid, ammonium monohydrogen phosphate, barium carbonate, magnesium chloride, potassium ferrocyanide, potassium ferricyanide, potassium dihydrogen phosphate, sodium hydrogen carbonate, sodium monohydrogen phosphate, and sodium thiosulphate, and a general correction for the gravimetric determination of sulphate is added.

E. S. Hedges.

Systematic analysis by drop reactions. C. J. van Nieuwenburg (Mikrochem., 1931, **9**, 199—219).—A scheme for the systematic detection of all the more common anions and cations has been developed by selection of available micro-reactions. For a complete analysis, involving the detection of constituents

present in proportions greater than 0·5%, a 100—200-mg. sample is required. H. F. GILLBE.

Glass electrode and its application to the determination of hydrogen-ion concentration. I, II. B. ELEMA (Chem. Weekblad, 1931, **28**, 223—229, 234—238).—I. The limits of usefulness of the colorimetric method and of the hydrogen and quinhydrone electrodes for the measurement of p_H are indicated, and the applications and technique of the glass electrode method are described.

II. Details are given of measurements, in buffered and biological solutions, of the influence of substances which interfere with the determination of p_H by other methods, of the examination of various types of soil with which the quinhydrone electrode yields unsatisfactory results owing to the existence of oxidation–reduction potentials, and of measurements with potato starch, for which a constant difference is observed between the results by the glass electrode and quinhydrone electrode methods. The glass electrode is applicable to measurements of p_H up to 9·5, even in presence of considerable quantities of oxidising and reducing agents. H. F. GILLBE.

The "pehameter" and its possible use in practice. R. HERRMANN (Z. Pflanz. Dung., 1931, **10 B**, 142—145).—Results of p_H determinations by the "pehameter" are compared with those by electrometric and colorimetric methods, and are shown to be unsatisfactory. A. G. POLLARD.

Tungsten electrode in potentiometric titrations and p_H measurements. H. T. S. BRITTON and E. N. DODD (J.C.S., 1931, 829—836).—The tungsten electrode has been calibrated against the Prideaux–Ward universal buffer mixture and employed in the potentiometric titration of several acids, for which the hydrogen electrode may not be used, with satisfactory results. F. J. WILKINS.

Solutions for colorimetric standards. IV. Factors affecting the colour of indicator solutions. M. G. MELLON and G. W. FERNER (J. Physical Chem., 1931, **35**, 1025—1043; cf. A., 1930, 871).—The effect on colour of (i) source of purity, (ii) method of preparing solutions, and (iii) exposure to ultra-violet light has been determined spectrophotometrically for methyl-orange, methyl-red, phenol-red, thymol-blue, cresol-red, tropæolin-OO, chlorophenol-red, bromophenol-blue, bromocresol-purple, bromothymol-blue, bromocresol-green, and bromophenol-red. All degrees of fading can result from (iii), and, in certain cases, considerable variations in colour arise from (i) and (ii). L. S. THEOBALD.

Manometric determination of hydrogen peroxide. A. FUJITA and T. KODAMA (Biochem. Z., 1931, **232**, 15—19).—Two manometric methods for the determination of hydrogen peroxide are described; both give results within 3% of those by permanganate titration. P. W. CLUTTERBUCK.

Test for halogens. H. E. TREMAIN (Ind. Eng. Chem. [Anal.], 1931, **3**, 225).—Free halogens give a sensitive colour reaction with p-aminodimethylaniline. The reagent is prepared by dissolving 5 g. of the base in 100 c.c. of absolute alcohol; 2 or 3 drops of the reagent are added to 5 c.c. of water and the solution to be tested is added slowly. A clear pink colour is obtained, but if excess of the halogen solution is added, other confusing colours appear. The limits of sensitivity are as follow: bromine, 1 in 1,300,000; chlorine, 1 in 65,000; iodine, 1 in 400,000. A convenient, although less sensitive, method of making the test is with test papers, made by immersing filter-paper in a solution of 10 c.c. of p-aminodimethylaniline in 100 c.c. of absolute alcohol. E. S. HEDGES.

Bromo-iodometric investigations. VI, VII. J. H. VAN DER MEULEN (Chem. Weekblad, 1931, **28**, 238—239, 258—260).—VI. The excess of hydrogen peroxide used for decomposing the excess of the hypochlorite employed to oxidise bromide to bromate (this vol., 325) is much more readily removed on boiling if 2—3 drops of a solution of osmic acid (0·5 g. per litre) be added. As an alternative to the peroxide method, M-sodium formate may be used at the b. p. to destroy the excess of hypochlorite. The titration of the bromate with iodide in acid solution may be accelerated by adding a few drops of sodium molybdate solution. Oxalate, carbamide, or phenol cannot be used satisfactorily in place of formate.

VII. Chlorate may be determined by reduction to chloride by heating at 85—90° for a few min. with standard arsenious acid solution, in presence of hydrobromic acid, using a few drops of osmic acid or osmate solution (0·5 g. OsO_4 per litre) as catalyst; the excess of arsenious acid is titrated with 0·1N-potassium bromate, using methyl-orange, which is destroyed at the end-point, as indicator. Alternatively, 0·1N-potassium iodate may be used for the titration, or the arsenious acid may be oxidised by an excess of iodate and iodide, and the excess of iodine titrated with 0·1N-arsenious acid after addition of potassium hydrogen carbonate. If iodate and bromate are present they may be determined as previously described (this vol., 325, and earlier papers), and the chlorate calculated by difference. H. F. GILLBE.

Determination of traces of iodine. V. Further refinements in technique. R. E. REMINGTON, J. F. MCCLENDON, and H. VON KOLNITZ (J. Amer. Chem. Soc., 1931, **53**, 1245—1249).—The oxygen–gas torch (A., 1930, 828) has been applied to the combustion of large samples of material; external heating of the silica tube is replaced by an internal electrically-heated platinum spiral or a coil of chromel wire just in front of the torch. A modified technique is described for pasty substances which cannot be introduced as pencils or sprays. The method of Glimm and Isenbruch (A., 1929, 838) is unsatisfactory for large samples. Contrary to Turner (A., 1930, 1143, 1463), it is found that the starch–iodine reaction is untrustworthy for the colorimetric determination of iodine. J. G. A. GRIFFITHS.

Preparation of starch solution for use in iodometric titrations. C. L. ALSBERG and E. P. GRIFFING (J. Amer. Chem. Soc., 1931, **53**, 1401—1402; cf. A., 1926, 701).—Grinding starch in a pebble mill can be avoided by using starch in the form of "puffed rice." J. G. A. GRIFFITHS.

Conductometric titration of sulphate and barium. I. M. KOLTHOFF and T. KAMEDA (Ind.

Eng. Chem. [Anal.], 1931, **3**, 129—133).—The conductometric method is applicable to the determination of alkali sulphates with barium chloride only if standard solutions are titrated under the same conditions as the unknown solutions. The break in the conductivity curve always occurs before the true end-point is reached, the magnitude of the error depending on the dilution, alcohol content, acidity, and nature of the cations present. In $0 \cdot 1N$-solutions the deviations are smaller with lithium sulphate than with potassium sulphate. In more dilute solutions the results are reproducible to within 1%. The conductivity is distinctly higher in the presence of the precipitate than that of the filtered solution, and the increase is attributed to the colloidal charge of the particles of barium sulphate and to the influence of the suspended matter on the cell constant. In the titration of barium with sulphate solutions, the break in the conductivity curve is nearer the end-point, although a deviation of about 1% is observed. The conductometric method is very useful in the titration of very dilute solutions in the presence of 30% of alcohol. Alcohol reduces the mobility of barium ions more than that of alkali metal, sulphate, or chloride ions. E. S. Hedges.

Ceric sulphate in volumetric analysis. IX. Standardisation of thiosulphate solutions. Determination of thiosulphate. N. H. Furman and J. H. Wallace, jun. (J. Amer. Chem. Soc., 1931, **53**, 1283—1288).—Interference by ferric iron in the method previously recorded (Martin, A., 1927, 1046) is prevented by the addition of phosphoric acid. A rapid determination accurate to 0·12% is effected by adding 0·3—0·4 g. of potassium iodide and 20 c.c. of 0·2% starch solution to 25 c.c. of approximately $0 \cdot 1N$-thiosulphate, diluting to 250 c.c., and titrating with $0 \cdot 1N$-ceric sulphate, until the starch–iodine blue appears. J. G. A. Griffiths.

Microanalysis with an ordinary balance. I. Determination of nitrogen by micro-Dumas method. W. J. Saschek (Ind. Eng. Chem. [Anal.], 1931, **3**, 198—199).—0·1 G. of the sample is ground with 5 g. of cupric oxide and after thorough mixing an aliquot portion (0·2 g.) is taken for analysis by the Pregl method. This method eliminates the use of a micro-balance when 0·1 g. of the sample is available and has the advantage that as many analyses as desired can be made and the unused portion of the sample can be recovered from the solid mixture by the use of a suitable solvent. E. S. Hedges.

Volumetric determination of phosphoric acid and its application to the determination of magnesium and zinc. R. Biazzo (Annali Chim. Appl., 1931, **21**, 105—109).—In the method previously described (this vol., 452), the titration of the excess of molybdate in the filtrate from the phosphate precipitate may be vitiated by various substances. This inconvenience may be avoided by dissolving the washed ammonium phosphomolybdate precipitate in ammonia, precipitating the phosphate as magnesium ammonium phosphate, and titrating the molybdate in an aliquot part of the filtrate with lead acetate. A similar procedure serves for the determination of zinc or magnesium, which is first precipitated as the corresponding ammonium phosphate. Magnesium may be determined also by precipitation with excess of standard sodium phosphate solution and determination of the excess of the phosphate in the precipitate. T. H. Pope.

Determination of carbon dioxide. C. A. Jacobson and J. W. Haught (Bull. West Va. Univ. Sci. Assoc., 1930, **2**, No. 4, 8—13).—Carbonate is decomposed with 15% perchloric acid, the gases being dried with "dehydrite" and the carbon dioxide absorbed in ascarite. Chemical Abstracts.

Determination of carbonyl chloride. J. C. Olsen, G. E. Ferguson, V. J. Sabetta, and L. Scheflan (Ind. Eng. Chem. [Anal.], 1931, **3**, 189—191).—The alcoholic sodium hydroxide method for determining carbonyl chloride cannot be used with samples containing other chlorine compounds. The silver nitrate method is unsatisfactory, owing to reduction of the silver nitrate by some of the decomposition products. Slight modifications of the aniline method and the sodium iodide–acetone method which lead to concordant results are described. By the modified acetone method it is possible to detect 0·1 mg. of carbonyl chloride when present in air at a concentration of only 1 in 10^6. E. S. Hedges.

Effect of silicic acid separated during analysis on the determination of small amounts of metals in rocks. A. Cissarz (Zentr. Min. Geol., 1930, 328—333; Chem. Zentr., 1930, ii, 2414).—The small metal content of the Mansfeld copper-bearing schists can be completely brought into solution for spectroscopic analysis by attack with hydrofluoric and sulphuric acids or aqua regia. Important amounts of metal can be lost through absorption by precipitated silica. L. S. Theobald.

Classical methods of analysis of silico-aluminous, calcareous, alkaline materials. J. Delforge.—See B., 1931, 491.

Conversion of alkali sulphate into chloride in silicate analysis. W. Mylius (Sprechsaal, 1930, **63**, 972—975; Chem. Zentr., 1931, i, 836).—The finely powdered neutral sulphates are twice heated to fuming with hydrazine hydrochloride. For 0·5 g. of silicate with 5—25% of alkali oxide the conversion occupied 85 min. and the chlorides contained 0·1 mg. or less of SO_3. The following procedure is more rapid than that of Lawrence Smith: opening up with hydrofluoric and sulphuric acids, removal of interfering bases with 8-hydroxyquinoline, isolation of alkalis by Robitschek's method, and conversion into chlorides as above. A. A. Eldridge.

Separation of alkalis from silicates and the volumetric determination of potassium. P. N. Grigoriev and S. S. Korol (J. Chem. Ind., Moscow, 1931, **8**, 68—70).—The following modifications of Drushel's method for the determination of potassium (A., 1909, ii, 94) have been introduced. Potassium is precipitated by sodium cobaltinitrite in the absence of sodium chloride. The reaction mixture is evaporated almost to dryness after the addition of the reagent, and it is filtered immediately after subsequent dilution with water. In this way the time necessary for the determination of potassium is reduced to 2·5—3 hrs. R. Truszkowski.

Simple test for silver in minerals. F. FEIGL and H. LEITMEIER (Tsch. Min. Petr. Mitt., 1931, **41**, 188—196).—A solution of *p*-dimethylaminobenzylidenerhodanine in acetone or alcohol gives with traces of silver a reddish-violet precipitate (A., 1928, 1108).
L. J. SPENCER.

Separation of calcium and magnesium by molybdate method. R. C. WILEY (Ind. Eng. Chem. [Anal.], 1931, **3**, 127—129).—Calcium may be determined accurately by precipitation as the molybdate in neutral or feebly alkaline solution, avoiding the use of excess of ammonium molybdate. The presence of residual ammonium molybdate in the washings from the calcium molybdate does not prevent the precipitation of magnesium as magnesium ammonium phosphate and the presence of ammonium salts does not interfere with the determination of calcium as molybdate. The calcium molybdate precipitate is dense and settles quickly and the results obtained in one precipitation are as exact as those obtained with two precipitations of calcium by the oxalate method. The procedure is time-saving and is specially suited to the analysis of limestones and dolomites.
E. S. HEDGES.

Semi-micro-determination of magnesium. M. JAVILLIER and D. DJELATIDES (Ann. Falsif., 1931, **24**, 133—138).—The magnesium is obtained as the ammonium phosphate, and the phosphoric acid in the precipitate is determined by Copaux's method (A., 1921, ii, 707); 0·5—2·5 mg. of magnesium may be determined with an accuracy of about 2%.
E. B. HUGHES.

Volumetric determination of magnesia and alumina in minerals and refractory bricks. H. ECKSTEIN.—See B., 1931, 440.

Detection of cadmium. J. S. PIERCE and W. T. FORSEE (Ind. Eng. Chem. [Anal.], 1931, **3**, 188—189).—Nickel powder is recommended for removing interfering cations in the test for cadmium. The finely-divided powder removes cupric ion from neutral or slightly acid solution and also removes all other cations which are precipitated together with cadmium by hydrogen sulphide in dilute acid solution. The presence of excess of nickel in the solution does not interfere with the test for cadmium with hydrogen sulphide. Lead is not readily removed by nickel powder and is best removed by adding a sulphate solution.
E. S. HEDGES.

Colorimetric determination of minute amounts of cadmium. L. T. FAIRHALL and L. PRODAN (J. Amer. Chem. Soc., 1931, **53**, 1321—1323; cf. Hessel, A., 1926, 1274).—Details of the extraction of cadmium from organic material by heating with nitric and sulphuric acids and the subsequent separations are given. By observing the colloidal cadmium sulphide in the light of the quartz mercury arc, the yellow colour is greatly intensified; 0·02 mg. of cadmium in 50 c.c. of solution can be detected and 0·4—1·0 mg. in 100 g. of original material can be determined to within 4%. Lead must be absent.
J. G. A. GRIFFITHS.

Determination of lead. E. BENESCH and E. ERDHEIM (Przemysł Chem., 1931, **15**, 153—155).—The solution is neutralised to methyl-orange, 100 c.c. of 0·4*N*-sodium carbonate are added, the solution is boiled, cooled, and water is added to 500 c.c. A portion of the filtrate is titrated with 0·5*N*-sulphuric acid, and the lead content is calculated from the volume of carbonate solution used for precipitation of the lead.
R. TRUSZKOWSKI.

Determination of lead as chromate in presence of perchloric acid. D. J. BROWN, J. A. MOSS, and J. B. WILLIAMS (Ind. Eng. Chem. [Anal.], 1931, **3**, 134—135).—Lead is precipitated more nearly quantitatively and more rapidly as chromate from dilute solutions of perchloric acid than by any of the methods in common use. This procedure provides a useful means of gravimetric determination. Lead may also be determined volumetrically by precipitating with a standard solution of potassium dichromate and determining the excess by adding potassium iodide and titrating with sodium thiosulphate.
E. S. HEDGES.

Relationship between sensitivity and molecular size of organic reagents. V. V. TAMCHYNA (Mikrochem., 1931, **9**, 229—241).—Comparison of the sensitivity of various xanthates when employed for the detection of copper and of molybdic acid indicates that the sensitivity of the reagent increases with increase of its mol. wt., probably as a result of the decrease of solubility of the complex formed. The same effect is observed with substituted derivatives of rhodanine when used for the detection of silver; the introduction of a benzene ring into the molecule causes a particularly large increase of sensitivity and a deepening of the coloration produced.
H. F. GILLBE.

Sensitive microchemical reaction of copper salts and heavy metals. I. M. KORENMAN (Pharm. Zentr., 1931, **72**, 225—226).—A mixture of saturated aqueous picric acid (2 vols.) with 10% ammonia yields with solutions of copper salts a characteristic crystalline precipitate, the limit of sensitivity being $0·05\times10^{-6}$ g. Cu. In slightly more concentrated solutions silver (limit 20), cobalt (0·3), nickel (0·1), cadmium (1), mercuric (0·15), and auric ($0·2\times10^{-6}$ g.) ions give characteristic crystals and lead gives an amorphous product.
H. E. F. NOTTON.

Micro-determination of copper ion. C. ZBINDEN (Bull. Soc. Chim. biol., 1931, **13**, 35—40).—The copper is deposited on a platinum cathode, the current is then reversed, and a suitable potential applied to effect redissolution. The current is kept constant by adjusting the potential until all the copper is dissolved. This point is marked by a sharp fall in the current. The quantity of copper redissolved, *i.e.*, the quantity originally present in solution, is then calculated from the formula $x=0·0003294IT$. mg., where I is the current in milliamp. and T the time in seconds. The error is about 3%.
W. O. KERMACK.

Electro-analytical separations in ammoniacal fluoride solutions. I. Separation of copper from arsenic and antimony. N. H. FURMAN (Ind. Eng. Chem. [Anal.], 1931, **3**, 217—218).—The material is dissolved in a mixture of hydrofluoric and nitric acids, with partial conversion of tervalent arsenic and antimony into the quinquevalent state.

The oxidation is completed by adding a moderate excess of potassium persulphate, boiling for 2 or 3 min., and immediately neutralising with ammonia. The solution is cooled, more ammonia is added, and pure copper is deposited cathodically on electrolysis.

E. S. HEDGES.

Quantitative X-ray analysis. Copper–silver and copper–zinc alloys. H. TERREY and E. G. V. BARRETT (J. Physical Chem., 1931, **35**, 1156—1167).—The relative intensities of the *K* lines in the *X*-ray emission spectra of copper–silver alloys have been determined by measurement of the ionising powers and by a method involving the penetration of an aluminium wedge. The relationship $I_{Ag}/I_{Cu}=MC_{Ag}/(C_{Ag}+C_{Cu})$, where I and C represent intensity and atomic concentration, respectively, holds for copper–silver alloys, whilst for those of copper and zinc the relationship between I and C is linear. The silver radiation is diminished and that of copper increased by partial absorption of the former in the copper.

L. S. THEOBALD.

Electrolytic determination of copper in presence of platinic ion. T. L. KELLY and J. J. MOLLOY (J. Amer. Chem. Soc., 1931, **53**, 1337—1341).—Platinum is deposited with the copper and is not removed from the cathode by 6*M*-nitric acid. The platinum deposited is independent of the weight of copper (0·06—0·3 g.).

The sodium diethyl dithiocarbamate test for copper (Callan and Henderson, A., 1930, 53) is not affected by the presence of bismuth, aluminium, manganese, or magnesium if the ammoniacal solution is boiled and filtered before adding the reagent. Cadmium gives a white turbidity, 1 mg. of nickel in 100 c.c. affords a light green precipitate, arsenate does not interfere, but arsenite affords a white turbidity unless the solution is strongly ammoniacal.

J. G. A. GRIFFITHS.

Determination of lanthanum by precipitation as oxalate or hydroxide and higher oxide formation of lanthanum. I. M. KOLTHOFF and R. ELMQUIST (J. Amer. Chem. Soc., 1931, 1225—1232).—The volumetric determination by means of the oxalate affords an accuracy of 0·1% when 50 c.c. of *N*-oxalic acid are added to 10 c.c. of 0·3*N*-lanthanum chloride and adsorbed oxalic acid is removed from the precipitate by prolonged washing. In the gravimetric determination, quantitative conversion of the oxalate into oxide does not occur below 800° (cf. Backer and Klaassens, A., 1930, 1148). Ignition at 800—850° affords results 0·15% too high. By adding lanthanum solution slowly to a large excess of sodium or ammonium hydroxide, precipitation of basic chloride with the hydrous oxide is avoided. The hydrous oxide, after being washed with 50% aqueous alcohol, is determined to within 0·15—0·1% by dissolution in excess of acid and titrating back. Ignition of the hydrous oxide at 800° affords values less than 0·3% too high. Increases in weight corresponding with the formation of La_2O_5 and La_2O_7 occur when lanthanum oxide is heated in air for many hours at a white heat in an electric muffle (cf. Pagel and Brinton, A., 1929, 280).

J. G. A. GRIFFITHS.

Precipitation of manganese salts by carbonates from the point of view of analysis. A. JÍLEK and J. LUKAS (Coll. Czech. Chem. Comm., 1931, **3**, 187—204).—Manganese is precipitated quantitatively by solutions of sodium and potassium carbonates; traces of manganese pass into the filtrate as an unstable double salt which is decomposed on heating the solution. Ammonium carbonate does not precipitate more than about 92% of the manganese present unless ammonium salts are present. The nature of the salt is of importance: with the chloride, at a concentration of about *N*, precipitation is practically complete, but at higher or lower concentrations, or with ammonium sulphate or nitrate, the results are less satisfactory. Guanidine carbonate causes quantitative precipitation if ammonium salts are absent, whilst with lithium and thallium carbonates results are high as a result of retention of lithium or thallium salts by the precipitate. Rubidium and cæsium carbonates precipitate manganese quantitatively.

H. F. GILLBE.

Determination of manganese in potable waters. E. BARTOW and H. THOMPSON.—See B., 1931, 516.

Rapid determination of iron. A. M. MALKOV (J. Chem. Ind., Moscow, 1931, **8**, 70—71).—40 C.c. of Fehling's solutions are boiled with 20 c.c. of 1% dextrose solution, and the precipitate of cuprous oxide is dissolved in a solution of the iron-containing substance under analysis in concentrated sulphuric acid. The ferrous sulphate content of the solution is then determined by titration with standard permanganate.

R. TRUSZKOWSKI.

Analysis of gasoline for iron carbonyl by means of a small quartz-prism spectrograph. G. L. CLARK, V. R. HARDY, and H. B. WILLMAN.—See B., 1931, 469.

Iodometric determination of vanadium in special steels and in ferrovanadium. W. WERZ.—See B., 1931, 443.

Determination of small quantities of bismuth in organic substances without decomposing them. N. A. VALIASCHKO and P. K. VIRUP (Ukrain. Chem. J., 1930, **5**, [Sci.], 275—293).—The organ is comminuted, and 30 g. of the mince are suspended in water. 5 C.c. of hydrochloric acid and 5 c.c. of 1% cupric chloride are added, and the mixture is boiled for 1 hr. with a copper plate (4 cm.² per mg. Bi). The plate is then washed and dissolved in nitric acid, and the solution is neutralised by addition of ammonia, 12—13 drops of dilute hydrochloric acid are added, and it is heated at 100° for 1 hr. The precipitate of bismuth oxychloride is washed and dissolved in sulphuric acid, and 10 drops of 5% sulphurous acid and 3 c.c. of 10% iodine in potassium iodide solution are added. The colour obtained is compared with that of a standard, and the bismuth content is hence calculated. This method serves for the detection of 0·5 mg. of bismuth per 100 g. of organ, and for the determination, with an error of ±1%, of 2—10 mg. per 100 g. of organ.

R. TRUSZKOWSKI.

Fluorescence microscope for strong illumination. M. HAITINGER (Mikrochem., 1931, **9**, 220—222; cf. A., 1930, 446).—Water-cooling of the electrodes renders the iron arc sufficiently steady for use in microscopy. A brilliant and detailed image is

obtained, and when used in conjunction with a black glass filter and a suitable reflector and dark-ground condenser, the iron arc is more satisfactory for the observation of fluorescence than is the mercury-vapour lamp. H. F. GILLBE.

Microscopic analysis of metalliferous minerals. M. BEREK (Z. Krist., 1931, **77**, 1—22; cf. (*ibid.*, 1931, **76**, 396—439).—A detailed description is given of the slit microphotometer for the measurement of the intensity of reflected light, and determination therefrom of the minerals present. C. A. SILBERRAD.

Method for registering and making corpuscular rays visible. E. REGENER (Festschr. Tech. Hochsch. Stuttgart, 1929, 331—338; Chem. Zentr., 1930, ii, 2410).—Descriptive. L. S. THEOBALD.

Monochromatic sodium light in polarimetry and refractometry. V. STANEK and K. SANDERA (Z. Zuckerind. Czechoslov., 1931, **55**, 307—312).—A powerful electric sodium lamp (Osram, Berlin) is simple and convenient, and is capable of lasting at least 3000 hrs. Its intensity is about 12 times that of the ordinary sodium flame lamp. The light is suitable for most technical work, being quite free from white light, and is superior to ordinary light passed through a dichromate filter. J. P. OGILVIE.

Colorimeter. K. MAYER (Biochem. Z., 1931, **231**, 314—316).—An apparatus for titration and colorimetric comparison of strongly coloured and other liquids is described. Light filters are used instead of solutions of standard colours. W. MCCARTNEY.

Nephelometric and Tyndallometric methods. E. HERZFELD (Biochem. Z., 1931, **232**, 78—81).—An adaptation of the use of the colorimeter for nephelometric and Tyndallometric measurements is described. P. W. CLUTTERBUCK.

Determination of hydrogen-ion concentration with photo-electric colorimeter. R. H. MULLER and H. M. PARTRIDGE (Ind. Eng. Chem. [Anal.], 1931, **3**, 169—171).—In a simple photo-electric colorimeter the feeble photo-electric current is amplified by a three-electrode vacuum tube and p_H values are read in terms of plate current. Greater accuracy is obtained than by the visual method of determination. E. S. HEDGES.

Thermometer for precision calorimetry. T. C. SUTTON (J. Sci. Instr., 1931, **8**, 98—103).—By filling mercury thermometers with nitrogen at 60 mm. the advantage of gas filling as regards stiction is retained and the effect on the readings of changes in the temperature of the upper part of the stem is minimised. The thermometer can be read from a distance without parallax by means of two lenses of 4 cm. focal length, 1·6 cm. apart, each etched with a pair of sights. This lens system is placed against the stem of the thermometer, and the parallax error can be reduced to 0·005 cm. of scale. This type of thermometer has a high precision for measuring rises of temperature, the necessary precautions being that the bulb should never be touched, that it should be chilled in ice-water before use, and that rising temperatures should always be read. C. W. GIBBY.

Simple electric immersion heater for constant-temperature baths. W. LEACH (Ann. Bot., 1931, **45**, 373—376).

Self-regulating induction furnace with ferromagnetic muffle. R. PERRIN and V. SORREL (Compt. rend., 1931, **192**, 1026—1029).—The furnace consists essentially of a muffle of ferromagnetic material showing rapid variation in induction at the transformation point (*e.g.*, ferrocobalt containing 30% Co). This is surrounded by a solenoid (of, *e.g.*, 4 layers of copper ribbon), and the whole by a conducting envelope of some material (*e.g.*, nickel) which is magnetic at low temperatures, but ceases to be so at the temperature (15—1100°) of the furnace. Industrial alternating current (*e.g.*, of 40—120 amp.) is passed through the solenoid. C. A. SILBERRAD.

Laboratory furnace for chemical reactions. E. BERL and K. WINNACKER (Chem. Fabr., 1931, **4**, 194).—The furnace consists of a copper cylinder coated with kieselguhr, around which is wound the electrical heating element, and the whole is lagged and insulated with an outer coating of kieselguhr. The cylinder is bored to a suitable size to carry the reaction tube. Owing to the high conductivity of the metal the temperature (1000°) of the interior is constant to within ±2° for 95% of its length. For higher temperatures platinum foil may be used, but the variation of temperature is then greater. H. F. GILLBE.

Apparatus for potentiometric analysis. P. DICKENS (Chem. Fabr., 1931, **4**, 145—147).—A simplified apparatus is illustrated in which the burette and motor-driven stirring device are both mounted on a stout retort stand the base of which carries a switch and regulating resistance for the motor. Two modified types of calomel electrodes are also described; the original must be consulted for details. A. R. POWELL.

Dipping electrodes for electrodialysis. J. LINDNER and N. FIGALA (Kolloid-Z., 1931, **55**, 3—6).—A simple apparatus for electrodialysis is described. The anode consists of a platinum wire and the cathode of silver wire; each electrode is separate and is enclosed by a sac of parchment paper. The electrodes can be dipped into the solution to be electrodialysed. E. S. HEDGES.

Measurement of the electricity liberated during the downgrade reactions of organic compounds. M. C. POTTER (Nature, 1931, **127**, 554—555).—An arrangement is described whereby the electricity liberated during the fermentation of sucrose by yeast and in the decay of organic matter in soil is determined by the weight of a copper deposit. L. S. THEOBALD.

Hydrogen electrode cell for determination of p_H. W. B. BOLLEN (Ind. Eng. Chem. [Anal.], 1931, **3**, 203—209).—The cell described and recommended for accurate and rapid p_H determinations has the following novel features: (1) a pyrex–alundum porous-tip calomel electrode, (2) a salt bridge giving sharp, reproducible liquid junctions, and (3) a stirrer which centrifugally circulates through the sample a small constant volume of hydrogen under constant pressure. This form of stirrer is specially suitable

for solutions containing dissolved carbon dioxide or other gases participating in hydrogen-ion equilibria and is also useful with foaming liquids. Saturation of the solution with hydrogen is effected in minimum time and the hydrogen-ion equilibrium is rapidly attained. E. S. HEDGES.

Cells sensitive to infra-red rays. F. MICHELSSEN (Z. tech. Physik, 1930, **11**, 511—515; Chem. Zentr., 1931, i, 1141).—The sensitivity of a selenium cell is extended from 0·75 to 1·2 by the use of tellurium, a thin film of the two elements being obtained by cathodic sputtering. A cell sensitive in the same region as Case's "thallofide" cell, but having a dark resistance of only $5—10\times10^6$ ohms, may be prepared by volatilisation of Tl_2S in oxygen at about 0·8 mm. A. A. ELDRIDGE.

Efficacies of some ordinary reflux condensers. F. MACH and R. HERRMANN (Chem. Fabr., 1931, 157—159, 170—173).—The efficacies of a number of types of laboratory reflux condenser have been compared by measuring the loss of ether vapour under strictly comparable conditions. The loss is greatest with the ordinary Liebig single-tube condenser, and is least with the multiple-tube Liebig; the narrow-jacket Liebig and the type wherein a number of spheres are formed on the inner tube are moderately satisfactory. In the worm type there is considerable loss, whilst the type wherein several jackets are placed one above the other and connected in series is not particularly efficacious. The form of the condenser, irrespective of the available cooling surface, is thus of great importance. Counter-current operation does not always result in a diminution of losses, and in the case of the more efficient types the loss is in general increased. H. F. GILLBE.

Automatic sampling apparatus. H. GEHLE (Chem. Fabr., 1931, 159—160).—A detailed description is given of an apparatus for the automatic intermittent sampling of liquids such as effluents, treated water, and distillate fractions. The flow is periodically interrupted and diverted into a funnel which feeds a segmented disc, whereby the liquid is run into a receiving vessel; when a sample of sufficient size has been collected the flow returns to its normal channel. When the next sample is required the funnel rotates and discharges into the next segment of the disc, which supplies a second receiver. The apparatus described permits of the collection of 24 samples, and is entirely self-contained and totally enclosed; the small amount of power required is supplied by a spring-operated motor. H. F. GILLBE.

Apparatus for extracting liquids with denser solvents. P. H. PRAUSNITZ (Chem. Fabr., 1931, 193—194).—By forcing a stream of air through a glass filter plate placed at the bottom of the extraction tube thorough mixing of the two liquids is assured. Extraction is very rapid compared with that obtained with other methods. H. F. GILLBE.

Fractional macro- and micro-sublimation at ordinary and reduced pressure. G. ILLARI (Annali Chim. Appl., 1931, **21**, 127—136).—The initial temperature of sublimation may be regarded as a characteristic physical constant, provided that certain conditions are observed in its measurement. By means of an apparatus described, the variation of this temperature with the pressure has been investigated for various compounds. An apparatus is also described for the qualitative and quantitative fractional macro- or micro-sublimation of the sublimable components of a mixture. T. H. POPE.

Device for producing slow constant flow of liquid. R. J. DAVIES (J. Sci. Instr., 1931, **8**, 110—111).—Mercury flows from a reservoir of adjustable height through a number of parallel horizontal glass capillary tubes connected by rubber pressure tubing, and falls into a constant-level trap of the usual type, also of adjustable height. Thence it passes by way of another similar set of capillary tubes into a vessel containing the liquid to be used. The latter is forced out and passes through a constant-level trap. C. W. GIBBY.

Fractional distillation of small amounts of substance in a high vacuum. S. KOBER (Biochem. Z., 1931, **232**, 274—277).—An apparatus which consists of a glass tube in which a succession of bulbs is blown is described. The tube is heated in a special form of combined air- and oil-bath. W. MCCARTNEY.

Flow divider for fractionation under diminished pressure. A. M. SCHWARTZ and M. T. BUSH (Ind. Eng. Chem. [Anal.], 1931, **3**, 138—139).—Details are given of the construction of a still head, with a mercury check valve, which allows total condensation and complete and easy control of the return of part of the condensate as reflux. The apparatus is especially useful for work under reduced pressure. E. S. HEDGES.

Precise fractional distillation analysis. New method of gas analysis. W. J. PODBIELNIAK (Ind. Eng. Chem. [Anal.], 1931, **3**, 177—188).—A survey is given of low-temperature methods of fractionation with a discussion of accuracy attainable, checking methods, sampling, and interpretation of results. Precision fractionating columns are described. These may be used to separate highly complex mixtures of saturated and unsaturated gaseous hydrocarbons into their components with high efficiency in a short time. Fractional distillation curves are given to show the behaviour of the apparatus. E. S. HEDGES.

Differential ebullioscope with still-head and its applications. W. SWIENTOSLAWSKI (Bull. Acad. Polonaise, 1930, *A*, 504—517).—A form of ebullioscope fitted with a still-head and suitable for studying the purity of pure liquids and of azeotropic and eutectic mixtures is described. A modification suitable for use with small quantities of liquid and a scheme to ensure optimum conditions in the filling of the apparatus have also been devised. The difference between the temperatures of ebullition and condensation is measured. A pure liquid should show no difference. The results obtained with several so-called pure liquids are quoted. The impurity, when known, can be determined. J. W. SMITH.

Pipette for removal of supernatant fluids. N. GAVRILESCO (Bull. Soc. Chim. biol., 1931, **13**, 110—112).—By the device described the supernatant liquid in a centrifuge tube can be readily removed from the centrifuged precipitate without disturbing the latter. W. O. KERMACK.

Comparative efficiencies of gas-washing bottles. F. H. RHODES and D. R. RAKESTRAW (Ind. Eng. Chem. [Anal.], 1931, **3**, 143—144).—The comparative efficiencies of different types of gas-washing bottles in common use have been measured by passing a mixture of air and carbon dioxide of known composition through a sodium hydroxide solution contained in the bottle and determining the percentage of carbon dioxide in the issuing gas at different rates of flow. The Friedrichs spiral wash-bottle was the most efficient of those examined; the poorest results were obtained with bottles of the Muencke and Habermann types. E. S. HEDGES.

Glass temperature and float regulators. D. F. OTHMER (Ind. Eng. Chem. [Anal.], 1931, **3**, 139—143).—A description of several types of temperature and float controllers at present in use. E. S. HEDGES.

Simple pipette for micro-filtration. R. EDGEWORTH-JOHNSTONE (J.S.C.I., 1931, **51**, 182T).—A simple form of pipette, constructed from capillary tubing, facilitates the filtration of single drops of liquid on a microscope slide.

Applications of the centrifugal filtration tube. E. L. SKAU and L. F. ROWE (Ind. Eng. Chem. [Anal.], 1931, **3**. 147—148).—The centrifugal filtration tube (A., 1929, 903) may be used for the approximate determination of solubilities at different temperatures. The binary f.-p. diagram of the system benzene–naphthalene has been constructed by this method. Measurements made with the systems benzene–naphthalene, water–sodium nitrate, and water–potassium iodide show that the eutectic composition may be obtained by a single determination by means of this device. The centrifugal filtration tube should be applicable in any plant-control work in which it is desired to carry any reaction to a stage where a certain consistency or f. p. is reached. Instead of roughly determining the f. p., a determination of the amount of solid separated at some arbitrary temperature can readily be made with suitable accuracy.

E. S. HEDGES.

Modified slow combustion pipette. K. A. KOBE (Ind. Eng. Chem. [Anal.], 1931, **3**, 159).—A pipette for use in the determination of combustible gases by the slow combustion method is described; the possibility of explosion is eliminated.

E. S. HEDGES.

Simple extraction apparatus. A. G. MILLIGAN (J.S.C.I., 1931, **50**, 144T).—The material to be extracted is contained in a siphon tube suspended in the wide mouth of an extraction flask. A short tube filled with glass beads connects the flask with a condenser. The solvent liquid, returning from the condenser through the beads, is re-heated to its b. p. by the ascending vapour before falling into the siphon tube, so that more rapid and more reproducible extraction is effected.

Burette for air-sensitive volumetric solutions. P. DICKENS (Chem. Fabr., 1931, 185).—In the apparatus described the solution is forced up into the burette by the pressure of hydrogen or nitrogen from a cylinder; a current of gas may be passed continuously through the apparatus during a titration, and the reservoir may be employed for storage of the solution in an inert atmosphere for an indefinite period. H. F. GILLBE.

Comparative methods for determining viscosities of liquids. A. TER-POGOSYAN (Azerbaid. Neft. Choz., 1930, No. 11, 120—127).—Engler's viscosimeter is satisfactory provided Vogel's formula is used. For kinematic viscosities below 2 Engler viscosimeter readings are not comparable with absolute viscosities, but Stokes' formula and the torsion balance method give satisfactory results.

CHEMICAL ABSTRACTS.

Viscosimeter with constant rate of flow. W. HEROLD and K. L. WOLF (Z. physikal. Chem., 1931, **154**, 183—186).—An apparatus of the above type and much superior in precision to Thorpe and Rodger's apparatus is described. R. CUTHILL.

Kampf viscosimeter. E. LANDT.—See B., 1931, 465.

Sealing substances in ampullæ with inert gases. A. B. WEINHAGEN (J. Amer. Chem. Soc., 1931, **53**, 1401).—The tubulure is closed with a Bunsen valve, and a hollow-pointed surgical needle is passed through one wall of the valve down the tubulure into the ampulla almost to the surface of the enclosed substance. After the inert gas has been passed in through the needle, the latter is partly withdrawn and the tubulure is sealed. J. G. A. GRIFFITHS.

Construction of Dewar flasks. T. E. PHIPPS, M. J. COPLEY, and E. J. SHAW (J. Amer. Chem. Soc., 1931, **53**, 1365—1366).—A durable 3-litre pyrex Dewar flask from which loss of liquid air by evaporation is very small is made by cutting equatorially a 5-litre pyrex flask and sealing this vessel round a 3-litre flask. The resulting hollow wall is silvered and evacuated for 36 hrs. at 400° under a high vacuum, by way of a side tube on the neck. Full details are given. J. G. A. GRIFFITHS.

Cooling apparatus. J. HALLER (Chem.-Ztg., 1931, **55**, 267—268).—A current of dry air is drawn successively through two vessels containing a volatile liquid (carbon disulphide, ether, or ethyl chloride), which is cooled by self-evaporation, the air after leaving the second vessel being utilised to cool the liquid still further in the first vessel and consequently the fresh air entering it; the substance to be cooled is placed in a tube which is inserted in the liquid in the second vessel. F. R. ENNOS.

Automatic vacuum pressure regulator. H. I. COLE (Philippine J. Sci., 1931, **44**, 411—413).—Mercury in a barometer column makes contact with a platinum wire at any desired height, and by means of an electromagnet opens a fine jet, consisting of the base of a hypodermic needle, admitting air. The pressure can be kept constant within 0·5 mm. C. W. GIBBY.

Use of steam for Kjeldahl distillation of nitrogen. J. GREEN (Ind. Eng. Chem. [Anal.],

1931, 3, 160—161).—A steam-distillation apparatus for use in the determination of nitrogen is described. The accuracy is equal to that obtained with stills heated by gas or electricity and the time required is less. The apparatus is entirely free from bumping and therefore may advantageously be used with soils.
E. S. Hedges.

Generator for production of carbon dioxide of high purity. E. J. Poth (Ind. Eng. Chem. [Anal.], 1931, 3, 202—203).—A continuous and automatic carbon dioxide generator, capable of modification for other gases, is made entirely of glass, without ground-glass connexions, and is sealed with mercury against contaminating atmospheric gases; it can be warmed and pumped free of occluded gases. The reactants recommended are 1 : 1 sulphuric acid and a saturated aqueous solution of potassium carbonate. The use of marble is inadvisable, because it is not possible completely to eliminate occluded air. E. S. Hedges.

Storage of carbon monoxide. O. H. Wagner.—See B., 1931, 438.

Laboratory autoclave. H. A. Cassar (Ind. Eng. Chem. [Anal.], 1931, 3, 197—198).—A dimensioned figure is given. E. S. Hedges.

Air separator for fine powders. P. S. Roller (Ind. Eng. Chem. [Anal.], 1931, 3, 212—216).—The apparatus described separates quantitatively a 1-kg. charge of fine powder into fractions of different particle size. Except for particles below 5 μ the particle sizes separated are very homogeneous within the limits given by Stokes' law. The rate of separation is proportional to the rate of flow of air, and at a flow of 140 litres per minute it is possible to fractionate 135 kg. per hr. The separation may be made continuous by the use of an offset separator tube.
E. S. Hedges.

Preparation of Debye–Scherrer diagrams of alloys sensitive to air. E. Zintl, A. Harder, and S. Neumayr (Z. physikal. Chem., 1931, 154, 92—96).—Apparatus suitable for the preparation of samples for X-ray examination of alloys which are hygroscopic or readily oxidised is described. R. Cuthill.

Geochemistry.

Influence of certain geophysical factors on the striking points of lightning. L. Bogoïavlenski (J. Phys. Radium, 1931, [vii], 2, 101—113).—Measurements by a variety of methods show that the normal conductivity of the atmosphere in the neighbourhood of regions at which lightning tends to strike is always unusually high. The effect is discussed in terms of ionisation resulting from the presence of traces of radioactive materials in the earth.
H. F. Gillbe.

Distribution of ozone in the atmosphere. D. Chalonge and E. Dubois (Compt. rend., 1931, 192, 808—810).—The thickness of the layer in which all the ozone in the atmosphere is assumed to be concentrated, as deduced from a comparison of the intensities of solar light of two wave-lengths (λ, λ'), should be the same as that deduced by an analogous method (cf. Cabannes, A., 1927, 1164) based on observations of the light diffused at the zenith, provided that the layer of ozone is wholly above the diffusing layer. The latter method, however, gives as the altitude of such layer a value that increases as the difference between λ and λ' increases. The distribution of ozone is therefore not in one definite layer, but appreciable quantities must exist at comparatively low altitudes.
C. A. Silberrad.

Oxygen absorption of natural waters in Nairobi with reference to anopheline mosquitoes. D. Harvey and C. B. Symes (Bull. Entom. Res., 1931, 22, 59—64).—In most cases examined waters producing anophelines show high variation in oxygen absorption values during the season, high organic contents, and high ratios of organic : inorganic constituents. A. G. Pollard.

True measure of the activity of natural waters. J. Tillmans and P. Hirsch (Z. anorg. Chem., 1931, 197, 182—188).—Polemical. Orlov's expression (A., 1930, 1130) for the activity of a water towards calcium carbonate is shown on both theoretical and experimental grounds to be invalid. H. F. Gillbe.

Karoonda (S.A.) meteorite of Nov. 25, 1930. K. Grant (Nature, 1931, 127, 631).—A preliminary report of a petrographic and chemical examination.
L. S. Theobald.

Composition of sarcolite from Monte Somma. F. Zambonini and V. Caglioti (Compt. rend., 1931, 192, 967—970).—New analyses of sarcolite (*a*) in the Naples Museum, and (*b*) recently collected, show, respectively, SiO_2 40·27, 36·05; Al_2O_3 23·81, 22·20; CaO 32·34, 35·03; K_2O 0·87, 2·98; Na_2O 2·05, 3·88; and in (*a*) [these substances were not determined in (*b*)], Fe_2O_3 0·29; BaO 0·23; SrO 0·08: MgO 0·28; Li_2O 0·008; CO_2 0·30; Cl 0·04. Total (*a*) 100·51%, (*b*) 100·14%. The formula suggested for (*a*) is $CaAl_2(SiO_4)_2,Ca_2SiO_4$, with some Ca replaced by K_2 and Na_2. X-Ray analysis and the optical properties show (*b*) also to be a true sarcolite; the difference in composition is attributed to the presence of some velardenite, $CaAl_2Si_2O_7$. These results disagree with Gossner and Mussgnug's views on the relations of sarcolite with the wernerites (cf. A., 1929, 18, 19).
C. A. Silberrad.

Two similar chlorites from the Tatra. S. Kozik (Bull. Acad. Polonaise, 1930, *A*, 536—542).—Two specimens of chlorite from the Tatra mountains show no essential differences. The analyses are given and formulæ are deduced according to the methods of Orcel and Winchell. From the circumstance that the chlorite was surrounded by unweathered granite it is concluded that the former is not a decomposition product of the latter, but is formed by hydrothermic action. This is confirmed by the existence of small particles of chlorite in the granite crust near the main chlorite nucleus. J. W. Smith.

Mineral composition of Doubrovka kaolin. T. KRASENSKAYA (Trans. Ceram. Res. Inst., Moscow, 1929, No. 21, 3—25).—The change in mineral composition of kaolin on alteration from coarse to fine fractions was determined, and mineral impurities were identified. In the finer fractions the proportion of kaolinite rises, but those of mica, felspar, and quartz diminish. CHEMICAL ABSTRACTS.

Composition of clay from Tshasov–Jar deposits. V. ISKYUL (Trans. Ceramic Inst. Res., Moscow, 1929, No. 20, 30—87).—The clay is mainly kaolinite in shredded flakes, muscovite in colourless scales, and slightly rounded quartz grains. Tourmaline, limonite, rutile, and zircon are present; strongly weathered felspar, lowigite, alunite, and biotite were also found. The alkali content is high. CHEMICAL ABSTRACTS.

Ramdohrite, a new mineral from Bolivia. F. AHLFELD (Zentr. Min. Geol., 1930, 365—367; Chem. Zentr., 1930, ii, 2362).—The new mineral appears with tetrahedrite and tin pyrites in a silver–tin vein as prismatic, lance-shaped crystals up to 2 cm. long. It is blackish-grey, with hardness 2, and *d* 4·18. It contains S 20·1, Sb 31·1, Pb 30·3, Bi 2·5, Ag 10·1, Cu 0·3, Fe 0·3, and gangue (SiO_2) 5·5%, corresponding with the formula $Ag_2S,3PbS,3Sb_2S_3$. L. S. THEOBALD.

Formula of eucolite. F. MACHATSCHKI (Zentr. Min. Geol., 1930, 360—364; Chem. Zentr., 1930, ii, 2362).—The empirical formula of eucolite is $X_5Y_2Si_6(O,OH)_{20}$, where X is Ca, Na (K), rare earths, and possibly Mn, and Y is Fe, Zr, Mg, Mn, Nb, and Ta. From the data of Gossner and Mussgnug (this vol., 289) eucolite should contain 4 mols. of the above formula per unit cell, but this formula does not correspond with a space-group D^5_{3d}. L. S. THEOBALD.

Allopalladium and clausthalite (Tilkerode, Harz) and the relation of allopalladium to potarite. A. CISSARZ (Z. Krist., 1930, **74**, 501—510; Chem. Zentr., 1930, ii, 2362).—Allopalladium and clausthalite have been examined spectroscopically and microscopically and the former has been compared with potarite. Clausthalite consists of two components of the potarite ground-mass and anisotropic potarite inclusions; both are soft and show no cleavage, and whilst the ground-mass is etched by concentrated nitric acid the inclusions are resistant to aqua regia. Both are probably compounds of mercury and palladium. Allopalladium, hexagonal with basal cleavage, is not identical with potarite or palladium. Spectroscopic examination shows it to be a palladium amalgam, poor in mercury, and to contain all the platinum metals and copper. Clausthalite contains some mercury and the platinum metals with the exception of rhodium; it also contains copper, silver, nickel, cobalt, and zinc. L. S. THEOBALD.

Minerogenetic rhythms. G. SILBERSTEIN (Tsch. Min. Petr. Mitt., 1931, **41**, 197—199).—Cylindrical ore-bodies of pneumatolytic origin in metamorphic limestone at Hopunvaara, Finland, show alternating layers of magnetite, idocrase, and fluorspar, the last two forming separate layers or being in part intergrown. This is explained by the action of the magmatic gases rising up the chimney. Magnetite is deposited by the reaction $2FeF_3+FeF_2+4H_2O \longrightarrow Fe_3O_4+8HF$. When the hydrofluoric acid reaches a certain concentration it acts on the limestone with the production of fluorspar and idocrase. This lowers the hydrofluoric acid concentration, and another ring of magnetite is then deposited. L. J. SPENCER.

Mottramite from Bolivia. E. DITTLER and H. HUEBER (Tsch. Min. Petr. Mitt., 1931, **41**, 173—179).—Small dark olive-green nodules, *d* 6·416, were found in sandstone. Analysis gave V_2O_5 21·89, As_2O_5 trace, PbO 53·76, CuO 17·72, ZnO 1·25, FeO 0·46, H_2O (+110°) 2·23, H_2O (−110°) 0·48, Cl trace, insol. 2·25%, total "100·36," agreeing with the formula $2R^{II}_3V_2O_8,R^{II}(OH)_2$. Analyses of crystals of descloizite and of massive cuprodescloizite from the Otavi district in South-West Africa also lead to the same formula. L. J. SPENCER.

Types of ore-deposits in Bulgaria. G. LADAME (Tsch. Min. Petr. Mitt., 1931, **41**, 145—172).—An account is given of a visit to the few mines in Bulgaria, and analyses of the ores (of lead, zinc, and copper) are quoted. L. J. SPENCER.

Geochemistry of granite-pegmatites. A. FERSMAN (Tsch. Min. Petr. Mitt., 1931, **41**, 200—213).—A repetition of earlier papers (this vol., 459). L. J. SPENCER.

Geochemistry of rhenium. I. NODDACK and W. NODDACK (Z. physikal. Chem., 1931, **154**, 207—244).—The chemical properties and relationships to other elements of rhenium are summarised. In its affinity towards oxygen and sulphur rhenium lies between molybdenum and osmium, but nearer the former. From chemical and X-ray analyses of 1600 minerals, of which 212 are tabulated, it is shown that rhenium is an extremely rare element. It is most abundant in certain molybdenum sulphide ores, in which the concentration is as high as 2×10^{-5} g. per g., but in the whole earth's crust the concentration is only $3·6\times10^{-9}$ g. per g. The geochemical behaviour of the element is discussed. O. J. WALKER.

Romanechite. F. ZAMBONINI and V. CAGLIOTI (Compt. rend., 1931, **192**, 750—753; cf. Lacroix, A., 1901, ii, 395; Orcel, A., 1929, 168).—A sample from Romaneche contained: MnO_2 67·69, BaO 16·03, MnO 6·14. CaO 1·55, Na_2O 1·30, As_2O_5 0·82, K_2O 0·60 SiO_2 0·34, MgO 0·33, Al_2O_3 0·25, WO_3 0·16, PbO 0·094, Fe_2O_3 0·05, CuO 0·046, ZnO 0 035, SrO 0·03, P_2O_5 0·015, TiO_2 0·01, Li_2O 0·0016, H_2O 4·68, total 100·17%. This corresponds with $H_2(MnBa)Mn_4O_{10}$ as a possible formula. Romanechite, coronadite, and hollandite are all best viewed as fundamentally MnO_2, with $3MnO_2$ partly replaced by $2BaMnO_3$, $2Mn_2O_3$, or $2Fe_2O_3$. C. A. SILBERRAD.

Morphology of azurite. H. BRASSEUR (Z. Krist., 1931, **77**, 177—238).—178 Forms occurring in varying numbers up to 27 on 693 crystals of azurite from 62 different localities are classified according to persistence, combination, and development. C. A. SILBERRAD.

Wavellite from Chernowitz (Bohemia) and the earth phosphates from its paragenesis. A. ORLOV (Z. Krist., 1931, **77**, 317—336).—The wavellite occurs in small spherulites in graphitic quartzite, accompanied by yellow earth phosphates and some

kaolinite. It is usually an intense blue and shows marked pleochroism—blue, green, and yellow; *d* 2·357; n^{α} 1·535, 1·543, $\gamma-\alpha$ 0·255; analysis: Al_2O_3 31·02, Fe_2O_3 3·18, Cr_2O_3 0·52, FeO 2·63, CaO 0·68, MgO 0·32, CuO 0·06, P_2O_5 32·72, SiO_2 0·96, F 0·60, H_2O 27·92; total (less O for F 0·25) 100·35%. Of the water 1·5% is regarded as hygroscopic, 22—23% as of crystallisation, and 6·3% as constitutional, evolved at 105°, 106—250°, and above 250°, respectively. The formula $(R^{III}OH)_3(PO_4)_2,5H_2O$, where part of the $(R^{III}OH)$ is replaced by R^{II}, is suggested. The accompanying earthy phosphates show varying optical properties; a selected light yellow sample contained Al_2O_3 36·31, Cr_2O_3 0·40, CaO 4·04, MgO 3·39, P_2O_5 21·54, SiO_2 12·81, H_2O (evolved below 105°) 1·56, (above 105°) 14·80, total 99·97%, corresponding approximately with a mixture of kaolinite and crandallite (cf. Loughlin, A., 1917, ii, 146).

C. A. SILBERRAD.

Mineralogical petrography of Pacific lavas. T. F. W. BARTH (Amer. J. Sci., 1931, [v], **21**, 377—405).—A detailed description of the rocks is given.

C. W. GIBBY.

Polyhedric concretions of magnesite and dolomite. F. RODOLICO (Atti R. Accad. Lincei, 1930, [vi], **12**, 457—460).—A chemical and microscopical examination of pea-shaped concretions of magnesite and dolomite found at Castigliocello (Livorno) and Monterufoli (Pisa) shows that the former are composed of magnesite, but it is not clear whether the latter are composed of dolomite, or of approximately equal amounts of calcite and magnesite. The dolomite hypothesis is confirmed by Feigl and Leitmeier's colorimetric test. Schrock's view of their origin is adopted (Amer. J. Sci., 1930, [v], **19**, 386).

F. G. TRYHORN.

Examination of clays associated with oil-bearing strata in the United States. E. McK. TAYLOR (J. Inst. Petroleum Tech., 1930, **16**, 681—683; cf. A., 1929, 168).—The p_H and replaceable sodium and calcium were determined for a number of clays overlying oil sands. All the specimens were alkaline and the amount of replaceable sodium was greatly in excess of the calcium, showing that base exchange between the clays and solutions of sodium salts had taken place and that the clay had been in contact with fresh water, leading to hydrolysis and the production of alkalinity. As a result of this alkalinity the clay is deflocculated and is consequently impermeable. The shales associated with oil-bearing strata irrespective of geological age are alkaline, containing sodium clay, and provide the alkaline anaerobic conditions postulated for the formation of oil from fats and proteins by bacteria. T. A. SMITH.

Black shale of Japanese oil measures and acid clay. K. KOBAYASHI and K. YAMAMOTO (J. Soc. Chem. Ind., Japan, 1931, **34**, 99—101B).—The so-called "black shales" of the Japanese oil measures are classified (beginning with the uppermost stratum) as black, siliceous, and flinty shales, analyses of which are given. The silica content increases and the absorptive power decreases in the above order. The black shale resembles Japanese acid clay in its solubility in alkali, absorptive power, and *X*-ray diffraction pattern, and it is concluded that the black shale is the residue of a mixture of acid clay (cf. A., 1930, 316) and organic matter after natural distillation. The siliceous shale is sandy acid clay, and flinty shale is a rock derived from sandy shale.

E. LEWKOWITSCH.

Origin and formation of Japanese petroleum. K. KOBAYASHI (J. Soc. Chem. Ind., Japan, 1931, **34**, 102—103B).—The evidence is reviewed for regarding Japanese petroleum as derived from fish oils, *e.g.*, as follows: the fish having been buried and their organic structure destroyed by volcanic action under the sea, the liberated oil floating on the surface is supposed to have been absorbed by volcanic muds (acid clay) and thus to form sedimentary strata; by geo-thermal action the oils were transformed into petroleum vapour, which was condensed in porous sedimentary overlying rocks (cf. preceding abstract). E. LEWKOWITSCH.

Origin of coal. W. FUCHS and O. HORN.—See B., 1931, 465.

Electrical properties of the soil. F. W. G. WHITE (Proc. Camb. Phil. Soc., 1931, **27**, 268—276)—Theoretical.

Air content of low moor soils. R. REINCKE (Z. Pflanz. Düng., 1931, **20A**, 217—232).—The soil-water-air relationships of moor soils are examined. In characterising these soils the air space is of considerable significance. The customary measurements of pore space are of little value. The bearing of the physical properties on the cultural condition of moor soils is considered. A. G. POLLARD.

Chemical composition of Hungarian lowland soils. A. ARANY (Z. Pflanz. Düng., 1931, **20A**, 130—142).—Analyses of numerous soils are recorded. There is a general deficiency of lime, phosphate, and nitrogen. Potash deficiency is less frequent.

A. G. POLLARD.

Effect of geological formation on soil structure in N. Germany. W. WOLFF (Z. Pflanz. Düng., 1931, **20A**, 170—183).—A discussion of certain soil types in relation to their geological origin.

A. G. POLLARD.

Organic Chemistry.

Relative hydration of anhydrous molecules in organic crystal hydrates. M. A. RAKUSIN (Chem.-Ztg., 1931, **55**, 333—335).—The number of mols. of water in organic crystal hydrates is generally small and seldom exceeds 7 or 8. The anhydrous substance is less soluble in water than the hydrate. The difference between the m. p. of the anhydrous and hydrated forms is less in the case of organic substances than with inorganic compounds. No organic hydrate is known in which the amount of water of hydration

exceeds the amount of the anhydrous substance. Data are given in illustration of the stability of these hydrates. E. S. HEDGES.

Configurational relationship of hydrocarbons. I. Optically active methane derivatives containing propyl, *iso*propyl, *iso*butyl, *iso*amyl, and *iso*hexyl groups. P. A. LEVENE and R. E. MARKER (J. Biol. Chem., 1931, **91**, 405—418).—By comparing the rotations of five hydrocarbons of identical configuration containing the *n*-propyl, *iso*propyl, *iso*butyl, *iso*amyl, and *iso*hexyl groups, it is observed that the hydrocarbons containing propyl and *iso*butyl groups rotate in the same and *iso*propyl in the opposite direction. This confirms the conclusion previously reached in the case of secondary carbinols containing the same groups. The maximum optical rotations of these hydrocarbons indicate that the polarity and distance from the asymmetric carbon atom of the polar group as well as the weight of the substituent group affects the sign and value of the rotation. An additional factor may be introduced by induced alternate polarity.

d-β-Bromobutane, b. p. 91°, d_4^{25} 1·2, $[\alpha]_D^{25}$ +10·81°, prepared from *l*-methylethylcarbinol with hydrogen bromide, was converted into l-β-*methylvaleric acid*, b. p. 110°/50 mm., d_4^{26} 0·923, $[\alpha]_D^{26}$ −2·54°, by condensation with ethyl malonate. l-β-*Methylbutane*, b. p. 91°, d_4^{25} 1·251, $[\alpha$ −13·79°, was converted by the same method into d-βγ-*dimethylvaleric acid*, b. p. 92°/15 mm., d_4^{25} 0·921, $[\alpha]_D^{25}$ +1·35° (*ethyl* ester, b. p. 78°/22 mm., d_4^{25} 0·875, $[\alpha]_D^{25}$ +1·88°), reduced by sodium in alcohol to l-βγ-*dimethylpentanol*, b. p. 75°/17 mm., d_4^{23} 0·836, $[\alpha]^{23}$ −0·97°, and this was converted into d-α-*bromo*-βγ-*dimethylpentane*, b. p. 67°/25 mm., d_4^{23} 1·166, $[\alpha]_D^{23}$ +2·99°, by phosphorus tribromide, followed by reduction to l-βγ-*dimethyl*-n-*pentane*, b. p. 89—90°, d_4^{21} 0·695, $[\alpha]_D^{21}$ −9·44°. *Ethyl* l-α-*ethylbutyrate*, b. p. 68°/25 mm., d_4^{20} 0·878, $[\alpha]_D^{20}$ −4·67°, with magnesium methyl iodide gave l-βδ-*dimethylhexan*-β-*ol*, b. p. 64°/20 mm., d_4^{21} 0·827, $[\alpha]_D^{21}$ −5·74°. This was dehydrated by means of iodine, and the unsaturated hydrocarbon reduced by hydrogen under pressure in presence of platinic oxide to l-βδ-*dimethylhexane*, b. p. 110—111°, d_4^{21} 0·703, $[\alpha]_D^{21}$ −10·85°. d-β-*Methylhexoic acid*, b. p. 115°/16 mm., d_4^{22} 0·923, $[\alpha]_D^{22}$ +6·24°, prepared by condensing *d*-α-bromo-β-methylbutane with ethyl malonate, was converted successively by the same reactions into the d-*ethyl* ester, b. p. 80°/20 mm., d_4^{22} 0·888, $[\alpha]_D^{22}$ +4·81°, d-βε-*dimethylhexan*-β-*ol*, b. p. 75°/15 mm., d_4^{22} 0·830, $[\alpha]_D^{22}$ +3·69°, and d-βε-*dimethyl*-n-*heptane*, b. p. 135°, d_4^{22} 0·714, $[\alpha]_D^{22}$ +3·33°. *n*-Propyl-*n*-butylcarbinol prepared from magnesium *n*-butyl bromide and *n*-butaldehyde was converted into its hydrogen phthalate and resolved through its strychnine and brucine salts into d-n-*propyl*-n-*butylcarbinol*, b. p. 79°/16 mm., d_4^{23} +0·74° (*hydrogen phthalate*, $[\alpha]_D^{23}$ +2·28° in alcohol). All the rotations recorded except when mentioned are of the substances in the homogeneous state. B. LEVIN.

Propadiene. W. A. LOTT and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1931, **20**, 207—209).—The toxic effects observed when propene, *cyclo*propane, and propadiene are used as anæsthetics are probably due to the presence of traces of bromo-derivatives which can be removed by adsorption on activated charcoal, but not by refrigeration alone. Attempts to obtain propadiene by passing acetone over phosphoric acid on pumice at 425—475° gave mainly carbon, carbon monoxide, and hydrogen. H. E. F. NOTTON.

Nuclear syntheses in the olefine series. II. αδ-Diolefines. B. H. SHOEMAKER and C. E. BOORD (J. Amer. Chem. Soc., 1931, **53**, 1505—1512).—Ethyl αβ-dibromoalkyl ethers are allowed to interact with magnesium allyl bromide, and the resulting ethyl β-bromo-α-allylalkyl ethers heated with zinc dust in propyl or butyl alcohol (cf. A., 1930, 1269). The following appear to be new: *ethyl α-chloropropyl ether*, b. p. 34—36°/25 mm., d_4^{20} 0·954, n^{20} 1·4120; *ethyl α-chloro-*n*-butyl ether*, b. p. 49—51°/25 mm., d_4^{20} 0·938, n^{20} 1·4168; *ethyl αβ-dibromo*-n-*propyl ether*, b. p. 79—82°/20 mm., d_4^{20} 1·649, n^{20} 1·50; *ethyl αβ-dibromo*-n-*butyl ether*, b. p. 99—101°/27 mm., d_4^{20} 1·564, n^{20} 1·4968; *ethyl δ-(ε-bromo-Δ^α-pentenyl) ether*, b. p. 69—71°/21 mm., 84—86°/33 mm., d_4^{20} 1·225, n^{20} 1·4592; *ethyl δ-(ε-bromo-Δ^α-hexenyl) ether*, b. p. 72—75°/15 mm., d_4^{20} 1·162, n^{20} 1·4592; *ethyl δ-(ε-bromo-Δ^α-heptenyl) ether*, b. p. 88—92°/18 mm., d_4^{20} 1·150, n^{20} 1·4606; *Δ^{αδ}-heptadiene*, b. p. 92—92·3°/755 mm., d_4^{20} 0·7176, n^{20} 1·4202 (*tetrabromide*, liquid, d_4^{20} 2·091, n^{20} 1·5734). The b. p. of the diolefines form a series in which an increase is caused by movement of the double linking towards the centre of the chain. H. A. PIGGOTT.

Action of allyl chloride, bromide, and iodide on monosodium acetylide. R. LESPIEAU and JOURNAUD (Bull. Soc. chim., 1931, [iv], **49**, 423—426).—When allyl chloride or bromide is added to a solution of acetylene and sodium in liquid ammonia, a true acetylene *hydrocarbon*,

(?)CH:C·CH(CH:CH$_2$)·CH$_2$·CH:CH$_2$, b. p. 29—30°/16 mm., d^{20} 0·794, is obtained in 25% yield. It rapidly turns yellow and slowly resinifies. With allyl chloride a *hydrocarbon* (?)CH:C·CH:CHMe, b. p. 62°/760 mm., d^{20} 0·759, n^{20} 1·438 (*silver* derivative), was also formed. With allyl iodide the yields of the hydrocarbon, C_8H_{10}, are lower and a small amount of an unstable *hydrocarbon*,

(?)CH:C·C(CH:CH$_2$)(CH$_2$·CH:CH$_2$)$_2$, b. p. 49°/20 mm., d^{20} 0·819, n^{20} 1·472 (*silver* salt), is formed. With allyl chloride about 25% of the reaction product distils above 120°/16 mm., three fourths of which distils at 120—150°/16 mm. and slowly polymerises at 120°. It yields no silver derivative. R. BRIGHTMAN.

Identification of alcohols. *p*-Nitrophenylurethanes. R. L. SHRINER and R. F. B. COX (J. Amer. Chem. Soc., 1931, **53**, 1601—1605).—*p*-Nitrophenylcarbamyl chloride, obtained from carbonyl chloride and *p*-nitroaniline (cf. Vittenet, A., 1899, i, 756), interacts readily with anhydrous alcohols in dry benzene to form crystalline *p*-nitrophenylurethanes, which serve to identify the alcohol. The following are described: *methyl*, m. p. 179·5°; *ethyl*, m. p. 129°; *propyl*, m. p. 115°; iso*propyl*, m. p. 116°; *butyl*, m. p. 95·5°; sec.-*butyl*, m. p. 75°; iso*butyl*, m. p. 80°; *amyl*, m. p. 86°; iso*amyl*, m. p. 97·5°; *hexyl*, m. p. 103°, and *heptyl*, m. p. 102°, p-*nitrophenylcarbamates*, and *glycol di*-p-*nitrophenylcarbamate*, m. p. 135·5°. H. A. PIGGOTT.

Catalysis by alumina and zinc oxide of disproportionation of alcohols, ethers, and hydroxy-esters. H. Adkins and K. Folkers (J. Amer. Chem. Soc., 1931, **53**, 1420—1424).—ββ-Dimethyl-Δ^{γ}-buten-α-ol when passed over alumina at 300° or zinc oxide at 300° and 330° gives ββ-dimethylbuten-α-al and (probably) γγ-dimethyl-Δ^{α}-butene, but in the case of zinc oxide with marked formation of hydrogen. In addition to disproportionation to aldehyde and hydrocarbon, therefore, dehydrogenation, also leading to aldehyde, is considered to occur over the latter catalyst. There is no evidence of formation of the corresponding saturated aldehyde as with allyl alcohol. The behaviour of benzyl alcohol and dibenzyl ether vapours in contact with alumina at 340° is strictly analogous, benzaldehyde and toluene being formed.

The passage of ethyl β-hydroxybutyrate over alumina at 325° and 350° leads to approximately equal amounts of dehydration to ethyl crotonate and disproportionation, with rupture of the molecule, to ethyl acetate and acetaldehyde. Ethyl crotonate is unaffected under the conditions of the experiment. Ethyl β-hydroxy-αα-dimethyl- and β-hydroxy-α-methyl-α-ethyl-butyrates, which cannot undergo dehydration, undergo the disproportionation reaction exclusively, giving ethyl *iso*butyrate and β-methylbutyrate, in yields of 36% and 61% of the theoretical, respectively, under approximately the same conditions. H. A. Piggott.

Preparation of glycerol mono- and di-chlorohydrin. A. Novelli (Anal. Farm. Bioquim., 1930, **1**, 8—19; Chem. Zentr., 1931, i, 250).—Formic, butyric, chloroacetic (1%), oxalic (1—5%), succinic or tartaric (2%) acid, or glycerol monoacetin (2%) promotes the formation of glycerol monochlorohydrin; formic (5%), acetic, propionic (1—5%), or butyric (5%) acid, or glycerol monoacetin (10%) promotes that of the dichlorohydrin.
A. A. Eldridge.

Synthesis of αβ-unsaturated ethers. W. M. Lauer and M. A. Spielman (J. Amer. Chem. Soc., 1931, **53**, 1533—1536).—β-Bromo-ethers, synthesised by the action of an appropriate Grignard reagent on αβ-dibromo-ethers (cf. Boord and collaborators, A., 1930, 450, 1269), are repeatedly distilled from powdered potassium hydroxide until free from bromine. Where new their structure was confirmed by hydrolysis to ketones, which occurs in the presence of a trace of acid: $CHR{:}CR''{\cdot}OR'+H_2O \longrightarrow CH_2R{\cdot}CO{\cdot}R''+R'{\cdot}OH$. The following are described: *α-phenyl-β-bromoethyl ethyl ether*, b. p. 129—133°/18 mm., n_D^{25} 1·5317; *γ-bromo -methoxyhexane*, b. p. 74—78°/20 mm., n_D^{25} 1·4495; *β-ethoxy-Δ^{α}-butene*, b. p. 85—87°, $n_D^{24\cdot5}$ 1·4011; α-ethoxystyrene (Tiffeneau, A., 1908, i, 19); α-methoxy-β-methylstyrene, b. p. 96—98°, n_D^{25} 1·5271 (Spath and Göhring, A., 1921, i, 45), and *γ-methoxy-Δ^{γ}-hexene*, b. p. 114—115°, 1·4130.
H. A. Piggott.

Ether-like compounds. IV. Synthesis and synthetic application of β-halogeno-ethers. M. H. Palomaa and A. Kenetti (Ber., 1931, **64**, [*B*], 797—801; cf. this vol., 197).—Alkyl β-halogenoethyl ethers are prepared by the action of phosphorus trihalide on β-alkoxyethyl alcohols in presence of pyridine; *β-chloroethyl* n-*butyl ether*, b. p. 154·5°/750 mm., d_4^{20} 0·9520, and *β-bromoethyl* n-*butyl ether*, b. p. 54—55°/7 mm., d_4^{20} 1·2292, are described. The application of the ethers in the malonic ester synthesis, the initial change being expedited by addition of sodium iodide, leads to the isolation of the following: *ethyl β-methoxyethylmalonate*, b. p. 110—111°/6 mm., d_4^{20} 1·0397; γ-methoxy-*n*-butyric acid, b. p. 105—105·5°/7 mm., d_4^{20} 1·0596, n_D^{20} 1·42509; *ethyl β-ethoxyethylmalonate*, b. p. 118—119°/6 mm., d_4^{20} 1·0199, and γ-ethoxy-*n*-butyric acid, b. p. 116·5—117°/8 mm., d_4^{20} 1·0194, n_D^{20} 1·42531; *ethyl β-*n*-propoxyethylmalonate*, b. p. 128·5—129·5°/7 mm., d_4^{20} 1·0041, and *γ-*n*-propoxy-*n*-butyric acid*, b. p. 106—107°/3 mm., d_4^{20} 0·9914, n_D^{20} 1·42722; *ethyl β-*n*-butoxyethylmalonate*, b. p. 128·5—129°/4 mm., d_4^{20} 0·9987, and *γ-*n*-butoxy-*n*-butyric acid*, b. p. 122·5—123°/4 mm., d_4^{20} 0·9741, n_D^{20} 1·43034. H. Wren.

Preparation of lactolides of aliphatic hydroxy-aldehydes and -ketones. M. Bergmann and A. Miekeley (Ber., 1931, **64**, [*B*], 802—804).—Bromoacetone is converted by cold, methyl-alcoholic potassium methoxide into *ββ-dimethoxy-*n*-propyl alcohol*, b. p. 64—65°/12 mm., n_D^{20} 1·4216, transformed when preserved or heated into acetomethyl-lactolide,

$OMe{\cdot}CMe\!<\!\begin{matrix}CH_2{\cdot}O\\O{\cdot}CH_2\end{matrix}\!>\!CMe{\cdot}OMe$, m. p. 128° (corr.).

Glycollaldehyde dimethylacetal passes when boiled into the corresponding methyl-lactolide, m. p. 72°.
H. Wren.

Reactions between organic and mineral compounds. I. Natural sulphides and certain acyclic compounds. R. de Fazi and A. Hemmeler (Atti R. Accad. Lincei, 1931, [vi], **12**, 583—586).—Pyrites gives (1) ferrous and ferric chlorides, ferrous sulphide, sulphur, carbon, and thiocarbonyl chloride when treated with carbon tetrachloride at 320—400° or 450°; (2) ethyl mercaptan and ethyl sulphide, respectively, with alcohol and ether at 450—500°; (3) thioacetic acid, methyl mercaptan, methyl sulphide, carbon dioxide, hydrogen sulphide, and sulphur with acetic acid at 480—500°; and (4) hydrogen sulphide, carbon and sulphur dioxides, and thioacetic anhydride with acetic anhydride at 450—480°. Stibine yields carbon disulphide and antimony trichloride with carbon tetrachloride at 300—325°, and thioacetic anhydride and antimony trichloride with acetyl chloride at 300—350°. T. H. Pope.

Reactions of [aliphatic] carboxylic acids. L. Ekkert (Pharm. Zentr., 1931, **72**, 228—229).—When the acid (0·01 g.) in ethyl alcohol (1 c.c.) with a 1% alcoholic solution (5 drops) of formaldehyde, phenylacetaldehyde, benzaldehyde, furfuraldehyde, anisaldehyde, salicylaldehyde, vanillin, cinnamaldehyde, piperonal, or sucrose is superposed on or mixed with sulphuric acid, formic, acetic, propionic, *n*- and *iso*-butyric, valeric, hexoic, and octoic acids do not give distinctive colorations, but palmitic, stearic, oleic, and ricinoleic acids give brilliant colour reactions which are described in detail. H. E. F. Notton.

Preparation of dichloroacetic acid. H. W. Doughty and C. J. Derge (J. Amer. Chem. Soc., 1931, **53**, 1594—1596; cf. A., 1925, i, 628).—By determination of the velocity coefficients of hydrolysis of trichloroacetic acid in aqueous solution at 60° and 100°,

the value $k_{t+10}/k_t=2\cdot576$ is found. The hydrolysis of trichloroacetic acid is relatively small at 60° ($k=0\cdot00009$), and yields of the order of 80% of the theoretical of dichloroacetic acid are obtained by its reduction in aqueous solution with a slight excess of copper-bronze. H. A. PIGGOTT.

Walden inversion. XV. Influence of substituting groups on optical rotation in disubstituted propionic acids containing a methyl group. P. A. LEVENE and R. E. MARKER (J. Biol. Chem., 1931, **91**, 77—103).—The effects of substituents in derivatives of disubstituted propionic acids involving transformations of the carboxyl group are almost identical, being in the following (descending) order as regards their optical rotations: $Me>CO\cdot NH_2>CO_2H>CH_2\cdot OH>CO_2Et>CH_2\cdot NH_2>COCl>CN>CH_2Br$. The configuratively related carbinols and halides rotate in the opposite direction, confirming the previous conclusion (A., 1930, 63), with the exception of the carbinol and halide derived from β-methyl-*n*-valeric acid. The explanation is that α-ethylbutyric acids and the higher acids of the same series are of opposite configuration.

β-Methyl-*n*-valeric acid was resolved through the brucine and quinine salts into the d-*acid*, b. p. 105°/30 mm., d_4^{25} 0·923, n_D^{25} 1·4152, $[\alpha]_D^{26}$ +4·01°, and the l-*acid*, $[\alpha]_D^{23}$ −4·67°. The *d*-acid was converted successively into the d-*ethyl* ester, b. p. 68°/25 mm., d_4^{25} 0·864, n_D^{25} 1·4062, $[\alpha]_D^{25}$ +3·26°; d-γ-*methyl*-n-*pentanol*, b. p. 72°/25 mm., d_4^{27} 0·822, n_D^{25} 1·4182, $[\alpha]_D^{27}$ +3·62°; d-α-*chloro*-γ-*methyl*-n-*pentane*, b. p. 73°/100 mm., d_4^{27} 0·892, n_D^{25} 1·4210, $[\alpha]_D^{27}$ +7·46°, d-β-*methyl*-n-*valeryl chloride*, b. p. 81°/100 mm., d_4^{29} 0·957, n_D^{25} 1·4245, $[\alpha]_D^{29}$ +5·43°, the d-*amide*, $[\alpha]_D^{27}$ +2·00° in 75% alcohol; d-β-*methylvaleronitrile*, b. p. 87°/100 mm., d_4^{25} 0·811, n_D^{25} 1·4070, $[\alpha]_D^{25}$ +3·72°; α-*amino*-γ-*methyl*-n-*pentane*, b. p. 67°/100 mm., d_4^{26} 0·767, n_D^{25} 1·4196, $[\alpha]_D^{26}$ −4·27°. β-Methyl-*n*-hexoic acid was resolved by means of cinchonidine, the l-*acid* having b. p. 113°/17 mm., d_4^{27} 0·911, n_D^{25} 1·4214, $[\alpha]_D^{27}$ −2·52°, which yielded successively the l-*ethyl* ester, b. p. 60°/10 mm., d_4^{27} 0·806, n_D^{30} 1·4102, $[\alpha]_D^{27}$ −0·42°; l-γ-*methyl*-n-*hexanol*, b. p. 80°/25 mm., d_4^{29} 0·8208, n_D^{30} 1·4202, $[\alpha]_D^{29}$ −1·65° (α-*naphthylurethane*, m. p. 73°); d-α-*chloro*-γ-*methyl*-n-*hexane*, b. p. 66°/25 mm., d_4^{29} 0·854, n_D^{25} 1·4282, $[\alpha]_D^{29}$ +3·68° (homogeneous); d-α-*bromo*-γ-*methyl*-n-*hexane*, b. p. 65°/20 mm., d_4^{20} 1·141, $[\alpha]_D^{21}$ +9·39°; l-γ-*methyl*-n-*hexane*, b. p. 92°, d_4^{21} 0·687, n_D^{25} 1·3854, $[\alpha]_D^{21}$ −7·75°, by decomposing the Grignard compound from the *d*-α-bromo-γ-methyl-*n*-hexane; d-β-*methyl*-n-*hexoyl chloride*, b. p. 82°/50 mm., d_4^{26} 0·954, n_D^{25} 1·4293, $[\alpha]_D^{26}$ +2·47°; l-*amide*, $[\alpha]_D^{26}$ −4·16° in 75% alcohol; d-β-*methyl*-n-*hexonitrile*, from the amide by means of phosphorus pentoxide, b. p. 95°/70 mm., d_4^{26} 0·810, n_D 1·4137, $[\alpha]_D^{26}$ +3·28°: and this by reduction with sodium in alcohol gave the l-*amine*, b. p. 67°/45 mm., d_4^{26} 0·772, n_D^{25} 1·4249, $[\alpha]_D^{26}$ −0·25°. β-Methyl-*n*-heptoic acid was resolved through the quinine salt into the l-*acid*, b. p. 131°/19 mm., d_4^{27} 0·909, n_D^{25} 1·4259, $[\alpha]_D$ −3·79°, which was converted successively into the l-*ethyl* ester, b. p. 104°/35 mm., d_4^{24} 0·862, n_D^{25} 1·4162, $[\alpha]_D$ −1·54°; l-γ-*methyl*-n-*hexanol*, b. p. 99°/25 mm., d_4^{24} 0·824, n_D^{25} 1·4295, $[\alpha]_D^{24}$ −2·75°; d-α-*bromo*-γ-*methyl*-n-*heptane*, by treatment with phosphorus tribromide, b. p. 85°/21 mm., d_4^{24} 1·106, n_D^{25} 1·4512, $[\alpha]_D^{24}$ +7·79°: d-*acid chloride*, b. p. 88°/30 mm., d_4^{24} 0·944, n_D^{25} 1·4331, $[\alpha]_D^{24}$ +1·95°; l-*amide*, $[\alpha]_D^{24}$ −6·19° in 75% alcohol; d-*nitrile*, b. p. 120°/85 mm., d_4^{25} 0·811, n_D^{25} 1·4196, $[\alpha]_D^{25}$ +4·33°; l-α-*amino*-γ-*methyl*-n-*heptane*, b. p. 87°/47 mm., d_4^{24} 0·782, n_D^{25} 1·4288, $[\alpha]_D^{24}$ −1·34°. *Methyl*-n-*octoic acid* was resolved through its quinine salt, the l-*acid* having b. p. 135°/16 mm., d_4^{23} 0·899, n_D^{25} 1·4298, $[\alpha]_D^{23}$ −4·57° (homogeneous), which was converted successively into the l-*ethyl* ester, b. p. 117°/35 mm., d_4^{23} 0·860, n_D^{25} 1·4209, $[\alpha]_D^{23}$ −2·03°; d-*acid chloride*, b. p. 95°/20 mm., d_4^{24} 0·935, n_D^{25} 1·4362, $[\alpha]_D^{24}$ +1·36°; l-*amide*, $[\alpha]_D$ −6·68° in 75% alcohol; d-*nitrile*, b. p. 135°/85 mm., d_4^{25} 0·813, n_D^{25} 1·4239, $[\alpha]_D^{25}$ +4·02°; l-α-*amino*-γ-*methyl*-n-*octane*, b. p. 87°/19 mm., d_4^{24} 0·788, n_D^{25} 1·4326, $[\alpha]_D^{24}$ −2·22°. The *l*-ethyl ester gave on reduction l-γ-*methyl*-n-*octanol*, b. p. 110°/25 mm., d_4^{24} 0·827, n_D^{25} 1·4328, $[\alpha]_D^{24}$ −3·74°, which gave on treatment with phosphorus tribromide d-*bromo*-γ-*methyl*-n-*octane*, b. p. 104°/25 mm., d_4^{24} 1·085, n_D^{25} 1·4536, $[\alpha]_D^{24}$ +6·13°. β-Methyl-*n*-nonoic acid was resolved through its quinine salt into the d-*acid*, b. p. 133°/8 mm., d_4^{26} 0·899, n_D^{25} 1·4339, $[\alpha]_D^{26}$ +0·78°, which was converted successively into the d-*ethyl* ester, b. p. 135°/36 mm., d_4^{25} 0·862, n_D^{25} 1·4232, $[\alpha]_D^{25}$ +0·38° (homogeneous); d-γ-*methyl*-n-*nonanol*, b. p. 122°/24 mm., d_4^{23} 0·837, n_D^{25} 1·4348, $[\alpha]_D^{23}$ +0·43°; l-α-*bromo*-γ-*methylnonane*, b. p. 116°/21 mm., d_4^{25} 1·063, n_D^{25} 1·4556, $[\alpha]^{25}$ −0·69°. The following were also prepared: d-α-*bromo*-γ-*methyl*-n-*pentane*, b. p. 80°/85 mm., d_4^{27} 1·171, n_D^{25} 1·4415, $[\alpha]_D^{27}$ +3·16°; d-δ-*methyl*-n-*hexanol*, b. p. 77°/20 mm., d_4^{23} 1·809, n_D^{25} 1·4233, $[\alpha]_D^{23}$ +1·94°, prepared by the action of paraformaldehyde on the Grignard reagent prepared from *d*-α-bromo-γ-methyl-*n*-pentane: d-α-*bromo*-δ-*methyl*-n-*hexane*, b. p. 78°/44 mm., d_4^{27} 1·070, $[\alpha]_D^{27}$ +2·36°; d-γ-*methyl*-n-*hexane*, b. p. 92°, d_4^{24} 0·684, n_D^{25} 1·3854, $[\alpha]_D^{24}$ −1·67°; l-δ-*methyl*-n-*octanol*, b. p. 106°/17 mm., $d_4^{27.5}$ 0·820, n_D^{25} 1·4335, $[\alpha]_D^{25}$ −0·45°: d-α-*bromo*-δ-*methyl*-n-*octane*, b. p. 95°/17 mm., $d_4^{27.5}$ 1·089, n_D^{25} 1·4540, $[\alpha]_D^{27.5}$ −3·63°; l-δ-*methyl*-n-*octane*, b. p. 141°/70 mm., d_4^{19} 0·717, $[\alpha]_D^{19}$ −1·06°; l-δ-*methyl*-n-*nonanol*, b. p. 120°/17 mm., d_4^{27} 0·826, n_D^{25} 1·4364, $[\alpha]_D^{27}$ −1·45°: d-α-*bromo*-δ-*methylnonane*, b. p. 115°/17 mm., $d_4^{27.5}$ 1·081, $[\alpha]_D^{27.5}$ +2·52°: l-γ-*methyl*-n-*octane*, b. p. 143°, d_4^{27} 0·714, n_D^{25} 1·4052, $[\alpha]_D^{27}$ −8·5°.

All rotations are in the homogeneous state unless otherwise given. B. LEVIN.

Intramolecular rearrangement during the hydrogenation of esters of mono-unsaturated fatty acids. I. II. A. STEGER and H. W. SCHEFFERS (Chem. Umschau, 1931, **38**, 45—53, 61—66).—I. Analysis of samples of olive oil hydrogenated with a nickel–kieselguhr catalyst at 80—240° indicated that solid fatty acids, chiefly unsaturated at first, are formed soon after the beginning of the hydrogenation. Linoleic acid is reduced more rapidly and more solid unsaturated acids are formed at higher temperatures, but in each case the amount of the latter became maximal when the iodine value was 50—60. Variation in the temperature of reduction of the nickel catalyst had no appreciable effect on the amount of solid unsaturated acids produced. Increasing the proportion of catalyst had little effect at 120°, but at 180° tended to yield more of the solid unsaturated acids. In the

hydrogenation of the ethyl esters of the liquid fatty acids (Twitchell) of olive oil, a palladium catalyst yielded more solid unsaturated acids than a nickel one, and was less affected by temperature variation; it was immaterial whether charcoal or kieselguhr supports were used. When hydrogenating mixtures of the ethyl esters of oleic (51, 30, and 8%) and linoleic acids with a nickel catalyst at 180°, no appreciable amounts of saturated acids were formed until the linoleic acid content had fallen to 10%. With each mixture the maximum content of solid unsaturated fatty acids (attained at iodine value 100—80) was about the same (45—50%); hence it appears that linoleic acid (ester) must yield primarily either (*a*) a solid singly unsaturated acid, which changes later into a liquid acid, or (*b*) a liquid acid which isomerises to a solid acid. In view of the earlier experiments (*b*) is considered the more probable course, although both processes may occur together. Solid unsaturated acids were also produced in the hydrogenation of the ethyl, glycol, glycerol, and erythritol esters of pure oleic acid, the amount decreasing after reaching a maximum; these acids were formed earlier in the process, and in greater amount, from the ethyl ester. In each case they had disappeared when the iodine value had fallen to 20. When the ethyl and glyceryl esters of elaidic acid were hydrogenated, liquid fatty acids were produced (42% and 27%, respectively, at the maximum, which occurred at iodine value 75—65), which persisted (in decreasing amount) practically up to the point of complete saturation. In most of the experiments the liquid fatty acids separated had iodine values below the theoretical 90, which could not be entirely accounted for by imperfect separation in the Twitchell method; some polymerisation appears to have occurred during the hydrogenation.

II. The ethyl esters of oleic and elaidic acids were hydrogenated over a nickel catalyst to iodine value 53·5 (representing the maximum content of solid unsaturated acids), and the component acids from the products were examined by ozonolysis. The C_7, C_8, C_9, and C_{10} monocarboxylic acids and the C_{10}, C_9, and C_8 dicarboxylic acids were recovered (in addition to the stearic acid produced by the hydrogenation) from both oleic and elaidic derivatives, but no undecanedicarboxylic acid corresponding with the heptoic acid could be detected. These products indicate that migration of the double linkings to the $\eta\theta$ and $\iota\kappa$ positions had occurred during hydrogenation; quantitatively, the latter position is favoured, and more of the position isomerides were produced from the oleic ester. The formation of heptoic acid may indicate a further shift of the unsaturated linking. Similar experiments on the partly hydrogenated ethyl ester of Δ^{ϵ}-oleic acid revealed the formation of Δ^{δ}- and Δ^{ζ}-octadecenoic acids. Ethyl stearate was heated with a nickel catalyst at 180—200° in nitrogen, hydrogen, or carbon dioxide, but no dehydrogenation could be observed. E. LEWKOWITSCH.

Palmitostearoazelain. A new triglyceride from cacao butter. J. BOUGAULT and G. SCHUSTER (Compt. rend., 1931, **192**, 953—954).—Oxidation of cacao butter with permanganate in acetone gives *palmitostearoazelain*, m. p. 58—59°, separated by means of its sodium salt. Partial hydrolysis of this gives a *palmitostearin*, m. p 34°. Palmitostearo-olein occurs in the original cacao butter to the extent of at least 36%. A. A. LEVI.

Hydrogenation of linolenic acid [methyl ester]. H. VAN DER VEEN (Chem. Umschau, 1931, **38**, 89—96).—Attempts to repeat Erdmann's zinc salt separation of linolenic acid (A., 1911, i, 832) were unsuccessful; methyl linolenate was prepared from the hexabromide and partly hydrogenated with a nickel–kieselguhr catalyst at 180° and the products were examined by ozonolysis (hot and cold) and elaidinisation. The thiocyanogen values were too erratic to be conclusive. It is concluded that on hydrogenation with 1 mol. of hydrogen the Δ^{λ}-linking is saturated, yielding $\Delta^{\theta\zeta}$-octadienoic acid, from which the $\Delta^{\iota\nu}$-isomeride is formed by shifting of the unsaturated linkings. On treatment with 2 mols. of hydrogen the remote double linkings of these acids are saturated, forming Δ^{ι}- and Δ^{θ}-oleic acids, the latter of which yields the Δ^{η}- (and probably Δ^{ι}-) acid by isomerisation (at this stage azelaic acid could not be found among the products of ozonolysis); considerable amounts of the elaidic forms are produced. Hydrogenation is not entirely selective, as 18% of stearic acid (Bertram method) was recovered from the second stage (iodine value 90). The formation of resinous substances, which are easily mistaken for dicarboxylic acid, is noted. The results are compared with those of Hilditch and Vidyarthi (A., 1929, 423), but ozonolysis is preferred as a method of isolating the lower component dicarboxylic acids. Bauer and Ermann's (A., 1930, 1271) use of the Twitchell separation is deprecated; also it is pointed out that, since the linolenic acid was prepared by reduction of the hexabromide, it is unjustifiable to assume that it can be quantitatively converted into the bromide and so removed from mixtures. E. LEWKOWITSCH.

Applicability of calcium carbide to syntheses with ethyl acetoacetate. K. PACKENDORFF (Ber., 1931, **64**, [*B*], 948—949).—Ethyl acetoacetate in cold benzene reacts readily with calcium carbide, and the calcium enolate is converted by acetyl chloride into ethyl diacetoacetate, b. p. 104°/15 mm., in 65% yield. Acetylacetone, ethyl oxalacetate, ethyl cyanoacetate, and malononitrile are readily attacked by calcium carbide, which does not affect fluorene, phenylacetonitrile, or ethyl malonate. H. WREN.

Preparation of ethyl dimethylacetoacetate and ββ-dimethyl-Δ^{γ}-buten-α-ol. K. FOLKERS and H. ADKINS (J. Amer. Chem. Soc., 1931, **53**, 1416—1419).—Detailed directions are given for the preparation of ethyl methyl- and dimethyl-acetoacetates, and for the reduction of ethyl αα-dimethyl-Δ^{β}-butenoate to ββ-dimethyl-Δ^{γ}-buten-α-ol, which is effected better by sodium and alcohol than by sodium alone in an inert solvent. H. A. PIGGOTT.

Electrolytic reduction of dicarboxylic acids. H. NAKATA.—See this vol., 578.

Lanthanum alkali oxalates. I. M. KOLTHOFF and R. ELMQUIST (J. Amer. Chem. Soc., 1931, **53**, 1232—1236).—Lanthanum oxalate forms no com-

pound with oxalic acid, but is in equilibrium with double salts of the formula $La_2(C_2O_4)_3,M_2C_2O_4,yH_2O$ in solutions of ammonium, potassium, and sodium oxalates at concentrations greater than about 0·012*N*, 0·01*N*, and 0·02*N*, respectively. The double salts $La_2(C_2O_4)_3,2M_2C_2O_4,zH_2O$ are formed in solutions of potassium and sodium oxalates at concentrations greater than about 0·125*N* and 0·225*N*, respectively.

J. G. A. GRIFFITHS.

Cork. III. F. ZETZSCHE and G. SONDEREGGER (Helv. Chim. Acta, 1931, **14**, 632—641).—Hydrolysis of pure cork (prepared by the action of boiling aqueous sodium sulphite on crude cork; cf. A., 1927, 541) with alcoholic sodium hydroxide affords the sparingly soluble sodium salts of the fatty acids from which sodium phellonate (α-hydroxybehenate) is separated by its insolubility in 5% aqueous sodium chloride solution. Fractional precipitation of the acids from the remaining sodium salts with alcoholic lead acetate affords a fraction containing insoluble lead salts, the acids from which are separated by extraction with benzene and carbon tetrachloride, and thus are isolated *phloionic* and *corticinic* acids. Similarly, from the acids of the soluble lead salts are separated *suberic*, *suberolic*, and *phloionolic* acids. These acids are purified by precipitation of their sodium salts with various concentrations of sodium hydroxide. The total fatty acid fraction is 28—36% of the crude cork. Contrary to Scurti and Tommasi (A., 1916, i, 789), separation of these acids by fractionation of their methyl esters in a high vacuum, or by Legg and Wheeler's copper salt method (A., 1925, i, 1025) were unsuccessful.

J. W. BAKER.

Cork. IV. Phellonic acid and eicosanedicarboxylic acid. F. ZETZSCHE and M. BAHLER (Helv. Chim. Acta, 1931, **14**, 642—645).—Phellonic acid is best purified by first heating with 35% potassium hydroxide to destroy acid colouring matter, and crystallisation of the potassium phellonate from alcohol and benzene (3 : 1) which separates 2·5—3% of an insoluble potassium salt which gives *n*-eicosane-ωω′-dicarboxylic acid [dimethyl ester, m. p. 72° (lit., m. p. 68—70°)], identical with a specimen synthesised by Fairweather's method (Proc. Roy. Soc. Edin., 1926, **45**, 283). With acetic anhydride at 100° phellonic acid affords its *acetyl* derivative, m. p. 79°.

J. W. BAKER.

Asymmetry of *anti*-tartaric acid. J. BÖESEKEN (Pharm. Weekblad, 1931, **68**, 246—248).—A reply to Scheringa (this vol., 465).

S. I. LEVY.

Esterification with thioacetic acid. F. B. STEWART and P. V. MCKINNEY (J. Amer. Chem. Soc., 1931, **53**, 1482—1490).—The esterification of methyl and ethyl alcohols with thioacetic acid at 76° gives approx. 78% of the acetate and hydrogen sulphide (i), and 22% of the thioacetate and water (ii): $CH_3\cdot CO_2R + H_2S$ (i) $\longleftarrow CH_3\cdot CO\cdot SH + R\cdot OH \longrightarrow$ (ii) $CH_3\cdot CO\cdot SR$. *iso*Propyl alcohol reacts to the extent of 97·7% according to reaction (i), whilst with triphenylcarbinol reaction (ii) alone occurs. In the case of *tert.*-butyl alcohol reaction was too slow for its direction to be determined.

H. A. PIGGOTT.

Production of thiol and sulphonic acids from dithio-acids by the action of silver sulphate. P. W. PREISLER and D. B. PREISLER (J. Biol. Chem., 1930, **89**, 631—645).—Dithiodiglycollic acid, dithiodilactic acid, cystine, and dithiodiacrylic acid give rise to reducing substances when heated with silver sulphate. For dithiodipropionic acid the reaction is shown to proceed quantitatively:

$$3[CO_2Na\cdot CH_2\cdot CH_2\cdot S\cdot]_2 + 5Ag_2SO_4 + 3H_2O = 5CO_2Ag\cdot CH_2\cdot CH_2\cdot SAg + CO_2Na\cdot CH_2\cdot CH_2\cdot SO_3H + 5NaHSO_4.$$

G. F. MARRIAN.

Effect of weak alkalis on trioses and methylglyoxal. H. A. SPOEHR and H. H. STRAIN (J. Biol. Chem., 1930, **89**, 503—525).—Glyceraldehyde and dihydroxyacetone in the presence of disodium phosphate or "neutral phosphate" at 37° slowly lose their reducing power towards Benedict's reagent and iodine. Neither methylglyoxal nor lactic acid was detected in the reaction products. The nature of the complex condensation products formed is unknown. In the presence of disodium phosphate at 37°, the reduction of Benedict's reagent by solutions of methylglyoxal increased for 24 hrs. and then became constant. The amount of methylglyoxal, determined as *m*-nitrobenzoylosazone, rapidly fell in the first 24 hrs. The product gave the iodoform reaction, and unidentified products with phenylhydrazine (m. p. 159—160°) and *p*-nitrophenylhydrazine (m. p. 140—160°). Trioses were absent.

G. F. MARRIAN.

Effect of amines on the conversion of trioses into methylglyoxal. H. H. STRAIN and H. A. SPOEHR (J. Biol. Chem., 1930, **89**, 527—534).—In the presence of dilute acetic acid and an amine, glyceraldehyde was slowly but completely converted into methylglyoxal. Quantitative conversion occurred in the presence of *m*-nitrobenzhydrazide with the formation of the insoluble methylglyoxal-*m*-nitrobenzoylosazone. The reaction did not take place in the absence of the amine. Dihydroxyacetone in the presence of acetic acid and *m*-nitrobenzhydrazide underwent the same change in the absence of an amine. The yield of methylglyoxal-*m*-nitrobenzoylosazone was not quantitative in this case and the addition of an amine had little effect. Determination of glyceraldehyde and methylgloxal in the presence of each other and the hexoses is possible.

G. F. MARRIAN.

Use of halogen acids as condensing agents for ketones. J. COLONGE (Bull. Soc. chim., 1931, [iv], **49**, 426—441).—At constant temperature (2°), the proportion of methyl ethyl ketone converted into ethylenic ketone, COEt·CH:CMeEt, is proportional to the hydrochloric acid used as condensing agent up to a ratio ketone : acid of 1·5, but increases with further increase in the amount of acid used. At a ketone : acid ratio of about 1·5, the velocity coefficient increases from 38 to 43 when the temperature is raised from 2° to 25°. The proportion of more condensed products increases slightly with a reaction time of 144 hrs. Addition of a dehydrating agent, *e.g.*, calcium chloride, does not accelerate the reaction, and a molecular ratio of ketone : acid of 1·5 at 25° and 48 hrs.' reaction give the best condensation yields. The coefficient of condensation of the methyl alkyl ketones decreases with the mol. wt. of the alkyl group to methyl *n*-amyl ketone and then remains constant. Condensation occurs only when the second radical is

primary; thus methyl *n*-butyl and *iso*butyl ketones condense, but not methyl *sec.*- or *tert.*-butyl ketones. Ketones which do not contain the group COMe are not condensed by this method. Use of hydrobromic acid in place of hydrochloric acid gives higher velocity coefficients, and condensation occurs with methyl ketones containing a secondary radical, and in the absence of the COMe group. Ketones of the pinacolin type are not condensed. Hydriodic acid gives still higher velocity coefficients for the condensation, *e.g.*, with methyl propyl ketone, but did not condense the tertiary ketones (pinacolins) which were uncondensed by hydrobromic acid.

Thus acetone saturated with hydrogen chloride (ratio 1·75) gives mesityl oxide and residue, the intermediate chloro-derivative being unstable. Methyl ethyl ketone with dry hydrogen chloride is converted into *δ-chloro-γδ-dimethylhexan-β-one*, b. p. 108—110°, d_4^{20} 0·988, n_D^{20} 1·4481, which with the theoretical amount of methyl-alcoholic sodium hydroxide yields γδ-dimethyl-Δ^{γ}-hexen-β-one, b. p. 157—159°/760 mm., d_4^{15} 0·866, n_D^{15} 1·4476 (semicarbazones, m. p. 182° and 142°; cf. Abbott and others, A., 1928, 1218), the structure of which is established by its oxidation with hypochlorous acid and scission of the phenylcarbinol, oxidation with permanganate, and by the synthesis of the corresponding saturated ketone. Alkaline condensation yields the isomeric δ-methyl-Δ^{δ}-hepten-γ-one. Methyl propyl ketone with hydrogen chloride or bromide, as well as with sodium methoxide, barium hydroxide, and magnesium butoxybromide, yields only δ-methyl-Δ^{δ}-nonen-ξ-one, b. p. 198—200°/760 mm., 76—77°/6 mm., d_4^{15} 0·867, n_D^{15} 1·4508, which yields no semicarbazone or hydrogen sulphite compound; the intermediate *o-chloro-δ-nonan-ξ-one* has b. p. 94—97°/8 mm., d_4^{20} 0·942. Methyl *n*-butyl ketone with hydrogen chloride yields *ε-methyl-Δ^{ϵ}-undecen-η-one*, b. p. 123—124°/18 mm., d_4^{17} 0·850, n_D^{17} 1·4540. *βδθ-Trimethyl-Δ^{δ}-nonen-ξ-one*, b. p. 95—96°/7 mm., d_4^{15} 0·842, n_D^{15} 1·4510, is similarly obtained. Methyl *n*-amyl ketone similarly yields a ketone, b. p. 146—149°/30 mm., d_4^{15} 0·849, n_D^{15} 1·4580; methyl nonyl ketone yields the ketone, C_9H_{19}·CMe:CH·CO·C_9H_{19}, b. p. 211—213°/11 mm., d_4^{14} 0·854, n_D^{14} 1·4637: acetophenone gives dypnone, b. p. 213—218°/17 mm., and triphenylbenzene, and methyl benzyl ketone affords *αε-diphenyl-β-methyl-Δ^{β}-penten-δ-one*, b. p. 193—196°/11 mm., d_4^{20} 1·048, n_D^{20} 1·5880. Diethyl ketone at 100° yields a small amount of condensation product, b. p. 180—185°/760 mm., and dipropyl ketone at 150° for 10 hrs. a little condensation product, b. p. 150—170°/20 mm., with hydrobromic acid; under the standard conditions, *ε-ethyl-o-propyl-Δ^{δ}-nonen-ξ-one*, b. p. 136—139°/30 mm., d_4^{20} 0·856, n_D^{20} 1·4510, is obtained. Methyl *sec.*-butyl ketone with hydrogen bromide yields *γδη-trimethyl-Δ^{δ}-nonen-ξ-one*, b. p. 218—220°, $d_4^{16·5}$ 0·856, $n_D^{16·5}$ 1·4522. Propiophenone similarly yields *αγ-diphenyl-γ-methyl-Δ^{γ}-penten-β-one*, m. p. 75°, b. p. 204—205°/6 mm. R. BRIGHTMAN.

Derivatives of methyl ethyl ketone and its condensation products. J. COLONGE (Bull. Soc. chim., 1931, [iv], 49, 441—451).—When refluxed with sodium methoxide for 2 hrs. methyl ethyl ketone is converted into γ-methyl-Δ^{γ}-hepten-ε-one, b. p. 163—164°, d_4^{15} 0·861, n_D^{15} 1·4473 [semicarbazone, m. p. 108°, and finally at 116° (cf. Abbott and others, A., 1928, 1218); semicarbazide-semicarbazone, m. p. 283° (decomp.)]; with magnesium butoxybromide or barium hydroxide it gives the corresponding ketol, d_4^{15} 0·931, n_D^{15} 1·4364 (*semicarbazone*, m. p. 124°), converted when distilled with 3—4% of oxalic acid into γ-methyl-Δ^{γ}-hepten-ε-one. The structure of the latter is established by its oxidation to methyl ethyl ketone, carbon dioxide, and propionic acid, and its hydrogenation in presence of platinum-black to γ-methylheptan-ε-one, b. p. 154—156°, d_4^{15} 0·825, n^{15} 1·4158 (semicarbazone, m. p. 101°), also obtained from *γ-methylvaleryl chloride*, b. p. 142—144°, by the action of zinc ethyl iodide. γ-Methylvaleric acid is obtained in 41% yield from *sec.*-butylmalonic acid. Similarly, γδ-dimethyl-Δ^{γ}-hexen-β-one (cf. preceding abstract) is converted into *γδ-dimethylhexan-β-one*, b. p. 152—154°, d_4^{15} 0·833, n_D^{15} 1·4186 (*semicarbazone*, m. p. 119°), which yields no hydrogen sulphite compound and does not give the iodoform reaction. The same ketone is obtained from ethyl *sec.*-butylacetoacetate, b. p. 72—74°/4 mm., by treating the sodio-derivative with methyl iodide and hydrolysing the *ethyl methyl* sec.-*butylacetoacetate*, b. p. 78—79°/3 mm., d_4^{22} 0·977, with 12% potassium hydroxide. *γδ-Dimethylhexan-β-ol*, b. p. 164—167°, d_4^{15} 0·840, n_D^{15} 1·4325 (*allophanate*, m. p. 182°), and *γ-methylheptan-ε-ol*, b. p. 165—167°, d_4^{15} 0·830, n_D^{15} 1·4282 (*allophanate*, m. p. 150°), are obtained by hydrogenation of the ethylenic ketones with sodium and moist ether, and finally over platinum-black. With magnesium phenyl bromide λδ-dimethyl-Δ^{γ}-hexen-β-one yields 38% of *β-phenyl-λδ-dimethyl-Δ^{γ}-hexen-β-ol*, b. p. 123—124°/5 mm., d_4^{15} 0·970, 1·5253, which when distilled under 80 mm. pressure yields acetophenone.

With acetaldehyde in presence of 3*N*-alcoholic potassium hydroxide, methyl ethyl ketone yields γ-methylpentan-β-ol-δ-one, b. p. 62—63°/3 mm., d_4^{15} 0·962, n_D^{15} 1·4357, converted by dehydration into *γ-methyl-Δ^{β}-penten-δ-one*, b. p. 136—138°, d_4^{15} 0·874, n_D^{15} 1·448 (*semicarbazone*, m. p. 199°). Catalytic hydrogenation of the latter yields γ-methylpentan-β-one, the sodium derivative of which with acetylene under pressure yields 69% of *γδ-dimethyl-Δ^{ϵ}-hexinen-δ-ol*, b. p. 153—154°, d_4^{15} 0·874, 1·4431, which on catalytic hydrogenation in presence of mercuric sulphate yields *γδ-dimethylhexan-δ-ol-ε-one*, b. p. 64—65°/7 mm., d_4^{19} 0·928, n_D^{19} 1·4332 (*semicarbazone*, m. p. 179°).

R. BRIGHTMAN.

Dioximes. LXXIV. G. PONZIO (Gazzetta, 1931, **61**, 138—149).—For the preparation of monobenzoyl derivatives of *as*-glyoximes, OBz·N:CR(or R′)·CR(or R′):N·OH, which have previously been obtainable only indirectly from oximinoketones by successive benzoylation and oximation, two methods have now been found. The first, applicable to the chloroglyoximes, consists in heating the glyoxime at 100° with benzoyl chloride (1 mol.), and yields the 2-benzoyl derivative. The second, applicable to the β-forms (those able to form nickel compounds) of aminoglyoximes, consists in treating the glyoxime in the cold with 1 mol. of benzoyl chloride in presence of acetic acid and sodium acetate, and gives the 1-benzoyl derivative (cf. A., 1930, 1409).

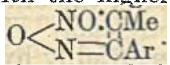
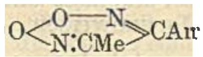
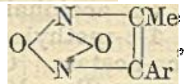
Amino-1-benzoylmethylglyoxime, OH·N:CMe·C(NH_2):N·OBz, m. p. 158°, thus obtained, gives the 1-*benzoyl*-2-*acetyl* compound, m. p. 143°. When heated with 20% sodium hydroxide solution and a little alcohol, either of these compounds yields aminomethylglyoxime and the oxime of 3-acetyl-5-phenylazoxime, m. p. 209° (cf. A., 1923, i, 854). At its m. p. the latter undergoes isomerisation into *benzamidomethylfurazan*, Me·C_2ON_2·NHBz, m. p. 119—120°, which forms a *copper* salt and may hence assume the lactim structure.

β-Aminophenylglyoxime yields the 1-*benzoyl* derivative, m. p. 168—169°, and the 1-*benzoyl*-2-*acetyl* derivative, m. p. 139—140°, either of which gives mainly the *oxime* of 3-*benzoyl*-5-*phenyl*-1 : 2 : 4-*oxadiazole*, m. p. 186—187°, when heated with 20% sodium hydroxide solution and a few drops of alcohol; this oxime forms a dark green *copper* salt, undergoes isomerisation into *phenylbenzamidofurazan*, m. p. 148°, when heated, and yields an *acetyl* derivative, m. p. 114—115°. When heated with 20% hydrochloric acid, the oxime of 3-benzoyl-5-phenyloxadiazole yields phenylbenzamidofurazan and 3-benzoyl-5-phenyloxadiazole, m. p. 87—88°; when heated with sodium ethoxide, the latter gives benzoylcyanoamide, 5-phenyloxadiazole being probably formed as an intermediate product. 3-Benzoyl-5-phenyloxadiazole forms a *semicarbazone*, m. p. 153—154°, and a *phenylhydrazone*, m. p. 130—131°.

With hydroxylamine, 3-benzoyl-5-phenyloxadiazole gives phenylbenzamidofurazan and the oxime of 3-benzoyl-5-phenyloxadiazole in about equal proportions. Since the latter is a stable form undergoing isomeric change into phenylbenzamidofurazan only at its m. p., oximation of 3-benzoyl-5-phenyl-1 : 2 : 4-oxadiazole evidently gives rise to the stable form of the oxime and to a labile form which undergoes spontaneous isomerisation in the cold.

When heated with 20% sodium hydroxide solution and a little alcohol, dibenzoyl-β-aminophenylglyoxime (cf. A., 1923, i, 857) yields a small proportion of β-aminophenylglyoxime, the main products being the oxime of 3-benzoyl-5-phenyl-1 : 2 : 4-oxadiazole and phenylbenzamidofurazan. In forming these two compounds, the dibenzoyl derivative apparently first loses a molecule of water to give the benzoyl derivative of the oxime of 3-benzoyl-5-phenyloxadiazole, which is then hydrolysed into the two forms of the corresponding oxime; the stable form persists as such, whereas the labile form undergoes spontaneous isomerisation into phenylbenzamidofurazan. T. H. Pope.

Dioximes. LXXV. I. de Paolini (Gazzetta, 1931, **61**, 149—153).—When the yellow dihydroxytrioxime, m. p. 111° (cf. A., 1930, 226; this vol., 199), is treated with concentrated hydrochloric acid, it yields a colourless chlorinated product, which gradually loses halogen, with formation of a colourless *compound*, m. p. 160°, showing the same composition and the same behaviour towards bromine as the original trioxime. To the compounds of m. p. 111° and 160°, respectively, the structures OH·N:C(OH)·C(NO):C(OH)·NH·OH (nitroso-enolic) and OH·N:C(OH)·C(N·OH)·CO·NH·OH (hydroxamic) are ascribed. The transformation of the nitroso-enolic form into the oxime of carbonyl bromide by the action of bromine water (this vol., 199) is explainable by assuming either the intermediate formation of an additive compound with hydrogen bromide or that the bromine acts on the nitroso-enolic form in equilibrium with the hydroxamic form. This equilibrium is established when the nitroso-enolic form is dissolved in water, giving a yellow solution. This becomes orange when heated and yellow when cooled again, the solution then containing the hydroxamic form in equilibrium with the colourless hydroximic form, C(N·OH)[C(OH):N·OH$)_2$, which has not been isolated. T. H. Pope.

Dioximes. LXXVI. M. Milone (Gazzetta, 1931, **61**, 153—158).—The chemical and chemico-physical properties of the two isomeric peroxides obtained on dehydrogenation of the β-form of an arylmethylglyoxime (A., 1928, 888; 1929, 334, 1072, 1316; 1930, 226, 581, 1409) indicate that only the peroxide with the higher m. p. possesses a furoxan structure, . For the other isomeride there remains a choice between the formula  and that suggested by Green and Rowe, , which alone are in accord with the behaviour towards magnesium methyl iodide (this vol., 225). Attempts to decide between these two formulæ by means of the parachor have been unsuccessful, owing to the conversion of one form into the other in the liquid phase or in solution. Determination of the heats of combustion supports the furoxan structure for the peroxide of higher m. p. and the dioxdiazine structure for that of lower m. p. T. H. Pope.

Mutarotation of fucose. J. Minsaas (Rec. trav. chim., 1931, **50**, 424—432).—The concentration of aqueous solutions of fucose is represented by the relationship $c=az+bz^2$ (c=concentration; $\log a=2{\cdot}4641174$; $\log b=1{\cdot}5610486$; $z=d^{20}-0{\cdot}998232$), whilst the relationship between the refractive index and the concentration of the solution is $\nu=0{\cdot}0_2144619c-0{\cdot}0_62282c^2$ ($\nu=1{\cdot}33300$). Dilatometric measurements of the change in volume of aqueous solutions during mutarotation of specimens crystallised from alcohol give different curves from those crystallised from water, whilst the curves are not identical with specimens crystallised from the same solvent. Similar discrepancies are observed in the mutarotation curves, the extreme initial rotation values observed for specimens crystallised from alcohol being $[\alpha]^{20}$ −155° and −111°, and for those crystallised from water, −158° and −151°. The final equilibrium value is −76·4° (lit. −72° to −77°). These results suggest the presence of several modifications of the sugar in solution, and the mutarotation can probably be accurately represented only by an equation involving more than two exponential terms. J. W. Baker.

Application of the fluorating process to lævulose. D. H. Brauns and H. L. Frush (Bur. Stand. J. Res., 1931, **6**, 449—456).—The prolonged action of anhydrous hydrofluoric acid on acetylated

lævulose (A., 1924, i, 265, 837; 1925, ii, 633; 1927, 93; 1928, 157; 1929, 913) leads to hydrolysis of the 1-acetyl group and replacement of the 2-hydroxyl group by fluorine. β-Tetra-, β-penta-, or fluorotetra-acetylfructose yields with hydrofluoric acid 2-*fluoro*-3 : 4 : 5-*triacetylfructose*, m. p. 134—135°, $[\alpha]_D^{17}$ −128·83°, yielding on acetylation fluorotetra-acetylfructose, and on methylation forming 2-*fluoro*-3 : 4 : 5-*triacetyl*-1-*methylfructose*, m. p. 94°, $[\alpha]^{20}$ −116·30°. *Triacetyl*-3-*methylfructose*, m. p. 156—157°, $[\alpha]^{20}$ −84·11°, on similar treatment forms 2-*fluorotriacetyl*-3-*methylfructose*, m. p. 113—114°, $[\alpha]^{20}$ −88·70° in chloroform.

G. DISCOMBE.

Isolation and identification of a polysaccharide from Southern yellow pine. E. L. FOREMAN and D. T. ENGLIS (Ind. Eng. Chem., 1931, **23**, 415—416).—An arabinogalactan was recovered from the "cyclone condensate" from the treatment of the wood of *Pinus palustris* by pressure-steam (Masonite process) and from the aqueous extract of the untreated wood (after extraction by light petroleum). The galactan was a white, tasteless powder, readily hydrolysed by dilute hydrochloric acid at 100° to *l*-arabinose and *d*-galactose.

E. LEWKOWITSCH.

Action of mercury salts on acetohalogenosugars. V. Synthesis of 1-β-methyl-α- and -β-cellobiosido-6-glucose deca-acetate. G. ZEMPLÉN, Z. BRUCKNER, and A. GERECS (Ber., 1931, **64**, [*B*], 744—751; cf. this vol., 72).—The action of 2 : 3 : 4-triacetyl-1-β-methylglucose on acetobromocellobiose in the presence of benzene and mercuric acetate leads to the production of mainly 1-β-*methyl*-α- or 1-β-*methyl*-β-*cellobiosido*-6-*glucose deca-acetate*, according to the relative excess of the triacetate employed. The β-compound has m. p. 248—249° (corr.), $[\alpha]_D$ −23·53° in chloroform, whereas the purest specimen of the more difficultly isolable α-compound has $[\alpha]_D$ +26·23° in chloroform. Both isomerides are converted by titanium tetrachloride into acetochlorocellobiose. The preparation of 1-α-*ethyl*-β-*cellobiosido*-6-*glucose deca-acetate*, m. p. 212°, $[\alpha]_D^{}$ +23·64° in chloroform, by use of a 100% excess of ethyl alcohol is described.

H. WREN.

Inulin. II. E. BERNER (Ber., 1931, **64**, [*B*], 842—850; cf. A., 1930, 1025).—Mainly a reply to Schlubach and Elsner (A., 1930, 1415) and to Pringsheim and Reilly (*ibid.*, 1562). The ready solubility in water of inulin precipitated by alcohol or ether from its solutions in glycerol, formamide, or acetamide is probably due to its amorphous condition; this property is enhanced but not caused by adsorbed solvent. The readily soluble form is also obtained when a hot, aqueous solution of inulin is poured into absolute alcohol. It absorbs organic solvents avidly and loses volatile solvents very slowly in a high vacuum at 110° in presence of phosphoric oxide. Adsorbed alcohol is more readily lost when the inulin is exposed to air of medium humidity. The residual alcohol-free inulin is permanently readily soluble in cold water, and causes the same depression of the f. p. as the original, sparingly soluble material. Elementary analysis of air-dried inulin without simultaneous determination of the water content is ill-adapted to the investigation of the purity of preparations.

H. WREN.

Cellulose. XL. Microstructure of fibre and swelling of cellulose. K. HESS and L. AKIM (Cellulosechem., 1931, **12**, 95—103).—An account of the microscopy of cellulose the swelling of which has been caused by various reagents.

J. D. A. JOHNSON.

Hydrolysis of cellulose and the intermediate products thereby formed. III. L. ZECHMEISTER and G. TOTH (Ber., 1931, **64**, [*B*], 854—870; cf. A., 1929, 544).—Cellulose is partly hydrolysed with very concentrated hydrochloric acid. The product is separated into fractions respectively soluble and insoluble in water and the carbohydrates are isolated from the aqueous solution by regulated addition of alcohol. The subsequent fractionation is controlled by determination of the iodine value (Willstatter and Schudel) and of the mol. wt. in freezing water. The latter determination is complicated by the obstinacy with which the products retain alcohol (overcome by evaporation with water previous to the final desiccation), but affords a very sensitive method for the detection of the presence of sugars of low mol. wt. The existence of cellotriose, $C_{18}H_{32}O_{16}$, m. p. 238° (corr. decomp.), $[\alpha]_D^{9}$ +31·8° to +23·2° in water, is confirmed and its *phenylosazone*, m. p. 208°, $[\alpha]^{20}$ −16·7° in alcohol, and *acetate*, $C_{40}H_{54}O_{27}$, m. p. 199—200° (corr.), $[\alpha]^{20}$ +7·2° in chloroform, are described. Cellotetraose has m. p. 251° (corr. decomp.), $[\alpha]_D^{21}$ +11·3° to +17·8° in water [*phenylosazone*, decomp. 228° (corr.); $[\alpha]_D$ −41° in ethyl alcohol; *acetate*, m. p. 225° (corr.), $[\alpha]_D^{20}$ −15·6° in chloroform]. The least soluble fractions give a *cellohexaose*, $C_{36}H_{62}O_{31}$, m. p. 266° (corr. decomp.), $[\alpha]_D^{20}$ +13·9° in water (*acetate*, $C_{76}H_{102}O_{51}$, $[\alpha]_D^{18}$ −7·6° in chloroform). Dextrose, cello-biose, -triose, -tetraose, and -hexaose form the initial members of a long condensation series, the properties of which are displaced continuously towards the cellodextrins and the polyoses. The solubility in water and alcohol diminishes with increasing length of the chain, as does the specific rotation. Dextrose and cellotriose show diminishing mutarotation, whereas cellobiose, cellotetraose, and cellohexaose exhibit increasing mutarotation. Cellotriose appears identical with the procellose of Bertrand and Benoist (A., 1923, i, 756).

H. WREN.

Cellulose. XXXIX. Determination of mol. wt. in glacial acetic acid. II. E. GARTHE and K. HESS (Ber., 1931, 64, [*B*], 882—897; cf. A., 1930, 456).—In part a reply to Freudenberg and others (A., 1930, 198, 457). Examination of the rate of crystallisation of solutions of the biosan acetate in glacial acetic acid and of the solvent in relation to bath temperature and supercooling by means of the f.-p. diagrams shows a normal behaviour of the compound; delay in crystallisation greater than that observed in solutions of known substances is not encountered. The method used is not "a process designed particularly for the biosan acetate," but is identical with that designed by Raoult, Nernst, and Abegg for the measurement of very small depressions. The latter are not caused by residues of solvent or by the presence of water. Up to 0·3% of the latter in the glacial acetic acid has no significant effect on the depressions, in contrast to the behaviour of membranised swelling cellulose acetates.

The previously observed small variations in the depressions of biosan acetate solutions are due to trivial causes. For concentrations between 0·034 and 0·295% the mean mol. wt. lies between the values 520 and 660. There is no evidence against the conception that the depressions are actually due to osmotically-active molecules of the size of a biosan hexa-acetate.

Further refinement of experimental technique is considered impossible with the type of apparatus employed. H. WREN.

Mechanism of formation of [cellulose] nitric esters. R. C. FARMER (J.S.C.I., 1931, **50**, 75—78T).—The nitration of cellulose is discussed on the basis of Hantzsch's theory of acids, and the conversion of nitric acid into nitronium salts. In accordance with these, it is found that in the mixed nitration acids only the nitric acid is active as an esterifying agent; the maximum degree of nitration always falls short of the trinitrate, and is not obtained with completely anhydrous acid, but with a mixture containing about 10% of water. Sulphuric esters have a detrimental effect on the stability of cellulose nitrates; they are removed by boiling with water in presence of acid, the cellulose nitrate being relatively little attacked. They are also readily removed by concentrated nitric acid or by nitric or acetic acid vapour. Some analogies are found in the nitration of benzene derivatives.

Action of formaldehyde on cellulose. M. SCHENK (Helv. Chim. Acta, 1931, **14**, 520—541).—The results of previous investigations on the action of formaldehyde and sulphuric acid on cellulose are confirmed. Microscopical examination shows that in the mercerisation of various samples of cellulose with sulphuric acid addition of formaldehyde protects the fibres, which retain their form and, after being freed from acid, the cellulose possesses a greatly enhanced affinity for substantive dyes, which is the greater the higher is the original degree of hydration of the cellulose. Addition of formaldehyde (as di*iso*propoxymethane) also retards the action of an acetic anhydride–acetic acid mixture at 100° on cellulose (viscose silk), especially in the initial stages, the inhibition being the greater the higher is the formaldehyde concentration. Even with prolonged treatment, acetylation of the cellulose never exceeds the diacetate stage (49·3% OAc), and the fibre, so treated, is immune to substantive dyes. The linear swelling of washed cellulose fibre, thus immunised by treatment with acetic anhydride–acetic acid and di*iso*propoxymethane for 5 hrs. at 100° (9—13% OAc) with various concentrations of sodium hydroxide reaches a maximum at the same concentration (10%) as does the untreated cellulose, but it is much flatter and of a much lower value, these effects being increased by increasing the formaldehyde concentration. It is suggested that formaldehyde so modifies the cellulose that the specific action of sodium hydroxide (cellulosate formation) is excluded, the base acting purely electrolytically. About the optimum concentration (10%) prolonged treatment with more concentrated sodium hydroxide at the ordinary temperature has very little effect on the swelling value. These results are confirmed by determination (by Vieweg's method, A., 1907, i, 893) of the amount of sodium hydroxide absorbed by the cellulose, which amount becomes the smaller the greater is the degree of immunity. Whilst the solubility of ordinary viscose in 2—5N-sodium hydroxide is considerable, the immunised cellulose is insoluble. It is concluded that the action of the formaldehyde is to form hydroxymethyl ethers of cellulose: $-C\cdot OH + CH_2O \longrightarrow -C\cdot O\cdot CH_2\cdot OH$ or $\longrightarrow CH_2(O\cdot C-)_2$; such action, however, fails to explain the increased affinity for substantive dyes, which possibly depends on the partial depolymerisation of the cellulose molecule into smaller, probably partly methylated, molecules.

J. W. BAKER.

Structure of nitrated cellulose. I. Swelling and disintegration of ramie cellulose in nitrating acids. F. D. MILES and M. MILBOURN. **II. X-Ray examination of nitroramie.** F. D. MILES and J. CRAIK.—See B., 1931, 92.

Lignin and related compounds. V. Action of halogens on lignin and wood. H. HIBBERT and C. A. SANKEY (Canad. J. Res., 1931, **4**, 110—118).—Bromine absorption experiments indicate that lignin contains an ethylenic linking. Di*iso*eugenol and di*iso*safrole contain two ethylenic linkings and cannot be derivatives of *cyclo*butane. The degree of conjugation of the ethylenic linking influences the reaction rate. Thus the addition of bromine to *iso*eugenol and *iso*safrole requires 4 hrs., whilst bromine addition to eugenol and safrole is complete in ½ hr. Of the ten bromine reagents tried, 0·2N-solutions of bromine in absolute methyl alcohol and carbon tetrachloride, respectively, gave the best results. The bromine absorbed varies with time, concentration, bromine solvent, and the acidity of the medium.

A. RENFREW.

Lignin and related compounds. VI. Mechanism of aqueous halogenation. K. A. TAYLOR, O. MAASS, and H. HIBBERT (Canad. J. Res., 1931, **4**, 119—132).—At 0° 0·025M-allyl alcohol absorbs at once the theoretical amount of 0·05M-hypochlorous acid. There is no oxidation in 24 hrs. In the reaction between M/800-hypochlorous acid and M/1600-allyl alcohol, M/10,000-sulphuric acid, M/5000-nitric acid, and M/5000-hydrochloric acid have the same catalytic effect. The catalytic effect of hydrochloric acid is proportional to the undissociated hydrochloric acid present. The addition of hypochlorous acid to $\delta\epsilon$-dihydroxy-$\Delta^{\beta\zeta}$-octadiene is similarly accelerated. Hydrochloric and hydrobromic acids hasten the addition of hypobromous acid to allyl alcohol to about the same extent. Nitric acid has a smaller effect. The addition of hypobromous acid to fumaric acid is retarded by hydrobromic acid and nitric acid and accelerated by hydrochloric acid. The conjugation of the ethylenic linking with two carbonyl groups may account for this behaviour. The reaction between m-nitrophenol and hypobromous acid is catalysed by hydrobromic acid and, to a smaller extent, by hydrochloric acid. Hypobromous acid addition accelerated by halogen acid is not the fastest reaction involved. The rate of reaction between hypochlorous acid and phloroglucinol and resorcinol, respectively, is of a much higher order than that of the reaction between hypo-

chlorous acid and the phenols studied by Soper and Smith (A., 1926, 831). The effect of various concentrations of hydrochloric and nitric acids on the reaction velocity suggests that chlorine reacts faster than hypochlorous acid. A. RENFREW.

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Hydrocarbons with phenyl and methyl groups alternating in the *para* position. E. CONNERADE (Bull. Soc. chim. Belg., 1931, **40**, 144—157).—*Di*-p-*methylbenzylbenzene*, m. p. 83·5°, prepared by heating *p*-xylylene dibromide, toluene, and anhydrous zinc bromide gives, on oxidation with potassium dichromate, p-*toluoyl*-p-*methylbenzylbenzene*, m. p. 192° (*oxime*, m. p. 155°), and *di*-p-*toluoylbenzene*, m. p. 194° (*dioxime*, m. p. 237°), synthesised by the action of terephthaloyl chloride on toluene in the presence of aluminium chloride. On oxidation with chromic acid, this diketone affords *di*-p-*carboxybenzoylbenzene*, m. p. 390·5°, decomp. 395°, also obtained by oxidation of the hydrocarbon. Reduction with hydriodic acid regenerates the hydrocarbon, whilst with sodium amalgam *di-α-hydroxy*-p-*methylbenzylbenzene*, m. p. 162°, is obtained, giving the corresponding *dichloro*-compound, m. p. 146—147°, on treatment with thionyl chloride. Reduction with sodium in toluene, or zinc dust and acetic acid with or without pyridine, affords a resinous *substance* which gives a marked yellowish-green fluorescence in alcoholic solution, and gives figures on analysis corresponding with the dimeride of the diketyl $[C_6H_4\dot{:}C(OH)\cdot C_6H_4Me]_2$. On oxidation of this substance, the diketodicarboxylic acid is obtained. B. LEVIN.

Conjugated systems. VIII. Catalytic hydrogenation of the geometrical isomerides of phenylbutadiene and vinylacrylic acid. I. E. MUSKAT and B. KNAPP (Ber., 1931, **64**, [*B*], 779—791).—Partial catalytic hydrogenation (Adams) of *cis*-phenylbutadiene affords *α-phenyl-Δ^{α}-butene*, b. p. 73—74·5°/12 mm., whereas *trans*-phenylbutadiene yields an *α-phenyl-Δ^{α}-butene*, b. p. 76—78°/12 mm. The structure of the butenes is established by their ozonisation to benzaldehyde and by addition of bromine to αβ-dibromo-α-phenylbutane, m. p. 70°. *cis*-Phenylbutadiene is more rapidly reduced than the *trans*-isomeride, and the difference in velocity appears more pronounced in the case of the second than in that of the first double linking. Vinylacrylic acid when reduced by Adams' method adds hydrogen first in the γδ-position, giving Δ^{α}-pentenoic acid, b. p. 93°/15 mm., ozonised to propaldehyde and oxalic acid. Hydrogenation occurs more rapidly in glacial acetic acid than in methyl alcohol.

H. WREN.

Hydrogenation of branched compounds over nickel. H. ADKINS, W. H. ZARTMAN, and H. CRAMER

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Reactions of organic lead compounds. C. D. HURD and P. R. AUSTIN (J. Amer. Chem. Soc., 1931, **53**, 1543—1548).—Lead tetraethyl is decomposed by nitric acid in boiling chloroform into *lead diethyl dinitrate* (an ionic compound, identified by conversion into the corresponding dichloride) and small quantities of lead triethyl nitrate and lead nitrate. Similar treatment of lead phenyltriethyl gives lead diethyl dinitrate and benzene: hydrochloric acid, however, gives lead triethyl chloride, possibly contaminated with the lower lead alkyl chlorides. Pyrolysis of lead tetrabenzoate gives lead benzoate and benzoic acid, there being no evidence of the formation of aromatic lead complexes; similar results are obtained with lead tetra-acetate. Lead benzoate has m. p. 118—119° (block) when crystallised from methyl alcohol, and m. p. 145—147° (block) when crystallised from ethylene dichloride.

H. A. PIGGOTT.

Hydrocarbons with phenyl and methyl groups alternating in the *para* position. E. CONNERADE (Bull. Soc. chim. Belg., 1931, **40**, 144—157).—*Di*-p-*methylbenzylbenzene*, m. p. 83·5°, prepared by heating *p*-xylylene dibromide, toluene, and anhydrous zinc bromide gives, on oxidation with potassium dichromate, p-*toluoyl*-p-*methylbenzylbenzene*, m. p. 192° (*oxime*, m. p. 155°), and *di*-p-*toluoylbenzene*, m. p. 194° (*dioxime*, m. p. 237°), synthesised by the action of terephthaloyl chloride on toluene in the presence of aluminium chloride. On oxidation with chromic acid, this diketone affords *di*-p-*carboxybenzoylbenzene*, m. p. 390·5°, decomp. 395°, also obtained by oxidation of the hydrocarbon. Reduction with hydriodic acid regenerates the hydrocarbon, whilst with sodium amalgam *di*-α-*hydroxy*-p-*methylbenzylbenzene*, m. p. 162°, is obtained, giving the corresponding *dichloro*-compound, m. p. 146—147°, on treatment with thionyl chloride. Reduction with sodium in toluene, or zinc dust and acetic acid with or without pyridine, affords a resinous *substance* which gives a marked yellowish-green fluorescence in alcoholic solution, and gives figures on analysis corresponding with the dimeride of the diketyl $[C_6H_4\!:\!C(OH)\cdot C_6H_4Me]_2$. On oxidation of this substance, the diketodicarboxylic acid is obtained.

B. LEVIN.

Conjugated systems. VIII. Catalytic hydrogenation of the geometrical isomerides of phenylbutadiene and vinylacrylic acid. I. E. MUSKAT and B. KNAPP (Ber., 1931, **64**, [*B*], 779—791).—Partial catalytic hydrogenation (Adams) of *cis*-phenylbutadiene affords *α-phenyl-Δ^α-butene*, b. p. 73—74·5°/12 mm., whereas *trans*-phenylbutadiene yields an *α-phenyl-Δ^α-butene*, b. p. 76—78°/12 mm. The structure of the butenes is established by their ozonisation to benzaldehyde and by addition of bromine to αβ-dibromo-α-phenylbutane, m. p. 70°. *cis*-Phenylbutadiene is more rapidly reduced than the *trans*-isomeride, and the difference in velocity appears more pronounced in the case of the second than in that of the first double linking. Vinylacrylic acid when reduced by Adams' method adds hydrogen first in the γδ-position, giving Δ^α-pentenoic acid, b. p. 93°/15 mm., ozonised to propaldehyde and oxalic acid. Hydrogenation occurs more rapidly in glacial acetic acid than in methyl alcohol.

H. WREN.

Hydrogenation of branched compounds over nickel. H. ADKINS, W. H. ZARTMAN, and H. CRAMER

(J. Amer. Chem. Soc., 1931, 53, 1425—1428).—The results of hydrogenation of a variety of substances in presence of nickel at 175—200°/98—124 atm. (in one experiment with triphenylamine 220 atm.) are tabulated. Triphenylmethane gives tri*cyclo*hexylmethane, m. p. 58·5—59·5° (lit. 48°), or di*cyclo*hexylphenylmethane according to the conditions. Triphenylcarbinol gives di*cyclo*hexylphenylmethane, which on further hydrogenation is converted into tri*cyclo*hexylmethane; this further reduction is, however, hindered by water or alcohol. Tri*cyclo*hexylamine, m. p. 160—161° (previously described as a liquid; cf. A., 1927, 552), is the sole product from triphenylamine, 1 : 3 : 5-trimethyl*cyclo*hexane from mesitylene, 1 : 3 : 5-*tri*cyclo*hexyl*cyclo*hexane*, m. p. 159—160°, b. p. 228—228·5°/3·5 mm., from 1 : 3 : 5-triphenylbenzene, and 2 : 2′ : 4 : 4′ : 6 : 6′-*hexamethyldi*cyclo*hexyl*, b. p. 123—126°/3 mm., from dimesityl.

H. A. Piggott.

Isomerisations of the dibromonaphthalenes by aluminium chloride. J. Salkind and Z. Stetzuro (Ber., 1931, 64, [*B*], 953—954).—The 1 : 2-dibromonaphthalene employed by Lohfert (A., 1930, 1424) is a mixture of 1 : 4- and 1 : 5-dibromonaphthalenes; his experiments therefore do not establish isomerisation under the influence of aluminium chloride. 2 : 6-Dibromonaphthalene, m. p. 159°, is obtained from 1 : 5- or 1 : 4-dibromonaphthalene and aluminium chloride in presence of carbon disulphide.

H. Wren.

Tribromonaphthalene of Glaser. J. Salkind and M. Belikov (Ber., 1931, 64, [*B*], 955—959).—The mixture of 1 : 4- and 1 : 5-dibromonaphthalene obtained by the bromination of naphthalene is transformed by bromine in presence of iron filings at 75—80° into Glaser's tribromonaphthalene, m. p. 86—87°, in 20·6% yield. It can be prepared in 43% yield from the 1 : 4-dibromide, whereas the 1 : 5-isomeride affords a *tetrabromonaphthalene*, m. p. 235°, and isomerides of lower m. p. Oxidation of the tribromo-compound gives 3 : 6-dibromophthalic acid. It is shown to be identical with 1 : 4 : 6-tribromonaphthalene prepared by bromination of potassium naphthalene-2-sulphonate to potassium 5 : 8-dibromonaphthalene-2-sulphonate and distillation of the last-named compound with phosphorus pentabromide or by sulphonating 1 : 4-dibromonaphthalene and subjection of the sulphonate thus produced to similar treatment. The structure of 1 : 4 : 5-tribromonaphthalene, m. p. 86—87°, is established, since the product of nitration of 1 : 4-dibromonaphthalene yields α-naphthylamine when strongly reduced and the tribromo-compound when distilled with phosphorus pentabromide.

H. Wren.

Piria reaction. I. The overall reaction. II. Rôle of the sulphamic acids. W. H. Hunter and M. M. Sprung (J. Amer. Chem. Soc., 1931, 53, 1432—1443, 1443—1447).—The name "Piria reaction" is applied to the preparation of aminoarylsulphonic acids by reduction of nitro-compounds with sulphites. The relative proportions of amine and sulphonic acid formed appear to be influenced in favour of the former by positive substituents, *e.g.*, the methyl group, and of the latter by negative substituents, such as a nitro- or carboxyl group, or a fused ring. 2-Nitronaphthalene gives a disulphonic acid as principal product. In most cases the velocity of reduction is greatest with partly neutralised sodium hydrogen sulphite. Sodium *p*-2-xylidine-5-sulphonate separates with $2H_2O$. A *salt* of *p*-aminobenzoic acid with *p*-amino-*m*-sulphobenzoic acid is described.

II. The sodium salts of arylsulphamic acids are hydrolysed quantitatively by 0·5—5·35*N*-hydrochloric acid to sulphuric acid and the corresponding amine, consequently as 2*N*-acid effects the second stage of the Piria reaction, the sulphamic acids are not formed intermediately. Sodium o-*tolyl*-, p-*tolyl*-, and p-*acetamidophenyl-sulphamate* ($+2H_2O$) are described.

H. A. Piggott.

Reactions of benzylamine and *iso*amylamine with propylene oxide. K. A. Krasuski and G. T. Piliugin (Ukrain. Chem. J., 1930, 5, [Sci.], 237—241).—The products of condensation of propylene oxide with benzylamine and *iso*amylamine are, respectively, α-benzylamino*iso*propyl alcohol (*picrate*, m. p. 126—128°) and α-iso*amylamino*iso*propyl alcohol*, b. p. 99—100°/14 mm. (*picrate*, m. p. 117°; *hydrochloride*, m. p. 193°), in 60% yields. Products of the condensation of 2 mols. of oxide with 1 mol. of amine are not formed.

R. Truszkowski.

Manufacture of sulphonic acids of 2-halogeno-3-chloro-*p*-toluidines and separation into their constituents of mixtures of 2 : 3- and 2 : 5-halogenochloro-*p*-toluidines. I. G. Farbenind. A.-G.—See B., 1931, 434.

Stereochemistry of diphenyl compounds. Preparation and resolution of 2 : 2′-difluoro-6 : 6′-diamino-3 : 5 : 3′ : 5′-tetramethyldiphenyl. E. C. Kleiderer and R. Adams (J. Amer. Chem. Soc., 1931, 53, 1575—1580).—5-*Bromo-4-nitro*-m-*xylene*-6-*diazonium fluoborate*, decomp. 195°, prepared from the corresponding amino-compound, is converted by heating under reduced pressure into 5-*bromo*-6-*fluoro*-4-*nitro*-m-*xylene*, m. p. 49—51°; this with copper-bronze at 200° gives 2 : 2′-*difluoro*-6 : 6′-*dinitro*-3 : 5 : 3′ : 5′-*tetramethyldiphenyl*, m. p. 234—236°, which is reduced by zinc dust in acetic and hydrochloric acids to the 6 : 6′-*diamino*-compound, m. p. 154—155°. This was resolved into l-, m. p. 150—152°, $[\alpha]_D^0$ −4·1° in acetone (d-*camphorsulphonate*, m. p. 171—173°, $[\alpha]_D^{20}$ +26° in alcohol), and d-, m. p. 150—151°, $[\alpha]_D^{20}$ +3·2° in acetone (d-*camphorsulphonate*, m. p. 125—130°, $[\alpha]^{20}$ +32·5° in alcohol), forms. The former is completely racemised in 30 min. to 4 hrs., according to the solvent, a result in agreement with the slight interference between the 2 : 2′- and 6 : 6′-groups determined by *X*-ray measurements.

By heating at 170° 5-*bromo*-m-*xylene*-6-*diazonium fluoborate*, decomp. 161°, is quantitatively decomposed into 5-*bromo*-6-*fluoro*-m-*xylene*, b. p. 87—89°/11 mm., d_{20}^{20} 1·452, n_D^{20} 1·3100, converted by nitric acid (*d* 1·6) at 0° into its 2 : 4-*dinitro*-derivative, m. p. 86—87°. This is converted in a similar manner to the preceding into 2 : 2′-*difluoro*-4 : 6 : 4′ : 6′-*tetranitro*-, m. p. 202—204°, and 2 : 2′-*difluoro*-4 : 6 : 4′ : 6′-*tetraamino*-3 : 5 : 3′ : 5′-*tetramethyldiphenyl*, m. p. 250—253°. Salts of the last-named suitable for resolution could not be prepared.

H. A. Piggott.

Reduction of azobenzene, azoxybenzene, and nitrosobenzene by the system magnesium + magnesium iodide. W. E. Bachmann (J. Amer. Chem. Soc., 1931, **53**, 1524—1531).—The product of interaction of equimolecular proportions of magnesium, magnesium iodide, and azobenzene in an inert solvent undergoes the following reactions. It is decomposed by water into hydrazobenzene (85—90% of the theoretical) and a little aniline; benzoyl chloride gives dibenzoylhydrazobenzene, and carbon dioxide gives the iodomagnesium salt of hydrazobenzene-*NN* dicarboxylic acid (the free acid rapidly decomposes into carbon dioxide and hydrazobenzene). Iodine, oxygen, nitrosobenzene, and azoxybenzene give azobenzene (2 mols. in the last-named case), and benzil gives azobenzene and benzoin. Benzaldehyde gives benzanilide. This behaviour, which is also shown by some substituted azobenzenes, is ascribed to the formation of dimagnesium hydrazobenzene di-iodide, $[MgI{\cdot}NPh{\cdot}]_2$; this conclusion is supported by the formation of a product with identical properties and ethane by interaction of hydrazobenzene and magnesium ethyl iodide.

Treatment of azoxybenzene with magnesium iodide and one atomic proportion of magnesium in an inert solvent and then hydrolysing gives azobenzene; the use of two equivalents of magnesium gives hydrazobenzene. Substituted azoxybenzenes behave similarly. In the same way nitrosobenzene may be reduced successively to azo- and hydrazo-benzene.

H. A. Piggott.

Action of organomagnesium halides and of the binary system MgI_2+Mg on some nitrogen compounds. H. Gilman and L. L. Heck (Rec. trav. chim., 1931, **50**, 522—524).—The binary system MgI_2+Mg acts as a reducing agent (cf. A., 1925, i, 1336) towards azobenzene (hydrazobenzene), azoxybenzene (azobenzene), nitrobenzene (aniline), nitrosobenzene (hydrazobenzene), phenylhydroxylamine (azobenzene and aniline), and diphenylhydroxylamine (diphenylamine), the substances in parentheses being the products isolated in each case. J. W. Baker.

Nitridation. III. Iodobenzene dichloride and *N*-chloro-acid amides as nitridising agents. A. L. Curl and W. C. Fernelius (J. Amer. Chem. Soc., 1931, **53**, 1478—1482).—Iodobenzene dichloride and iodine chloride interact with hydrazobenzene in liquid ammonia at −33° with formation of azobenzene: $PhICl_2+[NHPh{\cdot}]_2+2NH_3 \longrightarrow PhI+[NPh{:}]_2+2NH_4Cl$, but chloramine-*T*, dichloramine-*T*, *N*-chloroacetanilide, and *N*-chlorosuccinimide react preferentially with the ammonia, with formation of nitrogen, ammonium chloride, and the acid amide. The *N*-chloroamides interact similarly with gaseous ammonia. Iodobenzene dichloride, dichloramine-*T*, and *N*-chloro-acetanilide and -succinimide give with hydrazobenzene in chloroform solution azobenzene and benzidine hydrochloride. H. A. Piggott.

Azo-derivatives of homophthalimide. A. Meyer and R. Vittenet (Compt. rend., 1931, **192**, 885—887).—By coupling the appropriate diazotised amine with homophthalimide the following are obtained. o-*Chlorobenzene*-, m. p. 282°; o-, m. p. 276—277°, and p-*nitrobenzene*-, m. p. 290—291°; o-, m. p. 266—267°, m-, m. p. 228—230°, and p-*toluene*-, m. p. 240—242°; o-, m. p. 270—272°, and m-*nitro*-p-*toluene*-, m. p. 305—307°; m-*xylene*-, m. p. 260—261°; α-, m. p. 283—285°, and 2-*naphthalene*-, m. p. 262—264°; o-, decomp. about 315°, and m-*carboxyphenyl*-, m. p. 305—307° (decomp.); *antipyryl*- (from aminoantipyrine), m. p. 252—254° (decomp.), -*azohomophthalimides*. Similarly, from the tetrazotised diamines, *diphenyl*-, decomp. above 320°; *ditolyl*-, decomp. above 320°, and *dimethoxydiphenyl-bisazobishomophthalimides* are obtained.

J. D. A. Johnson.

Azo-chromophores. III. J. S. P. Blumberger (Chem. Weekblad, 1930, **28**, 190—198; cf. A., 1928, 996).—It is shown by examination of the absorption spectra of some 20 azo-dyes that the *o*-hydroxy-compounds differ from other classes of azo-dyes in the effect on them of substituting groups. Whereas in the other classes of azo-dyes both kinds of substituent (*loc. cit.*) in the *p*-position to the azo-group have a bathochromic effect, and particularly substituents of the second or electronegative kind, with the *o*-hydroxyazo-compounds only substituents of the first class, particularly the amino-group, have a bathochromic effect, the other substituents tending to diminish the depth of colour. The behaviour is attributed to co-ordination between the neighbouring azo- and hydroxy-groups. The conclusion that selective absorption is closely related to the polarity of the azo-group is strengthened. S. I. Levy.

Reactions of carbonyl compounds with phenylhydrazine. L. C. Raiford and W. T. Daddow (J. Amer. Chem. Soc., 1931, **53**, 1552—1558).—Formylphenylhydrazine, m. p. 143—144° (cf. Just, A., 1886, 700), is obtained by heating formanilide or substituted formanilides with phenylhydrazine and acetic acid, the corresponding aniline being formed at the same time. The interaction of diphenylcarbamide and phenylhydrazine at 80—90° or in boiling alcoholic solution gives diphenylsemicarbazide; with thiocarbanilide the reaction occurs more readily, giving diphenylthiosemicarbazide [*mercury* salt, $(C_{13}H_{13}N_3S)_2Hg$], and a number of other diarylthiosemicarbazides are similarly prepared. The *s*-diarylanilinoguanidines, $NHAr{\cdot}C({:}NAr){\cdot}NH{\cdot}NHPh$, are prepared by interaction of phenylhydrazine with the carbodi-imide, itself obtained by desulphurisation of the thiocarbamide with litharge in benzene. This method of formation, and their oxidation by mercuric oxide to azo-compounds, favour the hydrazo- (above) rather than the hydrazone formula. The following are described: s-*di*-2 : 4-*dibromophenylthiocarbamide*, m. p. 203°; 1-*phenyl*-4-p-*bromophenyl*-, m. p. 179—180°, 1-*phenyl*-4-2′ : 5-*dibromophenyl*-, m. p. 188°, 1-*phenyl*-4-2′ : 4′-*dibromophenyl*-, m. p. 177—178°, 1-phenyl-4-*o*-tolyl-, m. p. 170—171° (Dixon, J.C.S., 1890, **57**, 258, gives m. p. 162—163°), 1-phenyl-4-α-naphthyl-, m. p. 192—193° (Dixon, J.C.S., 1892, **61**, 1019, gives m. p. 183°), and 1-*phenyl*-4-m-*nitrophenylthiosemicarbazide*, m. p. 172°; *carbodi*-m-*tolylimide*, m. p. 118—119°; *carbodi-o-bromophenyl*-, m. p. 98—100°, -p-*bromophenyl*-, m. p. 144° (cf. Ingold, A., 1924, i, 322), -2 : 4-*dibromophenyl*-, m. p. 156—157°, and -2 : 5-*dibromophenyl-imide*, m. p. 172—173°; *di*-o-

tolyl-, m. p. 137° (*azo*-compound, m. p. 113—114°, by oxidation), *di*-m-*tolyl*, m. p. 158—159° (*azo*-compound, m. p. 107—108°), *di-o-bromophenyl-*, m. p. 147—148° (*azo*-compound, m. p. 132—133°), *di*-m-*bromophenyl-*, m. p. 162—163° (*azo*-compound, m. p. 131—132°), *di*-p-*bromophenyl-*, m. p. 202—203° (*azo*-compound, m. p. 163—164°), *di-α-naphthyl-*, m. p. 157—159°, and *di-β-naphthyl-anilinoguanidine*, m. p. 181—182°.

H. A. PIGGOTT.

Condensation of butyl chloral hydrate with arylhydrazines. F. D. CHATTAWAY and H. IRVING (J.C.S., 1931, 751—753).—*β-Chloro-α-ketobutaldehyde-phenylhydrazone*, m. p. 144°, $Ar\cdot NH\cdot N\colon CH\cdot CO\cdot CHCl\cdot CH_3$, -o-*tolylhydrazone*, m. p. 118—120°, -m-*tolylhydrazone*, m. p. 157·5°, -p-*tolylhydrazone*, m. p. 145—146°, -p-*chlorophenylhydrazone*, m. p. 156—157°, and -p-*bromophenylhydrazone*, m. p. 153°, are prepared by the condensation of butyl chloral hydrate and the appropriate arylhydrazine. The reaction proceeds more violently than with the corresponding 2 : 4-dihalogen-substituted phenylhydrazines (A., 1930, 324).

F. R. SHAW.

Diazo-compounds sensitive to light. I. Diazonaphtholsulphonic acid (1 : 2 : 4). J. SCHMIDT and W. MAIER (Ber., 1931, **64**, [*B*], 767—777).—Analyses of diazotised 1-amino-β-naphthol-4-sulphonic acid and its salts uniformly indicate the presence of the compound in an anhydrous form. The following salts are described: *sodium*, *potassium*, *barium* (*di-* and *tri-hydrate*), *silver* (*anhydrous* and *monohydrate*), *zinc* (*anhydrous* and *hexahydrate*), *cadmium* (*di-* and *hexa-hydrate*), *copper* (*hexahydrate* and anhydrous), *ferrous* (*hexahydrate* and *anhydrous*), *hexahydrated manganous*, *trihydrated uranium*. When exposed to light in the presence of sufficient acid to prevent the coupling of unchanged material with the products of decomposition, diazonaphtholsulphonic acid decomposes quantitatively into dihydroxynaphthalenesulphonic acid (*calcium* and *potassium* salts). *p*-Diazodiphenylamine and its complex compound with zinc chloride passes smoothly when illuminated into *p*-hydroxydiphenylamine, m. p. 70°.

H. WREN.

Action of diazonium salts on unsaturated compounds. IV. A. QUILICO and M. FRERI (Gazzetta, 1930, **60**, 606—619; cf. A., 1930, 82).—The secondary products of the reaction between diazonium salts and unsaturated phenols or their ethers (cf. A., 1928, 997; 1929, 559) are considered. The red compound, m. p. 228° (decomp.), formed during the action of *p*-nitrobenzenediazonium sulphate on anethole, *iso*safrole, etc. accompanied by a small amount of the *p*-nitrophenylhydrazone of the corresponding aldehyde, is found to be p-*nitromethylformazyl*, $NO_2\cdot C_6H_4\cdot N\colon N\cdot CMe\colon N\cdot NH\cdot C_6H_4\cdot NO_2$, also produced by the action of *p*-nitrobenzenediazonium sulphate on acetaldehyde. The action of *p*-nitrobenzenediazonium sulphate on ethyl alcohol yields glyoxal-*p*-nitrophenylhydrazone and on *p*-propenyldimethylaniline in alcoholic solution yields either dimethylaminobenzaldehyde-*p*-nitrophenylhydrazone (cf. Vecchiotti, A., 1913, i, 1100) or (?)2-p-*nitrophenyl*-4-p-*dimethylaminophenyl*-5-*methyl*-1 : 2 : 3-*triazole*, m. p. 232—233°, according to whether the diazo-compound is added to the amine solution or *vice versa* In aqueous solution the reaction gives the *aminoazo-compound*, $CHMe\colon CH\cdot C_6H_3(NMe_2)\cdot N\colon N\cdot C_6H_4\cdot NO_2$, softening at about 65° and decomposing completely at 85°, in almost theoretical yield.

T. H. POPE.

Chemistry of diazo-compounds. W. SWIENTOSŁAWSKI (Rocz. Chem., 1931, **11**, 221—225).—Polemical, in reply to Hantzsch (A., 1930, 1032).

R. TRUSZKOWSKI.

Aromatic thiocyanates and thiocarbimides. J. W. DIENSKE (Rec. trav. chim., 1931, **50**, 407—414).—The oily by-products obtained in the preparation of *p*-thiocyano-anisole and -phenetole (this vol., 474) by the action of cuprous thiocyanate on diazotised *p*-anisidine and *p*-phenetidine are the thiocarbimides, since they are converted by the action of alcoholic ammonia into the corresponding arylthiocarbamides and by the bases into the *s*-diarylthiocarbamides. Since the thiocyano-derivatives are not converted into the thiocarbimides by heating, the latter must be formed simultaneously in the original Sandmeyer reaction.

J. W. BAKER.

3-Fluoro-2-, -4-, and -6-amino- and -2-, -4-, and -6-halogeno-anisoles. H. H. HODGSON and J. NIXON (J.C.S., 1931, 981).—3-*Fluoro*-2-, b. p. 208°/756 mm., 3-*fluoro*-4-, m. p. 50°, and 3-*fluoro*-6-*amino-anisoles*, b. p. 215°/756 mm., prepared from the corresponding nitro-compounds, are converted by the Sandmeyer reaction into 2-, b. p. 198°/757 mm., 4-, b. p. 196°/757 mm., and 6-*chloro*-, b. p. 195°/757 mm., 2-, b. p. 220°/755 mm., 4-, b. p. 215°/755 mm., and 6-*bromo*-, b. p. 208°/755 m., 2-, b. p. 240°/756 mm., 4-, b. p. 238°/756 mm., and 6-*iodo*-3-*fluoroanisole*, b. p. 236°/746 mm.

F. R. SHAW.

Glycerol ethers of nitrophenols. L. DESVERGNES (Chim. et Ind., 1931, **25**, 811—818).—Chloro-2 : 4-dinitrobenzene gives with glycerol in the presence of sodium hydroxide, not only the glycerol ether of 2 : 4-dinitrophenol (cf. Willgerodt, A., 1879, 716), but also a *di*-(2 : 4-*dinitrophenyl*)*glyceryl ether*, m. p. 173·5—174°. Nitration of 2 : 4-dinitrophenyl glyceryl ether gives two isomeric 2 : 4 : 6-*trinitrophenyl mononitroglyceryl ethers*, m. p. 72·5—72·8° and 116·3—116·5°, respectively, and 2 : 4 : 6-*trinitrophenyl dinitroglyceryl ether*, m .p. 126—126·1°. Nitration of di-(2 : 4-dinitrophenyl)glyceryl ether gives *di*-(2 : 4 : 6-*trinitrophenyl*)*glyceryl ether*, m. p. 173—173·5°. Neither *p*-chloronitrobenzene nor chloro-2 : 4 : 6-trinitrobenzene forms glyceryl ethers. From the water-soluble portion of the products of the reaction between chloro-2 : 4 : 6-trinitrobenzene and glycerol in the presence of sodium hydroxide, *iso*picric acid can be isolated.

A. RENFREW.

De Haas fluorescence reaction for β-naphthol. N. SCHOORL (Pharm. Weekblad, 1931, **68**, 279—280; cf. this vol., 347).—The reaction is best carried out with commercial glacial acetic acid. With pure acid the fluorescence develops only after long keeping, but an immediate result is obtained if a trace of acetaldehyde be added.

S. I. LEVY.

Condensations of secondary amines with naphthols and aldehydes. II. W. R. BRODE and J. B. LITTMAN (J. Amer. Chem. Soc., 1931, **53**,

1531—1532).—The following are prepared by interaction of the appropriate aldehyde and secondary amine with β- or α-naphthol in alcoholic solution (cf. this vol., 362): ω-*di*-n-*propylaminophenyl*-, m. p. 95°; ω-*dimethylaminoanisyl*-, m. p. 132°; ω-1-*piperidylanisyl*-, m. p. 134·5°, and ω-*dimethylaminopiperonyl*-2-*hydroxynaphthylmethane*, m. p. 120°; and ω-1-*piperidylphenyl*-1-*hydroxy*-2-*naphthylmethane*, m. p. 110°. The last-named was also prepared by condensation of benzylidenepiperidine with α-naphthol.

H. A. PIGGOTT.

Intramolecular strain in substituted dihydroresorcinols. I. L. E. HINKEL, E. E. AYLING, J. F. J. DIPPY, and T. H. ANGEL (J.C.S., 1931, 814—820).—In presence of a large excess of alkali, ring fission of dihydroresorcinols to the δ-ketohexoic acids is unimolecular, the change being followed by oxidation with potassium permanganate solution under conditions which do not affect the acids. The effect of substituents on the ring stability of a series of ten dihydroresorcinols has been examined from the point of view of the valency deflexion hypothesis. 5-Phenyl-, 5-methyl-, 5-*iso*propyl-, 5-*n*-propyl-, 5-cinnamyl-, 4 : 5-dimethyl-, 5 : 5-dimethyl-, and unsubstituted dihydroresorcinols behave normally, although the results obtained are not entirely in harmony with conceptions based solely on spatial considerations. Whilst the monosubstituted compounds yield results in accordance with theoretical requirements, the unsubstituted and dimethyl compounds occupy anomalous positions, which, it is suggested, are due to the operation of polar influences. The hydrolysis of 2-methyl-5-*iso*propyl- and 2-methyl-5-phenyl-dihydroresorcinols is characterised by the rapid intervention of secondary reactions not observed in the previous cases. γ-*Methyl*-Δ^{β}-*penten*-δ-*one*, b. p. 138° [*semicarbazone*, m. p. 201° (decomp.); *oxime*, m. p. 75—76°], from methyl ethyl ketone and acetaldehyde is converted by ethyl malonate and sodium ethoxide into two *forms* of 4 : 5-*dimethyldihydroresorcinol*, m. p. 68—70° (*monohydrate*, m. p. 55°) and m. p. 109°. 2-*Methyl*-5-iso*propyl*-, m. p. 186° (from β-methyl-Δ^{γ}-hepten-ε-one); 5-*n*-propyl-, m. p. 107° (cf. Eccott and Linstead, A., 1930, 893) (*monohydrate*, m. p. 76°), and 2-methyl-5-phenyl-dihydroresorcinol, m. p. 215° (cf. Mattar, Hastings, and Walker, this vol., 92), are also described.

F. R. SHAW.

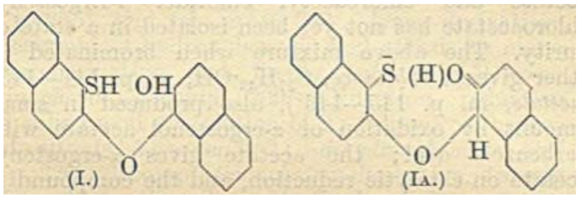
Hoesch–Houben synthesis in the preparation of aromatic ketimines and hydroxyphenyliminoesters. E. BRESSON and J. B. CULBERTSON (Proc. Iowa Acad. Sci., 1929, 36, 266).—Definite condensation products could not be obtained from benzonitrile and phenol, cresols, pyrocatechol, pyrogallol, or carvacrol. The products from quinol and resorcinol monomethyl ether form additive compounds with zinc chloride.

CHEMICAL ABSTRACTS.

Primary additive products in indirect substitution in the benzene nucleus. II. Additive products with nitric acid and 4 : 4′-dialkoxydiphenyls. J. VAN ALPHEN (Rec. trav. chim., 1931, 50, 415—423).—The effect of various substituent groups (R) on the formation and stability of the blue additive dinitrates formed when substituted 4 : 4′-dihydroxydiphenyl derivatives, $RO\cdot C_6H_4\cdot C_6H_4\cdot OR$, are treated in carbon tetrachloride with an emulsion of absolute nitric acid in the same solvent (A., 1930, 1284) has been investigated. Additive *dinitrates* (oxonium salts) are formed when R=Me, Et, $\cdot CH_2\cdot CO_2H$, $\cdot CH_2\cdot CO_2Et$, $\cdot CH_2Ph$, or *o*-, *m*-, and *p*-$\cdot CH_2\cdot C_6H_4\cdot NO_2$, but not when R=$CO_2Et$, Ac, or Ph. 4 : 4′-*Dimethoxydiphenyl*-ωω′-*dicarboxylic acid*, m. p. 274°, and its *ethyl* ester, m. p. 130°, are obtained by the action of chloroacetic acid or its ester, respectively, on the sodium derivative of 4 : 4′-dihydroxydiphenyl. The dinitrate of the ester is decomposed at 100°, giving *ethyl* 3 : 3′-*dinitro*-4 : 4′-*dimethoxydiphenyl*-ωω′-*dicarboxylate*, m. p. 152°, identical with a specimen obtained by nitration with absolute nitric acid and acetic anhydride. Similarly, by heating 4 : 4′-dihydroxydiphenyl with the appropriate nitrobenzyl chloride and alcoholic sodium ethoxide are obtained 4 : 4′-*dibenzyloxy*-, m. p. 215° (not sharp), 4 : 4′-*di*-o-, m. p. 179° (together with *o* : *o*′-dinitrostilbene), 4 : 4′-*di*-m-, m. p. 166°, and 4 : 4′-*di*-p-, m. p. 216°, -*nitrobenzyloxy-diphenyl*.

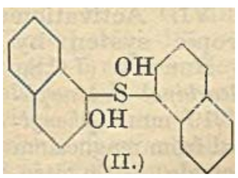
J. W. BAKER.

Conversion of *iso*-β-naphthol sulphide into β-naphthol 1-sulphide. L. A. WARREN and S. SMILES (J.C.S., 1931, 914—922).—The conversion of I into II (cf. A., 1930, 908) is effected by heat either alone or in solvents, but it may proceed more rapidly in alkaline media. When SH in I is replaced by SO_2H, no conversion into β-naphthol-1-sulphone has been observed; and the facts may be interpreted



(I.) (IA.)

as showing that the negative character of sulphur in the thiol is of fundamental importance. 2′-*Methoxy*-1-*thiol*-1 : 2′-*dinaphthyl ether* (I, OMe for OH), m. p. 112°, prepared by reducing 2′-*methoxy*-1-*dithio*-1 : 2′-*dinaphthyl ether*, m. p. 128° [1 mol. of ethyl acetate, m. p. 107° (decomp.); 1 mol. of benzene, m. p. 122—123° (decomp.)], is unaltered by boiling alkali and does not give the expected *monomethyl ether* of β-*naphthol* 1-*sulphide*, m. p. 155—156° (prepared from *di*-2-*methoxy*-α-*naphthyl disulphide*, m. p. 20°, which reduces to 1-*thiol*-2-*methoxynaphthalene*, m. p. 68°, converted into 2-*methoxy*-1-*naphthylthiolacetic acid*, m. p. 130°). From this result it appears that the freedom of the tautomeric system (I ⇌ IA) is an important factor. The hypothesis that IA undergoes fission yielding 1-thiol-2-naphthol or its ion and the quinonoid radical, which reunite to form II, is abandoned, since the S-*picryl* derivative of the iso-*sulphide*, m. p. 134° (*acetyl* derivative, m. p. 225°), should yield with alkali, according to the hypothesis, 9 : 11-dinitrobenz-αβ-naphthathioxin (III), but actually gives picric acid and the sulphide II. III is obtained



(II.)

from the S-*picryl* derivative, m. p. 191° (decomp.), of 1-*thiol*-2-*acetoxynaphthalene*, m. p. 120°

(obtained by reducing *di-2-acetoxy-1-naphthyl disulphide*, m. p. 200°). *1-Thiol-2-acetoxynaphthalene* forms with sodium chloroacetate *2-hydroxy-1-naphthylthiolacetic acid*, m. p. 118°, but attempts to isolate the isomeric acid from β-naphthol 1-disulphide result in *1-carboxymethyl-2-naphthoxyacetic acid*, m. p. 161°. *1-Thiopicryl-2-methoxynaphthalene*, m. p. 183°, is also described.

The change is regarded as a displacement of oxidic oxygen in I by the more highly negative S from the positive carbon in the 1-position. The rearrangement is inhibited either by conversion of S into SO_2H or by depressing the positive character of the 1-carbon atom. Conversely, the change is favoured by the attachment of a powerful electron-attracting group to O in I, since the presence of picryl chloride assists the change, although *O*-picryl derivatives of I could not be isolated (forms an additive *compound*, m. p. 182—184°). F. R. SHAW.

Phenolic decomposition of mixed ethers. II. Effect of substitution. Rate constant. D. M. BIROSEL.—See this vol., 691.

Ergostenyl chloroacetate. M. C. HART and F. W. HEYL (J. Amer. Chem. Soc., 1931, **53**, 1413—1416).—"β-Ergostenyl chloroacetate" (cf. Reindel and others, A., 1927, 241) is found by fractional crystallisation from ether to be a mixture of the chloroacetates of *allo*-α-ergostanol, α- and β-ergostenols, and an additive *compound*, m. p. 129—130°, of ergostenyl chloroacetate and chloroacetyl chloride. β-Ergostenyl chloroacetate has not yet been isolated in a state of purity. The above mixture when brominated in ether gives a *substance*, $C_{27}H_{43}\cdot OH$, m. p. 144—145° (*acetate*, m. p. 145—146°), also produced in small amount by oxidation of α-ergostenol acetate with perbenzoic acid; the acetate gives α-ergostenyl acetate on catalytic reduction, and the compound is undoubtedly a dehydroergostenol, but appears different from the compound prepared in the latter way by Windaus and Luttringhaus, A., 1930, 1178). H. A. PIGGOTT.

Sivadjian's colour reaction for ephedrine. W. H. HARTUNG, F. CROSSLEY, and J. C. MUNCH (J. Pharm. Chim., 1931, [viii], **13**, 474—478; cf. A., 1930, 1460).—By standardising the technique of this reaction it is shown to be not specific for amino-alcohols of the ephedrine type. Aliphatic compounds give no colour, but aromatic compounds respond according to their groups with the following increasing intensity: amines, amino-ketones, amino-alcohols, phenols, and amino-phenols. The reaction helps to differentiate isomeric compounds such as the toluidines, and whilst the carboxyl group does not affect the intensity of the colour, it appears to hasten its development. T. MCLACHLAN.

Mobile anion tautomerism. VI. Activation of the three-carbon anionotropic system by polynuclear aryl groups. H. BURTON (J.C.S., 1931, 759—763).—*α-Naphthylvinylcarbinol* (*α-1-naphthylallyl alcohol*), b. p. 186—187°/19 mm. (*phenylurethane*, m. p. 108—109°), prepared from magnesium α-naphthyl bromide and acraldehyde, is *p*-nitrobenzoylated in pyridine, after 3 hrs., to *α-naphthylvinylcarbinyl* p-*nitrobenzoate*, m. p. 79—80°, and after 16 hrs. to *γ-1-naphthylallyl* p-*nitrobenzoate*, m. p. 138—139° [also prepared from *γ-1-naphthylallyl alcohol*, m. p. 39—40° (*phenylurethane*, m. p. 120°)]. *β-Naphthylvinylcarbinol*, b. p. 195—198°/21 mm. (*phenylurethane*, m. p. 134—135°), similarly prepared, gives no solid derivative when heated with *p*-nitrobenzoyl chloride in pyridine for 3 hrs., but after 16 hrs. a small amount of *γ-2-naphthylallyl* p-*nitrobenzoate*, m. p. 148° (also formed from *γ-2-naphthylallyl alcohol*, m. p. 116°), is obtained. The results show the increased activation of the three-carbon anionotropic system by the polynuclear aryl groups. F. R. SHAW.

Synthesis of simple and substituted 2-alkylcinnamyl alcohols, including a unimolecular cubebin. M. T. BOGERT and G. POWELL (J. Amer. Chem. Soc., 1931, **53**, 1605—1609).—The following are obtained by reduction of the corresponding cinnamaldehyde derivatives with ethoxymagnesium chloride (prepared by dissolving magnesium in absolute-alcoholic hydrogen chloride; cf. Meerwein and Schmidt, A., 1925, i, 1239) or aluminium ethoxide: *β-ethyl-*, b. p. 131—132°/9 mm. (p-*nitrobenzoate*, m. p. 110—111°; *phenylurethane*, m. p. 63—64°); *β-n-amyl-*, b. p. 141—143°/5 mm. [*phenylurethane*, m. p. 61—62° (uncorr.)]; *β:4-dimethyl-*, b. p. 142—143°/11 mm., and *3:4-methylenedioxy-cinnamyl alcohol*, b. p. 167—168°/5 mm., m. p. 78—78·8° [*benzoate*, m. p. 96—97°; *phenylurethane*, m. p. 96—97° (uncorr.)]. The last (cubebin) is different from the product obtained by Pauly, Schmidt, and Bohme (A., 1924, i, 1189) by reduction with iron and acetic acid. H. A. PIGGOTT.

Reduction of aromatic carbinols by mixtures of stannous chloride and hydriodic acid. A. VANSCHEIDT and B. MOLDAVSKI (Ber., 1931, **64**, [*B*], 917—925; cf. A., 1930, 1035, 1576).—Many aromatic triarylcarbinols are smoothly reduced to the corresponding triarylmethane by stannous chloride and a little hydriodic acid in glacial acetic acid: $CAr_3\cdot OH+2HI \longrightarrow CHAr_3+I_2+H_2O$ and $I_2+SnCl_3+2HCl \longrightarrow 2HI+SnCl_4$. The established unimolecular nature of the change proves that the concentration of the hydrogen iodide is constant and that the acid is the actual reducing agent. Examples cited are triphenylcarbinol to triphenylmethane, diphenyl-α-naphthylcarbinol to diphenyl-α-naphthylmethane, and 9-phenylxanthenol to 9-phenylxanthen. More drastic conditions are required with 9-phenylfluorenol, which affords diphenyldibiphenylene-ethane and ultimately 9-phenylfluorene. Xanthhydrol yields dixanthyl. 9-Alkylfluorenols are readily dehydrated to dibenzofulvenes by stannous chloride and hydrochloric acid and 9-ethylfluorenol yields 9-ethylidenefluorene under the influence of hydriodic and glacial acetic acids. With stannous chloride and hydriodic acid they yield dibiphenylenedialkylethanes, which are much more stable than the tetraphenyldialkylethanes. Diphenyldibiphenylene-ethane is also obtained from 9-phenylfluorenol by means of hydriodic acid and passes into 9-phenylfluorene when the mixture is boiled. 9-Alkylfluorenols are smoothly and rapidly reduced to the corresponding 9-alkylfluorenes by hydriodic acid in glacial acetic acid. *Dibiphenylenediethylethane*, m. p.

210° (corr.) when rapidly heated, *dibiphenylenedimethylethane*, m. p. 209° (corr.), and *dibiphenylenedibenzylethane*, m. p. 203° (corr.), are described.

H. WREN.

N-Phenylalkyl-N-methylaminoalkyl benzoates and p-aminobenzoates. A. C. COPE and S. M. MCELVAIN (J. Amer. Chem. Soc., 1931, 53, 1587—1594).—Pharmacological data are given for a series of local anæsthetics of the type $Ph\cdot[CH_2]_{1-4}\cdot NMe\cdot[CH_2]_{2-3}\cdot CO_2R$ (R=Ph or p-$C_6H_4\cdot NH_2$–). The requisite series of phenylalkylmethylamines was prepared by methylation of the *p*-toluenesulphonyl derivatives of the corresponding phenylalkylamines and hydrolysis of the products (cf. A., 1928, 54). The resulting amines were condensed with β-chloroethyl or γ-chloropropyl benzoates or *p*-nitrobenzoates, and in the case of the nitro-compounds the products were reduced catalytically or by iron and a little hydrochloric acid to the amino-compounds. The following are described: *γ-chloropropyl* p-*nitrobenzoate*, b. p. 168·5—169·5°, d_{25}^{25} 1·3222, n_D^{25} 1·54736 (from trimethylene chlorohydrin and *p*-nitrobenzoyl chloride); N-*γ-phenylpropyl*-p-*toluenesulphonamide*, m. p. 65·1—65·7° [N-*methyl* derivative, m. p. 41·8—42·4°, b. p. 234—238°/3 mm. (uncorr.)]; NN-*di-γ-phenylpropyl*-, m. p. 113·3—113·7°, and N-*δ-phenylbutyl*-p-*toluenesulphonamide*, m. p. 53·5—53·9° [N-*methyl* derivative, b. p. 241—245°/2 mm. (uncorr.), m. p. 60·5—61·1°]; β-phenylethyl-(hydrochloride, m. p. 164·1—164·9°), γ-phenylpropyl-, b. p. 85·5—86·1°/5 mm. (*hydrochloride*, m. p. 145·6—146·1°), and *δ-phenylbutyl-methylamine*, b. p. 95—95·4°/5 mm., d_{25}^{25} 0·9126, n_D^{25} 1·5035 (*hydrochloride*, m. p. 126·2—126·8°); *β-benzylmethylaminoethyl benzoate hydrochloride*, m. p. 145·6—146·4° [p-*nitro*-, m. p. 216·6—217·6°, and p-*amino*- (*dihydrochloride*), m. p. 209·6—210·6°, derivatives]; *β-(β-phenylethylmethylamino)ethyl benzoate hydrochloride*, m. p. 134·2—134·8° (softens at 114°) [p-*nitro*-, m. p. 170·9—171·9°, and p-*amino*- (*dihydrochloride*), m. p. 245·2—247·4°, derivatives]; *β-(γ-phenylpropylmethylamino)ethyl benzoate hydrochloride*, m. p. 106·3—107·1° [p-*nitro*-, m. p. 122·6—123·6°, and p-*amino*- (*dihydrochloride*), m. p. 182·3—184·3°, derivatives]; *β-(δ-phenylbutylmethylamino)ethyl benzoate hydrochloride*, m. p. 106·9—107·5° (p-*nitro*-derivative, m. p. 120·6—121·6°); *γ-benzylmethylaminopropyl benzoate hydrochloride*, m. p. 145·4—146·3° [p-*nitro*-, m. p. 206·6—207·4°, and p-*amino*- (*dihydrochloride*), m. p. 219·1—220·1°, derivatives]; *γ-(β-phenylethylmethylamino)propyl benzoate hydrochloride*, m. p. 128·8—129·4° (p-*nitro*-, m. p. 147·2—148·2°, and p-*amino*-, m. p. 190·7—192·2°, derivatives); *γ-(γ-phenylpropylmethylamino)propyl benzoate hydrochloride*, m. p. 117·5—118·3° (p-*nitro*-, m. p. 99·5—100·3°, and p-*amino*-, m. p. 178·8—179·8°, derivatives); *γ-(δ-phenylbutylmethylamino)propyl benzoate hydrochloride*, m. p. 124·7—125·7° (p-*nitro*-, m. p. 159·3—160·3°, and p-*amino*-, m. p. 156—158°, derivatives); *γ-phenylpropylmethylaminoethanol*, b. p. 132·6—133°/5 mm., d_{25}^{25} 0·9883, n_D^{25} 1·51723 (from γ-phenylpropylmethylamine and ethylene chlorohydrin at 100—120°); and *γ-phenylpropylmethylaminopropanol*, b. p. 147·3—147·9°/5 mm., d_{25}^{25} 0·9785, n_D^{25} 1·51335 (as above using trimethylene chlorohydrin).

H. A. PIGGOTT.

Manufacture of derivatives of 3-nitro-4-hydroxybenzamide. I. G. FARBENIND. A.-G.—See B., 1931, 434.

Action of bromine on acetamidohydroxybenzoic acids and acetamidophenols. G. HELLER [with F. SOLDNER] (J. pr. Chem., 1931, [ii], 129, 257—267).—5-Acetamido-2-hydroxybenzoic acid is converted even by excess of bromine in acetic acid at 100° into a *monobromo*-derivative, m. p. 247° (decomp.), and by acetic acid and 25% nitric acid into its *nitro*-derivative, decomp. 300°. Reduction of 3-nitro-4-hydroxybenzoic acid with tin and hydrochloric acid and subsequent acetylation affords *3-acetamido-4-hydroxybenzoic acid*, m. p. 251—252° (decomp.), converted successively by bromine in acetic acid into its *mono*-, m. p. 254° (decomp.), *di*-, m. p. 219°, and *tri*-, m. p. 230° (decomp.), *-bromo*-derivatives. No fission of the benzene nucleus is observed. When the bromination is carried out in the hot, *tribromo-2-bromoaminophenol* (?), m. p. 305°, is obtained. Acetic and nitric (*d* 1·53) acids convert 3-acetamido-4-hydroxybenzoic acid into its 2 : 5 : 6-*trinitro*-derivative, m. p. 204°, converted by bromine in acetic acid into *pentabromoacetanilide*, m. p. 222°. Similarly, 4-nitro-3-hydroxybenzoic acid is converted into *4-acetamido-3-hydroxybenzoic acid*, m. p. 250—251°, brominated to a *monobromo*-derivative, m. p. 255° (decomp.), and finally to the tribromo-2-bromoaminophenol (above), whilst *3-acetamido-2-hydroxybenzoic acid*, m. p. 230° (decomp.) (prepared from 3-nitrosalicylic acid), is brominated to its *mono*-, m. p. 255°, and *tri*-, m. p. 259°, *-bromo*-derivatives. 6-Acetamido-4-hydroxybenzoic acid affords its monobromo-derivative and finally *tribromo*-p(?)-*bromoaminophenol*, decomp. 200°. Nitration, reduction, and subsequent acetylation of 2 : 4-dihydroxybenzoic acid affords *o-acetamido-2 : 4-dihydroxybenzoic acid*, m. p. 220° (decomp.) (*monobromo*-derivative, decomp. 260°). Acetanthranilic acid affords, on bromination, its 5-bromo- and 3 : 5-dibromo-derivatives; 3 : 5-dibromoanthranilic acid, and *tetrabromo-2-acetamidobenzoic acid*, m. p. 228° (darkens at 200°), and, under certain conditions, a trace of pentabromoacetanilide. Bromination of *p*-acetamidophenol with 5 mols. of bromine and acetic acid affords the 2 : 6-*dibromo*-derivative, m. p. 188°, and bromoanil, and with 10 mols. of bromine at 100°, the *tetrabromo*-derivative, m. p. 246—247° [hydrolysed to *tetrabromo*-p-*aminophenol*, m. p. 215° (decomp.)], is obtained together with a little tetrabromoquinol. Bromine and acetic acid in the cold converts *o*-acetamidophenol into its *tribromo*-derivative, m. p. 163° (decomp.), and in the hot into *tetrabromo*-, m. p. 185° (decomp.), further brominated to *pentabromo*-, m. p. 207—208°, -N-*bromoacetanilide*.

J. W. BAKER.

New nitro-dye from aminosulphosalicylic acid. V. G. GULINOV (Ukrain. Chem. J., 1930, 5, [Tech.], 155—161).—Salicylic acid is converted into cupric 5-nitrososalicylate by treatment with sodium nitrite and copper sulphate (86% yield). The product yields 5-amino-6-sulphosalicylic acid on treatment with sodium sulphite, and this condenses with chloro-2 : 4-dinitrobenzene to yield *2′ : 4′-dinitro-4-hydroxy-2-sulphodiphenylamine-3-carboxylic acid*. This dyes animal fibres yellow, with acid mordants orange-

yellow, with chrome and iron golden-brown, and with alum yellow. R. TRUSZKOWSKI.

Titrimetric and spectrometric analysis of keto–enol mixtures. Ethyl α-phenylacetoacetate. K. VON AUWERS and (in part) E. WOLTER (J. Amer. Chem. Soc., 1931, **53**, 1496—1500).—The values of the spectrochemical data determined for ethyl α-phenylacetoacetate by Post and Michalek (this vol., 88) are confirmed, but their method of calculating the enol content is fallacious; the true value is 36·6%, which agrees with the results both of direct and indirect bromine titration. The increased enolisation caused by the phenyl group may be regarded as an example of the tendency of Δ^{β}-styrenes to isomerise into Δ^{α}-styrenes. H. A. PIGGOTT.

Preparation of β-hydroxy-αβγ-triarylbutyric acids. D. IVANOV and A. SPASSOV (Bull. Soc. chim., 1931, [iv], **49**, 371—375).—When chloromagnesium phenylacetate is treated with magnesium aryl bromides, β-hydroxy-αβγ-triarylbutyric acids are obtained in 60—65% yield on the aryl halide. The formation of dibenzyl, diaryls, and the corresponding tertiary alcohols as secondary products and of 3—4% of phenylmalonic acids by treating the reaction mixture with carbon dioxide indicates the following mechanism: $CH_2Ph\cdot CO_2MgCl \longrightarrow CH_2Ph\cdot CO\cdot Ph \longrightarrow CH_2Ph\cdot CPh(OMgBr)\cdot CHPh\cdot CO_2MgCl \longrightarrow CH_2Ph\cdot CPh(OH)\cdot CHPh\cdot CO_2H$, and the alternative: $CH_2Ph\cdot CO_2MgCl \longrightarrow MgBr\cdot CHPh\cdot CO_2MgCl$, yielding malonic acid derivatives. Chloromagnesium *o*-chlorophenylacetate does not condense thus, and magnesium *o*-tolyl bromide behaves differently from the *m*- and *p*-compounds. Magnesium phenyl bromide and chloromagnesium phenylacetate give 61% of β-*hydroxy-αβγ-triphenylbutyric acid*, m. p. 176—177°. β-*Hydroxy-αγ-diphenyl*-β-m-*tolyl*-, m. p. 158—159°, and -p-*tolylbutyric acid*, m. p. 169—170°, are similarly obtained. The derivative $C_6H_4Cl\cdot CH(MgCl)\cdot CO_2MgCl$, with 2 mols. of magnesium phenyl bromide yields 49·8% of β-*hydroxy-αγ-di*-p-*chlorophenyl*-β-*phenylbutyric acid*(?), m. p. 182·5—183·5°, and a *substance*, m. p. 135—137°, probably the corresponding tertiary alcohol. β-*Hydroxy-αγ-di*-p-*chlorophenyl*-β-m-*tolyl*- (yield, 64·5%), m. p. 157—158°, β-*hydroxy-αγ-di*-p-*chlorophenyl*-β-p-*tolyl*- (yield 63·5%), m. p. 175—176°, and β-*hydroxy-αγ-di*-p-*chlorophenyl*-β-p *bromophenyl-butyric acid*, m. p. 181—182°, are similarly obtained. β-Hydroxy-αβγ-triphenylbutyric acid is also obtained from deoxybenzoin and the compound $BrMg\cdot CHPh\cdot CO_2\cdot MgCl$. Magnesium phenyl bromide and ethyl αγ-diphenylacetoacetate yielded benzene and the original ester, the latter reacting in its enolic form.

R. BRIGHTMAN.

Condensation of ethyl phenyl- and *p*-chlorophenyl-acetate with magnesium *iso*propyl halides. D. IVANOV and A. SPASSOV (Bull. Soc. chim., 1931, [iv], **49**, 375—377).—When ethyl phenylacetate is treated with 1·5 mols. of a magnesium *iso*propyl halide, *ethyl αγ-diphenylacetoacetate*, m. p. 78—78·5°, is obtained quantitatively. Ethyl *p*-chlorophenylacetate similarly gives *ethyl αγ-di*-p-*chlorophenylacetoacetate* (yield 93%), m. p. 119—120°. Other magnesium organo-halides react normally, magnesium ethyl bromide, however, giving a little ethyl phenylacetate. The abnormal behaviour of the *iso*propyl halides is attributed to their enolising power.

R. BRIGHTMAN.

Preparation of ββ-dialkyl-, diaryl-, or diaralkyl-substituted β-hydroxy-α-phenylpropionic acids. D. IVANOV and A. SPASSOV (Bull. Soc. chim., 1931, [iv], **49**, 377—379).—When the dimagnesium derivative of phenylacetyl chloride, $MgX\cdot CHPh\cdot CO_2MgCl$, is heated with ketones, ββ-substituted derivatives of β-hydroxy-α-phenylpropionic acid are obtained in almost quantitative yield calculated on the dimagnesium derivative and up to 85% yield on the ketone. Thus di-*n*-propyl ketone gives 88% of β-*hydroxy-α-phenyl*-β-n-*propylhexoic acid*, m. p. 171°. β-*Hydroxy-αγ-diphenyl*-β-*methylbutyric acid*, m. p. 182—183° (decomp.), β-*hydroxy-αγ-diphenyl*-β-*benzylbutyric acid*, m. p. 183—184°, β-*hydroxy-αββ-triphenylpropionic acid*, m. p. 186—187°, and *α-hydroxy-α-phenyl-α*-cyclo*hexylacetic acid* (yield 80%), m. p. 135°, are similarly obtained from acetophenone, dibenzyl ketone, benzophenone, and *cyclo*hexanone. β-Hydroxy-αββ-triphenylpropionic acid is also obtained (yield 60%) from benzophenone and sodium α-bromomagnesium phenylacetate, $MgBr\cdot CHPh\cdot CO_2Na$, obtained from magnesium *iso*propyl bromide (or chloride) and sodium phenylacetate. Diphenylcarbinol is also formed. R. BRIGHTMAN.

Hydrolysis of γ-keto-nitriles of the type $R\cdot CH(CN)\cdot CH_2\cdot COPh$. (MISS) M. ROBERTSON and H. STEPHEN (J.C.S., 1931, 863—867).—β-Benzoyl-α-phenylpropionitrile is hydrolysed through the enolic form of the corresponding acid into αγ-diphenyl*iso*-(I), $CHPh{<}\begin{matrix}CO\cdot O\\ CH:CPh\end{matrix}$, m. p. 109°, and αγ-diphenylcrotonolactone (II), $CPh{\lessdot}\begin{matrix}CO\cdot O\\ CH\cdot CHPh\end{matrix}$, m. p. 284—286° (cf. Anschutz and Montfort, A., 1895, i, 179; Lapworth and Wechsler, J.C.S., 1910, **97**, 39). I is reduced to αγ-diphenylbutyrolactone, m. p. 103°, and II to phenylacetic acid; I may be converted into II (less soluble) by heating or repeated crystallisation. Treatment of a solution of β-benzoyl-α-phenylpropionitrile in acetic acid with hydrogen chloride yields a third form, m. p. 206°, which passes into II during crystallisation and affords acetophenone and β-benzoyl-α-phenylpropionic acid on boiling with alkali. β-*Benzoyl*-α-(p-*methoxyphenyl*)*propionitrile*, m. p. 118°, is converted into the corresponding *acid*, m. p. 155°, which with acetic anhydride gives α-(p-*methoxyphenyl*)-γ-*phenyl*isocrotonolactone, m. p. 96°, transformed by prolonged boiling in alcohol into the *crotonolactone*, sublimes at 266°, m. p. 270—275° (decomp.), also formed by the action of heat on the acid. The nitrile dissolved in 75% sulphuric acid gives the corresponding *amide*, m. p. 153°, from which α-(p-*methoxyphenyl*)-γ-*phenyl*isocrotonoiminolactone, m. p. 114°, is prepared. The following are similarly obtained: β-*benzoyl-α-phenylpropionamide*, m. p. 149°; *αγ-diphenylcrotono*-, decomp. above 290°; *αγ-diphenyl*iso*crotono-iminolactone*, m. p. 122°; β-*benzoyl*-α-(3 : 4-*methylenedioxyphenyl*)*propionitrile*, m. p. 129°; *acid*, m. p. 134°; *amide*, m. p. 149°; α-(3 : 4-*methylenedioxyphenyl*)-γ-*phenyl*-isocrotonolactone, m. p. 143°; -*crotonolactone*, m. p. 285—290°; and -*crotonoimino*-

lactone, m. p. 265°. The iminolactones exhibit the same isomeric change as the lactones.

F. R. SHAW.

Synthesis of cyclic compounds. VIII. Conversion of β-methyladipic acid into 3-methyl*cyclo*pentanone and the preparation of 3-methyl*cyclo*pentane-1 : 1-diacetic acid. A. I. VOGEL (J.C.S., 1931, 907—914).—Theoretical considerations indicate, if spatial effects alone are operative, a greater ease of ring-formation for β-methyladipic acid than for adipic acid. The method selected is that of slow thermal decomposition of the dibasic acids, by which β-methyladipic acid gives a 75·8±0·4% yield of 3-methyl*cyclo*pentanone together with a small quantity of γ-methyl-*n*-valeric acid, and adipic acid gives an 80% yield of *cyclo*pentanone (cf. A., 1929, 700). The smaller yield from β-methyladipic acid is attributed to a polar effect due to the methyl group. A method for preparing β-methyladipic acid in quantity is given.

3-Methyl*cyclo*pentanone condenses with ethyl cyanoacetate and ammonia to form a *dicyano-imide*, m. p. 189—190°, hydrolysed by sulphuric acid to the ω-*imide* of *αα'-dicarbamyl-3-methyl*cyclo*pentane-*1 : 1-*diacetic acid*, m. p. 232—233° (decomp.), or to 3-*methyl*cyclo*pentane*-1 : 1-*diacetic acid*, m. p. 134—135° (*silver* salt; *anhydride*, b. p. 192°/20 mm., or 185°/12 mm.; *ethyl* ester, b. p. 155·5°/15 mm., n_D^{15} 1·4485, d_4^{15} 1·0602; β-*naphthylamic acid*, m. p. 162—163°).

F. R. SHAW.

Constitution of phthalhydrazides and 6-nitrophthalhydrazide. D. RADULESCO (Bul. Soc. Chim. Romania, 1930, **12**, 137—139).—Polemical against Mihăilescu and Protopopescu (A., 1930, 1434). 6-Nitrophthalhydrazide and its derivatives are not new (cf., *e.g.*, Bogert and Boroschek, A., 1902, i, 98). The aminophthalimide formula for phthalhydrazide is untenable, since anhydrous salts, $C_8H_5O_2N_2X$, are known.

A. RENFREW.

New synthesis of phthalimidoacetonitriles and a note on aminoacetonitrile sulphates. H. STEPHEN [with W. W. ADAMSON] (J.C.S., 1931, 871—875).—Phthalic anhydride or a substitution product when heated with methyleneaminoacetonitrile gives formaldehyde and the corresponding *phthalimidoacetonitrile*, $C_6H_4{<}^{CO}_{CO}{>}N{\cdot}CH_2{\cdot}CN$, m. p. 123—124°, acted on by sulphuric acid to form *phthalimidoacetamide*, m. p. 257°, which can be converted into *phthalamic acid* N-*acetamide*, m. p. 204—205°. 4-*Chloro*-, m. p. 146·5° (*acid*, m. p. 205°; *chloride*, m. p. 93·5°; *amide*, m. p. 241°; *ethyl* ester, m. p. 95·5°); 3-*nitro*-, m. p. 156° (*acid*, m. p. 208°; *chloride*, m. p. 119·5°; *ethyl* ester, m. p. 77·5°; *amide*, m. p. 212°); 4-*nitro*-, m. p. 134—135° (*acid*, m. p. 193°; *chloride*, m. p. 129°; *ethyl* ester, m. p. 78°; *amide*, m. p. 214°); 3 : 6-*dichloro*-, m. p. 175—176° (*acid*, m. p. 243—244·5°; *chloride*, m. p. 135°; *ethyl* ester, m p. 193°; *amide*, m. p. 262—263°); 3 : 6-*dibromo*-, m. p. 228° (*acid*, m. p. 239—242°; *amide*, m. p. 285—287°); and *tetrachloro-phthalimidoacetonitrile*, m. p. 259° [*acid*, m. p. 298° (decomp.); *chloride*, m. p. 209°; *methyl* ester, m. p. 181°; *ethyl* ester, m. p. 180·5°; *amide*, m. p. 294°], are described; *naphthalimidoacetonitrile* has m. p. 248° (decomp.) [*acid*, m. p. 259—260°; *chloride*, m. p. 232°; *amide*, m. p. 319° (decomp.)].

The monosulphate of aminoacetonitrile obtained by Klages (A., 1903, i, 469) is a mixture and the *monosulphate*, m. p. 121°, now obtained is entirely different; the disulphate has m. p. 166° (decomp.). Each reacts with phthalic anhydride and derivatives to give the corresponding amides.

F. R. SHAW.

4-Aminophthalide and some derivatives. L. F. LEVY and H. STEPHEN (J.C.S., 1931, 867—871).—4-Aminophthalimide is reduced by Reissert's method (A., 1913, 621) to 4-*aminophthalide*, m. p. 194°, and the corresponding 5-isomeride is not obtained. *m*-Toluidine was identified in the product obtained by heating the base with hydriodic acid and phosphorus and establishes the constitution. Neutralisation of the base affords 4-*amino*-2-*hydroxymethylbenzoic acid*, m. p. 182° (efferv. and re-melting at 193°), and by use of the appropriate reagents the following are obtained: 4-*acetamido*-, m. p. 205°; 4-*benzamido*-, m. p. 191°; 5-*benzamido*-, m. p. 225°; 4-*chloro*-, m. p. 153·5° (acidified to 4-*chloro*-2-*hydroxymethylbenzoic acid*, m. p. 135—136°); 4-*bromo*-, m. p. 161° (4-*bromo*-2-*hydroxymethylbenzoic acid*, m. p. 155°); 4-*iodo*-, m. p. 193·5°; 4-*hydroxy*-, m. p. 222° (*acetyl* derivative, m. p. 126·5°); and 4-*cyano-phthalide*, m. p. 200° [hydrolysed to *phthalide-4-carboxylamide*, m. p. 245—248°, or to *phthalide-4-carboxylic acid*, m. p. 293—294° (*chloride*, m. p. 128°; *methyl* ester, m. p. 164·5°; *ethyl* ester, m. p. 148°)]. Phthalide-4-carboxylic acid is oxidised by potassium permanganate to 1 : 2 : 4-trimellitic acid and the *silver* salt prepared from it is that of 2-hydroxymethylterephthalic acid, resulting from fission of the lactone ring.

Reduction of 3-aminophthalimide by the same method gives the two possible isomeric aminophthalides.

F. R. SHAW.

***oo'*-Dicyanostilbene.** P. RUGGLI (Helv. Chim. Acta, 1931, **14**, 541—545).—*o*-Cyanobenzyl chloride is converted by heating with aqueous sodium sulphite into *sodium* o-*cyanobenzylsulphonate* $+H_2O$, m. p. 252—254°, converted by phosphorus pentachloride into the corresponding *sulphonyl chloride*, m. p. 85—86°. Anhydrous trimethylamine in benzene removes 1 mol. of hydrogen chloride from this and the sulphone $CN{\cdot}C_6H_4{\cdot}CH{:}SO_2$ so formed immediately loses sulphur dioxide to give oo'-*dicyanostilbene*, m. p. 191·5—192·5°. Nitration of *o*-cyanobenzyl chloride with mixed acids affords the 4-*nitro*-derivative, m. p. 94·5—95·5° (identical with the product erroneously described as the 5-nitro-compound by Gabriel and Landsberger, A., 1899, i, 133), converted by cold alcoholic sodium ethoxide directly into 4 : 4'-*dinitro*-2 : 2'-*dicyanostilbene*, decomp. 270—280°.

J. W. BAKER.

Decarboxylation of quinic acid. H. O. L. FISCHER and G. DANGSCHAT (Naturwiss., 1931, **19**, 310—311).—*iso*Propylidenequinide (A., 1921, i, 419) is converted through the hydrazide and the azide into iso*propylidenetrihydroxy*cyclo*hexanone*, m. p. 73—75°, α_D^{15} +116° in alcohol [*phenylhydrazone*, m. p. 150° (decomp.); *monoacetate*, m. p. 68°]. Methyl*iso*propylidenequinide by the same treatment gives a cyclic *urethane*, $C_{11}H_{17}O_5N$, m. p. 145°, α_D^{20} +73° in

chloroform. It is concluded that the free hydroxyl group in *iso*propylidenequinide is in the α-position to the carboxyl group. A. A. Levi.

Dicyclic systems. II. Influence of *cis*- and *trans*-hexahydrohydrindene nuclei on the carbon tetrahedral angle. A. Kandiah (J.C.S., 1931, 952—976).—The *cis*-form of hexahydrohydrindene should, according to the models, be strainless and the *trans*-form show an appreciable molecular strain. The results obtained from a comparative study of the products of hydrolysis of mono- and di-bromo-esters on the basis of the Thorpe–Ingold valency-deflexion hypothesis lead to the conclusion that when the *cyclo*hexane ring participates in the formation of condensed systems, it does so in its strainless " *cis* " and " *trans* " forms.

Monobromination of *ethyl hydrogen* trans-*hexahydrohydrindene*-2 : 2-*diacetate* affords the *neutral* α-*bromo*-ester (converted into the *lactonic* ester, b. p. 210°/13 mm., by distillation in a vacuum) and a small quantity of the *monobromo-acid* ester. Hydrolysis of the neutral bromo-ester gives a mixture of cis-, m. p. 225° (*anhydride*, m. p. 180°; *anilic acid*, m. p. 175°), and trans-1 : 2-*dicarboxy*cyclo*propane*-3(2′)-spiro-trans-*hexahydrohydrindene*, m. p. 262° (*dianilide*, m. p. 310°), and the *lactone* of α-*hydroxy*-trans-*hexahydrohydrindene*-2 : 2-*diacetic acid*, m. p. 115° (*aniline* salt, m. p. 192°), also obtained by treatment of the monobromo-esters with sodium carbonate solution. The *trans*-acid is completely decomposed with 10% hydrochloric acid at 240°, indicating the instability of the associated *cyclo*propane ring. *trans*-Hexahydrohydrindene-2 : 2-diacetic acid is dibrominated to form *ethyl* αα′-*dibromo*-trans-*hexahydrohydrindene*-2 : 2-*diacetate* (I), which cannot be purified without decomposition (with some *lactone* of α-*bromo*-α′-*hydroxy*-trans-*hexahydrohydrindene*-2 : 2-*diacetic acid*, m. p. 145°), and the corresponding *acid*, m. p. 200°. Hydrolysis of the ester with 64% potassium hydroxide affords mainly α-*keto*-trans-*hexahydrohydrindene*-2 : 2-*diacetic acid* (II), m. p. 164° [*quinoxaline* derivative, m. p. 238°; *phenylhydrazone*, m. p. 176°; *semicarbazone* of monosodium salt, m. p. 245°; *methyl* ester, b. p. 208°/18 mm. (*semicarbazone*, m. p. 150° (decomp.); *phenylhydrazone*, m. p. 186°)], a small quantity of 2-carboxy-*trans*-hexahydrohydrindene-2-acetic acid, and a mixture of stereoisomeric hydroxy-lactonic acids. When the hydrolysis of the ester is effected with methyl-alcoholic alkali a complex mixture of products is obtained, chief of which are: cis-1 : 2-*dicarboxy*-1-*hydroxy*-, m. p. 187° (decomp.) (*anhydride*, m. p. 110°); cis-1 : 2-*dicarboxy*-1-*methoxy*-, m. p. 180° (decomp.) (*ethyl* ester, m. p. 80°; *anhydride*, m. p. 91°; *anilic acid*, m. p. 193°; *anil*, m. p. 140°); trans-1 : 2-*dicarboxy*-1-*methoxy*-cyclo*propane*-3(2′)-spiro-trans-*hexahydrohydrindene*, m. p. 185°; and α-*hydroxy*-α′-*methoxy*-trans-*hexahydrohydrindene*-2 : 2-*diacetic acid*, m. p. 171°. The methoxy-*spiro*-acids when boiled with hydrobromic acid are converted into 2-carboxy-*trans*-hexahydrohydrindene-2-acetic acid.

Hydrolysis of I with aqueous sodium carbonate gives a mixture including: trans-*lactone*, m. p. 212° (*aniline* salt, m. p. 130°; *acetyl* derivative, m. p. 205°); cis-*lactone* of αα′-*dihydroxy*-trans-*hexahydrohydrindene*-2 : 2-*diacetic acid*, m. p. 195° (*aniline* salt, m. p. 126°); *ethyl* ester of one of the hydroxy-lactonic acids, m. p. 127°; and the keto-acid, II. The dibromo-ester of the *cis*-diacetic acid gives the α-keto-glutaric acid on alkaline hydrolysis. The theoretical significance of the above results with regard to strain in the molecule is discussed.

trans-*Hexahydrohydrindylidene*-2-*acetone*, b. p. 142—144°/25 mm. (*semicarbazone*, m. p. 218°), obtained from the acid chloride of *trans*-hexahydrohydrindene-2-acetic acid by the Blaise–Maire reaction, condenses with sodiocyanoacetamide to form 6-*hydroxy*-2-*keto*-3-*cyano*-6-*methylpiperidine*-4(2′)-spiro-trans-*hexahydrohydrindene*, m. p. 293°, which is hydrolysed with concentrated alkali to 2-*acetonyl*-trans-*hexahydrohydrindene*-2-*malonic acid* (III), m. p. 169° (decomp.) (*ethyl* ester, b. p. 214°/15 mm., n_D^{18} 1·48025, d_4^{18} 1·057; *semicarbazone*, m. p. 130°), or with concentrated hydrochloric acid to a *dilactone*, m. p. 154°. Pyrogenic decomposition of III yields the dilactone and 2-*acetonyl*-trans-*hexahydrohydrindene*-2-*acetic acid* (IV), m. p. 87° (*semicarbazone*, m. p. 202°), in the ratio of 1 : 3, indicating that III exists in the liquid state probably as an equilibrium mixture of keto- and lactol forms. The action of zinc methyl iodide on the acid chloride of ethyl *trans*-hexahydrohydrindene-2 : 2-diacetate affords the *ethyl* ester of IV, b. p. 180°/15 mm. (*semicarbazone*, m. p. 138°), converted by sodium into cyclo*hexane*-3 : 5-*dione*-1(2′)-spiro-trans-*hexahydrohydrindene*, m. p. 199° (*methylene* compound, m. p. 275°), and hydrolysed to IV. IV reacts in the lactol form with acetic anhydride to form an unsaturated *lactone*, m. p. 58—59°. The results show that the *trans*-hexahydrohydrindene ring closely resembles the *gem*-dimethyl group in its effect on the tautomerism of δ-ketonic acids.

Methyl *trans*-hexahydrohydrindene-2 : 2-diacetate condenses with methyl oxalate to form 2 : 5-*dicarbomethoxy*cyclo*pentane*-3 : 4-*dione*-1(2′)-spiro-trans-*hexahydrohydrindene*, m. p. 112° (*semicarbazone*, m. p. 202°), half the ester being converted into the parent acid. The ketonic ester hydrolyses to cyclo*pentane*-3 : 4-*dione*-1(2′)-spiro-trans-*hexahydrohydrindene*, m. p. 111° (*disemicarbazone*, m. p. 270°). *Ethyl* 2-*acetyl*-trans-*hexahydrohydrindene*-2-*acetate*, b. p. 164°/10 mm., n^{15} 1·48142, d_4^{15} 1·030 (*acid*, m. p. 123°), is converted by sodium ethoxide into cyclo*pentane*-2 : 4-*dione*-1(2′)-spiro-trans-*hexahydrohydrindene*, m. p. 190°, in 30% yield. The yield, smaller than in the case of the *cyclo*hexane derivative, is to be expected on the basis of a strainless configuration for the *trans*-hexahydrohydrindene nucleus. F. R. Shaw.

Dicyclic systems. I. 2-Substituted *cis*- and *trans*-hexahydrohydrindenes. A. Kandiah (J.C.S., 1931, 922—952).—Oxidation of *trans* decalone with hot concentrated nitric acid gives an excellent yield of *trans*-*cyclo*hexane-1 : 2-diacetic acid (cf. Hückel and Friedrich, A., 1927, 238) and the corresponding *cis*-acid is similarly obtained in 30% yield. These acids are almost quantitatively converted into *trans*- and *cis*-hexahydro-2-hydrindones on dry distillation with barium hydroxide. The *trans*-hydrindone condenses with ethyl cyanoacetate and ethyl-alcoholic ammonia to the ω-*imide* of trans-*hexahydrohydrindene*-2 : 2-*dicyanoacetic acid* (I), m. p.

291°, which separates as the ammonium salt (60% yield) and is transformed by concentrated sulphuric acid into the *αα'-dicarbamylimide*, m. p. 260°, the latter hydrolysed to trans-*hexahydrohydrindene*-2 : 2-*diacetic acid*, m. p. 224° (*methyl* ester, b. p. 172°/15 mm., d_4^{19} 1·074, n_D^{19} 1·4769; *ethyl* ester, b. p. 182°/16 mm., d_4^{19} 1·043, n_D^{19} 1·4687; di-p-*toluidide*, m. p. 197°; *anhydride*, m. p. 107°; *anilic acid*, m. p. 203°; *anil*, m. p. 197°; *methyl hydrogen* ester, m. p. 73°). The *cis*-hydrindone gives only 5% of the corresponding cis-*dicyanoimide*, m. p. 262°, similarly hydrolysed to cis-*hexahydrohydrindene*-2 : 2-*diacetic acid*, m. p. 188°, the *anhydride*, m. p. 88°, of which affords two *anilic acids*, m. p. 184° and 180°, respectively, each forming the same *anil*, m. p. 140°, indicating that they are stereoisomerides.

The mother-liquor of I when saturated with ammonia deposits the *ωω'-di-imide* of trans-*hexahydrohydrindene*-2 : 2-*dimalonic acid*, m. p. 308°, and *α*-*cyano*-trans-*hexahydrohydrindylidene*-2-*acetamide* (II), m. p. 149°; the latter is also obtained together with the *ωω'-di-iminodi-imide* of trans-*hexahydrohydrindene*-2 : 2-*dimalonic acid*, m. p. 284°, by condensing the hydrindone with cyanoacetamide. II is converted quantitatively into trans-*hexahydrohydrindylidene*-2-*cyanoacetic acid* (III), m. p. 179°. Condensation of the *cis*-hydrindone with cyanoacetamide gives only *α*-*cyano*-cis-*hexahydrohydrindylidene*-2-*acetamide* (IV), m. p. 118°, from which the *ω-di-iminodi-imide* of cis-*hexahydrohydrindene*-2 : 2-*dimalonic acid*, m. p. above 325°, is obtained by condensing with another molecule of cyanoacetamide.

The *trans*-hydrindone condenses readily with ethyl cyanoacetate, giving the *ethyl* ester of III (V), m. p. 55°, its oxidation to the parent ketone and inability to combine with bromine showing that it has the αβ-structure. In the presence of alkaline catalysts, it can react in either the αβ- or βγ-forms (in the latter form it is methylated to give *ethyl α-cyano*-trans-*hexahydroindenyl*-2-*propionate*, b. p. 175°/16 mm., which when treated with sodium ethoxide affords α-trans-*hexahydrohydrindylidene*-2-*propionitrile*, m. p. 60°). The action of sodium ethoxide on the ester yields a *compound*, m. p. 265°, under investigation. III is obtained by hydrolysis of its ester or in poor yield by condensing the hydrindone with cyanoacetic acid. Distillation under reduced pressure converts it into trans-*hexahydroindenyl*-2-*acetonitrile*, b. p. 136°/14 mm., d_4^{19} 0·9690, 1·4956, which can react in the αβ-form (physical properties and condensation with piperonal) and in the βγ-form (condensation with cyanoacetamide to the *imide* of *α-cyano*-trans-*hexahydrohydrindene*-2 : 2-*diacetic acid*, m. p. 224°). The *cis*-hydrindone gives a similar series: *ethyl* cis-*hexahydrohydrindylidene*-2-*cyanoacetate*, b. p. 200°/19 mm., $d_4^{21·4}$ 1·064, $n_D^{21·4}$ 1·5126, and the corresponding *acid*, m. p. 143°, by condensation of the hydrindone with ethyl sodiocyanoacetate or by the action of nitrous acid on IV. Distillation of the acid under reduced pressure gives cis-*hexahydroindenyl*-2-*acetonitrile*, b. p. 140°/15 mm., d_4^{19} 0·9750, $n_D^{19·5}$ 1·4968. Methylation of the unsaturated ester affords *ethyl α-cyano-α*-cis-*hexahydroindenyl*-2-*propionate*, b. p. 165°/15 mm., $d_4^{18·1}$ 1·028, $n_D^{18·1}$ 1·4843, transformed by heating with sodium ethoxide into cis-*hexahydrohydrindylidene*-2-*propionitrile*, b. p. 154°/15 mm., $d_4^{18·4}$ 0·9703, $n_D^{18·}$ 1·5101.

Reduction of V with moist aluminium amalgam gives *ethyl* r-trans-*hexahydrohydrindyl*-2-*cyanoacetate*, b. p. 178°/15 mm., d_4^{18} 1·021, 1·4700 (*anilide*, m. p. 150°), and 18% of a bimolecular compound. The ester is hydrolysed to the corresponding -2-*malonic acid*, m. p. 181—182° (*methyl* ester, b. p. 138°/13 mm., $d_4^{19·}$ 1·067, 1·4721; *dianilide*, m. p. 296°), which, when heated above its m. p., gives the -2-*acetic acid*, m. p. 120° (*ethyl* ester, b. p. 138°/18 mm., $d_4^{19·4}$ 0·9627, $n_D^{19·4}$ 1·4643; *anilide*, m. p. 135°). Condensation of V with potassium cyanide affords a mixture of 2-*carboxy*-trans-*hexahydrohydrindene*-2-*acetic acid* (VI), m. p. 202° (decomp.) (*methyl* ester, b. p. 172°/30 mm., $d_4^{18·2}$ 1·083, $n_D^{18·}$ 1·47526; *ethyl* ester, b. p. 176°/14 mm., $d_4^{18·}$ 1·043, $n_D^{18·}$ 1·46876; p-*tolylimide*, m. p. 154°; *anhydride*, m. p. 181°; *anilic acid*, m. p. 185°; *methyl hydrogen* ester, m. p. 124°), and its *imide*, m. p. 258°.

The *trans*-hydrindone gave its *cyanohydrin*, b. p. 165°/15 mm. (slight decomp.) (converted into 2-*hydroxy*-trans-*hexahydrohydrindene*-2-*carboxylic acid*, m. p. 134°, when boiled with concentrated hydrochloric acid), which condenses with ethyl sodiocyanoacetate to form *ethyl* 2-*cyano*-trans-*hexahydrohydrindene*-2-*cyanoacetate*, b. p. 212°/15 mm., hydrolysed to VI. The additive compound of V with potassium cyanide decomposes to a mixture of 2-*cyano*-trans-*hexahydrohydrindene*-2-*cyanoacetic acid*, m. p. 154° (when heated gives the *nitrile*, m. p. 179°), and the *imide* of 2-*carboxy*-trans-*hexahydrohydrindene*-2-*cyanoacetic acid*, m. p. 173°, which on hydrolysis and decarboxylation is transformed into VI. Ethyl *cis*-hexahydrohydrindylidene-2-cyanoacetate adds alcoholic potassium cyanide to give dicyano-esters, *A* and *B*, hydrolysed to two series of acids and imides, purified through the anhydrides. *A* series: 2-*carboxy*-cis-*hexahydrohydrindene*-2-*acetic acid*, m. p. 205° (decomp.) (*anhydride*, m. p. 137°; *ethyl* ester, b. p. 170°/15 mm., $d_4^{19·4}$ 1·1045, $n_D^{·4}$ 1·4720; *anilic acid*, m. p. 197°; *anil*, m. p. 127°; *imide*, m. p. 216°). *B* series: *acid*, m. p. 159° (*anhydride*, m. p. 68°; *anilic acid*, m. p. 182°; *anil*, m. p. 120°; *imide*, m. p. 170°).

The *trans*-hydrindone reacts with ethyl bromoacetate in presence of zinc to form *ethyl* 2-*hydroxy*-trans-*hexahydrohydrindene*-2-*acetate* (VII), b. p. 160°/16 mm., d_4^{19} 1·038, n_D^{19} 1·47279, and a little trans-*hexahydrohydrindylidenehexahydro*-2-*hydrindone*, m. p. 126° (*semicarbazone*, m. p. 140°), the ester being hydrolysed to the acid, m. p. 91° (*acetyl* derivative, m. p. 106°). The latter is dehydrated to trans-*hexahydrohydrindylidene*-2-*acetic acid* (αβ-acid), m. p. 155° (*dibromide*, m. p. 150°). When VII is dehydrated with phosphoryl chloride it gives *ethyl* trans-*hexahydroindenyl*-2-*acetate* (βγ-ester), b. p. 152°/15 mm., hydrolysed to the corresponding *acid*, m. p. 144° (*dibromide*, m. p. 146°; *hydrobromide*, from either αβ- or βγ-acid, m. p. 97°). The *cis*-hydrindone reacts similarly but less vigorously with ethyl bromoacetate and gives two series of acids: *ethyl* 2-*hydroxy*-cis-*hexahydrohydrindene*-2-*acetate* (probably a mixture), b. p. 158°/10 mm., $d_4^{15·5}$ 1·043, $n_D^{15·5}$ 1·4817; *acids*, m. p. 130° and 84°, respectively, which on dehydration form cis-*hexahydrindylidene*-2-*acetic acid*, m. p. 140°. The hydroxy-ester is dehydrated to *ethyl* cis-*hexahydroindenyl*-2-*acetate*, b. p. 143°/10 mm., $d_4^{15·6}$ 1·007, $n_D^{15·6}$ 1·48917; corresponding *acid*, m. p. 138°.

The isolation of two forms in the *cis*- and of one form in the *trans*-series is in accordance with the demands from consideration of the models for the two dicyclic systems, and isomerism persists when the two dissimilar groups attached to the quaternary carbon atom participate in ring-formation. F. R. SHAW.

Syntheses of *o*- and *m*-methoxyphthalic acids. A. GIRARDET (Helv. Chim. Acta, 1931, **14**, 511—512).—Experimental modifications for the preparation of 3- and 4-methoxyphthalic acids and their anhydrides by nitration of phthalic acid, reduction to the amino-acids, diazotisation, and methylation of the hydroxy-acids (cf. Kenner and Mathews, J.C.S., 1914, **105**, 2477; Bentley and others, *ibid.*, 1907, **91**, 118) are given. J. W. BAKER.

Synthesis of unsymmetrical diphenyl derivatives. J. KENNER and H. SHAW (J.C.S., 1931, 769—773).—Knoevenagel's synthesis of aromatic compounds from derivatives of *cyclo*hexen-2-one has been successfully extended to the preparation of unsymmetrical derivatives of diphenyl by the use of carbethoxy-compounds. Ethyl 5-phenyl-3-methyl-Δ^2-*cyclo*hexen-1-one-4 : 6-dicarboxylate forms a *dibromide*, m. p. 93—94°, which readily loses hydrogen bromide on keeping, and is converted by quinoline into *ethyl 3-hydroxy-5-methyldiphenyl-2 : 6-dicarboxylate*, m. p. 94° (*methyl ether*, m. p. 98°). The corresponding *dicarboxylic acid*, m. p. 297° (decomp.) (*ethyl hydrogen* ester, m. p. 153°), could not be resolved through either its *acid quinine* salt, m. p. 186° (decomp.) ($[\alpha]^{20\cdot5}$ —43° in chloroform), or its *acid codeine* salt, m. p. 161—165° ($[\alpha]^{16}_{D}$ —99·1° in water). Bromination of ethyl 3 : 5-diphenyl-Δ^2-*cyclo*hexen-1-one-6-carboxylate in cold acetic acid affords on warming *ethyl 4 : 6-diphenylsalicylate*, m. p. 89° (*methyl ether*, m. p. 115°), and the corresponding *acid*, m. p. 204° (decomp.) [converted by distillation with lime into 3 : 5-*diphenylphenol*, m. p. 95° (*benzoyl* derivative, m. p. 124°)]. 4 : 6-*Diphenyl*-o-*anisic acid*, m. p. 218°, is prepared from its methyl ester. F. R. SHAW.

Synthesis of 6 : 7-methylenedioxy-4-methoxyphenanthrene and of 5 : 6-methylenedioxy-4-methoxyphenanthrene-9-carboxylic acid. A. GIRARDET (Helv. Chim. Acta, 1931, **14**, 513—515).—Condensation of 3 : 4-methylenedioxyphenylacetic acid and 2-nitro-3-methoxybenzaldehyde in acetic anhydride in the presence of stannous chloride at 120° in an atmosphere of nitrogen affords 2-*nitro*-α-(3 : 4-*methylenedioxyphenyl*)-3-*methoxycinnamic acid*, m. p. 225°, reduced by ferrous sulphate in aqueous ammonia at 93° to the corresponding 2-*amino-acid*, m. p. 221°, converted by diazotisation and subsequent boiling with molecular copper in 2*N*-sulphuric acid into 6 : 7-*methylenedioxy* - 4 - *methoxyphenanthrene* - 9 - *carboxylic acid*, m. p. 271°, decarboxylated by prolonged heating at 300°/760 mm. to the corresponding phenanthrene (*picrate*, m. p. 160—161°, not identical with the phenanthrene picrate obtained from methylpukateine, this vol., 749). Similarly, condensation of 2-*bromo*-4 : 5-*methylenedioxyphenylacetic acid*, m. p. 192° [prepared from 6-bromopiperonal (Oelker, A., 1891, 1474) through the azlactone, m. p. 226°, hydrolysed to the pyruvic acid, m. p. 232°, oxidised with hydrogen peroxide to the phenylacetic acid], with 2-nitro-3-methoxybenzaldehyde affords 2-*nitro*-3-*methoxy*-α-(2-*bromo*-4 : 5-*methylenedioxyphenyl*)*cinnamic acid*, m. p. 210°, reduced to the *amino-acid*, m. p. 216°, diazotisation and ring closure of which gives 8-*bromo*-5 : 6-*methylenedioxy* - 4 - *methoxyphenanthrene* - 9 - *carboxylic acid*, m. p. 223°, debromination of which with a zinc–copper couple in aqueous-alcoholic sodium hydroxide affords the corresponding *acid*, m. p. 202—203°. This resists decarboxylation, distillation under reduced pressure giving a neutral substance (picrate, m. p. 201—202°) which regenerates the original 9-carboxylic acid with alkali. J. W. BAKER.

Additive properties, and a new reaction of glycocholic acid. S. MINOVICI and M. VANGHELOVICI (Bull. Sci. Acad. Roumaine, 1931, **14**, 53—58).—In the complete absence of water glycocholic acid forms crystalline additive *compounds* with aniline, m. p. 90° (decomp.), benzaldehyde, m. p. 81°, nitrobenzene, m. p. 105° (decomp.), benzyl alcohol, m. p. 87°, amyl alcohol, m. p. 75°, and triolein, m. p. 145°. All are decomposed by water, alkalis, and ethyl alcohol. The brilliant fluorescence shown by the compound with nitrobenzene, even in dilute solution, may be used as a test for the acid if water be absent; it is not shown by cholesterol or by other bile acids. H. A. PIGGOTT.

Perylene and derivatives. XXXII. Degradation of perylene to phenanthrene-1 : 8 : 9 : 10-tetracarboxylic acid and mellitic acid. A. ZINKE [with G. HAUSWIRTH and V. GRIMM] (Monatsh., 1931, **57**, 405—420).—Oxidation of 1 : 9-benzanthrone-(2)-5 : 10-dicarboxylic anhydride (A., 1930, 1587), or dichloro- or di-(*p*-chlorophenyl)-perylene-3 : 10-quinone with a mixture of nitric and acetic acids gives *phenanthrene*-1 : 8 : 9 : 10-*tetracarboxylic dianhydride*, unchanged at 400° (*dianil*), with intermediate formation in the case of the first of the 3(or 4)-*nitrobenzanthronedicarboxylic anhydride*, decomp. above 315° (the position of the nitro-group being indicated by the subsequent oxidation). The *silver* salt and, by its aid, the *tetramethyl* ester, m. p. 181—183°, and a *calcium hydrogen* salt, $[C_{14}H_6 \cdot CO_2H(CO_2)_3]_2Ca_3$, are prepared. The anhydride is reduced to phenanthrene by distillation with zinc dust. Its solution in aqueous alkali is not precipitated by mineral acids in the cold; when warmed to 60—70° *phenanthrene*-9 : 10-*dicarboxylic anhydride*-1 : 8-*dicarboxylic acid*(?), m. p. above 360° (*dimethyl* ester, m. p. 225—227°), separates. Oxidation of perylene-3 : 4 : 9 : 10-diquinone with nitric acid at 230—250° gives mellitic acid.

The annexed formula, or its Thiele equivalent, is suggested for perylene on account of its marked similarity to naphthalene in chemical behaviour. H. A. PIGGOTT.

Manufacture of cyclic ketones of the acenaphthene series and of 1 : 4 : 5 : 8-naphthalenetetracarboxylic acid and derivatives thereof. I. G. FARBENIND. A.-G.—See B., 1931, 476.

2 : 4 : 6-Trinitrobenzaldehyde. S. SECAREANU (Ber., 1931, **64**, [*B*], 837—842).—2 : 4 : 6-Trinitrobenzaldehyde, m. p. 119°, is obtained in 80% yield by the action of concentrated hydrochloric acid on tri-

nitrobenzylidenedimethyl-*p*-phenylenediamine (cf. this vol., 752). When warmed with aniline in alcohol it affords 2 : 4 : 6-*trinitrobenzylideneaniline*, m. p. 170°, transformed by aniline at 100° into 4 : 6-*dinitro-2-anilinobenzylideneaniline*, m. p. 177°, which yields 1 : 3-*dinitroacridine*, m. p. 218°, and aniline with glacial acetic acid. When warmed with an excess of aniline, 2 : 4 : 6-trinitrobenzaldehyde affords the *compound* $[C_6H_3(NO_2)_3]_2,NHPh\cdot C_6H_2(NO_2)_2\cdot CH:NPh$, m. p. 110°, converted by boiling alcohol into 4 : 6-dinitro-2-anilinobenzylideneaniline and *s*-trinitrobenzene. The unusual mobility of all the atomic groups of trinitrobenzaldehyde is explained by the theory of the electromerism of the nitro-group and alternating polarity in the benzene nucleus (cf. Rădulescu and Alexa, A., 1930, 1087). H. Wren.

Diphenyl ether series. III. Derivatives of local anæsthetic type. C. M. Suter and E. Oberg (J. Amer. Chem. Soc., 1931, **53**, 1566—1569).—Interaction of *p*-chloronitrobenzene with the crude potassium salt of *p*-hydroxybenzaldehyde at 190—200° gives 4-p-*nitrophenoxybenzaldehyde*, m. p. 104—105°; with *o*-chloronitrobenzene 4-o-*nitrophenoxybenzaldehyde*, m. p. 84—85°, is obtained. The former is oxidised by chromic acid to 4-*p*-nitrophenoxybenzoic acid (cf. Haeussermann and Bauer, A., 1896, i, 676), from which, by means of the *chloride*, m. p. 79—80°, the *ethyl*, m. p. 74—75°, *butyl*, b. p. 250—255°/5 mm., and β-*diethylaminoethyl* (*hydrochloride*, decomp. 100—110°) esters are obtained. These are reduced by platinum and hydrogen to the *ethyl* (*hydrochloride*, decomp. 165°), *butyl* (*hydrochloride*, decomp. 155—160°), and β-*diethylaminoethyl* (*hydrochloride*) esters of 4-p-*aminophenoxybenzoic acid*, all of which exert considerable anæsthetic action, but are too toxic to be of practical value. 4-Nitro-4′-acetyldiphenyl ether (A., 1928, 180) is obtained by interaction of 4-nitrodiphenyl ether and acetyl chloride in carbon disulphide in presence of aluminium chloride. H. A. Piggott.

Action of diazomethane on piperonal. III. E. Mosettig and K. Czadek (Monatsh., 1931, 57, 291—304).—The suggestion that the intermediate formation of homopiperonal is responsible for the course of the reaction between diazomethane and piperonal (cf. A., 1929, 814) is supported by the formation of piperonylacetone and safrole oxide by the interaction of diazomethane and homopiperonal. 6-Nitropiperonal behaves towards diazomethane in methyl alcohol similarly to *o*-nitrobenzaldehyde (Arndt, A., 1928, 752), giving 6-*nitropiperonylethylene oxide*, m. p. 109—110°, as the principal product, and 6-*nitropiperonylacetone*, m. p. 144—144·5° [*semicarbazone*, m. p. 216° (decomp.)], as by-product. The former was identified by conversion into the *piperidinoalcohol*, m. p. 79°, and *chlorohydrin*, m. p. 128—129° (cf. Arndt, *loc. cit.*), and the latter by direct comparison with the product (and its semicarbazone) synthesised by nitration of piperonylacetone. 6-*Nitropiperonyl methyl ketone*, m. p. 122—123·5° (*semicarbazone*, m. p. 224—225°), was prepared by nitration of piperonyl methyl ketone for comparison with the isomeric ethylene oxide; it is oxidised by sodium hypochlorite in a water–chloroform emulsion to 6-*nitropiperonylic acid*, m. p. 172°, also obtained by oxidation of 6-nitropiperonal.

In contrast to diazomethane, diazoethane gives both with piperonal and 6-nitropiperonal the corresponding propiophenone as main product. 6-*Nitropiperonoylethane*, m. p. 68—69°, prepared in this way, is also obtained by nitration of piperonoylethane. It does not give a semicarbazone. H. A. Piggott.

Experiments on the production of a "tetrahydropyrone" [of 2-methyl-6-benzylidene*cyclo*hexanone]. R. Cornubert (Compt. rend., 1931, **192**, 958—959; cf. A., 1930, 343).—2-Methyl-6-benzylidene*cyclo*hexanone with hydrochloric acid gives a small amount of *substance*, m. p. 85—86°, and 2-*methyl*-6-(ω-*chlorobenzyl*)cyclo*hexanone*, m. p. 90—91°. The latter, as well as the original methylbenzylidene*cyclo*hexanone, give with benzaldehyde and hydrochloric acid two isomeric "*tetrahydropyrone*" derivatives of 2-methyl-6-(ω-chlorobenzyl)*cyclo*hexanone, m. p. 170—172° and 199—200°, respectively. A. A. Levi.

New derivatives in the *cyclo*octane series. M. Godchot and G. Cauquil (Compt. rend., 1931, **192**, 962—964; cf. A., 1928, 65).—Pure *cyclo*octanone b. p. 196—197°, new m. p. 38° (*carbanilido-oxime*, m. p. 98—99°; *dibenzylidene* derivative, b. p. 210—215°/10 mm.), was regenerated from the oxime, m. p. 35—36°. It is converted into *cyclo*octene, which when oxidised with perbenzoic acid gives cyclo*octene oxide*, b. p. 189—190°, m. p. 45°. Hydrolysis with dilute acid gives cyclo*octene*-1 : 2-*diol*, b. p. 135—140°/6 mm. (*diphenylurethane*, m. p. 166—167°). *cyclo*Octanone with sodamide and methyl iodide gives 2-*methyl*cyclo*octanone*, b. p. 74—75°/7 mm., d_{14}^{14} 0·9478, n_D^{14} 1·4675, purified by regeneration from the *semicarbazone*, m. p. 127—128° (*oxime*, b. p. 115°/7 mm.; *carbanilido-oxime*, m. p. 117—118°). Oxidation of this methyl*cyclo*octanone gives 3-keto-*n*-octoic acid. Further methylation of *cyclo*octanone gives a mixture of 2 : 2- and 2 : 8-dimethyl*cyclo*octanone. A. A. Levi.

Indones. XI. Stereoisomerism of indones and indenes. R. de Fazi (Gazzetta, 1931, **61**, 131—137).—The results of the author and of a number of others on these compounds are discussed. Theoretical considerations indicate the existence of two diphenylindenes, two diphenylhydrindenes, and two 2 : 3-diphenylhydrindones. Stereoisomeric formulæ are proposed for these compounds and the possible existence of two 2 : 3-diphenylindones is shown. T. H. Pope.

αβ-Unsaturated ketones. α-Bromo-β-aminobenzylideneacetophenones. C. Dufraisse and R. Netter (Compt. rend., 1931, **192**, 960—962; cf. A., 1927, 884).—Both stereoisomerides of phenyl α-bromo-β-ethoxystyryl ketone when treated with piperidine, benzylamine, or diethylamine give *phenyl α-bromo-β-piperidino-*, m. p. 144°, -β-*benzylamino-*, m. p. 114°, and -β-*diethylamino-styryl ketone*, m. p. 100°, respectively. On hydrolysis these give bromodibenzoylmethane. On similar treatment the same products are formed from phenyl α-bromo-ββ-diethoxy-β-phenylethyl, phenyl αβ-dibromo-β-ethoxy-β-phenylethyl, phenyl α-bromo-β-methoxystyryl, and

phenyl αβ-dibromostyryl ketones. In each case the same single stereoisomeride is produced. The bromoamino-derivatives readily lose bromine on reduction.

A. A. LEVI.

Oximes of o-hydroxybenzophenone. E. P. KOHLER and W. F. BRUCE (J. Amer. Chem. Soc., 1931, **53**, 1569—1574).—The preparation of anti-, m. p. 142—153° (*hydrochloride*, m. p. 118—120°), and syn-o-*hydroxybenzophenoneoxime*, m. p. 141—142° (*hydrochloride*, m. p. 132—134°), is described. The former is converted into the latter by aqueous alkalis or by subliming at 180—200°; the reverse change is effected by formic acid. Their configurations are assigned on account of the Beckmann rearrangement with phosphorus pentachloride by which they are converted into 1-phenylbenzoxazole and salicylanilide, respectively. In none of the above reactions could the formation of a benz*iso*oxazole derivative by dehydration of the oxime be detected; both hydrochlorides when heated at 140—145° likewise gave 1-phenylbenzoxazole free from phenylbenz*iso*oxazole.

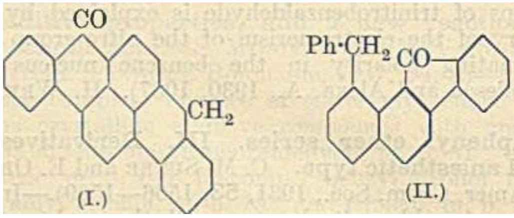
H. A. PIGGOTT.

Mixed benzoins. III. Structure of unsymmetrically substituted deoxybenzoins. J. S. BUCK and W. S. IDE (J. Amer. Chem. Soc., 1931, **53**, 1536—1542).—The oximes of the deoxybenzoins are subjected to the Beckmann rearrangement, and the arylamide produced is identified by hydrolysis, and by synthesis by the Schotten–Baumann reaction or by heating together the requisite acid and amine at 180—200°. The method was tested by application to *anisyl benzyl ketone*, m. p. 73° (synthesised by the Friedel–Crafts method from anisole and phenylacetyl chloride), the *oxime*, m. p. 114°, of which gives *phenylacetanisidide*, m. p. 121°, when treated with benzenesulphonyl chloride and aqueous sodium hydroxide. The oxime has therefore the *anti*-configuration; transposition of radicals, as suggested by Meisenheimer (A., 1922, i, 152), does not occur in this case, and is therefore considered unlikely in the others.

The constitutions of the following hydrobenzoins, prepared by reduction of the corresponding mixed benzoins with tin and alcoholic hydrochloric acid, were determined in this manner: 3 : 4-dimethoxyphenyl o-chlorobenzyl ketone (anti-*oxime*, m. p. 137°; cf. A., 1930, 1586); anisyl o-chlorobenzyl ketone (anti-*oxime*, m. p. 97°; cf. *loc. cit.*); p-*dimethylaminophenyl* o-*chlorobenzyl ketone*, m. p. 122° (anti-*oxime*, m. p. 173°); *piperonyl* o-*chlorobenzyl ketone*, m. p. 105° (anti-*oxime*, m. p. 120°); phenyl *p*-methoxybenzyl ketone (anti-*oxime*, m. p. 133°; syn-*oxime*, m. p. 94°; cf. Kinney, A., 1929, 829); *piperonyl benzyl ketone*, m. p. 86° (anti-*oxime*, m. p. 103°; syn-*oxime* [?], m. p. 130°), and *p*-dimethylaminophenyl benzyl ketone (*anti*-oxime; cf. this vol., 224). The following appear to be new: o-*chlorophenylacetoanisidide*, m. p. 163°; o-*chlorophenylaceto*-p-*dimethylaminoanilide*, m. p. 165°, and -3 : 4-*methylenedioxyanilide*, m. p. 175°; *anisylacetanilide*, m. p. 113°; *benzoyl*-p-*methoxybenzylamine*, m. p. 96°; *phenylacet*-3 : 4-*methylenedioxyanilide*, m. p. 146°, and -p-*dimethylaminoanilide*, m. p. 144°.

H. A. PIGGOTT.

Naphthalene group. I. New hydrocarbons and ketones derived from phenylnaphthylmethane and phenyl naphthyl ketone. K. DZIEWOŃSKI and J. MOSZEW (Rocz. Chem., 1931, **11**, 169—192).—4-Benzoyl-1-benzylnaphthalene (A., 1930, 763) yields 5-*nitro*-4-*benzoyl*-1-*benzylnaphthalene*, m. p. 165—166°, on nitration, whilst with chlorosulphonic acid 4-*benzoyl*-1-*benzylnaphthalene*-5-*sulphonic acid* (*aniline* salt, m. p. 221—222°; *chloride*, m. p. 155—156°; *amide*, m. p. 182—183°) is obtained. When heated for 3 hrs. at 130—150° with aluminium chloride 4 : 5 : 8 : 9-*dibenzo*-10-*keto*-3-*hydropyrene* (I), m. p. 169—170°, is obtained. 1-Benzoyl-8-benzylnaphthalene (see A., 1930, 606) is converted by heat-



(I.) (II.)

ing with aluminium chloride at 120—145° into *benzylchrysofluorene* (II), m. p. 167—168°. The following derivatives are described: 1-*benzoyl*-4-*propionylnaphthalene*, m. p. 69—70° (*oxime*, m. p. 129—130°); 1-*benzoylnaphthalene*-4-*sulphonic acid* (*aniline* salt, m. p. 236—237°; *chloride*, m. p. 117—119°; *amide*, m. p. 199—200°; *anilide*, m. p. 175—177°) (see also A., 1930, 917).

R. TRUSZKOWSKI.

Synthesis of 4-hydroxy-3-methoxyphenylethyl n-pentadecyl ketone. T. NISHIMURA (Sci. Rep. Tohoku, 1931, **20**, 97—100).—4-*Hydroxy*-3-*methoxyphenylethyl* n-*pentadecyl ketone*, m. p. 68·5—69·5°, obtained by catalytic reduction of 4-*hydroxy*-3-*methoxystyryl* n-*pentadecyl ketone*, m. p. (anhydrous) 76—77·5°, formed by the condensation of vanillin with methyl *n*-pentadecyl ketone (from ethyl palmitylacetoacetate) in the presence of aqueous-alcoholic potassium hydroxide, has no pungent taste (cf. Nomura and Hotta, A., 1925, i, 1156; Nomura and Tsurumi, A., 1927, 1078; Oyamada, A., 1930, 476).

A. RENFREW.

Anthraquinone azo-compounds. II. Insoluble disazo-dyes from 1 : 5-diaminoanthraquinone. T. MAKI (J. Soc. Chem. Ind. Japan, 1931, **34**, 51—56B; cf. A., 1930, 346).—1 : 5-Diaminoanthraquinone is tetrazotised in sulphuric acid with powdered sodium nitrite, and after keeping for 20 hrs. at 0—5° the mixture is poured into ice-water and neutralised with sodium hydroxide. The tetrazo-compound is coupled with 2 mols. of α-naphthylamine [m. p. 256° (decomp.); violet-brown on acetate silk], β-naphthylamine [m. p. 269·9° (decomp.); similar on acetate silk], aniline [m. p. 248·5° (decomp.); reddish-orange on acetate silk], *m*-phenylenediamine [m. p. 259·6° (decomp.); brown on acetate silk], α-naphthol (decomp. above 340°; brown on acetate silk), phenol [m. p. 280·8° (decomp.); small affinity for acetate silk and useless as ice colour], and resorcinol (decomp. above 400°; reddish-brown on acetate silk).

C. HOLLINS.

Flavanthrene. E. SCHWENK and H WALDMANN (J. pr. Chem., 1931, [ii], **130**, 79—80).—The interaction of 1 : 2-dibromoanthraquinone with copper powder in nitrobenzene at 200—210° gives 2 : 2′-*di*-

bromo-1 : 1′-*dianthraquinonyl*, m. p. above 400°, which with aqueous ammonia and copper sulphate at 230—240° gives flavanthrene (cf. B.P. 336,983; B., 1931, 150). H. A. PIGGOTT.

Fractionation and isomerisation of carotene. R. KUHN and E. LEDERER (Naturwiss., 1931, **19**, 306).—Carotene from various sources has a positive rotation after repeated crystallisation. By fractional adsorption or fractional precipitation with iodine it is separated into α-*carotene* (5—15%), m. p. 172—173°, $[\alpha]_{Cd}^{20}$ +380°, in benzene, and β-*carotene*, m. p. 180—181°, $[\alpha]_{Cd}^{20}$ <±5°. Carotene tetraiodide, decomposed with mercury or thiosulphate, gives iso*carotene*, m. p. 183—185°, in good yield. All three have the formula $C_{40}H_{56}$. Absorption spectra data are given for these substances and for their coloured solutions with antimony trichloride in chloroform. A. A. LEVI.

Plant colouring matters. XXX. Carotene, xanthophyll, fucoxanthin, and capsanthin. P. KARRER, A. HELFENSTEIN, H. WEHRLI, B. PIEPER, and R. MORF (Helv. Chim. Acta, 1931, **14**, 614—632). —The fraction of carotene (α), m. p. 170°, more soluble in light petroleum is strongly dextrorotatory $[\alpha]_C^{18}$ +136°, and is reduced with aluminium amalgam to a mixture of di- and tetra-hydro-derivatives, $[\alpha]_D$ +60°, whilst pure β-carotene, m. p. 181—182°, is probably optically inactive and affords a reduction product, $[\alpha]_D$ +13°, from which a least-soluble fraction, $[\alpha]_D$ +4°, can be separated. The inactive β-carotene is probably represented by the structure previously suggested (A., 1930, 1422), whilst three possible modified structures, containing an asymmetric carbon atom in one or both of the dimethyl*cyclo*hexene rings, are suggested for the α-isomeride. The existence of isomeric carotenes suggests the similar existence of related isomeric xanthophylls, and by extraction of dried stinging-nettle leaves with ether, hydrolysis of the chlorophyll in the extract with methyl-alcoholic potassium hydroxide, extraction of the residue from the ether solution with light petroleum, and repeated crystallisation from methyl alcohol is obtained a xanthophyll, m. p. 192°, $[\alpha]_C$+110° to +130°, whereas from the same source Zechmeister and Tuzson (A., 1929, 1306) obtained a specimen of m. p. 172—174°, $[\alpha]_C$ +137° to 192°. No appreciable amount of xanthophyll esters is present in the leaves. Extraction of *Fucus vesiculosus* on similar lines with 90% alcohol affords fucoxanthin (2 g. from 15 kg. of the air-dried algæ), which on oxidation with cold, alkaline potassium permanganate gives acetic acid (4·24 mols.) and dimethylmalonic acid. Similar oxidation of xanthophyll and capsanthin, $C_{35}H_{50}O_3$, affords acetic acid (3·77 mols.), dimethylmalonic and αα-dimethylsuccinic acids, whilst carotene gives these acids and αα′-dimethylglutaric acid in addition. In the presence of platinum-black in acetic acid fucoxanthin absorbs hydrogen equivalent to 10 or 11 double linkings, but evidence relating to the number of hydroxyl groups is inconclusive. Capsanthin contains two hydroxyl groups. J. W. BAKER.

Tauro*iso*lithocholic acid from chicken bile. T. HOSIZIMA, H. TAKATA, Z. URAKI, and S. SIBUYA (J. Biochem., Japan, 1930, **12**, 393—397).—Chicken bile is freed from mucus with alcohol and concentrated at 100° to the original volume. Ferric chloride is added until no further precipitate is obtained; the precipitate is collected and decomposed with warm sodium carbonate solution. The filtrate is evaporated and the dry residue extracted with alcohol. The alcoholic solution is decolorised and evaporated, the residue being dissolved in alcohol, decomposed with sulphuric acid, and mixed with ether. The flocculent precipitate is dissolved in dilute sodium carbonate solution, gradually acidified with hydrochloric acid, and extracted with ether. The precipitate, m. p. 210—211°, [α] +65·74°, is tauro*iso*lithocholic acid, $C_{23}H_{39}O\cdot CO\cdot NH\cdot CH_2\cdot CH_2\cdot SO_3H$ (sodium and barium salts). CHEMICAL ABSTRACTS.

Caoutchouc. XII. Lævulic peroxide from caoutchouc. XIII. Degradation of caoutchouc by ozone. R. PUMMERER, G. EBERMAYER, and K. GERLACH (Ber., 1931, **64**, [*B*], 804—809, 809—825).—XII. The "lævulaldehyde diperoxide" obtained by Harries is formed by over-ozonisation of caoutchouc ozonide or when solutions of the latter compound are preserved at a low temperature. Determination of mol. wt. in boiling ethyl alcohol or freezing dioxan indicates the formula $(C_5H_8O_4)_2$. The compound dissolves readily in cold sodium hydrogen carbonate solution and can be sharply titrated. It reacts very slowly with 2 : 4-dinitrophenylhydrazine. With aluminium amalgam in alkaline solution it affords lævulic acid in more than 90% yield. It reacts slowly with cold titanium trichloride, yielding lævulic, succinic, and formic acids. Hydrogen in presence of platinum gives lævulic and succinic acids. The compound is therefore regarded as the ketoperoxide of lævulic acid, $\left| CO_2H\cdot CH_2\cdot CH_2\cdot CMe{<}{}^{O\cdot}_{O\cdot} \right|$

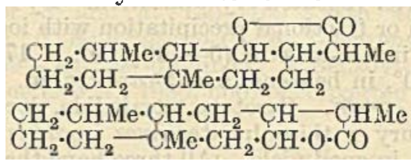
XIII. Decomposition of caoutchouc ozonide with boiling water and removal of volatile products with steam involves secondary changes (oxidative fission of lævulic acid and transformation of lævulic peroxide). For the detection of acetone short decomposition with steam followed by distillation with steam in a vacuum is advantageous, but anomalous products are best excluded by avoiding rise in temperature. After ozonisation in chloroform, the product is therefore treated with hydrogen in presence of spongy platinum, with calcium filings and oxalic acid, or with aluminium amalgam in neutral solution. The caoutchouc ozonide at first remains dissolved in chloroform, but when the solution is kept at 0° lævulic acid peroxide separates in considerable amount, thereby affording a convenient means of weighing a portion of the lævulic acid. After removal of the chloroform the residual ozonide is soluble in ether and readily reduced. Immediately after ozonisation it is sparingly soluble in ether and requires intense agitation during reduction. The various products are determined by titration or quantitative precipitation. The yield of derivatives of the lævulic series approaches 90%. The occurrence of acetic acid (minimal 2%), traces of acetone (probably arising from an impurity), and of a substance fermentable by dried yeast (probably pyruvic acid) has not been observed previously. Carbon dioxide and formic acid each occur to the extent of 1—2% (minimum 0·9%). Succinic acid appears in varying amount, probably

derived from lævulic acid peroxide. The total yield of products, calculated on the carbon skeleton of the caoutchouc used, reaches 95% with conservative calculation. The conception that caoutchouc is formed by agglomeration of *iso*pentene groups receives strong support, but Harries' dictum that no fission products with less than five carbon atoms can be obtained which might be regarded as terminal members of an open chain cannot be maintained definitely. Acetic acid and the supposed pyruvic acid cannot be assigned to definite terminal groups. The question of the existence of terminal groups is regarded as open. H. WREN.

Caoutchouc. XIV. Behaviour of caoutchouc towards iodine chloride and dithiocyanogen. R. PUMMERER and H. STARK (Ber., 1931, **64**, [*B*], 825—830).—Consistent results are obtained in the titration of caoutchouc with iodine chloride only when a 10—20% excess of the latter substance is used. Within these limits very little or no acid is produced. With larger excesses of iodine chloride, higher iodine and acid values are obtained, denoting substitution. Similar observations are made with gutta-percha. Various fractions of sol caoutchouc give iodine values lying very close to 100, whilst for gel caoutchouc the data 99·1, 99·3, and 99·1 are obtained. There is no fundamental difference between sol and gel caoutchouc with regard to readiness of substitution by iodine chloride. It is not possible to establish the presence of a terminal isoprene group in caoutchouc by means of iodine chloride; the optical method is definitely preferable. With hentriacontene and *cyclo*hexene an excess of iodine chloride is harmless, whereas with limonene and trimethylethylene more than two double linkings are indicated by the use of a considerable excess. Vinyl bromide reacts more slowly than a normal olefine, but complete saturation is obtained after 50 hrs. with use of 180% of iodine chloride. *s*-Dichloroethylene does not react.

Thiocyanogen is less suitable than iodine chloride, since partial gelatinisation occurs, which hampers the withdrawal of samples. There is only a relatively short interval within which the consumption of thiocyanogen remains constant; subsequently, caused either by the caoutchouc thiocyanate or by traces of eliminated thiocyanic acid, gradual decomposition of the excess of thiocyanogen ensues. During the short, constant interval the addition of 1 mol. of dithiocyanogen per C_5H_8 residue is observed. *Caoutchouc thiocyanate*, $C_5H_8(SCN)_2$, has been isolated. H. WREN.

Bitter substances. II. Bitter substances from the elecampane root. K. F. W. HANSEN (Ber., 1931, **64**, [*B*], 943—947; cf. this vol., 360).—When slowly reduced with sodium amalgam, alantolactone, like *iso*alantolactone, gives a *dihydro*-derivative, m. p. 126°. Hydrogenation of alantolactone, *iso*alantolactone, or bitter substance III (*loc. cit.*) in presence of spongy platinum affords *tetrahydroalantolactone*, $C_{15}H_{24}O_2$, m. p. 147·5°. The isomerism of alanto- and *iso*alanto-lactones is therefore conditioned by the arrangement of the double linkings. Tetrahydroalantolactone is converted by the successive action of potassium hydroxide and diazomethane into *methyl tetrahydroalantolate*, $C_{16}H_{28}O_3$, m. p. 114°, reduced by sodium and alcohol to the corresponding glycol, from which the hydrocarbon is obtained by means of phosphorus and hydriodic acid; this is dehydrogenated to endalin (picrate, m. p. 90°; styphnate, m. p. 118°). The formula I or II is therefore assigned to tetrahydroalantolactone

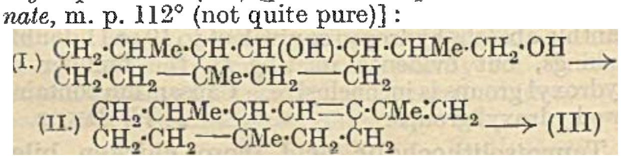


(I.)

(II.)

It is suggested that the alantolactones are derived from αβ-unsaturated acids and that the so-called amides are really additive products of lactone and ammonia. Confirmation of this view is found in the formation of additive *products* from diazomethane and *iso*alantolactone, $C_{16}H_{23}O_2N_3$, m. p. 157° (decomp.) (corresponding *acid*, m. p. 143°), and alantolactone, m. p. 116—117° (decomp.) (corresponding *acid*, m. p. 135—136°). Bitter substance III gives the *methyl* ester, $C_{16}H_{26}O_2$, m. p. 101°. H. WREN.

Higher terpene compounds. XLV. Alantolactone and *iso*alantolactone. L. RUZICKA and J. A. VAN MELSEN. **XLVI. Stepwise degradation of caryophyllene with ozone and hypobromite.** L. RUZICKA and A. H. WIND. **XLVII. Caryophyllenic acid.** L. RUZICKA, J. C. BARDHAN, and A. H. WIND (Helv. Chim. Acta, 1931, **14**, 397—410, 410—423, 423—435).—XLV. (cf. Hansen, this vol., 360). Both alanto- and *iso*alanto-lactones are dehydrogenated by selenium, giving 1-methyl-7-ethylnaphthalene, and hydrogenated (platinum-black) to the same *tetrahydro*-derivative, m. p. 143—144°, $[\alpha]_D$ +15·2°, +16·0° in alcohol; this has the same m. p. as, and is probably a stereoisomeride of, deoxytetrahydrosantonin (Clemo and Haworth, this vol., 227). There is evidence of the intermediate formation of dihydro-derivatives in each case, although from the products of incomplete hydrogenation of *iso*alantolactone a new *tetrahydro*-derivative, m. p. 159—160°, may be isolated. Reduction of alantolactone with sodium and alcohol gives the *glycol*, $C_{15}H_{26}O_2$, b. p. 168—170°/0·4 mm., from which no definite product could be isolated by heating with aqueous hydrobromic acid, etc. With the *glycol* (I), b. p. 167—170°/0·4 mm., from tetrahydrolantolactone, however, hydrobromic acid gives the *dibromide*, $C_{15}H_{26}Br_2$, which with quinoline at 200° gives a *hydrocarbon* (II), b. p. 130—133°/12 mm., of sesquiterpene character, dehydrogenated by selenium to 1-*methyl*-7-iso*propenylnaphthalene* (III) [*picrate*, m. p. 87—88°; *styphnate*, m. p. 112° (not quite pure)]:

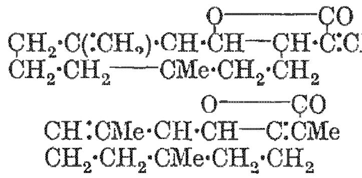


Hydrolysis of the ozonide of a somewhat impure alantolactone (m. p. 66—72°) and oxidation of the product with alkaline permanganate after removal of the acetic acid gives β-3-*keto*-1-*methyl*cyclo*hexane*-1-

propionic acid, m. p. 92—93° [*semicarbazone*, m. p. 183—185° (*methyl* ester, m. p. 207—208°)], and a *ketonic lactone*, $C_{14}H_{20}O_3$, m. p. 203—205°, probably

$CH_2{\cdot}CO{-}CH{-}CH{\cdot}O{\cdot}CO$
$CH_2{\cdot}CH_2{\cdot}CMe\ CH{-}CHMe$, derived from a dihydro-
$CH_2{-}CH_2$

derivative in the crude alantolactone. The annexed structures are suggested for the isomeric alanto-



lactones, as agreeing best with the above evidence, their behaviour on reduction with sodium amalgam, and the existence of distinct dihydrochlorides of each form. It is suggested, however, that the present products, although crystalline, may contain isomerides. In elecampane oil they are accompanied by oily isomerides which give 1-methyl-7-ethylnaphthalene on dehydrogenation, and sesquiterpenes, $C_{15}H_{24}$, b. p. 135—138°/12 mm., converted by dehydrogenation into 1-methyl-7-*iso*propylnaphthalene.

Oxidation of 1-methyl-7-ethylnaphthalene with alkaline ferricyanide gives naphthalene-1 : 7-dicarboxylic acid, m. p. 294—296° (dimethyl ester, m. p. 86—87°; cf. A., 1923, i, 119).

XLVI. The acid, $C_{11}H_{18}O_3$, derived by degrading caryophyllene with ozone (Semmler and Mayer, A., 1912, i, 120), is oxidised by aqueous hypobromite to a *dicarboxylic acid*, $C_{10}H_{16}O_4$, b. p. 175°/0·4 mm. (*dimethyl* ester, b. p. 140—142°/12 mm.), and therefore contains the acetyl group. The diketocarboxylic acid, $C_{14}H_{22}O_4$, α_D +50·5° (*loc. cit.*), when similarly treated, gives a *ketodicarboxylic acid*, $C_{13}H_{20}O_5$ (isolated as *dimethyl* ester, b. p. 155—160°/0·5 mm., n_D^{20} 1·4873, d_4^{20} 1·1390), the acid $C_{13}H_{18}O_4$ (below), and unidentified products. The methyl ester of the acid $C_{14}H_{22}O_4$ is dehydrated by boiling 10% alcoholic sodium hydroxide or by sodium methoxide to an unsaturated acid, $C_{14}H_{20}O_3$ (isolated as an impure *methyl* ester, b. p. 140—143°/0·5 mm.), which is oxidised by hypobromite to a *dicarboxylic acid*, $C_{13}H_{18}O_4$, m. p. 148—149° (*dimethyl* ester, b. p. 128—129°/0·3 mm., 139—140°/0·6 mm., d_4^{17} 1·0775, n_D^{17} 1·4894); this is hydrogenated (platinum oxide) to a *dihydro*-derivative, m. p. 149°, and converted by ozonisation into a *ketodicarboxylic acid*, $C_{12}H_{18}O_5,H_2O$, m. p. 70° (*dimethyl* ester, b. p. 135—136°/0·3 mm., d_4^{18} 1·0856, n_D^{18} 1·4625). It is considered that the acid $C_{13}H_{18}O_4$ is formed thus:

$$CO_2H{\cdot}C_9H_{16}\begin{cases}{-}CH_2Ac\\ {:}CO\end{cases}\xrightarrow{-H_2O} CO_2H{\cdot}C_9H_{16}\begin{cases}{-}CAc\\ {:}C\end{cases}\xrightarrow{\text{oxidation}} CO_2H{\cdot}C_9H_{16}\begin{cases}{-}C{\cdot}CO_2H\\ {:}C\end{cases}.$$

XLVII. The dimethyl ester of caryophyllenic acid, prepared by a slight modification of the method of Semmler and Mayer (*loc. cit.*), can be separated into four main fractions ($C_{11}H_{18}O_4$) boiling between 110° and 125°/12 mm. Hydrolysis of the individual fractions, conversion into the anhydride, and regeneration of the acid by hydration gave with the three lower fractions an acid of m. p. 145—150°, intermediate in composition between caryophyllenic acid and its next lower homologue, and with the fraction of b. p. 124—125°/12 mm. an acid, m. p. 66—75°, approximating more nearly in composition to caryophyllenic acid. Interaction of the ester (b. p. 120—121°/12 mm.) with the appropriate Grignard reagent gives a *tetramethyl*-, m. p. 99—100°, and a *tetraphenyl-glycol*, $C_7H_{12}(CPh_2{\cdot}OH)_2$, m. p. 198—199°. The former is oxidised by chromic anhydride in acetic acid to $\alpha\alpha\alpha'\alpha'$-tetramethylglutaric acid, but the latter gives benzophenone (1·8 mols.) and *as*-dimethylsuccinic acid (0·5—0·6 mol.); the behaviour of the former is regarded as due to rearrangement involving the entry of the carbinol C-atom into the ring-system. The tetraphenylglycol loses $2H_2O$ when heated with a mixture of formic and acetic acids to give a *hydrocarbon*, $C_{33}H_{30}$, b. p. about 235°/0·2 mm. With acetic acid alone only 1 mol. of water is lost, and the *substance* $C_{33}H_{32}O$, b. p. about 240°/0·3 mm., results; this gives benzophenone on oxidation, so that dehydration appears to be unaccompanied by alteration in ring structure. The results of oxidation of the tetraphenylglycol and the marked contrast of the ready hydrolysis of the methyl ester of caryophyllenic acid to the *methyl hydrogen* ester, b. p. 130—134°/0·4 mm. (*chloride*, b. p. 115—118°/12 mm.; *amide*, b. p. 135°/0·4 mm.; *hydrazo*-derivative (?), b. p. 240°/0·3 mm.), with the behaviour of methyl camphorate, do not accord with the structure suggested for caryophyllenic acid by Semmler and Mayer.

H. A. PIGGOTT.

Ascaridole. I. F. RICHTER and W. PRESTING (Ber., 1931, **64**, [*B*], 878—882).—Ascaridole is converted by palladium saturated with hydrogen in presence of methyl alcohol into Δ^2-p-*menthene*-1 : 4-*diol*, m. p. 78—79°, oxidised by potassium permanganate to $\alpha\alpha'$-dihydroxy-α-methyl-α-*iso*propyladipic acid, m. p. 208—209° (corr.), and hydrogenated to *cis*-*p*-menthane-1 : 4-diol. The unsaturated diol is smoothly oxidised by perbenzoic acid to a *compound*, $C_{10}H_{20}O_3,H_2O$, readily dehydrated to 2 : 3-oxido-*p*-menthane-1 : 4-diol, m. p. 102°, apparently identical with the β-glycol of Nelson (A., 1911, i, 797; 1913, i, 189). Confirmation is thus given of Wallach's formula for ascaridole (A., 1912, i, 878). *γ-Terpinine dioxide*, b. p. 105—107°/6 mm., $d_4^{18\cdot5}$ 1·0295, n_D^{19} 1·468, is described incidentally.

H. WREN.

Decomposition of rotenone in solution. H. A. JONES (Ind. Eng. Chem., 1931, **23**, 387—388).—In solution, rotenone decomposes in the presence of air, as the change in colour indicates. The yellow crystals formed in stale pyridine solution and other solvents are a mixture of dehydrorotenone and rotenonone (H. L. HALLER). Decomposition proceeds most rapidly in pyridine solution, but slowly in acetone; no appreciable change in colour occurs in benzene or water during several months. Dry rotenone is stable.

E. LEWKOWITSCH.

Action of Japanese clay on terpene compounds. II. Cyclisation of citronellal. T. KUWATA (J. Soc. Chem. Ind. Japan, 1931, **34**, 70—72B).—The violent action of Japanese acid clay on citronellal is moderated by suspending the clay in 10 parts of methyl alcohol. The product under these conditions contained *iso*pulegol (32% crude yield, b. p. 80—90°/10

mm.) and methoxylated compounds derived from the acetal of citronellal. Both *iso*pulegol and the alkoxy-compounds are stable towards the acid clay, and may be used as diluents instead o1 the alcohol, the products then being *iso*pulegol and polymerides (b. p. 190—200°/20 mm., d_4^{20} 0·9072, n_D^{20} 1·4758). C. HOLLINS.

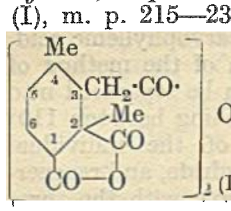
Action of hydroferrocyanic acid on dicyclic terpenes: new partial synthesis of terpene bases and alcohols. K. STEPHAN and T. HAMMERICH (J. pr. Chem., 1931, [ii], **129**, 285—308).—Various dicyclic terpenes form stable crystalline compounds of the type $(C_{10}H_{17})_2H_2Fe(CN)_6$ with hydroferrocyanic acid. These are decomposed by heating with 15% aqueous potassium hydroxide at 160°/9—10 atm., forming (in addition to iron oxide, potassium formate, and ammonia) terpenes, terpene alcohols, $C_{10}H_{17}\cdot OH$, and bases, $C_{10}H_{17}\cdot NH_2$. The terpenes and alcohols are formed by hydrolysis of true esters of hydroferrocyanic acid, and the bases by hydrolysis of the unstable carbylamines resulting from the isomerides in which the terpene framework (or the isomerised skeleton) is directly attached to the nitrogen of the cyano-group. The *compound* from camphene decomposes to give 7% of iso*bornylamine*, b. p. 199—203°, m. p. 162—163° (corr.), d^{20} 0·888 [*phenylurethane*, m. p. 253—254° (corr.); *phenylthiourethane*, m. p. 181·5° (corr.)], 50% of camphene, and 43% of a mixture of camphene (74·4%), camphene hydrate (23·1%), and *iso*borneol (2·5%). With α-pinene hydroferrocyanic acid forms a *compound*, decomposed to give 70% of a mixture of α-terpineol, limonene, and dipentene, and 30% of a mixture of *iso*bornyl- and *iso*fenchyl-amine. In addition, the autoxidation products of pinene, verbenol, and verbenone, and its hydration product, α-terpineol, are isolated as *oxonium* salts with the hydroferrocyanic acid, whilst terpin hydrate is also formed. Similarly with β-pinene (nopinene), α-terpineol is isolated as its *oxonium* salt with hydroferrocyanic acid, or is further hydrated to terpin hydrate, and the *compound* formed is decomposed, giving 45% of iso*fenchylamine*, b. p. 88—95°/16 mm., d^{20} 0·914, n_D 1·4867, $[\alpha]_D$ −40·5° [*phenylurethane*, m. p. 258° (corr.) (decomp.); *phenylthiourethane*, m. p. 175—176° (corr.)], and 55% of a mixture of α-terpineol and limonene. The mechanisms of the formation of these products are discussed.

J. W. BAKER.

Complex sodium and gold salts of camphordithiocarbonic acid. L. LECOQ (Compt. rend., 1931, **192**, 846—849).—Sodium camphordithiocarbonate (Tschugaev and Pigulevski, A., 1911, i, 797) and gold chloride in aqueous solution give *sodium aurous camphordithiocarbonate nonahydrate*, $NaAu(C_{10}H_{14}O\cdot CS_2)_2,9H_2O$ (*trihydrate*, *monohydrate*, and *anhydrous* salts described). Acidification of solutions of the salt in ether precipitates *aurocamphordithiocarbonic acid*, which readily loses hydrogen sulphide. G. DISCOMBE.

Catalytic hydrogenation of sabinene. I. F. RICHTER, W. WOLFF, and W. PRESTING (Ber., 1931, **64**, [*B*], 871—878).—Catalytic hydrogenation of sabinene at the ordinary temperature in presence of palladium-black gives a product, $C_{10}H_{18}$, b. p. 156—156·8°/757·5 mm., d_4^{15} 0·811, identical with the dihydrosabinene of Wallach (A., 1912, i, 202). Titration of the product with perbenzoic acid reveals the presence of a double linking. Since instability towards the reagent is shown not to be due to the three-membered ring (established by the behaviour of sabinaketone, carone, thujone, and thujane), the product is considered to be unsaturated and to be 1 : 2-*dimethyl*-3-iso*propyl*cyclo*pentene*, in which the position of the double linking is undecided. Confirmation of this view is found in the further hydrogenation of "dihydrosabinene" to 1 : 2-dimethyl-3-*iso*propyl*cyclo*pentane (cf. Kasanski, A., 1929, 1286). Hydrogenation of sabinene in presence of platinum-black gives thujane, stable towards perbenzoic acid and further hydrogenation and identical with the product of Tschugaev and Fomin (A., 1911, i, 72). H. WREN.

Higher terpene compounds. XLVIII. Constitution of the tricarboxylic acids, $C_{11}H_{16}O_6$ and $C_{12}H_{18}O_6$, obtained by oxidation of abietic acid. Carbon skeleton of abietic acid. L. RUZICKA, M. W. GOLDBERG, H. W. HUYSER, and C. F. SIEDEL (Helv. Chim. Acta, 1931, **14**, 545—570).—In the oxidation of abietic acid (3 kg.) with potassium permanganate (24 and 12 atoms of oxygen) (Ruzicka and others, A., 1925, i, 1419) or with potassium permanganate (10 atoms of oxygen) and subsequent oxidation with nitric acid, both the *cyclo*hexane acids,
(22 g.) and $C_{11}H_{16}O_6$ (24 g.), are formed and are separated either by fractional hydrolysis of their trimethyl esters (ester of C_{12} acid completely hydrolysed) or by fractional esterification (C_{12} acid completely esterified). Thus are obtained the 3-*monomethyl* ester, m. p. 188—190° (converted by acetyl chloride at 100° into its *anhydride*, m. p. 137—137·5°), and 1 : 2-*dimethyl* ester, m. p. 119—120° (crystallographic and optical data by NANNINGA), of the C_{11} acid. Dehydrogenation of the C_{11} acid with selenium affords *m*-xylene (25% yield). The C_{12} acid similarly gives 1 : 2 : 3-trimethylbenzene, hemellitic acid, and its trimethyl ester. Hence the methyl group which is eliminated in the dehydrogenation of abietic acid to retene must be in the 12 position, and not at position 11 as previously supposed. The C_{11} acid is converted by heating above its m. p. or, better, by heating with acetyl chloride into two isomeric *anhydrides*, separated by fractional crystallisation from benzene, m. p. 170—172° (least soluble) (converted by methyl-alcoholic sodium methoxide into a *substance*, m. p. 150—160°) and m. p. 98—100°, respectively. Partial esterification of the C_{11} acid with 3·5% methyl-alcoholic hydrogen chloride affords the 1-*monomethyl* ester, m. p. 154—156° (*anhydride*, m. p. 103—104°). Similarly, the C_{12} acid affords a unimolecular *anhydride*, m. p. 182—183°, and a bimolecular *anhydride* (I), m. p. 215—235° indefinite, which is hydrolysed to the parent acid only with difficulty. Partial esterification of the C_{12} acid with 5% methyl-alcoholic hydrogen chloride gives the 1 : 3-*dimethyl* ester, m. p. 148—149°, the *trimethyl* ester, b. p. 133—134°/0·1 mm., being obtained by the silver salt method. Oxidation of the C_{12} to the C_{11} acid could not be effected. Quantit-



(I.)

ative investigations on the relative ease of hydrolysis of these various methyl esters are described, the results indicating that a neighbouring carboxyl group has a greater steric effect than has the $\cdot CH_2\cdot CO_2H$ group in the C_{12} acid. Electrolysis of the 1 : 2-dimethyl ester of the C_{11} acid affords a bimolecular *ester* (45%), b. p. 200—220 /0·3 mm., and a unimolecular *ester*, b. p. 120—155°/11 mm., which is hydrolysed to 2 : 4-*dimethyl*-Δ^3-cyclo*hexene*-1 : 2-*dicarboxylic acid*, m. p. 163—165°. J. W. BAKER.

Higher terpene compounds. XLIX. Clovene. L. RUZICKA, D. T. GIBSON, and [in part] R. BLAIR (Helv. Chim. Acta, 1931, **14**, 570—577).—Fractionation of clovene (prepared from caryophyllene by a modification of Asahina and Tsukamoto's method, A., 1922, i, 845) affords two main fractions, b. p. 117—119°/16 mm. and b. p. 122—124°/16 mm. The best yields of crystalline products are obtained by oxidation of these fractions with chromic oxide (4 atoms of oxygen) and acetic acid, which affords *clovenic acid*, $C_{15}H_{24}O_4$, in 50% yield (*methyl*, b. p. 136—137°/0·3 mm., d_4^{20} 1·088, n_D 1·4901, and *ethyl*, b. p. 135—138°/0·2 mm., esters). This is readily converted into its *anhydride*, m. p. 50—51°, by short heating above its m. p. or by heating with thionyl chloride or phosphorus tribromide. Magnesium methyl iodide converts methyl clovenate into a neutral *product*, b. p. 150—155°/0·2 mm., and an alkali-soluble substance, $C_{16}H_{24}O_2$, m. p. 137—138° (possibly

oxidised either by chromic anhydride or by sodium hypobromite to clovenic acid, whilst with magnesium ethyl iodide the anhydride yields a *substance*, $C_{17}H_{28}O_3$, m. p. 137—138° (depresses m. p. of above substance) (possibly $COEt\cdot C_{13}H_{22}\cdot CO_2H$), also oxidised to clovenic acid. These results are not in agreement with the structure previously suggested for caryophyllene and clovene (Henderson and others, A., 1929, 931). J. W. BAKER.

Sclareol and its derivatives. M. JANOT (Compt. rend., 1931, **192**, 845—846).—Sclareol, a dihydric alcohol, $C_{20}H_{36}O_2$, from *Salvia sclarea*, L. (this vol., 94), has b. p. 163—164°/0·25 mm., m. p. 105—106°, and is reduced, according to conditions, to *dihydrosclareol*, or to a monohydric *alcohol*, b. p. 130—132°/0·1 mm. *Sclareolic acid*, $C_{19}H_{34}O_4$, m. p. 153—155°, on complete dehydration gives *sclarene* and cyclo*sclarene*, $C_{20}H_{32}$. G. DISCOMBE.

Higher terpene compounds. L. Sclareol. L. RUZICKA and M. M. JANOT (Helv. Chim. Acta, 1931, **14**, 645—650).—Sclareol (Volmar and Jermstad, A., 1928, 524; Janot, preceding abstract) is reduced by hydrogen at platinum-black in ethyl acetate to the dihydro-compound, m. p. 114—115°, which also contains two hydroxyl groups. When heated with naphthalene-2-sulphonic acid at 140° in a current of carbon dioxide it yields sclarene, b. p. 125—128°/0·8 mm., d_4^{17} 0·9388, n_D^{17} 1·5217, which contains three double linkings and is cyclised by heating with 100% formic acid at 120° to give a *substance*, b. p. 118—122°/0·1 mm., d_4^{16} 0·9462, n_D^{16} 1·5190, which contains two double linkings. Dehydrogenation of sclareol with selenium gives 1 : 5 : 6-trimethylnaphthalene. Ozonolysis of sclareol affords formaldehyde in good yield. Oxidation of sclareol with chromic oxide and acetic acid affords a neutral *substance*, $C_{16}H_{26}O_2$, the nature of which is still uncertain. The structure

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                          CH2·CMe·OH
CH2·CMe2·CH·CH2  |
CH2·CH2—CMe——CH·CH2·CH2·CMe(OH)·CH2:CH2
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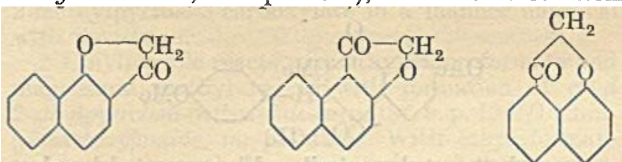
is provisionally assigned to sclareol. J. W. BAKER.

Coumaranone series. III. Dihydro-α- and -β-naphthafuranones and their condensation products with aromatic aldehydes. B. H. INGHAM, H. STEPHEN, and R. TIMPE (J.C.S., 1931, 895—900; cf. *ibid.*, 1922, **121**, 1598).—Chloroacetic acid and α-naphthol in alkaline solution give α-naphthyloxyacetic acid (Spitzer, A., 1901, i, 715), converted into the *chloride*, b. p. 194°/10 mm. (*anilide*, m. p. 144°), which with aluminium chloride gives *dihydro-α-naphthafuran*-2-*one* (I), m. p. 119° (*acetyl* derivative, m. p. 85—86°). This substance may be 1-keto-1 : 2-dihydro*peri*naphthapyran (III) (cf. Ullmann, A., 1897, i, 482). With *p*-nitrosodimethylaniline it gives 1-*p*-*dimethylaminoanilodihydro*-α-*naphthafuran*-2-*one*, m. p. 210—211°. With benzaldehyde in acetic anhydride 1-*benzylidenedihydro*-α-*naphthafuran*-2-*one*, m. p. 130° (*dibromide*, m. p. 195°), is obtained, but in alcoholic hydrogen chloride some *benzylidenebis*(*dihydro*-α-*naphthafuran*-2-*one*), m. p. 197—198°, is also formed. From the condensation of dihydro-α-naphthafuran-2-one and *o*-vanillin 8-*methoxy*-α-*naphthafurano*-(1′ : 2′-2 : 3)-*benzopyrylium ferrichloride*, m. p. 230—231°, is obtained (cf. Ridgeway and Robinson, J.C.S., 1924, **125**, 221). Chloroacetic acid and β-naphthol give β-naphthyloxyacetic acid, converted into the *chloride*, m. p. 54°, b. p. 207°/10 mm. (*anilide*, m. p. 145°), which gives dihydro-β-naphthafuran-1-one (II), m. p. 133° (*acetyl* derivative, m. p. 87—88°; 2-*p*-*dimethylaminoanil*, m. p. 231°), also obtained from



(I.) (II.) (III.)

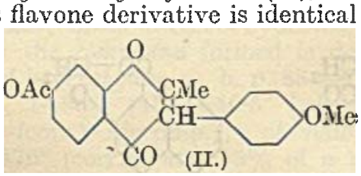
β-naphthyl chloroacetate (cf. Fries and Frellstedt, A., 1921, i, 431). Benzaldehyde with II in acetic anhydride gives 2-*benzylidenedihydro*-β-*naphthafuran*-1-*one*, m. p. 150° (*dibromide*, m. p. 168°). The above dibromide with alcoholic potassium hydroxide gives 5 : 6-*benzflavanol*, m. p. 147°. Dihydro-β-naphthafuran-1-one with vanillin in acetic anhydride gives *acetyl*-2-*vanillylidenedihydro*-β-*naphthafuran*-1-*one*, m. p. 178°, also obtained with alcoholic hydrogen chloride. The latter condensation, with 2 mols. of vanillin, gives *vanillylidenebis*(*dihydro*-β-*naphthafuran*-1-*one*), m. p. 223°. *Piperonylidene*-, m. p. 244°, and *piperonylidenebis*-(*dihydro*-β-*naphthafuran*-1-*one*), m. p. 234—345° (? 235°), are similarly obtained. A. A. LEVI.

Synthesis of scopoletin. R. SEKA and P. KALLIR (Ber., 1931, **64**, [*B*], 909—917).—4-Nitroguaiacol is reduced by tin and hydrochloric acid in alcohol to 4-*aminoguaiacol hydrochloride*, converted by diazotis-

ation and heating of the product with water into 2 : 4-*dihydroxyanisole*, m. p. 63°. The ether is transformed by hydrocyanic acid and zinc chloride in ether into 2 : 4-*dihydroxy-5-methoxybenzaldehyde*, m. p. 152° (*phenylhydrazone*, m. p. 161°), converted by acetic anhydride and sodium acetate into scopoletin acetate and thence into scopoletin [7-hydroxy-6-methoxycoumarin], m. p. 202°, identical with the product obtained from Radix Gelsemii sempervirentis.

Treatment of æsculetin with acetobromoglucose according to the method of Glaser and Kraus (A., 1923, i, 820) affords a *tetra-acetylæsculetin glucoside*, hydrolysed by methyl-alcoholic ammonia to *æsculetin glucoside*, m. p. 216°, $[\alpha]_D^{22}$ −88·5° in pyridine, not identical with natural æsculin or the synthetic product of Glaser and Kraus. Methylation followed by hydrolysis of the *methyl ether*, m. p. 208°, yields scopoletin. The formation of æsculin in the glucoside synthesis has not been established, since the second fraction of the æsculetin methyl ether has a lower m. p. (184—191°) but also a low methoxyl content.
H. WREN.

Ononin. I. "Ononetin." F. WESSELY and F. LECHNER (Monatsh., 1931, **57**, 395—404; cf. Hemmelmayr, A., 1904, i, 814).—Ononetin, prepared by alkaline hydrolysis of formononetin, is separable into 2 : 4-*dihydroxyphenyl* 4'-*methoxybenzyl ketone* (I), 157·5°, and a substance which could be isolated only as an impure methyl ether, m. p. 131—136°. Hydrolysis of onospin by acid or emulsin gives the same products. The constitution of I is proved by its synthesis by the Hoesch condensation of resorcinol and *p*-methoxyphenylacetonitrile. Both the natural and synthetic products give an *oxime*, m. p. 218° (decomp.), and a 4-*methyl ether* (dimorphous), m. p. 92—93° and 104°, and are converted by acetic anhydride and sodium acetate at 160—170° into 7-*acetoxy-4'-methoxy-2-methyl*iso*flavone* (II), m. p. 194—195°. This flavone derivative is identical with Hem-


(II.)

melmayr's "acetylononin," and is converted by alcoholic sulphuric acid into 7-*hydroxy-4'-methoxy-2-methyl*iso*flavone*, m. p. 276—280°, and by hydriodic acid (*d* 1·7) into 7 : 4'-*dihydroxy-2-methyl*iso*flavone*, m. p. 317° (decomp.). The 4-position of the methoxyl group in the methyl ether of I is proved by its cyclisation by acetic anhydride and sodium acetate to 7 : 4'-*dimethoxy-2-methyl*iso*flavone*, m. p. 166—168°, also obtained from the corresponding dihydroxy-compound and diazomethane.

In spite of its behaviour on hydrolysis, formononetin appears from its acetyl derivative and methyl ether to be homogeneous. Alkaline hydrolysis of the latter gives the methyl ethers of the constituents of "ononetin." Acetylation of ononin in pyridine gives an *acetyl* derivative, m. p. 182·5°. H. A. PIGGOTT.

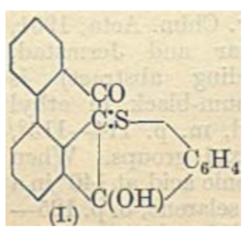
Constitution of the dye of the corn poppy. (*Papaver rhœas*). L. SCHMID and R. HUBER (Monatsh., 1931, **57**, 383—394).—Two anthocyan glucosides are extracted from the fresh petals of the wild poppy by glacial acetic acid, and separated by virtue of the different solubilities of their hydrochlorides in alcohol. The more soluble of these is hydrolysed by 20% hydrochloric acid to a hexose (2 mols., converted by phenylhydrazine into glucosazone) and cyanidin, of which therefore it is a *diglucoside*. H. A. PIGGOTT.

Dye of acacia wood. L. SCHMID and K. PIETSCH (Monatsh., 1931, **57**, 305—322).—A yellow *glucoside*, decomp. 270—280°, is extracted from acacia wood by alcohol. Acetylation gives the *penta-acetyl* derivative, m. p. 216°, of the *aglucone*, $C_{15}H_{10}O_7$, decomp. 324—334° (*pentamethyl ether*, m. p. 148—149°); the latter is formed by hydrolysis of the acetyl derivative or of the glucoside. Fusion of the aglucone with potassium hydroxide at 180—200° in hydrogen gives β-resorcylic acid and a mixture of phenols.
H. A. PIGGOTT.

Anthochlor of *Linarea vulgaris* (common toadflax). L. SCHMID and W. RUMPEL (Monatsh., 1931, 57, 421—435).—A pale yellow *substance*, decomp. 240°, $C_xH_yO_z$, is extracted from the blossoms of *L. vulgaris* by alcohol. Hydrolysis with acid gives a methylpentose (1 mol.), a hexose (1 mol.) convertible into glucosazone, and an *aglucone*, $C_{17}H_{14}O_6$, m. p. 200°. The last-named may be obtained crystalline by sublimation in a high vacuum at 130—155°, contains two methoxyl groups, and gives a *diacetyl* derivative, m. p. 145—146°, from which it is regenerated by alcoholic hydrochloric acid. Fusion with 72% potassium hydroxide in hydrogen at 170° gives anisic acid. H. A. PIGGOTT.

Stereoisomeric catechins. R. P. BIGGS, W. L. COOPER, E. O. HAZLETON, M. NIERENSTEIN, and P. H. PRICE (J. Amer. Chem. Soc., 1931, **53**, 1500—1505). —The isolation of d-*acacatechin* (*penta-acetyl* derivative, m. p. 151°, $[\alpha]_D$ +12·0°) from the Australian kinos from *Eucalyptus viminalis*, *E. leucoxylon*, and *Angophora intermedia*, and of d-iso*acacatechin* (*penta-acetyl* derivative, m. p. 171°, $[\alpha]_D$ +29·3°) from the heartwood of *Anarcadium occidentale* is described. A study of other possible sources did not lead to the isolation of any more new isomerides. The occurrence in nature of at least eight isomeric catechins is difficult to reconcile with the hypothesis that they are stereoisomerides of a single substance containing two asymmetric carbon atoms (cf. A., 1930, 206).
H. A. PIGGOTT.

"2-Thionaphthen-9-phenanthreneindigo" and its isomerisation. R. PUMMERER and F. LUTHER (Ber., 1931, **64**, [*B*], 831—833). —A detailed description is given of the preparation of homogeneous "2-thionaphthen-9-phenanthreneindigo" [10-oxy-9-anthraquinone and 3-oxythionaphthen (cf. Friedländer and others, A., 1922, i, 764). It is isomerised in boiling nitrobenzene to the *compound* I, m. p. 318° (*acetyl* derivative, m. p. 284°). H. WREN.


(I.)

Syntheses of thioxins. H. A. STEVENSON and S. SMILES (J.C.S., 1931, 718—723).—A review of ex-

isting methods. Those previously described (J.C.S., 1914, **105**, 1744; A., 1929, 327) have been extended. 2-*Iodophenyl disulphoxide*, m. p. 147° (from the sulphinic acid), with sodium 2-naphthoxide gives 2-iodophenyl 2-hydroxy-1-naphthyl sulphide (*methyl ether*, m. p. 162°). The sodium salt of this (prepared with sodium ethoxide) when sublimed in a vacuum with a little copper sulphate gives *benz-αβ-naphthathioxin*, m. p. 63°. 2 : 5-*Dibromophenyl* 2-*hydroxy*-1-*naphthyl sulphide*, m. p. 148°, is obtained similarly, or by condensing 2 : 5-dibromo-1-chlorothiolbenzene with 2-naphthol. This, when treated as above, gives 10-*bromobenz-αβ-naphthathioxin*, m. p. 142°. The above chlorothiol with 4-bromophenol gives 2 : 5 : 5′-tribromo-2′-hydroxydiphenyl sulphide (*methyl ether*, m. p. 142°), and by further treatment 2 : 8-*dibromodibenzthioxin*, m. p. 92°. Alcoholic 2-hydroxy-1-naphthyl mercaptan with picryl chloride and alkali gives 9 : 11-*dinitrobenz-αβ-naphthathioxin*, m. p. 300°. The yield in the preparation of αβα′β′-dinaphthathioxin (J.C.S., 1912, **101**, 714) is improved (60—70%) by adding zinc chloride. 6 : 6′-Dibromo-β-naphthol 1-sulphide gives by this process 3 : 11-*dibromo-αβα′β′-dinaphthathioxin*, m. p. 275°, not identical with the product obtained by brominating the parent thioxin (J.C.S., 1913, **103**, 907). Similarly, 4-bromo-β-naphthol 1-sulphide gives 3-*bromo-αβα′β′-dinaphthathioxin*, m. p. 119°. Dehydration of 4-chloro-1 : 2′-dihydroxy-2 : 1′-dinaphthyl sulphide (A., 1926, 734) gives αβα′β′-dinaphthathioxin (10% yield). Derivatives of α-naphthol 2-sulphide cannot be dehydrated to give thioxins (cf. Mauthner, A., 1906, i, 447). 6-Bromo-β-naphthol 1-sulphide with alkaline ferricyanide gives the dehydro-derivative (cf. Lesser and Gad, A., 1923, i, 561) converted by acetyl iodide (90% yield) into 3 : 10-*dibromo-αββ′α′-dinaphthathioxin*, m. p. 273°, not identical with other dibromonaphthathioxins obtained (see above). 1 : 6-Dibromo-β-naphthol and 1-bromothiol-β-naphthol with pyridine and sodium hydroxide give (30% yield) a dehydrosulphide, converted by acetyl iodide into 10-*bromo-αββ′α′-dinaphthathioxin*, m. p. 173°. 4-Bromo-β-naphthol 1-sulphide may give rise to two isomeric dehydro-derivatives with alkaline ferricyanide. The product, when treated with acetyl iodide, and subsequently fractionated, gives the above 10-bromo-αββ′α′-dinaphthathioxin. A. A. LEVI.

Ring-synthesis of 4-acetyl-3-methylpyrrole-5-carboxylic acid. H. FISCHER, H. BEYER, and E. ZAUCKER (Annalen, 1931, **486**, 55—70).—The interaction of aminoacetone and ethyl acetylpyruvate gives in addition to ethyl 4-acetyl-3-methylpyrrole-5-carboxylate an isomeride (I), m. p. 125° (cf. A., 1928, 776). The former is the sole product in an alkaline solution and the latter in an acid medium (p_H 6), a mixture of the two being formed under intermediate conditions. By hydrolysis to the acid [m. p. 305° (decomp.), and not 281° as previously stated] and decarboxylation I is converted into 5-*acetyl-2-methylpyrrole* (II), m. p. 89°, and is therefore *ethyl 5-acetyl-2-methylpyrrole-4-carboxylate*. The constitution of II was arrived at by reduction by the Wolff–Kishner method to an oily alkylpyrrole from which no crystalline picrate or oxidation product could be isolated; 2 : 3 : 4-trimethylpyrrole (known) was thus excluded, and the product could only be 2-methyl-5-ethylpyrrole derived from either 2-ethylpyrrole-5-aldehyde or 5-acetyl-2-methylpyrrole; these were synthesised and directly compared with II.

With hydrazine hydrate in alcohol II or the corresponding carboxylic acid gives a *pyridazine*, m. p. above 300°, probably $\begin{array}{l}\mathrm{CH{-}{-}{-}C{\cdot}CO{-}NH}\\ \mathrm{CMe{\cdot}NH{\cdot}C{\cdot}CMe{:}N}\end{array}$; the same product is obtained in presence of sodium methoxide. The *phenylhydrazone*, m. p. 238°, of the free acid is formed normally in absence of a solvent, but in presence of 80% acetic acid both the acid and its ester (II) give the corresponding N-*phenylpyridazine*, decomp. 324°. The *oxime* (of the acid?), decomp. 244° (*monobromo*-derivative), is dehydrated by aqueous sodium hydroxide to an *isooxazole* (above formula, ‒CO·O·N‒ in place of ‒CO·NH·N=), m. p. 233° (decomp.), converted by hydrazine hydrate and sodium methoxide into the pyridazine. The *dibromo-*, m. p. 185°, *tribromo-*, m. p. 165°, and p-*dimethylaminobenzylidene*, m. p. 231°, derivatives of I, also the *carbinol*, m. p. 142° (prepared by reduction with aluminium amalgam in ether), are described.

5-Acetyl-2-methylpyrrole (II) [*phenylhydrazone*; *oxime*, m. p. 150° (*acetyl* derivative, m. p. 147°); *ketazine*, $C_{14}H_{18}N_4$, m. p. 183°; *semicarbazone*, m. p. 200°; *benzylidene*, m. p. 197°, *dibromo-*, m. p. 161°, and *tribromo*-derivatives] was synthesised by interaction of 2-methylpyrrole, acetyl bromide, and magnesium ethyl bromide. Reduction by the Wolff–Kishner method gives 2-*methyl-5-ethylpyrrole* (*benzeneazo-*, decomp. 174°, *tolueneazo-*, decomp. 178°, and *sulphobenzeneazo-*, m. p. 240—250°, derivatives), converted by hydroxylamine at 100° into *heptane-βε-diketoxime*, m. p. 150°. *Ethyl 5-acetyl-2-methylpyrrole-3-carboxylate*, m. p. 152° (*phenylhydrazone*, m. p. 144°; *hydrazone*, m. p. 116°; *oxime*, m. p. 191°; *dibromo-*, m. p. 214°, derivatives), is prepared from ethyl 2-methylpyrrole-3-carboxylate in a manner identical with the above.

2-Ethylpyrrole reacts with ethyl chloroformate and magnesium methyl iodide with formation of *ethyl 2-ethylpyrrole-5-carboxylate*, m. p. 48°, b. p. 134°/15 mm. (-5-*carboxylamide*, m. p. 112°). With ethyl formate and magnesium ethyl bromide it gives the corresponding *tripyrrylmethane*, m. p. 162°, decomposed by boiling with alcohol into 2-*ethylpyrrole-5-aldehyde*, m. p. 52°. Using 2-methylpyrrole in place of 2-ethylpyrrole, however, 2-methylpyrrole-5-aldehyde (*oxime*, m. p. 153°) is formed in the initial condensation.

The interaction of ethyl 2-methylpyrrole-3-carboxylate with acetyl chloride and aluminium chloride in carbon disulphide gives ethyl 5-acetyl-2-methylpyrrole-3-carboxylate and a *substance*, decomp. 194°, to which the formula
$\begin{array}{l}\mathrm{C(CO_2Et){\cdot}CH\qquad\qquad C(CO_2Et){\cdot}CH}\\ \mathrm{CMe{\cdot}NH{-}C{\cdot}CMe{:}CH{\cdot}C{\cdot}NH{-}{-}{-}CAc}\end{array}$ is assigned. p-*Dimethylaminobenzylidene-2-acetylpyrrole* has m. p. 206°.
H. A. PIGGOTT.

Nitration of benzylpiperidine. R. ROBINSON and J. S. WATT (J.C.S., 1931, 980).—The addition of varying quantities of rubidium nitrate has little effect on the proportion of *m*-isomeride formed in the nitration of benzylpiperidine. A. A. LEVI.

2-Nitropyridine. A. KIRPAL and W. BOHM (Ber., 1930, **64**, [*B*], 767; cf. den Hertog and Overhoff, A., 1930, 925).—2-Aminopyridine is oxidised by ammonium persulphate and hydrogen peroxide in presence of sulphuric acid to 2-nitropyridine, m. p. 71°, b. p. 256°. H. WREN.

Pyridine derivatives. IX. Preparation of 2-chloropyridines. C. RATH (Annalen, 1931, **486**, 71—80).—2-Chloropyridine and its derivatives are readily prepared in good yield by heating 1-alkyl-2-pyridones with carbonyl chloride alone or in toluene at 150—200°. The reaction, which involves the elimination of the 1-alkyl group as alkyl chloride (cf. Fischer, A., 1898, i, 180), appears to be unaffected by the size of the alkyl group or by the presence of nuclear substituents: it may be applied to 1-methyl-2-thiopyridone and -2-quinolone, and in no case is there a tendency to further chlorination. Its application to the preparation of the following is described: 2-chloropyridine; 2-chloroquinoline; 2-chloro-5-nitropyridine (from the 1-methyl-, 1-ethyl-, and 1-benzyl-pyridones); 2:5-*dichloro*-, m. p. 60°; 2-*chloro*-5-*bromo*-, m. p. 71°; 2-*chloro*-5-*iodo*-, m. p. 98°; 2:3:5-*trichloro*-, m. p. 49—50°; 2-*chloro*-3:5-*dibromo*-, m. p. 43°, and 2-*chloro*-3:5-*di-iodo-pyridines*, m. p. 72—73°. Thionyl chloride may replace carbonyl chloride in some cases, but gives poorer yields; there is a tendency, not only to further nuclear chlorination, but also to the replacement of other halogen substituents by chlorine. Both 5-chloro- and 5-bromo-1-methyl-2-pyridones give 3:5-dichloro-1-methyl-2-pyridone with thionyl chloride.

The following are obtained by interaction of the potassium salts of the correspondingly substituted 2-hydroxypyridine with methyl iodide in alcoholic solution: 5-*chloro*-, m. p. 44—45°; 5-*bromo*-, m. p. 53°; 3:5-*dichloro*-, m. p. 142°; 3:5-*dibromo*-, m. p. 182°, and 3:5-*di-iodo*-1-*methyl*-2-*pyridone*, m. p. 227°. H. A. PIGGOTT.

Pyridine derivatives. X. 3-Aminopyridine. C. RÄTH (Annalen, 1931, **486**, 95—106).—The preparation of 3-aminopyridine [*benzoyl* derivative, m. p. 119° (*hydrochloride*, decomp. 206°)] from 2-chloro-5-nitropyridine by conversion into the 2-hydrazino-derivative, elimination of the hydrazino-group, and reduction is reported. Its conversion by diazo-reactions into the following is described: 3-*fluoro*-, b. p. 106—108°/750 mm. (the *hydrochloride* is hygroscopic and immediately decomposed by air); 3-chloro-; 3-bromo-; 3-*iodo*-, m. p. 50° [*dichloride*, m. p. 128—130° (decomp.)]; 3-cyano-; 3-*acetyl*-, b. p. 222—223° [*hydrochloride*, m. p. 80° (decomp.)] (from the cyano-derivative and magnesium methyl iodide), and 3-*hydrazino-pyridine*, m. p. 53—55° [*acetophenone*-, m. p. 156°, *propaldehyde*-, m. p. 68°, and *pyruvic acid* 3-*pyridylhydrazone*, m. p. 166° (decomp.); 3-*pyridylglucosazone*, m. p. 196°]; *pyridine*-3-*azo*-β-*naphthol*, m. p. 152° [*hydrochloride*, m. p. 160° (decomp.)], and -3-*azo*-p-*dimethylaniline*, m. p. 121° [*hydrochloride*, m. p. 105° (decomp.)]. s-3:3′-*Dipyridylthiocarbamide*, m. p. 176° (*hydrochloride*), is obtained by interaction of the aminopyridine with carbon disulphide and alcoholic sodium hydroxide; it is completely hydrolysed by concentrated hydrochloric acid without the intermediate formation of the thiocarbimide. Attempts to prepare arsinic and stibinic acids and thiophenols in this series failed. H. A. PIGGOTT.

Amides of heterocyclic carboxylic acids. E. GRISCHKEVITSCH-TROCHIMOVSKI (Rocz. Chem., 1931, **11**, 193—202).—The *diethylamides* of picolinic acid, m. p. 26—28°, b. p. 122·5—123°/3 mm., d_4^{16} 1·0603, of nicotinic acid ("coramine"), m. p. 21—23°, b. p. 128·5—129°/3 mm., d^{16} 1·0652, and of *iso*nicotinic acid, m. p. 22—24°, b. p. 123—123·5°/3 mm., d_4^{16} 1·0630, are prepared from the corresponding acid chlorides and diethylamine. The pharmacological action of picolinoyldiethylamide is similar to that of "coramine," but it stimulates the nervous system. The diethylamide of 2:2:5:5-tetramethylpyrrolidine-3-carboxylic acid, $NH{<}{\scriptstyle CMe_2\cdot CH \atop CMe_2\cdot C\cdot CO\cdot NEt_2}$, m. p. 33—34°, b. p. 129·5—130°/9 mm., is prepared by the action of diethylamine on dibromoacetonamine. R. TRUSZKOWSKI.

Molecular compounds of dipyridylium and pyridinium salts. B. EMMERT, O. SCHNEIDER, and M. KOBERNE (Ber., 1931, **64**, [*B*], 950—953).—Dibenzyldipyridylium dibromide and barium salicylate in water afford *dibenzyldipyridylium salicylate* $\left(-\langle\rangle N(C_7H_7){\scriptstyle O_2C\cdot C_6H_4 \atop \cdots\cdots OH}\right)_2,4H_2O$ the corresponding tetrahydrated *anthranilate* is analogously prepared. *Dipyridyl anthranilate*, m. p. 150—152° after softening, is described. The following molecular pyridinium salts have been prepared, the ratio of the components being placed within parentheses: 1-*methylpyridinium iodide*, with p-*phenylenediamine* (2:1), 4:4′-*diaminodiphenylmethane* (1:1), 4:4′-*diaminostilbene* (1:1) and 4:4′-*diaminotolane* (1:1); 1-*ethylpyridinium bromide, benzidine* (1:2); 1-*iso-amylpyridinium iodide, benzidine* (1:2); 1-*benzylpyridinium chloride, benzidine* (2:3); 1-*methylcollidinium iodide, benzidine* (1:1); 1-*methylquinolinium iodide*, o-*phenylenediamine* (1:1); 1-*methylquinolinium iodide*, p-*phenylenediamine* (2:1); 1-*methylquinolinium iodide*, 4:4′-*diaminodiphenylethane* (1:1); 1-*methylquinolinium iodide*, 4:4′-*diaminostilbene* (1:1); 1-*methylquinolinium iodide*, 4:4′-*diaminotolane* (1:1); *diisoamyldipyridylium dibromide, diphenylamine* (1:6); 4:4′-*dipyridyl* with o-*phenylenediamine* (1:1), m. p. 95—97°, with p-*phenylenediamine* (2:1), m. p. 113—115°, with *benzidine* (1:1), m. p. 193—195°, with 4:4-*diaminostilbene* (1:1), m. p. 224—227°, with 4:4′-*diaminotolane* (1:1), m. p. 205—207°. H. WREN.

Reduction of nitrosophenol by iron and hydrochloric acid. K. MATSUMURA and C. SONE (J. Amer. Chem. Soc., 1931, **53**, 1406—1408).—Reduction of 7-*nitroso*-8-*hydroxy*-5-*quinolyl methyl ketone*, decomp. 180—195° (prepared by nitrosation in dilute acetic acid), with stannous chloride and hydrochloric acid gives 7-*amino*-8-*hydroxy*-5-*quinolyl methyl ketone*, m. p. 148—149° (decomp.) (*picrate*, decomp. 201—222°; *hydrochloride*, sinters 145°), in poor yield, but with iron and dilute hydrochloric acid 7:8-*dihydroxy*-5-*quinolyl methyl ketone* [$+1{\cdot}5H_2O$, and colourless, m. p. 235—236°, and red, m. p. 241—242° (decomp.),

anhydrous forms : *hydrochloride*, yellow, m. p. 280—305° (decomp.); *oxime*, decomp. 215—220°; *diacetyl* derivative, m. p. 121—122°]. By the latter method of reduction 5 : 8-*dihydroxyquinoline*, m. p. 181—183° (*sulphate*, decomp. 250°), is obtained from 5-nitroso-8-hydroxyquinoline, and quinol, mixed with very little *p*-aminophenol, from *p*-nitrosophenol; its application to *p*-nitrophenol gives 20% and 35% of the theoretical of quinol and *p*-aminophenol, respectively, whereas with *o*-nitrophenol the sole product is *o*-aminophenol.

H. A. PIGGOTT.

Condensations between formaldehyde and monoketones. I. Condensation of 8-hydroxy-5-acetylquinoline with aldehydes. K. MATSUMURA and C. SONE (J. Amer. Chem. Soc., 1931, **53**, 1490—1492).—ω - *Methylenebis* - 8 - *hydroxy* - 5 - *quinolyl methyl ketone*, m. p. above 315° [*hydrochloride*; *monoxime*, m. p. 295—300° (decomp.); *diacetyl* derivative, m. p. 234—235°], and its *dibenzoyl* derivative, m. p. above 315°, are prepared by interaction of aqueous formaldehyde with 8-hydroxy-5-acetylquinoline, and its *benzoyl* derivative, m. p. 168°, respectively. ω-*Piperonylidene*-8-*hydroxy* - 5 - *quinolyl methyl ketone*, m. p. 178—179°, is similarly prepared by the use of piperonal in alcoholic solution.

H. A. PIGGOTT.

Beckmann rearrangement with quinoline compounds. K. MATSUMURA and C. SONE (J. Amer. Chem. Soc., 1931, **53**, 1493—1496).—Phenyl 8-hydroxy-5-quinolyl ketoxime is converted by thionyl chloride in ether into 8-*hydroxyquinoline*-5-*carboxyanilide*, m. p. 211—212°, and by concentrated sulphuric acid into a *sulphonic acid* of the anilide, in which the sulphonyl group is considered to be in the anilido-residue. Both on hydrolysis give 8-hydroxyquinoline-5-carboxylic acid (Lippmann and Fleissner, A., 1887, 63, 1119) [*barium* salt; *acetyl* derivative, decomp. 312°; *methyl ether*, m. p. 225—226° (decomp.)]. This behaviour contrasts with the Beckmann rearrangement by other agents (cf. this vol., 98), but this divergence is not shown by 8-hydroxy-5-quinolyl methyl ketone, which gives 5-acetamido-8-hydroxyquinoline both with thionyl chloride and sulphuric acid.

H. A. PIGGOTT.

Fission and transformation of *iso*quinoline into 2-phenylnaphthalene-5 : 2′-dialdehyde and conversion of the latter substance into two isomeric benzofluorenones. P. BAUMGARTEN and J. OLSHAUSEN (Ber., 1931, **64**, [*B*], 925—942; cf. 1927, 674).—*iso*Quinoline is converted by chlorosulphonic acid in cold chloroform into *N*-iso*quinoliniumsulphonic acid*, m. p. 250—254°; if ethyl chlorosulphonate is used the base is ethylated to a minor extent. The acid is immediately hydrolysed by boiling water to *iso*quinoline and sulphuric acid. When treated with cold, aqueous sodium hydroxide it is transformed into the *disodium* salt of *o*-aldehydostyrylaminosulphonic acid, $CHO{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}NNa{\cdot}SO_3Na$, which readily decomposes when preserved into *iso*quinoline and sodium sulphate; when acidified it gives *o*-*aldehydostyrylaminosulphonic acid*, m. p. 245—248° (*dihydrate*, m. p. 205°), quantitatively isomerised by boiling water to *iso*quinolinium sulphate. When the disodium salt is heated in aqueous solution, 2-*phenylnaphthalene*-5 : 2′-*dialdehyde*, $CHO{\cdot}C_{10}H_6{\cdot}C_6H_4{\cdot}CHO$, m. p. 126·5°, is precipitated. The corresponding *monophenylhydrazone*, decomp. 70—80°, *diphenylhydrazone*, decomp. 198—200°, and *dioxime*, m. p. 199°, are described. Oxidation of the aldehyde with ammoniacal silver oxide or potassium permanganate affords 2-*phenylnaphthalene*-5 : 2′-*dicarboxylic acid*, m. p. 267—268° (normal *potassium* salt and its *trihydrate*; *silver*, *lead*, *copper*, *ferric*, *cobalt*, and *nickel* salts); when heated with calcium hydroxide, the acid yields 2 : 3-benzoylfluorenone, m. p. 153·5°, and a little 2-phenylnaphthalene, m. p. 101·5—102°. Distillation in a vacuum transforms the acid into *chrysofluorenone*-4-*carboxylic acid*, m. p. 320°, the barium salt of which affords 1 : 2-benzofluorenone, m. p. 132° (oxime, decomp. 203°), when distilled with lime.

H. WREN.

ψ-Cyanine dyes containing pyridine or β-naphthaquinoline nuclei. (MISS) F. M. HAMER and (MRS.) M. I. KELLY (J.C.S., 1931, 777—786; cf. this vol., 103).—Improved preparations are described for 1-methyl-, 1-ethyl-, and 1-benzyl-2-pyridone from pyridine metho-*p*-toluenesulphonate, etho-*p*-toluenesulphonate, and benzochloride (*benzoferricyanide*, m. p. 102—103°), respectively (cf. Fargher and Furness, A., 1915, i, 842). 2-Chloropyridine, obtained from the above methyl- or ethyl-pyridones (*loc. cit.*) with methyl iodide gives 2-iodopyridine methiodide, and with ethyl iodide the *ethiodide*, m. p. 156—157°. Attempts to condense these with α-picoline methiodide or ethiodide were unsuccessful. The product from condensation of 2-iodopyridine methiodide with quinaldine methiodide in presence of alcoholic potassium hydroxide gives, on fractional crystallisation, a ψ-*cyanine*, m. p. 238—241° (decomp.) (yield 17%) (photographic sensitising action extends to λ 5600, maximum at 5200 Å.). Similarly, 2-iodopyridine ethiodide and quinaldine methiodide give a ψ-*cyanine*, m. p. 249° (decomp.) [sensitising action extends to λ 6000, maxima at 5200, and 5700 Å. (weak); absorption spectrum maximum λ 4800 Å.]. 2-Iodopyridine ethiodide and quinaldine ethiodide give a ψ-*cyanine* (10% yield) (absorption spectrum maximum at λ 4950 Å.). β-Naphthaquinoline metho- and etho-*p*-toluenesulphonate give 1-*methyl*-, m. p. 174° (previous shrinking and darkening) (yield 79%), and 1-*ethyl*-β-*naphtha*-2-*quinoline*, m. p. 138° (yield 68%), respectively, both converted by phosphorus pentachloride and oxychloride into 2-chloro-β-naphthaquinoline, m. p. 114°, which is converted by methyl and ethyl iodides into 2-iodo-β-naphthaquinoline methiodide, m. p. (varies with rate of heating) 202—211° (decomp.), and ethiodide, m. p. 202—210° (decomp.), respectively. 2-Iodo-β-naphthaquinoline methiodide and β-naphthaquinaldine methiodide give 1 : 1′-*dimethyl*-5 : 6 : 5′ : 6′-*dibenz*-ψ-*cyanine iodide*, m. p. 286° (decomp. commences 240°) (yield 21%) [sensitising action extends to λ 6300, maxima at 5900, and 5200 Å. (weak); absorption spectrum maxima λ 5150, and 5300 Å. (stronger)]. 2-Iodo-β-naphthaquinoline methiodide and β-naphthaquinaldine ethiodide give 1(or 1′)-*methyl*-1′(or 1)-*ethyl*-5 : 6 : 5′ : 6′-*dibenz*-ψ-*cyanine iodide*, m. p. 300° (decomp.) (yield 28%) [strong sensitising action extends

to λ 6400 (weaker extension due to an impurity with maximum at 6750), maxima at 5900 and 5200 Å. (stronger); absorption spectrum maxima λ 5100 and 5450 Å. (stronger)]. 2-Iodo-β-naphthaquinoline ethiodide and β-naphthaquinaldine ethiodide give 1 : 1′-*diethyl*-5 : 6 : 5′ : 6′-*dibenz-ψ-cyanine iodide*, m. p. 310° (decomp.) (yield 25%), sensitising action extends to λ 6300, maxima at 5700, and 6700 Å. (weak, due to impurity): absorption spectrum maxima at λ 5100 and 5500 Å. (stronger)]. 2-Iodo-β-naphthaquinoline methiodide and quinaldine methiodide give 1 : 1′-dimethyl-5 : 6(or 5′ : 6′)-benz-ψ-cyanine iodide, also obtained from 2-iodoquinoline methiodide and β-naphthaquinaldine (cf. A., 1928, 307). 2-Iodo-β-naphthaquinoline methiodide and quinaldine ethiodide give 1(or 1′)-*methyl*-1′(or 1)-*ethyl*-5 : 6(or 5′ : 6′)-*benz-ψ-cyanine iodide*, m. p. 275—276° (decomp.) (yield 5%) [strong sensitising action extends to λ 6150, maximum at 5700 Å.; absorption spectrum maxima at λ 5300 and 5000 Å. (weaker)]. 2-Iodo-β-naphthaquinoline ethiodide and quinaldine methiodide give 1(or 1′)-*methyl*-1′(or 1)-*ethyl*-5′ : 6′-(or 5 : 6)-*benz-ψ-cyanine iodide*, m. p. 277—278° (decomp.) (yield 17%) [strong sensitising action extends to λ 6200, maximum at 5750 Å.; absorption spectrum maxima at λ 5300 and 5000 Å. (weaker)]. 2-Iodo-β-naphthaquinoline ethiodide and 1-methylbenzthiazole methiodide give 2-*methyl*-1′-*ethyl*-5′ : 6′-*benzthio-ψ-cyanine iodide*, m. p. 282° (softens 279°) (yield 18%) (sensitising action extends to λ 6000, maximum at 5350 Å.; absorption spectrum maximum at λ 4850 Å.). 2-Iodo-β-naphthaquinoline methiodide and 1-methylbenzthiazole methiodide give 1′ : 2-*dimethyl*-5′ : 6′-*benzthio-ψ-cyanine iodide*, m. p. 275° (decomp.) (yield 20%) (sensitising action extends to λ 6000, maximum at 5300 Å.; absorption spectrum maximum at λ 4900 Å.).

A. A. Levi.

Reaction between barbital (diethylbarbituric acid) and phosphorus pentachloride. A. W. Dox (J. Amer. Chem. Soc., 1931, 53, 1559—1566).—Barbital is unacted on by phosphoryl chloride at 175—180°; in marked contrast, *sec.*-butylbarbituric acid readily gives 2 : 4 : 6-*trichloro*-5-sec.-*butylpyrimidine*, m. p. 40°, under similar conditions. Interaction of barbital with phosphorus pentachloride at 115—120° gives diethylcyanoacetyl chloride (identified by conversion into the acid and *amide*, m. p. 121°) and 2 : 2 : 4 : 6-*tetrachloro*-5 : 5-*diethyldihydropyrimidine*, m. p. 127°, whilst from the residues were isolated, by methods involving hydrolysis, *diethylmalononitrile*, m. p. 44°, and 5 : 5-diethylmalonoguanidine (cf. Fischer and Dilthey, A., 1905, i, 35). The tetrachloropyrimidine is hydrolysed by boiling water, with quantitative liberation of hydrogen chloride, to diethylmalononitrile; in presence of zinc dust, however, it is reduced to 4 : 6-*dichloro*-5 : 5-*diethyldihydropyrimidine*, m. p. 117°. The action of dry ammonia in an inert solvent gives 2 : 4 : 6-tri-imino-5 : 5-diethylhexahydropyrimidine (*hydrochloride*) (or 2 : 4 : 6-triamino-5 : 5-diethylpyrimidine; cf. G.P. 165,692).

H. A. Piggott.

4-Hydroxy-1-aryl-5-methylpyrazoles. F. D. Chattaway and H. Irving (J.C.S., 1931, 786—794).—4-Hydroxy-1-aryl-5-methylpyrazoles are obtained in good yield from β-chloro-α-ketobutaldehydearylhydrazones (cf. this vol., 722) by treatment with sodium ethoxide, or from butyl chloral hydrate and arylhydrazine in alcohol, and subsequent treatment with potassium hydroxide. The following are described: 1-*phenyl*-, m. p. 136·5—137·5°, monoclinic, $a : b : c$ = 1·3383 : 1 : 0·78035, β=95° 57′ [*hydrochloride*, m. p. 83°; *chloroplatinate*, m. p. 205° (decomp.); *picrate*, m. p. 154—154·5°; *benzoate*, m. p. 91·5°; p-*chlorobenzenesulphonate*, m. p. 87°; *methiodide*, m. p. 201—202°], 1-o-*tolyl*-, m. p. 157·5° (*methiodide*, m. p. 198°), 1-m-*tolyl*-, m. p. 120°, 1-p-*tolyl*-, m. p. 125°, 1-p-*chlorophenyl*-, m. p. 141—142° [*hydrochloride*, m. p. 99—102° (decomp.); *picrate*, m. p. 125—126°; *methiodide*, m. p. 196—197° (slight decomp.); *benzoate*, m. p. 95—96°], 1-p-*bromophenyl*-, m. p. 143° (*benzoate*, m. p. 108·5—109°), 1-(2′ : 4′-*dichlorophenyl*)-, m. p. 184°, orthorhombic, $a : b : c$=1·1250 : 1 : 1·0649 [*hydrochloride*, m. p. 96° (decomp.); *benzoate*, m. p. 112·5—113°], and 1-(2′ : 4′-*dibromophenyl*)-4-*hydroxy*-5-*methylpyrazole*, m. p. 186° (*benzoate*, m. p. 112—113°). 4-Hydroxy-1-phenyl-5-methylpyrazole methiodide gives with silver oxide 4-*hydroxy*-1-*phenyl*-1(or 2) : 5-*dimethylpyrazolinium hydroxide*, m. p. 150—155° (decomp., darkens 145°) [*methochloride*, m. p. 225° (decomp.); *chloroplatinate*, m. p. 190—195° (decomp., darkens 140°)]. When heated with phosphorus tribromide and phosphorus 4-hydroxy-1-phenyl-5-methylpyrazole gives 1-phenyl-5-methylpyrazole (cf. Stoermer and Martinsen, A., 1907, i, 446), oxidised by permanganate to 1-phenylpyrazole-5-carboxylic acid (cf. Claisen and Roosen, A., 1894, i, 345). No 4-chloro-1-phenyl-5-methylpyrazole was obtained by the action of phosphoryl chloride on the 4-hydroxy-compound (cf. Wolff and Fertig, A., 1900, i, 691). β-Acetyl-2 : 4-dichlorophenylhydrazine and ethyl acetoacetate give with phosphorus trichloride 1-(2′ : 4′-*dichlorophenyl*)-5-*methyl*-3-*pyrazolone*, m. p. 208—209° (cf. Michaelis, A., 1908, i, 209) (*benzoate*, m. p. 98—99°), brominated to 4-*bromo*-1-(2′ : 4′-*dichlorophenyl*)-5-*methyl*-3-*pyrazolone*, m. p. 241—242° (decomp.).

A. A. Levi.

ψ-Bases. II. Equilibria and rate of change of tautomeric bases in the pyrazine series. Effect of conjugation. J. G. Aston (J. Amer. Chem. Soc., 1931, 53, 1448—1470).—The anomalously high conductivities of solutions of 5-phenyl-10-methylacridinium chloride and sodium hydroxide (cf. Hantzsch and Kalb, A., 1900, i, 113) are shown by solubility determinations to be due to supersaturation with the base, which is slightly soluble in water to a highly-ionised solution. The nature of the changes undergone and the final equilibria reached by pyrazinium bases in aqueous solutions are determined by conductivity measurements. The disappearance of strong base from solutions of equivalent proportions of 1 : 2 : 5-trimethylpyrazinium iodide and sodium hydroxide is the result of two simultaneous reactions, one of which is proportional to the product of the hydroxyl-ion concentration and the square of the concentration of pyrazinium ion, and the other to the product of the squares of both. Both lead to the ether of the ψ-base, which has not been obtained pure, but with acids regenerates the pyrazinium salt. The equilibria between 1 : 2 : 2 : 5 : 5-pentamethyldihydropyrazinium hydroxide and its ψ-base, and

1 : 2 : 2 : 3 : 5 : 5 : 6 - heptamethyldihydropyrazinium hydroxide and its methylene base are established too quickly for measurement, the low basic dissociation coefficients reached indicating the presence of small amounts only of ammonium base.

H. A. PIGGOTT.

Electrochemical bromination of indigo. F. FICHTER and F. CUENI (Helv. Chim. Acta, 1931, **14**, 651—660).—Indigo is converted in 90% yield into 5 : 5′-dibromoindigotin by electrolysis of a suspension in 51% hydrobromic acid using a carbon anode. The by-products include 2 : 4 : 6-tribromoaniline, 5-bromo- and 5 : 7-dibromo-isatin, 2 : 4-dibromoaniline, and unchanged indigotin. Purification of the product is best effected by extraction with boiling nitrobenzene, reduction of the insoluble dibromoindigotin with sodium hyposulphite, and re-oxidation, which affords a product 98·6% pure. Neither increasing the total current passed nor the current density effects further bromination or appreciably increases the amount of decomposition products, owing to the stability and insolubility of the initial substitution product. Decrease in the bromide-ion concentration or increase in the amount of water present decreases the yield of dibromoindigotin and favours the formation of oxidation products. Thus in 40% hydrobromic acid only 8·69% of dibromoindigotin is formed. The use of pyridine dihydrobromide in nitrobenzene as a non-aqueous medium for the electrolysis is not recommended, incomplete bromination or the formation of higher brominated products resulting according to the conditions. The electrolytic chlorination of indigotin in hydrochloric acid cannot be effected owing to the formation of oxidation products. J. W. BAKER.

Chemotherapy (antimalarials). I. A derivative of glyoxalinoquinoline. K. S. NARANG and J. N. RAY (J.C.S., 1931, 976—980).—The azlactone from piperonal and hippuric acid when heated with *m*-toluidine and a little copper-bronze gives *piperonylidenebenzamidoaceto*-m-*toluidide*, m. p. 233°, and a little 5-*keto*-2-*phenyl*-1-m-*tolyl*-4-*piperonylidene*-4 : 5-*dihydroglyoxaline*, m. p. 167°, also obtained by treating the former with phosphoryl chloride. Similarly, the azlactone with *p*-toluidine gives *piperonylidenebenzamido*-p-*toluidide*, m. p. 248—249°, and 5-*keto*-2-*phenyl*-1-p-*tolyl*-4-*piperonylidene*-4 : 5-*dihydroglyoxaline*, m. p. 230°. The *azlactone*, m. p. 166°, from *o*-nitrobenzaldehyde and hippuric acid, with aniline as above yields o-*nitrobenzylidenebenzamidoacetanilide*, m. p. 213°, converted by phosphoryl chloride into 5-*keto*-1 : 2-*diphenyl*-4-o-*nitrobenzylidene*-4 : 5-*dihydroglyoxaline*, m. p. 178°, which is reduced by zinc dust and acetic acid to 1 : 2-*diphenylglyoxalino*-4 : 5-(3′ : 2′)-*quinoline*, m. p. 239°. *o*-Nitrobenzylidenebenzamidoacetanilide with zinc dust and acetic acid gives 2-*anilino*-3-*benzamidoquinoline*, m. p. 254°. The following are obtained by similar reactions: o-*nitrobenzylidenebenzamidoaceto*-o-*toluidide*, m. p. 172—173°, -m-*toluidide*, m. p. 215°, and -p-*toluidide*, m. p. 206°; 2-o-*toluidino*-, m. p. 247°, 2-m-*toluidino*-, m. p. 238—239°, and (in small yield) 2-p-*toluidino*-3-*benzamidoquinoline*, m. p. 259°. 6-Nitropiperonal and hippuric acid when heated with acetic anhydride and sodium acetate give an *azlactone*, m. p. 196°, from which the following are obtained; 6-*nitropiperonylidenebenzamidoacet-anilide*, m. p. 225°, -o-*toluidide*, m. p. 223°, m-*toluidide*, m. p. 186°, and -p-*toluidide*, m. p. 229° (also with the last a *substance*, m. p. 259°). Reduction to quinoline derivatives gave small yields. The following are described: 2-*anilino*-, m. p. 315°, 2-o-*toluidino*-, m. p. 298°, 2-m-*toluidino*-, m. p. 286°, 2-p-*toluidino*-3-*benzamido*-6 : 7-*methylenedioxyquinoline*, m. p. 305°.

A. A. LEVI.

Reactivity of the position 8 in xanthines and *iso*xanthines and the conception of them as aromatic compounds. H. BILTZ and J. SAUER (Ber., 1931, **64**, [*B*], 752—766).—8-Thiouric acids, which contain an NH group proximate to the CS group, react as 8-thiolxanthines. The salt formation of xanthines depends on nitrogen doubly linked towards position 8. The tendency is considerable when hydrogen or methyl is attached to 8, but diminishes when negative substituents are placed there. Correspondingly, thiolxanthines and thiol*iso*xanthines are incapable of salt formation. In uric acids the double linking between the atoms 4 and 5 gives opportunity for numerous additive reactions, whereas its absence from the xanthines results in their incapacity for addition. The xanthines, and particularly the *iso*xanthines, have pronouncedly aromatic character. The double linking in the five-membered ring cannot be detected additively, whereas substitution occurs readily in position 8, giving stable halogeno-, nitroso-, and nitro-compounds which can be reduced to amino-derivatives.

Uramil is converted by allylthiocarbimide and aqueous potassium hydroxide into 9-*allyl*-8-*thio*-ψ-*uric acid*, m. p. 264° (decomp.), converted by boiling hydrochloric acid into 9-*allyl*-8-*thiouric acid*, m. p. 319° (decomp.). The following compounds are prepared similarly: 7-*methyl*-9-*allyl*-8-*thio*-ψ-*uric acid*, m. p. 226° (decomp.), and 7-*methyl*-9-*allyl*-8-*thiouric acid*, m. p. 317° (decomp.); 1-*methyl*-9-*allyl*-8-*thio*-ψ-*uric acid*, m. p. 242° (decomp.), and 1-*methyl*-9-*allyl*-8-*thiouric acid*, m. p. 309° (decomp.); 1 : 7-*dimethyl*-9-*allyl*-8-*thio*-ψ-*uric acid*, m. p. 186° (decomp.), and 1 : 7-*dimethyl*-9-*allyl*-8-*thiouric acid*, m. p. 256° (decomp.); 1 : 3-*dimethyl*-9-*allyl*-8-*thio*-ψ-*uric acid*, m. p. 192°, and 1 : 3-*dimethyl*-9-*allyl*-8-*thiouric acid*, m. p. 326° (decomp.). The following 9-alkyl*iso*xanthine-8-thiolacetic acids are prepared by the action of chloroacetic acid on 9-alkyl-8-thiouric acids: 9-*allyl*-, m. p. 257°; 9-*methyl*-, m. p. 329°; 9-*ethyl*-, m. p. 289°; 9-*propyl*-, m. p. 268° [9-*propyl*-8-*thiouric acid*, m. p. 354° (decomp.)]. 9-Allyl- and 9-methyl-*iso*xanthine-8-thiolacetic acids are converted by concentrated hydrochloric acid into 9-*allyluric acid*, m. p. (indef.) 355—365° (decomp.), and 9-methyluric acid, m. p. (indef.) 385—400° (decomp.), respectively. Chloroacetic acid and the requisite 8-thiouric acid afford the following xanthine-8-thiolacetic acids: 1 : 3 : 7-*trimethyl*-, m. p. 240° [*sodium* salt, m. p. 305° (decomp.)]; 3 : 7-*dimethyl*-, m. p. 302° (darkening) [*sodium* salt, m. p. 360° (decomp.)]; 1 : 3-*dimethyl*-, m. p. 265°, -*xanthine*-8-*thiolacetic acid*, m. p. 343° (decomp.). Sodium nitrite converts 9-methyl-8-thiouric acid in boiling nitric acid into 8-*nitroso*-9-*methyl*iso*xanthine*, m. p. (indef.) 355—360° after darkening at 290° (isolated through the *monohydrated ammonium* salt), also obtained similarly from 9-methyl*iso*xanthine.

8-*Nitroso*-9-*allyl*isoxanthine, m. p. 305—307° (decomp.) after darkening at 270° (monohydrated *ammonium* salt), is described. Under milder conditions, 9-allyl-8-thiouric acid is converted by nitrous acid into 9-allyl-Δ^7-*iso*xanthine, m. p. about 310°. 8-*Nitroso*-1 : 3 : 9-*trimethyl*isoxanthine has m. p. 257° (decomp.). Caffeine, theobromine, and theophylline could not be nitrosated. 7-Methyl-9-allyl-8-thiouric acid and nitrous acid afford 7-*methyl*-9-*allyldeoxyuric acid*, m. p. 326° (decomp.) (*hydrochloride*, m. p. 222°). Treatment of 9-methyl- and 9-allyl-8-thiouric acid with bromine water gives 8-*bromo*-9-*methyl*isoxanthine, darkening above 290°, and 8-*bromo*-9-*dibromopropyl*isoxanthine, becoming yellow above 120°, respectively, whereas 3 : 9-dimethyluric acid affords the corresponding glycol. 1 : 3 : 9-Trimethyl*iso*xanthine is transformed by methyl sulphate and sodium hydroxide into 1 : 3 : 8 : 9-*tetramethyl*isoxanthine, m. p. 249°, converted by bromine water into 8-bromo-1 : 3 : 9-trimethyl*iso*xanthine, m. p. 256° (decomp.). 1 : 3 : 7 : 8-Tetramethylxanthine similarly yields 8-bromo-1 : 3 : 7-trimethylxanthine. 9-Methyl*iso*xanthine and methyl sulphate give 8 : 9-*dimethyl*isoxanthine, m. p. 363° (decomp.). H. WREN.

Constitution of 4′-hydroxyphthalazone [phthalylhydrazide] and its derivatives. D. RADULESCO and V. ALEXA (Bul. Soc. Chim. Romania, 1930, **12**, 140—163).—Hantzsch's quinonoid theory of the colour of nitro-derivatives is untenable. When a nitro-compound is coloured, the nitrogen has negative polarity. In nitrophenol salts the metal replaces the hydrogen of the hydroxy-group.

From the sodium salt of 4′-hydroxyphthalazone the calcium, silver, cobalt, nickel, and copper salts can be prepared by double decomposition [phthalylhydrazide salts according to Curtius and Fosterling (A., 1895, i, 354) and Radenhausen (A., 1896, i, 137)], and the existence of pyridine–metal salt complexes (prepared by evaporating pyridine solutions of the salts) of the type

$\left(C_6H_4<\begin{matrix}CO\cdot NH\cdot N\\ \text{——}C\cdot O\end{matrix}>\right)_2$ metal . . . $(C_5H_4N)_{2(\text{or }4)}$ can be shown by a determination of their co-ordination numbers and by a study of their absorption spectra (cf. Radulescu and Barbulescu, A., 1929, 1213), which differ profoundly from those of metal salts having a co-ordination number of 6. Similar phenomena are exhibited by the pyridine complexes of the metal salts of 5- and 6-nitro-4′-hydroxyphthalazone [nitrophthalylhydrazides according to Bogert and Boroschek (A., 1902, i, 98) and Curtius and Hoesch (A., 1907, i, 1079)] and of 5 : 6 : 7 : 8-tetrachloro-4′-hydroxyphthalazone [a chlorophthalylhydrazide according to Phelps (A., 1905, i, 528)]; and similar absorption phenomena by aqueous solutions of 5- and 6-amino-4′-hydroxyphthalazone [aminophthalylhydrazides according to Curtius and Hoesch (A., 1907, i, 1079)]. The changes in the ultra-violet absorption which should result, according to Hantzsch's theory, from the introduction of a nitro-group are not found, nor are the absorption curves for the isomeric nitro-derivatives identical. The absorption curve of quinolhydrazide agrees with that expected on the new theory.

The liberation of 4′-hydroxyphthalazone (phthalylhydrazide) from its sodium salt by bubbling carbon dioxide through its aqueous solution, a reaction doubted by Mihailescu and Protopopescu (A., 1930, 1434), takes place readily.

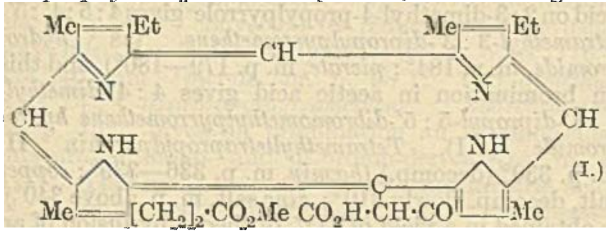
The 5-nitro-4′-hydroxyphthalazone (nitrophthalylhydrazide) used was prepared in increased yield by a modification of the original method. A. RENFREW.

Benzoylenearyliminazoles and diphthalimido-derivatives. G. B. CRIPPA and P. GALIMBERTI (Gazzetta, 1931, **61**, 91—98; cf. A., 1930, 205).—Whereas *o*-aminoazobenzene condenses with phthalic anhydride to give the corresponding phthalimide derivative, which is readily convertible into benzoylenebenziminazole, 4 : 6-diphenylazo-1 : 3-phenylenediamine behaves towards phthalic anhydride like the *o*-aminoazo-derivatives of the naphthalene series, giving *m*-diphthalimidobenzene and not *s*-bisbenzoylenebenziminazole. The latter may, however, be obtained as follows. 1 : 5-Dinitro-2 : 4-diaminobenzene condenses with phthalic anhydride to form 1 : 5-*dinitro*-2 : 4-*diphthalimidobenzene*, m. p. 249°, which, on reduction with acetic acid and iron, yields s-*bisbenzoylenebenziminazole*, m. p. 300°; this was purified by hydrolysing it to *benzenebis*-(2 : 3 and 2 : 5)-*azimido*-C-*phenyl*-o-*carboxylic acid* and subjecting this to dehydration.

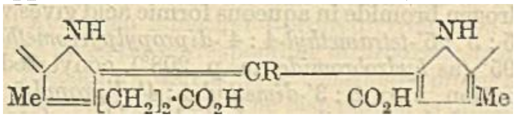
2 : 3-Diamino-9 : 10-phenazine readily condenses with phthalic anhydride to give 2 : 3-(*benzoyleneazimino*)-9 : 10-*phenazine*, m. p. 358°, which forms 9 : 10-*phenazine*-2 : 3-*azimino*-C-*phenyl*-o-*carboxylic acid* on hydrolysis. The *o*-diaminic character of 2 : 3-diamino-9 : 10-phenazine is shown by its condensation with phenanthrenequinone to yield *phenanthrazinephenazine*, decomp. above 300°. Although aromatic *o*-diamines react with nitrous acid with formation of azimino-derivatives, 9 : 10-diaminophenanthrene gives no such condensation product with nitrous acid, which merely oxidises it to phenanthrenequinone. With phthalic anhydride, 9 : 10-diaminophenanthrene reacts to form 9 : 10-*phenanthrenediphthalamic acid*, $\begin{matrix}C_6H_4\cdot\\ C_6H_4\cdot\end{matrix}\begin{matrix}\cdot NH\cdot C_6H_4\cdot CO_2H\\ \cdot NH\cdot C_6H_4\cdot CO_2H\end{matrix}$ (*sodium* salt), which gives 9 : 10-*phenanthrylenebisphthalimide*, m. p. 257°, on sublimation. T. H. POPE.

Chlorophyll. XVI. Constitution of chlorophyll *a*. Phæophorbide, methylphæophorbide, and chlorin *e*. H. FISCHER, O. MOLDENHAUER, and O. SÜS. **XVII. Conversion of chlorophyll-pyrroporphyrin into the mesoporphyrin from hæmin.** H. FISCHER and H. J. RIEDL (Annalen, 1931, **486**, 107—177, 178—190).—XVI. Phæoporphyrins a_6, a_5, and a_4 give the same *oxime*, with diazomethane the same *dimethyl* ester, m. p. 273°, and are identical in all respects. Phæoporphyrin a_5 is formed by the degradation of phæophytin with hydriodic acid, and similarly, but in smaller yield, from methylchlorophyllide and allomerised methylchlorophyllide. Attempted esterification with methyl-alcoholic hydrogen chloride gives the esters of phylloerythrin and chloroporphyrin e_6. The dimethyl ester, however, gives only the latter, and in phæoporphyrin a_5 a free carboxyl group must be attached to the *cyclo*pentenone ring; in phæophytin this must be esterified

by phytol. The formula I is therefore suggested for phæoporphyrin a_5 monomethyl ester, necessitating the


(I.)

reformulation of chloroporphyrin e_6 (cf. A., 1930, 482) as rhodoporphyrin-γ-acetic acid (II, R=$\cdot CH_2\cdot CO_2H$; the upper half of this formula is as in I).


(II.)

Similarly, alcoholic potassium hydroxide gives the *monomethyl* ester of chloroporphyrin e_6, m. p. 235° (decomp. into pyrroporphyrin and phylloerythrin), identified by complete esterification with diazomethane. The reverse change of chloroporphyrin e_6 or its ester into I is effected by sodium hydroxide and pyridine at its b. p. (chloroporphyrin e_5 and e_4 and phylloerythrin are stable to this reagent), or by hydroxylamine hydrochloride and barium carbonate in alcohol, which gives phæoporphyrin a_5 oxime. Chloroporphyrin e_6 is degraded to phyllo-, rhodo-, and pyrro-porphyrins by 30% methyl-alcoholic potassium hydroxide at 150—155°, which confirms the newly suggested structure; hydrogen bromide in acetic acid at 50—55° gives ψ-phylloerythrin, and at 165° deoxyphylloerythrin, and formic acid at its b. p. gives chloroporphyrin e_4.

The tricarboxylic acid of Noack and Kiessling (this vol., 247) was obtained in minute yield only by their method; it is best prepared by interaction of phylloerythrin and 10% alcoholic potassium hydroxide at the ordinary temperature in a stream of oxygen, in the absence of which not a trace is formed. Its reconversion into phylloerythrin (*loc. cit.*) has not been effected. The action of methyl-alcoholic hydrogen chloride gives a *monomethyl* ester of the anhydride, m. p. 167—168° (264° after drying at 90°); 30% methyl-alcoholic potassium hydroxide at 150—154°, hydrogen bromide and acetic acid at 50°, or formic acid at its b. p., gives rhodoporphyrin with loss of 1 mol. of carbon dioxide; it is therefore considered to be rhodoporphyrin-γ-carboxylic acid (II, R=CO_2H). A further proof of the essential identity of phyllo- and ψ-phyllo-erythrins is afforded by the conversion of the latter into this acid. By repeated recrystallisation from pyridine and acetic acid the latter gradually acquires the power of crystallising with combined chloroform characteristic of phylloerythrin.

*iso*Phæoporphyrin a_3 is identical with deoxyphylloerythrin; a small amount of impurity is removed by catalytic reduction and reoxidation.

Reduction of methylphæophorbide *a* with hydriodic acid gives phæoporphyrin a_5 dimethyl ester, also obtained with iron and formic acid (cf. Noack and Kiessling, this vol., 247; the spectral differences observed by these authors are caused by a removable impurity). Formic acid at its b. p. gives phylloerythrin and a chlorin. Chloroporphyrin e_5 (*potassium* salt; *oxime*) is reduced by the Wolff–Kishner method to phyllo-, pyrro-, and rhodo-porphyrins, confirming the structure of γ-formylrhodoporphyrin (II, R=·CHO) already assigned. The formula previously given for chloroporphyrin e_4 (II, R=Me) is supported by the formation of phylloporphyrin with loss of 1 mol. of carbon dioxide with hydrogen bromide in acetic acid at 180°. Phyllo- and pyrroporphyrins are formed by the Wolff–Kishner reduction of chlorin *e* or its trimethyl ester. Formulæ are suggested for phæophorbide *a* (based on work of Conant, this vol., 368) and chlorophyll.

XVII. The interaction of pyrrohæmin with chloromethyl ether and stannic chloride (cf. this vol., 101) gives the *hæmin* of 1 : 3 : 5 : 8-*tetramethyl*-2 : 4-*diethyl*-6-*acetoxymethylporphin*-7-*propionic acid*, simultaneous hydrolysis and acetylation having occurred. Hydrolysis with hydrogen bromide in acetic acid and interaction of the crude bromo-derivative with methyl alcohol give the corresponding *ether-ester*, m. p. 232° [*hæmin*, m. p. 242°; *copper* complex, m. p. 192°, of the acetoxyporphyrin (see below)], readily hydrolysed to the free *hydroxymethylpyrroporphyrin*, m. p. above 290°, with intermediate formation of the bromo-derivative (*hydrobromide*). The bromo-derivative reacts with ethyl potassiomalonate in dry acetone with formation of *methyl* 1 : 3 : 5 : 8-*tetramethyl*-2 : 4-*diethylporphin*-7-*propionate*-6-*methylmalonate*, m. p. 235° (*hæmin*, m. p. 224°), and a *substance*, m. p. 205°. Hydrolysis of the former with hydrochloric acid at 180° with simultaneous decarboxylation gives mesoporphyrin.

The ether-ester of dihydroxymethyldeuteroporphyrin gives with cupric chloride in hot glacial acetic acid the complex *copper* salts, m. p. 220° (sinters 180°), and 200° (sinters 170°), of the *di*- and *monoacetyl* derivatives, respectively, of the methyl ester. It differs in this respect from the above pyrroporphyrin derivative, in which the ester group is also hydrolysed.

H. A. PIGGOTT.

Allomerisation of chlorophyll. J. B. CONANT, S. E. KAMERLING, and C. C. STEELE (J. Amer. Chem. Soc., 1931, 53, 1615—1616).—The dehydrogenation of chlorophyll during allomerisation is brought about by atmospheric oxygen, which is absorbed to an extent corresponding with the removal of 1 mol. of hydrogen with formation of hydrogen peroxide. Chlorophyll or its magnesium-free derivatives of the *a* or *b* series may be dehydrogenated by potassium molybdicyanide in acetone and pyridine, two equivalents of the oxidising agent being needed per mol. Dehydrogenated chlorophyll *a* thus prepared is identical with allomerised chlorophyll; on removal of magnesium the product is spectroscopically indistinguishable from methyl dehydrophæophorbide, which is obtained in quantity by action of the molybdicyanide on methyl phæophorbide, and on hot alkaline hydrolysis yields the unstable chlorins obtained from allomerised chlorophyll.

H. A. PIGGOTT.

Crystallisation of protoporphyrin. A. HAMSÍK (Z. physiol. Chem., 1931, 196, 195—198).—Crude protoporphyrin prepared by various methods from

hæmatin, chlorohæmin, and directly from blood was purified by way of the sodium or potassium salt and with pyridine. The purified product was obtained in various interconvertible crystalline forms according to the method of crystallisation selected.

J. H. Birkinshaw.

Porphyrin syntheses. XXXVII. Synthesis of tetramethyltetrapropylporphins I—IV and octapropylporphin. H. Fischer, M. Goldschmidt, and W. Nussler (Annalen, 1931, 486, 1—54).—*Ethyl* 3-*propionyl*-2 : 4-*dimethylpyrrole*-5-*carboxylate*, m. p. 140°, is obtained from ethyl 2 : 4-dimethylpyrrole-5-carboxylate by the Friedel–Crafts reaction (50°; no solvent). Bromination in acetic acid gives *ethyl* 3-*propionyl*-4-*methyl*-2-*bromomethylpyrrole*-5-*carboxylate*, m. p. 145°, and reduction with hydrazine hydrate and alcoholic sodium ethoxide gives 2 : 4-*dimethyl*-3-*propylpyrrole* (I), b. p. 98—100°/15 mm., m. p. 13·5°, d^{-0} 0·8988, $n_D^{21\cdot5}$ 1·49243 [*picrate*, m. p. 134°; *ketazine*, $C_{18}H_{26}N_4$, m. p. 159° (? or of 3-propionyl-2 : 4-dimethylpyrrole); p-(?)-*sulphobenzeneazo*-derivative, m. p. 248°], and a *substance*, b. p. 141—145°/15—16 mm. (*dihydrochloride*, m. p. 145°, *dipicrate*, m. p. 137°), to which the formula

$$NH<\begin{matrix} N=\!=CR \\ CEt(R)\cdot CHMe \end{matrix}$$

(R being a 2 : 4-dimethylpyrrole residue) is provisionally assigned. An *oxime*, $C_8H_{12}O_2N_2$, m. p. 198°, is obtained from I by the action of nitrous acid, and the corresponding 5-*aldehyde*, m. p. 105°, and 5-*glyoxylic* (*ethyl*) ester, m. p. 192°, by treating with hydrogen cyanide and ethyl cyanoformate, respectively, in ethereal solution in presence of hydrogen chloride. Oxidation of I with chromic acid or treatment of the derived oxime with sulphuric acid gives methylpropylmaleimide (cf. Kuster, A., 1906, i, 337). Bromination of I gives 5-*bromo*-4 : 3′-*dimethyl*-3 : 4′-*dipropyl*-5′-*bromomethylpyrromethene hydrobromide*, m. p. 130°, which is capable of brominating acetone and is converted by crystallisation into 5-*bromo*-4 : 3′ : 5′-*trimethyl*-3 : 4′-*dipropylpyrromethene hydrobromide*, decomp. 207° (*hydrochloride*, m. p. 178°; *picrate*, m. p. 182°). Both pyrromethene hydrobromides yield the porphyrin with some difficulty by most of the ordinary methods, but on fusion with succinic acid at 180° give *tetramethyltetrapropylporphin* I, m. p. 290° (corresponding with ætioporphyrin I) [*copper* salt, m. p. 295°; *magnesium* salt, m. p. 249°; *chlorohæmin*, m. p. 338°; *bromohæmin*, m. p. 333°; *iodohæmin*, m. p. 310°; *nitro*-derivative, m. p. 272°; *xanthoporphyrinogen*, m. p. 262° (from which the original porphyrin is regenerated by reduction, and which gives methylpropylmaleimide on photo-oxidation)].

Ethyl 2 : 4-*dimethyl*-3-*propylpyrrole*-5-*carboxylate*, m. p. 98°, is obtained by the interaction of I, ethyl chloroformate, and magnesium ethyl bromide. Its 2-ω-*bromo*-derivative, m. p. 148°, gives with methyl alcohol containing a little formaldehyde *ethyl* 4 : 4′ *dimethyl*-3 : 3′-*dipropylpyrromethane*-5 : 5′-*dicarboxylate*, m. p. 166°, hydrolysed by alcoholic sodium hydroxide to the free *dicarboxylic acid*, m. p. 140°, which when boiled with glacial acetic acid gives a little porphyrin and 2-methyl-4-propylpyrrole (below). Bromination of the acid in formic acid gives 5 : 5′-*dibromo*-4 : 4′-*dimethyl*-3 : 3′-*dipropylpyrromethene*, m. p. 146° [isolated as *hydrobromide* (II); *picrate*, m. p. 181°]. The action of hydrogen bromide in aqueous formic acid on 2 : 3-dimethyl-4-propylpyrrole gives 4 : 5 : 4′ : 5′-*tetramethyl*-3 : 3′-*dipropylpyrromethene* (as *hydrobromide*, m. p. 184°; *picrate*, m. p. 179—180°), and this on bromination in acetic acid gives 4 : 4′-*dimethyl*-3 : 3′-*dipropyl*-5 : 5′-*dibromomethylpyrromethene hydrobromide* (III). *Tetramethyltetrapropylporphin* II, m. p. 330° (decomp.) (*hæmin*, m. p. 336—339°; *copper* salt, decomp. slowly 310°; *zinc* salt, m. p. above 340°), is obtained in a yield of 41% of theory by fusion of an equimolecular mixture of II and III with succinic acid, and in minute yield by the long-continued air-oxidation of the pyrromethane in acetic acid at 30—40°.

Hydrogen bromide in aqueous formic acid gives with I 3 : 5 : 3′ : 5′-*tetramethyl*-4 : 4′-*dipropylpyrromethene*, m. p. 95° (as *hydrobromide*, m. p. 208°), converted by bromination into 3 : 3′-*dimethyl*-4 : 4′-*dipropyl*-5 : 5′-*dibromomethylpyrromethene hydrobromide*, decomp. above 200°. A mixture of equimolecular amounts of this and II when fused with a mixture of succinic and tartaric acids (9 : 1) at 190°, or heated with hydrogen bromide in glacial acetic acid at 170—175°, gives *tetramethyltetrapropylporphin* IV, m. p. 218° (*hæmin*, m. p. 276°; *silver* salt, m. p. 267°; *copper* salt, m. p. 255°).

Ethyl 2-*methyl*-4-*propylpyrrole*-3 : 5-*dicarboxylate*, m. p. 102°, is synthesised by the action of nitrous acid, followed by ethyl acetoacetate, and zinc and acetic acid, on ethyl butyrylacetate (cf. Knorr, A., 1887, 277; Zanetti, A., 1894, i, 109). The ethyl residue attached to the 3-carboxyl group is removed by concentrated sulphuric acid at 140°, the *ethyl hydrogen* ester having m. p. 217° (decomp.). On careful distillation this gives *ethyl* 2-*methyl*-4-*propylpyrrole*-5-*carboxylate*, m. p. 80°, converted by Gattermann's method into the corresponding 3-*aldehydo*-compound, m. p. 117°, which on Wolff–Kishner reduction gives 2 : 3-*dimethyl*-4-*propylpyrrole*, b. p. 96—98° (*picrate*, m. p. 127°). A mixture of this with an equimolecular proportion of 2 : 4-dimethyl-3-propylpyrrole-5-aldehyde gives with alcoholic hydrobromic acid 4 : 5 : 3′ : 5′-*tetramethyl*-3 : 4′-*dipropylpyrromethene hydrobromide*, decomp. 182° (sinters 177°) (*picrate*, decomp. 162°; *perbromide*, m. p. 100°), converted in the usual way into 4 : 3′-*dimethyl*-3 : 4′-*dipropyl*-5 : 5′-*dibromomethylpyrromethene hydrobromide* (IV). Introduction of the carbethoxy-group in the usual manner into 2 : 3-dimethyl-4-propylpyrrole, gives the corresponding 5-*carbethoxy*-derivative, m. p. 102°, converted by bromination into *ethyl* 3-*methyl*-4-*propyl*-2-*bromomethylpyrrole*-5-*carboxylate*, m. p. 156°. With methyl alcohol and a little formaldehyde this gives *ethyl* 3 : 3′-*dimethyl*-4 : 4′-*dipropylpyrromethane*-5 : 5′-*dicarboxylate*, m. p. 132°; the free *dicarboxylic acid*, m. p. 168°, is converted into 5 : 5′-*dibromo*-3 : 3′-*dimethyl*-4 : 4′-*dipropylpyrromethene*, m. p. 141° (*hydrobromide*), in the usual way. *Tetramethyltetrapropylporphin* III, m. p. 206° (*hæmin*, m. p. 297°; *copper* salt, m. p. 235°; *zinc* salt, m. p. 250°; *picrate*, decomp. 190—204°), is obtained by heating an equimolecular mixture of this and IV or of IV and II with hydrobromic and formic acids at 130—135°, or of the latter pair with acetic and hydrobromic acids at 170—175°.

Introduction of the propionyl group into the corresponding pyrrole by the Friedel–Crafts reaction gives *ethyl 3-propionyl-2-methyl-4-propylpyrrole-5-carboxylate*, m. p. 119°, converted by reduction in the usual way into *2-methyl-3 : 4-dipropylpyrrole*, b. p. 116—124°/40 mm. (*picrate*, m. p. 98°); *5 : 5′-dimethyl-3 : 3′ : 4 : 4′-tetrapropylpyrromethene hydrobromide*, m. p. 152°, gives on bromination an equimolecular mixture of mono- and di-bromo-derivatives, m. p. 113°. This on fusion with succinic and tartaric acids (4 : 1) gives *octapropylporphin*, m. p. 276° (*hæmin*, sinters 225°, no m. p.; *copper* salt, m. p. 327°).

The spectra of these new porphyrins are described, those of the isomeric tetramethyltetrapropylporphins being identical. The alkaline hydrolysis of ethyl or ethyl hydrogen 2-methyl-4-propylpyrrole-3 : 5-dicarboxylate gives the corresponding *dicarboxylic acid*, m. p. 251° (decomp.), and a little *2-methyl-4-propylpyrrole*, b. p. 86—88°/15 mm. The last-named is prepared by thermal decomposition of the acid, and gives with hydrogen bromide in formic acid *2 : 2′-dimethyl-4 : 4′-dipropylpyrromethene hydrobromide*, m. p. 190° (*picrate*; *copper* complex salt, sinters 160°), and with bromine in acetic acid a *perbromide* ($C_{16}H_{22}N_2Br_4$) of 2-bromo-2′-methyl-4 : 4′-dipropylpyrromethene hydrobromide. *Ethyl 2-formyl-4-propylpyrrole-3 : 5-dicarboxylate*, m. p. 88° [*hydrazone*, m. p. 118°; *semicarbazone*, m. p. 199°; *phenylhydrazone*, m. p. 85° (decomp.)], results from the action of sulphuryl chloride on ethyl 2-methyl-4-propylpyrrole-3 : 5-dicarboxylate; the corresponding *dicarboxylic acid*, decomp. above 210°, condenses with 2-methyl-4-propylpyrrole in presence of alcoholic hydrogen bromide to *5′-methyl-4 : 3′-dipropylpyrromethene-3-carboxylic acid hydrobromide*, decomp. 100°.

3-Propionyl-2 : 4-dimethylpyrrole-5-carboxylic acid, m. p. 214° (decomp.), gives on distillation *3-propionyl-2 : 4-dimethylpyrrole*, m. p. 122°. It gives on bromination *3 : 5-dibromo-4′-propionyl-4 : 5′-dimethylpyrromethene hydrobromide* (free base, m. p. 175° (decomp.)] with elimination of a propionyl group, and with hydrogen cyanide and chloride in ether *3-propionyl-2 : 4-dimethylpyrrole-5-aldehyde*, m. p. 169°, from which *4 : 4′-dipropionyl-3 : 5 : 3′ : 5′-tetramethylpyrromethene hydrobromide*, m. p. 197°, is prepared; on bromination this loses both propionyl groups, and gives the dibromopyrromethene of 2 : 4-dimethylpyrrole. *4 : 4′-Dipropionyl-3 : 5 : 3′ : 5′-tetramethylpyrromethane*, m. p. 225°, is prepared from the pyrrole and formaldehyde.

Improvements in the preparation of ethyl butyroacetate are described, and the composition of the keto-enol mixture in a large variety of organic solvents and also in the pure liquid was determined by Kurt Meyer's method. By condensation with the substances in parentheses by Zanetti's modification of Knorr's method, the following are prepared: *ethyl 2-ethyl-4-propylpyrrole-3 : 5-dicarboxylate*, m. p. 91° (propionacetic ester); *ethyl 2 : 4-dipropylpyrrole-3 : 5-dicarboxylate*, m. p. 87° (itself), and *ethyl 3-acetyl-2-methyl-4-propylpyrrole-5-carboxylate*, m. p. 112° (acetylacetone). *2 : 3-Dimethyl-4-propylpyrrole-5-aldehyde*, m. p. 75°, is prepared by Gattermann's method. In the preparation of 3 : 5 - diacetyl - 2 : 4 - dimethylpyrrole (Zanetti, *loc. cit.*), *3 : 6-diacetyl-2 : 5-dimethylpyrazine*, m. p. 101°, is obtained as a by-product.

H. A. Piggott.

Porphyrin syntheses. XXXVIII. New syntheses of coproporphyrin III and coprorhodin II. H. Fischer and J. Hierneis (Z. physiol. Chem., 1931, **196**, 155—168; cf. preceding abstract).—Coproporphyrin III was synthesised by succinic acid fusion from (*a*) (4 : 3′-dimethyl-5 : 5′-dibromomethyl-3-methyl propionate-4′-propionic acid)pyrromethane hydrobromide and (3 : 3′-dimethyl-4 : 4′-dipropionic acid)pyrromethene hydrobromide and (*b*) (4 : 5 : 3′ : 5′-tetramethyl-3-methyl propionate-4′-propionic acid)-pyrromethene hydrobromide and (3 : 3′-dimethyl-5 : 5′-dibromo-4 : 4′-dipropionic acid)pyrromethene hydrobromide. It was isolated as the methyl ester, m. p. 142—143° and 169°; the two forms are interconvertible. A mixture of coproporphyrins I and III was obtained from (4 : 3′ : 5′-trimethyl-5-bromo-3 : 4′-dipropionic acid)pyrromethene hydrobromide and (3 : 5 : 3′-trimethyl-4 : 4′-dipropionic acid)pyrromethene hydrobromide, I being formed by condensation of the bromo-compound with itself. The esters were separated by fractionation. The ester of coproporphyrin III, m. p. 142—143°, yields complex salts: *zinc*, m. p. 190—195°, *copper*, m. p. 206—207° (sinters at 195°), *iron*, m. p. 179°. The ester of m. p. 169° forms complex salts: *zinc*, m. p. 216—217°, *copper*, m. p. 206—207°, *iron*, m. p. 179°.

The occurrence of coproporphyrins I, II, and III together is explained by the primary fission of the methanedicarboxylic acid to form the opso-acid and the radical of hæmopyrrolecarboxylic acid. Thus (3 : 3′-dipropionic acid-4 : 4′-dimethyl-5 : 5′-dicarboxy)pyrromethane in boiling acetic acid yields opsopyrrolecarboxylic acid. Coproporphyrin II by the action of fuming sulphuric acid produces rhodin (*methyl* ester, m. p. 220°). Hæmin when heated with resorcinol and β-chloropropionic acid gives deuteroporphyrin.

J. H. Birkinshaw.

Ketophenmorpholine syntheses. E. Puxeddu and G. Sanna (Gazzetta, 1931, **61**, 158—168; cf. A., 1930, 225).—*2-Chloroacetamidophenol*, m. p. 138°, is readily obtained from *o*-aminophenol and chloroacetyl chloride. Ketophenmorpholine (cf. Aschan, A., 1887, 814), m. p. 168—169°, subliming at about 100°, may be obtained by the action of potassium hydroxide, diethylamine, or other organic base on 2-chloroacetamidophenol or by reducing *o*-nitrophenoxyacetic acid. The *o*-aminophenoxyacetic acid formed as intermediate product in the last reaction was obtained only as *potassium* salt. *2 : 3-Diketophenmorpholine*, m. p. 258—259°, may be prepared by treating *o*-aminophenol with oxalyl chloride. *5-Chloroacetamido-p-cresol*, m. p. 173°, yields *6-methyl-2-ketophenmorpholine*, m. p. 206°, when treated with either aqueous potassium hydroxide or anhydrous diethylamine. Treatment of 5-amino-*p*-cresol with oxalyl chloride yields two isomeric *compounds*, m. p. 272—273° and 230°, respectively, which are probably 6-methyl-2 : 3-diketophenmorpholine and its enolic form.

T. H. Pope.

Synthesis of 4-phenyl-2-hydroxymethylthiazole and derivatives. J. F. Olin and T. B. Johnson (J. Amer. Chem. Soc., 1931, **53**, 1470—1473).—The *benzoate*, m. p. 73—74°, of 4-phenyl-2-hydroxymethylthiazole is obtained from benzoylglycollthioamide

and phenacyl bromide in pyridine; the corresponding *ethyl ether*, b. p. 187—188°/15 mm., is similarly prepared. 4-*Phenyl-2-hydroxymethylthiazole*, m. p. 88—89°, b. p. 210—215°/20 mm. (*acetyl*, m. p. 40°, b. p. 193°/4 mm., and *benzoyl*, m. p. 73—74°, derivatives), is obtained from the above derivatives by hydrolysis with alcoholic potassium hydroxide and 80% sulphuric acid, respectively, and is converted by hydrogen bromide in acetic anhydride into 4-*phenyl-2-bromomethyl-*, b. p. 195°/15 mm., by phosphoryl chloride into 4-*phenyl-2-chloromethyl-thiazole*, b. p. 184°/16 mm., and by oxidation with chromic acid into 4-*phenylthiazole-2-aldehyde*, b. p. 160—162°/14 mm. [*phenylhydrazone*, m. p. 131—132°; *aldoin*, $C_9H_6NS\cdot CO\cdot CH(OH)\cdot C_9H_6NS$, m. p. 256°].

H. A. Piggott.

Synthesis of 2-acetyl-4-phenylthiazole. J. F. Olin and T. B. Johnson (J. Amer. Chem. Soc., 1931, **53**, 1473—1475).—Interaction of the thioamide of benzoyl-lactic acid (this vol., 353) and ω-bromoacetophenone in boiling alcohol gives 4-*phenyl-2-α-hydroxyethylthiazole benzoate*, b. p. 252—254°/14 mm.; this is readily hydrolysed by alcoholic potassium hydroxide to the corresponding *alcohol*, m. p. 76°, b. p. 191—194°/16 mm., which is oxidised by sodium dichromate and acetic acid to 4-*phenyl-2-thiazolyl methyl ketone*, m. p. 78—79° (*phenylhydrazone*, m. p. 208—209°; ω-*bromo*-derivative, m. p. 106—107°).

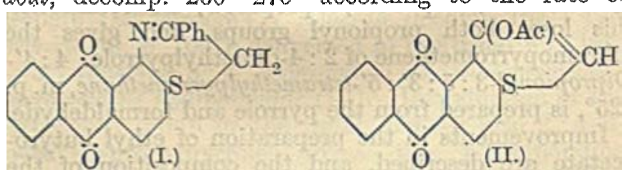
H. A. Piggott.

Synthesis of thiazole amines containing the pyrocatechol group. J. F. Olin and T. B. Johnson (J. Amer. Chem. Soc., 1931, **53**, 1475—1477).—γ-Phthalimidobutyronitrile (Gabriel, A., 1890, 360) is converted by alcoholic ammonium sulphide into the corresponding *thioamide*, m. p. 181—182°, which with 3 : 4-dihydroxyphenacyl chloride in alcohol gives 2-γ-*phthalimidopropyl*-4-(3′ : 4′-*dihydroxyphenyl*)-*thiazole*, m. p. 114—115°, hydrolysed by the hydrazine method (Ing and Manske, A., 1926, 1132) to 2-γ-*aminopropyl*-4-(3′ : 4′-*dihydroxyphenyl*)*thiazole*, [isolated as *sulphate* (+3½H_2O), m. p. 120—140° (decomp., in a closed tube); (anhyd.), m. p. 226—228°]. β-*Chloropropionitrile*, b. p. 76°/20 mm., prepared from ethylene cyanohydrin and thionyl chloride, is converted in the usual way into β-*phthalimidopropionitrile*, m. p. 147—148°, and -*thioamide*, m. p. 187—189°. The last-named is converted as before into 2-β-*phthalimidoethyl*-, m. p. 203—205°, and 2-β-*amino-ethyl*-4-(3′ : 4′-*dihydroxyphenyl*)*thiazole* (*sulphate*).

H. A. Piggott.

Thioindigotins of naphthalene. A. Corbellini and L. Albenga (Gazzetta, 1931, **61**, 111—130).—Reduction of naphthalene-1 : 5-disulphonyl chloride (cf. A., 1927, 551) with sodium sulphide yields *naphthalene-1 : 5-disulphinic acid*, m. p. 174—175° (decomp.), which reacts readily with quinones, giving, for instance, with *p*-benzoquinone (2 mols.), 1 : 5-*naphthylenedi-(1 : 4-dihydroxybenzene)disulphone*, $C_{10}H_6[\cdot SO_2\cdot C_6H_3(OH)_2]_2$, m. p. 294° (uncorr.), probably by way of an intermediate quinolic compound (cf. Hinsberg, A., 1917, i, 575). Other methods of reduction of naphthalene-1 : 5-disulphonyl chloride yield, as intermediate products, the 1 : 5-naphthylene ester of naphthalene-1 : 5-dithiodisulphonic acid and di-1 : 5-naphthylene didisulphide, these two compounds being obtained only as a mixture (?), m. p. 234° (decomp.). The ultimate product of the reduction is naphthalene 1 : 5-dimercaptan (cf. Braun and Ebert, A., 1892, 1471). Treatment of the latter with an alkaline solution of chloroacetic acid yields *naphthalene-1 : 5-dithioglycollic acid*, m. p. 251° (uncorr.), which forms a *dichloride*, m. p. 119°, a *dimethyl* ester, m. p. 86°, a *diethyl* ester, m. p. 59°, and a *diamide*, m. p. 239°, and, under the action of sulphuric acid, is converted into 1 : 2-naphtho-(3′-oxy-1′-thiophen)-5-thioglycollic acid and a violet thioindigo, *bis-1 : 2-naphthothioindigotin-5 : 5′-dithioglycollic acid*, probably formed by oxidation of the preceding compound and analogous to indirubin; this compound imparts a fast greenish-blue colour to cotton. T. H. Pope.

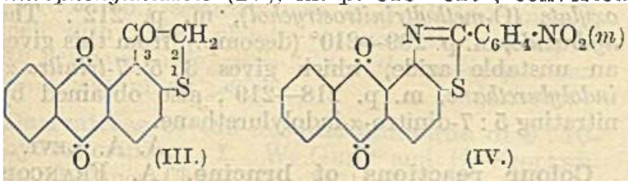
Anthracene derivatives. V. 2 : 1-Thioindigotins of the anthraquinone series. VI. Derivatives of anthraquinone-2 : 1-thiazole and other compounds from 1-amino-2-thiolanthraquinone and halogeno-compounds. P. Ruggli and W. Heitz (Helv. Chim. Acta, 1931, **14**, 257—275, 275—285).—V. 1-Aminoanthraquinone and sodium sulphide at 70—140° (cf. G.P. 290,080) give the sodium salt of 1-amino-2-thiolanthraquinone, converted by methyl sulphate into 1-*amino-2-methylthiolanthraquinone*, red, m. p. 186°, and by phenacyl bromide into 1-*amino-2-phenacylthiolanthraquinone*, red. When the last-named compound is heated above 130°, dissolved in sulphuric acid, or heated with nitrobenzene, water is eliminated and the *thiazine* (I), bluish-black, m. p. 262°, results. Chloroacetic acid and the above sodium salt give 1-aminoanthraquinone-2-thioglycollic acid [*sodium* salt; *methyl* ester, m. p. 135°; *ethyl* ester, m. p. 116·5° (prepared similarly using ethyl bromoacetate)], readily converted by warm sulphuric acid or boiling acetic acid into the corresponding *lactam*, decomp. about 250°. The diazonium perchlorate from ethyl 1-aminoanthraquinone-2-thioglycollate and potassium cuprous cyanide afford *ethyl 1-cyanoanthraquinone-2-thioglycollate*, m. p. 222° (*methyl* ester, m. p. 217°), hydrolysed by hydrochloric and acetic acids to 1-*cyanoanthraquinone-2-thioglycollic acid*, decomp. 260—270° according to the rate of



heating, and by warm sulphuric acid to 2-*carboxymethylthiolanthraquinone-1-carboxylamide*, decomp. 276°. Alkaline hydrolysis of this gives the corresponding *dicarboxylic acid*, m. p. 243—244° when heated slowly, which when heated with acetic anhydride and sodium acetate affords the *acetoxythiophen* (II), m. p. 154°. Alkaline hydrolysis of this yields the *compound* (III), violet-black, m. p. 230—240° (decomp.) [2-*bromo*-derivative, m. p. 220° (decomp.)], which is re-acetylated to II and *p*-bromobenzoylated (pyridine method) to the p-*bromobenzoyloxythiophen* (II, Ac=$\cdot CO\cdot C_6H_4\cdot Br$), m. p. 228°. *Thioindigotins* are prepared from 1 mol. of III and 1 mol. of the following compounds: isatin (isatin-2-anil is used in the condensation), m. p. 290° (decomp.); acenaphth-

enequinone, m. p. 320° (decomp.). and 1 : 2-diketo-1 : 2-dihydrothionaphthen, decomp. from 360°. These dyes have no affinity for cotton. The *benzylidene* derivative of III has m. p. 257—261°.

VI. 1-Amino-2-thiolanthraquinone and *m*-nitrobenzoyl chloride in nitrobenzene at 170° give the *nitrophenylthiazole* (IV), m. p. 318—320°, converted

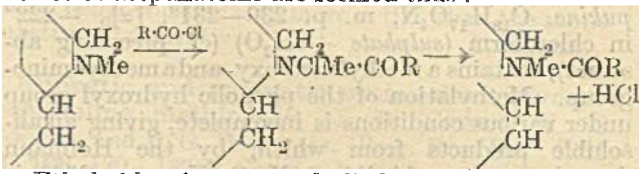


by nitric (*d* 1·52) and sulphuric acids at 60—70° into a *dinitro*-derivative, decomp. 350—355°, and reduced by alkaline sodium sulphide or hyposulphite to the corresponding *aminophenylthiazole*, m. p. 241° (*acetyl* derivative, m. p. 286°).

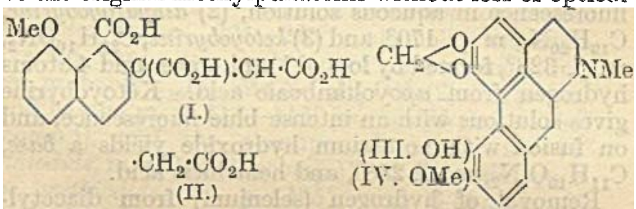
Diazotisation of this with nitrosylsulphuric acid and alkaline coupling of the resulting diazo-compound with β-naphthol, β-naphthol-6-sulphonic acid, and α-naphthol-3 : 8-disulphonic acid yields red *azo*-dyes. Treatment of the amino-derivative with carbonyl chloride in toluene at 90—95° affords a *carbimide* (IV, NO_2=NCO), m. p. 350—360°, which reacts with amyl alcohol forming the corresponding *urethane* (IV, NO_2=NH·$CO_2C_5H_{11}$), m. p. 221°, with aniline, yielding the *phenylcarbamide* derivative (IV, NO_2=NH·CO·NHPh), not melted at 300°, and with the above aminophenylthiazole furnishing the corresponding *carbamide*, not melted at 300°.

1-Amino-2-thiolanthraquinone and cyanogen chloride in warm nitrobenzene give the *compound* N$\lessdot$CR:N / CR·N$\gtrdot$CR [R=$C_{14}H_6O_2(NH_2)S$·], sinters about 210° and then decomposes gradually. Dichloroethylene and 1-amino-2-thiolanthraquinone in aqueous-alcoholic alkali afford *αβ-di-(1-amino-2-anthraquinonylthiol)ethylene*, decomp. about 270°; with an excess of dichloroethylene, *1-amino-2-β-chlorovinylthiolanthraquinone*, m. p. 180°, is also produced. H. Burton.

Constitution of pukateine and laureline. G. Barger and A. Girardet (Helv. Chim. Acta, 1931, 14, 481—504).—Extraction of the bark of *Laurelia Novæ Zealandiæ* with 70% alcohol containing 0·5% of acetic acid (cf. Aston, J.C.S., 1910, 97, 1381; improved method of isolation is described) affords pukateine, $C_{18}H_{17}O_3N$, b. p. 210—215°/2 mm., laureline, $C_{19}H_{19}O_3N$, m. p. 97°, $[\alpha]_D$ −98·5° (hydrochloride, m. p. 280°; *hydrobromide*; nitrate, m. p. 238—240°; *tartrate*, m. p. 220°, $[\alpha]_D$ −25·1°±3·14°), and a new alkaloid to which the name *laurapukine* is given (cf. following abstract), the substance originally so named (*loc. cit.*) being a mixture of the first two alkaloids. Methylation of the phenolic group in pukateine with nitrosomethylurethane affords *methylpukateine*, m. p. 137° (*methiodide*, m. p. 240—241°; *hydriodide*; *hydrochloride*, m. p. 281°; *hydrobromide*, m. p. 234°; *tartrate*, m. p. 238°, $[\alpha]_D$ −173° to −174·3°), which is not identical with laureline. Acetic anhydride and pyridine at 100° convert pukateine into its *O*-acetyl derivative, isolated as the *methiodide*, m. p. 245°. With acetic anhydride or benzoyl chloride at the b. p., inactive, non-crystalline, non-basic derivatives of despukateine are formed thus :

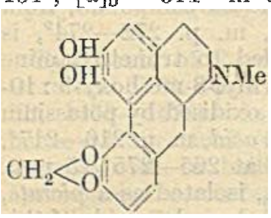


Ethyl chloroformate and alkali at 0° give a similar *derivative*, m. p. 101—103°. Attempts to hydrolyse the methylenedioxy-group in pukateine by various methods afford a substance with the reactions of pyrocatechol. Methylpukateine is converted by the Hofmann degradation first into a mixture of an optically active and an inactive unsaturated compound, from which an inactive *methiodide*, m. p. 272—274°, is isolated and is further degraded to trimethylamine and a *vinylphenanthrene* (? 2-vinyl-8-methoxy-9 : 10-methylenedioxyphenanthrene). oxidised by potassium permanganate in acetone to an *acid*, m. p. 216—217°, decarboxylated by distillation at 265—275°/15 mm. to the phenanthrene, $C_{16}H_{12}O_3$, isolated as a *picrate*, m. p. 183—184°. Oxidation of the polymeride of this vinylphenanthrene with potassium permanganate in aqueous pyridine at 90° affords an *acid*, m. p. 203—204°, converted by distillation at 150°/15 mm. into an *acid*, m. p. 131° (*methyl* ester, m. p. 98°), to which the structures I and II, respectively, are assigned. Oxidation of methylpukateine with iodine affords an amorphous product, reduced by zinc and acetic acid to the original methylpukateine without loss of optical



activity. Oxidation of pukateine with nitric acid after scission of the molecule between the nitrogen and asymmetric carbon atoms (Warnat, A., 1926, 185) affords mellophanic acid, whilst with permanganate in acetone is obtained(?) 4 : 5-methylenedioxybenzene-1 : 2 : 3-tricarboxylic acid, converted by sublimation at 150—180°/15 mm. into the anhydride, m. p. 110°, of *iso*hydrastic acid, characterised as its ethylimide (also obtained by similar oxidation of the ethyl carbonate derivative of despukateine). Oxidation of methylpukateine (or of its initial Hofmann degradation product) with alkaline potassium permanganate affords 3-methoxyphthalic acid. Similar results are obtained with laureline, which has the same nuclear skeleton. The *methiodide*, m. p. 223°, on exhaustive methylation affords, initially, a *substance*, m. p. 171°, further degraded to a *vinylphenanthrene*, m. p. 158°. oxidised by permanganate in acetone and chloroform to an *acid*, m. p. 279—281°, decarboxylated to a *methylenedioxymethoxyphenanthrene*, m. p. 132° (*picrate*, m. p. 172°). Oxidation of laureline with permanganate first in acid and then in alkaline solution affords 4-methoxyphthalic acid, identified as its anhydride and its anil. On the basis of these results the structures III and IV are assigned to pukateine and laureline, respectively. J. W. Baker.

Constitution of laurepukine. A. GIRARDET (Helv. Chim. Acta, 1931, **14**, 504—510).—*Laurepukine*, $C_{18}H_{17}O_4N$, m. p. 230—231°, $[\alpha]_D$ −222° in chloroform (*sulphate* $+6H_2O$) (cf. preceding abstract), contains a methylenedioxy- and a methylimino-group. Methylation of the phenolic hydroxyl group under various conditions is incomplete, giving alkali-soluble products from which, by the Hofmann degradation, a *methiodide* $C_{22}H_{26}O_4NI$, m. p. 262°, is obtained, but by use of the method employed with corytuberine (nitrosomethylurethane and 25% alcoholic potassium hydroxide on the alkaloid in amyl ether solution, Gadamer, A., 1912, i, 46) is obtained *dimethyl-laurapukine*, b. p. 200—210°/10 mm., m. p. 134°, $[\alpha]_D$ −314° in chloroform (*methiodide*, m. p. 249—250°), which gives an absorption spectrum (bands at λ 3720 and 3260) similar to but not identical with that of bulbocapnine and dicentrine methyl ether. On the basis of these and other considerations laurapukine is most probably represented by the annexed structure.



J. W. BAKER.

Structure of yohimbine. F. MENDLIK (Pharm. Weekblad, 1931, **68**, 257—271).—Selenium dehydrogenation of yohimbine gave (1) *yobyrine*, $C_{19}H_{18}N_2$, m. p. 217°, formed by removal of 1 mol. of carbon dioxide and 4 hydrogen atoms from *apo*yohimboaic acid, a base of which the salts show violet-blue fluorescence in aqueous solution, (2) *dihydroyobyrine*, $C_{19}H_{20}N_2$, m. p. 170°, and (3) *ketoyobyrine*, $C_{20}H_{16}ON_2$, m. p. 328°, formed by loss of 1 mol. water and 4 atoms hydrogen from *apo*yohimboaic acid. Ketoyobyrine gives solutions with an intense blue fluorescence, and on fusion with potassium hydroxide yields a *base*, $C_{11}H_{10}O_2N_2$, m. p. 258°, and hemellitic acid. Removal of hydrogen (selenium) from diacetylyohimbine gave yobyrine and dihydroyobyrine only, no ketoyobyrine being detected. The bearing of these results on the probable structure of yohimbine is discussed. S. I. LEVY.

Constitution of lupinene. P. KARRER (Ber., 1931, **64**, [*B*], 942; cf. Winterfeld and Holschneider, this vol., 370).—Exhaustive examination of the lupinene used by the author (A., 1929, 200) has failed to give evidence of non-homogeneity. H. WREN.

[**Constitution of chelidonine.**] F. VON BRUCHHAUSEN and H. W. BERSCH (Ber., 1931, **64**, [*B*], 947; cf. A., 1930, 1600).—A reply to Spath and Kuffner (this vol., 500). H. WREN.

Strychnine and brucine. XII. Constitution of dinitrostrycholcarboxylic acid. K. N. MENON and R. ROBINSON (J.C.S., 1931, 773—777; cf. A., 1930, 795).—Dinitrostrychol is shown to be 5 : 7-dinitroindole-2-carboxylic acid, whence dinitrostrycholcarboxylic acid is 5 : 7-dinitroindole-2 : 3-dicarboxylic acid. The bearing of this on the constitution of strychnine is discussed. Previous preparations (*loc. cit.*) of dinitrohydrazinodeoxystrychol (5 : 7-dinitroindole-2-carboxyhydrazide) gave a by-product (m. p. 202—204°) of 5 : 7-*dinitro 3-carbomethoxy-2-carboxyhydrazide* arising from dinitrostrycholcarboxylic acid in the dinitrostrychol employed. 5 : 7-Dinitroindole-2-carboxyhydrazide with sodium nitrite in acetic acid gives the *azide*, m. p. 160° (decomp.), converted by boiling alcohol into 5 : 7-*dinitro-α-indolylurethane*, m. p. 194°. Methyl-alcoholic sulphuric acid converts trinitrostrychol into *methyl* 3 : 5 : 7-*trinitroindole-2-carboxylate* (O-*methyltrinitrostrychol*), m. p. 212°. The *hydrazide*, m. p. 209—210° (decomp.), from this gives an unstable azide, which gives 3 : 5 : 7-*trinitro-α-indolylurethane*, m. p. 218—219°, also obtained by nitrating 5 : 7-dinitro-α-indolylurethane. A. A. LEVI.

Colour reactions of brucine. A. FRANÇOIS (Bull. Soc. Pharm. Bordeaux, 1930, **68**, 156—158; Chem. Zentr., 1931, i, 977—978).—(*a*) Bromine water is added dropwise in slight excess, with shaking, to a solution of brucine in 0·2% acetic acid; the liquid is decolorised with 1 drop of hydrogen sulphite solution, treated with hydrochloric acid, and heated for 1 min. at 100°. A stable red colour is produced. (*b*) After oxidation and decolorisation as above, ammonia is added; a brown is followed by a green coloration. After boiling, cooling, and saturating with hydrogen chloride the liquid is yellow, and on dilution shows a strong green fluorescence. (*c*) Hydrogen sulphite solution (2 c.c.) is added to the oxidised brucine solution (4 c.c.); half is boiled and treated with ammonia solution (1 c.c.), a violet coloration being produced. Half is treated dropwise, with shaking, with dilute (1 : 4) ammonia solution; the colour is yellow, then green, and with increasing alkalinity becomes blue, violet, and finally amethyst. The reverse changes are observed on acidification. A. A. ELDRIDGE.

Fluorescence of alkaloids. A. ANDANT (Bull. Sci. pharmacol., 1930, **37**, 28—44, 89—104, 169—183; Chem. Zentr., 1931, i, 948).—The behaviour of a number of alkaloids is described. A. A. ELDRIDGE.

Bromination of methylarsepedine. Existence of a radical with quadrivalent arsenic. E. V. ZAPPI and H. DEGIORGI (Bull. Soc. chim., 1931, [iv], **49**, 366—371).—Bromine (1 mol.) converts methylarsepedine in carbon tetrachloride at 0° into *bis-arsepedine dimethobromide*,

$$\left[CH_2{<}\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}{>}AsMeBr\cdot\right]_2,$$ m. p. 60° (decomp.)

which appears to dissociate or decompose in benzene and with water gives arsenious oxide. When kept in air the carbon tetrachloride solution becomes turbid and deposits 1-*bromo*-1-*methylarsepedyl* 1-*peroxide*, decomp. 110°, and when it is allowed to warm to the ordinary temperature and is then treated with bromine gives 1 : 1-dibromo-1-methylarsepedine (cf. A., 1916, i, 575, 683); this in warm carbon tetrachloride gives 1-bromoarsepedine, which with 2 mols. of bromine yields 1 : 1 : 1-*tribromoarsepedine*, m. p. 102°, decomposed in hot carbon tetrachloride or xylene into hydrogen bromide and arsenic tribromide. Since hydrolysis yields hydrogen bromide and a *cyclo*pentylarsinic acid, $C_5H_{10}{:}AsO\cdot OH$, immediately decomposed, yielding arsenious oxide, the affinity of arsenic for the carbon linkings is very small. The existence of the free radical, $C_5H_{10}{:}\dot{A}sMeBr$, in solution

is indicated by the dissociation of 1 : 1′-dibromo-1 : 1′-dimethylbisarsepedine and its conversion into the peroxide. R. BRIGHTMAN.

Piperonal-6-arsinic acid. I. E. BALABAN (J.C.S., 1931, 885—886).—6-Aminopiperonal by the Bart-Schmidt reaction gives *piperonal*-6-*arsinic acid*, m. p. 268° (decomp.) [*semicarbazone*, m. p. 213° (decomp.)], which with hydroxylamine in neutral solution, or with permanganate, gives 3 : 4-*methylenedioxy*-6-*benzarsinic acid*, m. p. >300°. A. A. LEVI.

Derivatives of the arsenic analogue of 9 : 10-dihydroacridine. I. W. GUMP and H. STOLZENBERG (J. Amer. Chem. Soc., 1931, **53**, 1428—1432).—*Diphenylmethane*-o-*arsinic acid*, m. p. 161—162°, prepared from *o*-aminodiphenylmethane, is cyclised by sulphuric acid at 100° to *acridarsinic acid*, $C_6H_4<\genfrac{}{}{0pt}{}{CH_2}{AsO(OH)}>C_6H_4$, m. p. 235—236°, which on reduction by sulphur dioxide in presence of a large excess of hydrochloric acid gives 10-*chloro*-9 : 10-*dihydroacridarsine*, $C_6H_4<\genfrac{}{}{0pt}{}{CH_2}{AsCl}>C_6H_4$ or $C_6H_4<\genfrac{}{}{0pt}{}{CH}{As(HCl)}\geqslant C_6H_4$ m. p. 114—115°. H. A. PIGGOTT.

Organic lead compounds. I. Action of acids on lead aryls. P. R. AUSTIN (J. Amer. Chem. Soc., 1931, **53**, 1548—1552).—*Lead tetra*-o-*tolyl*, m. p. 201—202°, is obtained by boiling lead tri-*o*-tolyl with xylene for 24 hrs. The action of 40% aqueous hydrobromic acid on lead tri-*o*-tolyl in chloroform gives *lead tri*-o-*tolyl bromide*, m. p. 129—130°, and *lead di*-o-*tolyl dibromide*, m. p. 150—151°; the latter is also produced by the action of bromine. *Lead phenyltri*-o-*tolyl*, m. p. 161—162°, prepared by the interaction of lead tri-*o*-tolyl and magnesium phenyl bromide, is successively converted by hydrobromic acid in boiling chloroform into *lead phenyldi*-o-*tolyl bromide*, m. p. 117—118°, *lead phenyl*-o-*tolyl dibromide*, m. p. 116—117°, and a substance, m. p. 232° (decomp.); nitric acid in chloroform or light petroleum (b. p. 65—110°) gives *lead phenyl*-o-*tolyl dinitrate* ($+2H_2O$), and in absence of a diluent gives in addition a product converted by sodium bromide into lead di-*o*-tolyl dibromide. A method for the determination of lead in lead aryls, based on oxidation to sulphate and titration with ammonium molybdate, is described. H. A. PIGGOTT.

Ureides of ***p*****-aminophenylstibinic acid.** W. H. GRAY, J. W. TREVAN, H. W. BAINBRIDGE, and A. P. ATWOOD (Proc. Roy. Soc., 1931, **B**, **108**, 54—83).—Commercial "urea stibamine" contains ammonium *p*-carbamidophenylstibinate, antimonic acid, *p*-acetamidophenylstibinic acid, and *s*-diphenylcarbamide-4 : 4′-distibinic acid in varying proportions. Carbamide and *p*-aminophenylstibinic acid yield (*a*) antimonic acid by hydrolysis, (*b*) either the mono- or the di-substituted carbamide, but neither product could be obtained pure. *s*-Diphenylcarbamide-4 : 4′-distibinic acid was prepared from carbonyl chloride and *p*-aminophenylstibinic acid. The mono-substituted carbamide was prepared by the potassium cyanate method. The toxicity and therapeutic activity were determined on mice infected with *T. equiperdum.* The activity of the commercial preparation depends on the amount of di-substituted carbamide present, the latter being considerably more active than the mono-substituted derivative. B. LEVIN.

Aliphatic and aromatic amino-derivatives of 1-quinoline methiodide. J. B. COHEN, K. E. COOPER, and P. G. MARSHALL (Proc. Roy. Soc., 1931, **B**, **108**, 130—137).—Some substances possessing the general formulæ $C_{10}H_6N(MeI)\cdot NX(2)$ ($X=HR$, HI, $H\cdot[CH_2]_n\cdot NR_2$ or $H\cdot C_6H_4\cdot[CH_2]_n\cdot NR_2$) have been examined for antiseptic, trypanocidal, and for anti-malarial activity. None of the compounds possessed marked action. 6-*Methoxy*-1-*methyl*-2-*quinolone*, m. p. 80°, was obtained by oxidation of 6-methoxyquinoline methiodide, and was converted into 2-chloro-6-methoxyquinoline, m. p. 107—108°, and this into 2-*iodo*-6-*methoxyquinoline methiodide*. *Diethylaminoethylamine*, b. p. 75°/20 mm., prepared by hydrolysis of the product obtained by heating β-bromoethylphthalimide with diethylamine; *diethylaminopropylamine*, b. p. 90°/20 mm., obtained similarly; p-*aminobenzyldiethylamine*, b. p. 177—178°/20 mm., from *p*-nitrobenzyl bromide and diethylamine in alcohol; p-*aminophenylethyldiethylamine*, b. p. 170—175°/20 mm., from the product obtained by heating phenylethyl bromide with diethylamine, are described. The following substances were prepared by boiling the necessary iodo-compound with ammonia or the amine in alcohol: 2-*diethylaminoquinoline methiodide*, m. p. 202° (decomp.); 2-p-*anisamidoquinoline methiodide*, m. p. 230—231°; 2-o-*anisamidoquinoline methiodide*, m. p. 224—225°; alcoholic ammonia converted these two substances into halogen-free bases, probably $C_{10}H_6NMe\colon N\cdot C_6H_4\cdot OMe(2)$, the *p*-compound having m. p. 114—115° [*methiodide*, m. p. 185° (decomp.)], and the *o*-compound, m. p. 95—96° [*methiodide*, m. p. 192° (decomp.)]. 2-*Piperidinoquinoline methiodide*, m. p. 195°, and 6-(6-*amino*-2′-*methylquinolyl*)*quinoline methiodide*, m. p. 170°. The following were prepared from iodoquinoline and 6-methoxyiodoquinoline by the action of the respective diamines: *ethylenediaminebisquinoline methiodide*, m. p. 286—288°; 2-γ-*diethylamino*-β-*hydroxypropylaminoquinoline methiodide hydriodide* (converted by boiling with alcoholic ammonia into 2-γ-*diethylamino*-β-*hydroxypropylaminoquinoline methiodide*, m. p. 180°); 2-*diethylaminoethylaminoquinoline methiodide*, m. p. 241° (decomp.); 2-*diethylaminoethylamino*-6-*methoxyquinoline methiodide hydriodide*, m. p. 203—206°; 2-*diethylaminopropylaminoquinoline methiodide hydriodide*, m. p. 216° (decomp.); 2-*diethylaminopropylamino*-6-*methoxyquinoline methiodide hydriodide*, m. p. 229—230°; 2-p-*aminophenylaminoquinoline dihydrochloride*, m. p. about 270° (decomp.), from *p*-aminoacetanilide and iodoquinoline, followed by hydrolysis with alcoholic hydrogen chloride; 2-p-*dimethylaminophenylaminoquinoline methiodide*, m. p. 241° (decomp.) [*hydrochloride*, m. p. about 205° (decomp.), converted by alcoholic ammonia into the base, $C_{10}H_6NMe\colon C_6H_4\cdot NMe_2$; *methiodide*, m. p. 223—224° (decomp.)]. 2-p-*Aminobenzyldiethylaminoquinoline methiodide hydriodide*, m. p. 241°; 2-p-*aminobenzyldiethylamino*-6-*methoxyquinoline methiodide hydrochloride*, m. p. 245° (decomp.); 2-p-*aminophenylethyldiethylaminoquinoline methiodide hydriodide*, and 2-p-*aminophenylethyldiethylamino*-6-

methoxyquinoline methiodide hydriodide and *hydrochloride*, m. p. 260° (decomp.), are also described.
B. LEVIN.

Deaminocaseinogen. III. H. STEUDEL and R. WOHINZ (Z. physiol. Chem., 1931, **196**, 78—80; cf. A., 1930, 638).—The cystine content of caseinogen is 0·81%, and of deaminocaseinogen 1·68%, as determined by the new method of Folin and Marenzi (A., 1929, 1093).
J. H. BIRKINSHAW.

Stoicheiometrical relations in the reactions between dye, nucleic acid, and gelatin. A. E. STEARN (J. Biol. Chem., 1931, **91**, 325—331).—The sodium salts of ash-free gelatin and yeast-nucleic acid were titrated conductometrically against methyl-violet solutions. The results are independent of the direction of titration and indicate definite equivalence values. The binding power of gelatin for basic dyes as found by Chapman, Greenberg, and Schmidt (A., 1927, 686) is confirmed and combination of the dye with gelatin or with nucleic acid in stoicheiometrical proportions is indicated.
F. O. HOWITT.

Mol. wts. of proteins. W. T. ASTBURY and H. J. WOODS (Nature, 1931, **127**, 663—665).—The sequence of the numbers 1, 2, 3, and 6 as multiples of Svedberg's value of 34,500 for the mol. wt. of proteins is discussed in terms of the ordinary peptide chain, ·CO·NH·CHR·CO·NH·CHR, and possible crystallographic combinations are outlined. The observed constant value of 34,500 is considered to be due to the vibrational instability of peptide chains of length greater than a certain limit. The disruptive action of high-energy quanta on the length and cohesion of peptide chains is shown by experiments on unstretched wool which, after exposure for many hrs. to the full beam of a Shearer *X*-ray tube, shows many of the properties characteristic of wool which has been exposed under tension to the action of steam.
L. S. THEOBALD.

Determination of nitrogen in organic compounds. Pregl's micro-method. O. R. TRAUTZ and J. B. NIEDERL (Ind. Eng. Chem. [Anal.], 1931, **3**, 151—152).—The accuracy of Pregl's micro-determination of nitrogen in organic compounds can be increased by using measured amounts of carbon dioxide and cupric oxide and applying empirical corrections for air and absorption errors.
E. S. HEDGES.

Micro-determination of organic substances in dilute solution by oxidation with dichromate-sulphuric acid mixture. Micro-determination of ethyl alcohol. M. NICLOUX (Compt. rend., 1931, **192**, 985—987).—Details for the determination of ethyl alcohol in dilute solution (0·1—5 mg.) are given. The method is applicable to other oxidisable organic substances.
A. A. LEVI.

Detection and determination of hydroxyl groups in organic compounds. HUPPMANN (Pharm. Ztg., 1931, **76**, 113—114).—The method of Verley and Bolsing (A., 1902, ii, 54; 1928, 615) for determining hydroxyl groups gives correct results with resorcinol, orcinol, methyl salicylate, and 2 : 7-dihydroxytetrahydronaphthalene.
H. E. F. NOTTON.

Volumetric determination of ketones containing the COMe group. V. CUCULESCU (Bul. Fac. Stiinte Cernauti, 1928, **2**, 143—146; Chem. Zentr., 1931, i, 819).—The method, for determining acetone, based on the formation of iodoform in alkaline solution, can be applied to many ketones containing the COMe group. A 50% excess of iodine is employed, the excess being determined with thiosulphate.
A. A. ELDRIDGE.

Accurate determination of trinitrotoluene in presence of other aromatic nitro-compounds. S. SECAREANU (Ber., 1931, **64**, [*B*], 834—836).—The method is based on the quantitative transformation of trinitrotoluene by *p*-nitrosodimethylaniline in presence of pyridine and a trace of iodine into trinitrobenzylidenedimethyl-*p*-phenylenediamine, $(NO_2)_3C_6H_2·CH:N·C_6H_4·NMe_2$, which is weighed. Dinitrobenzene and trinitroxylene do not react with *p*-nitrosodimethylaniline under these conditions. The results are accurate except in the presence of very large amounts of foreign substances. The explosive nature of trinitrobenzylidenedimethyl-*p*-phenylenediamine is emphasised.
H. WREN.

Diazo-compounds sensitive to light. II. Determination of diazo-nitrogen. J. SCHMIDT and W. MAIER (Ber., 1931, **64**, [*B*], 778—779).—The compound, dissolved in water acidified sufficiently with hydrochloric acid to prevent the formation of coupled compounds, is exposed to direct sunlight and the evolved nitrogen is measured.
H. WREN.

Determination of tannic and gallic acids. P. D. DALVI (J. Indian Inst. Sci., 1930, **13**, A, 193—195).—The method of Gardner and Hodgson (J.C.S., 1909, **95**, 1819) together with the precipitation of tannic acid by gelatin and acid sodium chloride (Lowenthal, J. pr. Chem., 1863, 3, 150) is recommended.
F. O. HOWITT.

Determination of chlorophyll in recent and fossil sediments. D. RAUSER-CERNOUSSOVA (Zentr. Min. Geol., 1930, *A*, 314—324; Chem. Zentr., 1930, ii, 2415).—Recent sediments are relatively low in chlorophyll (1 mg. per 100 g. of air-dried substance); coastal sediments contain less than deep-sea sediments (up to 99 mg.).
A. A. ELDRIDGE.

Volumetric determination of narcotine, santonin, and other compounds containing the lactone group. A. P. SNESAROV (J. Chem. Ind. Moscow, 1931, **8**, 161—163).—Narcotine or santonin (0·3—0·6 g.) is heated at 100° with 15—20 c.c. of 0·1*N*-alcoholic potassium hydroxide to complete evaporation of alcohol, 15—20 c.c. of water and 10—15 c.c. of ether are added to the residue, and excess of alkali is titrated, using 0·1*N*-acid in presence of phenolphthalein. The end-point is greatly retarded in the absence of ether, when low values are obtained. The number of c.c. of alkali used multiplied by 0·0413 gives g. of narcotine, and by 0·0246 the number of g. of santonin present. The results are accurate to within 1%. Where the narcotine content of "pantopon" is determined, the sum of the narcotine and papaverine contents is determined by precipitation by one of the usual methods and weighing, and narcotine is determined separately as above.
R. TRUSZKOWSKI.

Titration of alkaloid salts. F. REIMERS (Dansk Tidsskr. Farm., 1931, **5**, 42—53).—The equivalents of many alkaloids have been determined by titration of their salts and compared with those afforded by

gravimetric methods. Determination of the halogen acid by Volhard's method is usually satisfactory, but gives too high results in the case of the hydrochlorides of narcotine and papaverine. Titration with sodium hydroxide using phenolphthalein or Poirrier's blue as indicator can frequently be used; with the latter indicator the titration is best carried out in 50% alcoholic solution, with phenolphthalein either in 50% alcohol or in an aqueous solution after addition of chloroform. Morphine hydrochloride is preferably titrated in acetone solution using Poirrier's blue as indicator. The results obtained in the titration of a number of different alkaloids are tabulated.

H. F. HARWOOD.

Determination of quinine iodobismuthate. L. BRACOLONI (J. Pharm. Chim., 1931, [viii], **13**, 422—425).—The iodobismuthate is treated with excess of sodium carbonate, the precipitated bismuth and quinine are collected, and after extraction of the filtrate with chloroform, its iodide content is determined volumetrically. The precipitate is extracted with chloroform until the extract gives no colour with the mercuric chloride–potassium iodide reagent. The combined extracts are evaporated to dryness, the residue is dissolved in dilute sulphuric acid, and the quinine determined polarimetrically. The bismuth is determined as oxide.

C. C. N. VASS.

Biochemistry.

Blood as a physico-chemical system. X. Physico-chemical properties of oxygenated human blood. L. J. HENDERSON, D. B. DILL, H. T. EDWARDS, and W. O. P. MORGAN (J. Biol. Chem., 1931, **90**, 697—724; cf. A., 1930, 1053).—A quantitative description is given of oxygenated human blood of standard concentration of chloride, plasma-protein, and cell-hæmoglobin, with special reference to the variables oxygen capacity, base, and carbon dioxide tension.

A. COHEN.

Action of phenylhydrazine and phenylhydroxylamine on the respiration of red blood-cells. O. WARBURG, F. KUBOWITZ, and W. CHRISTIAN (Biochem. Z., 1931, **233**, 240—242).—When phenylhydrazine is added to a suspension of rabbit's red blood-cells, the colour changes to brown and the respiration of the brown cells suspended in Ringer–hydrogen carbonate solution is 10—12 times as great as that of the original cells. When the brown cells are hæmolysed with water, a thick white precipitate of globin is obtained and the solution contains hæmin. When the cells contain no sugar the oxygen capacity of the brown cells decreases and methæmoglobin is produced. The hæmin produced by phenylhydrazine is oxidised by atmospheric oxygen and oxidises hæmoglobin to methæmoglobin, which in turn oxidises sugar. If phenylhydroxylamine is added to a suspension of the red cells, they become brown, but methæmoglobin is formed and disintegration to hæmin and globin does not occur. If these brown cells are shaken with dextrose in air, the sugar is oxidised and 0·8 mol. of carbon dioxide is produced per mol. of oxygen used. If the brown cells are hæmolysed, respiration ceases, but the solution readily oxidises Robison's sodium hexosemonophosphate. Sugar is not oxidised.

P. W. CLUTTERBUCK.

Manometric determination of hæmoglobin by the oxygen capacity method. J. SENDROY, jun. (J. Biol. Chem., 1931, **91**, 307—323).—The technique employed by Lundsgaard and Moller (A., 1922, ii, 724) was modified for use with the apparatus of Van Slyke and Neill (A., 1924, ii, 872) by dilution of the blood with 0·9% saline. Nomograms for amounts of blood as low as 0·2 c.c. are given.

F. O. HOWITT.

Synthetic rations and hæmoglobin building. C. A. ELVEHJEM and E. B. HART (J. Biol. Chem., 1931, **91**, 37—42).—The finding of Drabkin and Waggoner (A., 1929, 1476; this vol., 247) that a copper-free synthetic diet containing iron maintains normal hæmoglobin formation is refuted on the grounds that their modification of the method of Elvehjem and Lindow (A., 1929, 614) does not give correct values of copper content and that sufficient amounts of copper were actually present.

F. O. HOWITT.

Structure of hæmocyanins. II. Reaction processes in the isolation of hæmocuprin. A. SCHMITZ (Z. physiol. Chem., 1931, **196**, 71—77; cf. this vol., 497).—When octopus hæmocyanin is degraded by alkali, the copper component is separated in combination with an organic sulphur compound as an undissociated, alkali-soluble complex. This complex can be separated into its components (*a*) by boiling alcohol, when hæmocuprin is obtained, or (*b*) by treatment with 50% acetic acid, which, by removal of copper from hæmocuprin, forms a synthetic copper–sulphur–nitrogen complex.

J. H. BIRKINSHAW.

Determination of f.-p. depression of aqueous solutions, particularly those containing protein. W. C. STADIE and F. W. SUNDERMAN (J. Biol. Chem., 1931, **91**, 217—226).—A method in which the solution is cooled to within 0·1° of its f. p. and then transferred to a second vessel containing ice and cooled to the same temperature is described. An accuracy of ±0·001° is claimed.

F. O. HOWITT.

Osmotic coefficient of sodium in sodium hæmoglobinate and of sodium chloride in hæmoglobin solution. W. C. STADIE and F. W. SUNDERMAN (J. Biol. Chem., 1931, **91**, 227—241).—Reduced hæmoglobin (horse) in the isoelectric state was treated in solution with varying amounts of sodium hydroxide and the f.-p. depression determined by the authors' method (cf. preceding abstract). Similar determinations were made on hæmoglobin from electrodialysed blood-cells alone and with the addition of dry sodium chloride in varying amounts. Sodium hæmoglobinate appears to be completely ionised, but the attraction and repulsion centres of the hæmoglobin molecule influence the sodium ions so

that the osmotic coefficient is diminished to 0·75. Hæmoglobin is without effect on the osmotic properties of sodium chloride, a finding contradictory to the activity coefficients of chlorine ion as determined by electrometric and membrane potential methods of other workers. F. O. Howitt.

Distribution of electrolytes between serum and the *in-vivo* dialysate. C. H. Greene and M. H. Power [with M. S. Bledsoe] (J. Biol. Chem., 1931, **91**, 183—202).—Dialysing tubes were anastomosed into the femoral vein and artery of anæsthetised dogs and surrounded by jackets containing modified Ringer's solution, hypotonic for one side and hypertonic for the other. The concentrations of the various cations were uniformly greater in the serum than in the dialysate. Thus the dialysate-calcium averaged only 61·5% of the serum-calcium, confirming the view of Rona and Takahashi (A., 1911, ii, 302) that the serum-calcium is partly non-diffusible. The serum-chloride and -hydrogen carbonate apparently existed in the free state, whilst approximately 11% of the sodium, 24% of the potassium, and 35—45% of the magnesium were present in a non-diffusible form. The role of serum-proteins in the binding of bases and the application of the Donnan equilibrium are discussed. F. O. Howitt.

Distribution of electrolytes between serum and transudates. C. H. Greene, J. L. Bollman, N. M. Keith, and E. G. Wakefield (J. Biol. Chem., 1931, **91**, 203—216).—Fluid from dogs with experimental ascites and ascitic and pleural fluids from human patients together with the appropriate blood samples were analysed for electrolyte content. Comparison with the results obtained by dialysis *in vivo* (cf. preceding abstract) indicates that the same physico-chemical laws apply to both series of phenomena.
F. O. Howitt.

Determination of the p_H of serum at 38° with the glass electrode and an improved electron tube potentiometer. W. C. Stadie, H. O'Brien, and E. P. Laug (J. Biol. Chem., 1931, **91**, 243—269).—A modification of the thermionic valve potentiometer of Stadie (A., 1929, 1262) having a deflexion of 10—15 mm. per millivolt together with a new type of glass electrode have been applied to the determination of the p_H of serum. Compared with the hydrogen electrode the variation in p_H for serum in equilibrium with carbon dioxide at 40 mm. of mercury was $\pm 0·007$ from the mean of 7·470, the time required for attainment of equilibrium with the glass electrode being 30 sec.
F. O. Howitt.

Influence of serum-lipins on the precipitation and determination of serum-globulins. P. Merklen, E. Le Breton, and A. Adnot (Compt. rend., 1931, **192**, 1053—1056).—Proteins are precipitated from serum by addition of acetone (8 vols.) and the process is repeated twice on the aqueous solution of the precipitate, which is finally washed with ether, dissolved in water, and globulins are precipitated by saturation with carbon dioxide. The globulin content by this method is much higher than that obtained by simple precipitation with carbon dioxide or ammonium sulphate, although the N : S ratio is the same for all methods. F. O. Howitt.

Low phospholipin values in dog plasma. E. M. Boyd (J. Biol. Chem., 1931, **91**, 1—12).—Using a modified technique of Bloor (A., 1929, 837) the plasma-phospholipins in dogs on a diet poor in fat but rich in carbohydrate were found to vary from 0·049 to 0·076%, about one sixth of the normal value, whereas those of the erythrocytes were normal. The leucocytes contained 0·71%. F. O. Howitt.

Amylase of horse serum during the course of numerous successive bleedings. Relation to serum-proteins. Z. Gruzewska and G. Roussel (Compt. rend., 1931, **192**, 897—900).—The amylase activity of the serum obtained from a horse on successive bleedings ran parallel to the protein content (cf. A., 1929, 236). Both curves showed a minimum between the 4th and 6th and another between the 30th and 40th bleedings. W. O. Kermack.

Catalytic activity of the blood. M. Giwjorra (Z. klin. Med., 1930, **114**, 799—807; Chem. Zentr., 1931, i, 799).—Conditions leading to an acute disturbance of equilibrium in human blood cause changes in catalytic activity. Inhalation of coal gas markedly inhibits the catalase activity, and is followed after 2—3 hrs. by a compensating increase.
A. A. Eldridge.

Influence of serum on enzymes with reference to its action on trypsin. J. Fine (Biochem. J., 1931, **25**, 647—670).—There is a preliminary inhibition of the activity of trypsin by unheated serum; on recovery, however, the enzyme shows a greater activity than when heated serum is used, although in the latter case there is no initial inhibition. When the concentration of trypsin is greatly in excess of the serum the latter does not produce any appreciable inhibition. When the concentration of the serum is greatly in excess of the trypsin the latter completely fails to recover from the inhibition. A rise in the antitryptic index of guinea-pig serum follows the injection of trypsin. The nature of inhibition produced by serum is essentially different from that produced by unsaturated soaps. With most enzymes true acceleration or inhibition by serum is not due to specific accelerators or anti-enzymes, but to various physical conditions. S. S. Zilva.

Physico-chemical condition of the mineral matter and dextrose in plasma. L. Brull (Arch. int. Physiol., 1930, **32**, 138—236; Chem. Zentr., 1931, i, 639).—Serum-phosphate is diffusible through collodion. Increase of the calcium × phosphorus product by the administration of phosphate or calcium and phosphorus affords colloidal calcium phosphate in quantity proportional to the product. Administration of calcium affects the colloidal calcium, but not the colloidal phosphate, content. The phosphorus is present chiefly in a non-ionised complex form, but a small part is ionised and can react with calcium. Calcium is present in three forms: ionised and diffusible, non-ionised and diffusible, and colloidal (30—40% in serum and plasma). For a constant protein content the colloidal portion is proportional to the increase in total calcium. The colloidal form does not consist of phosphate. The effect of the administration of citrate is discussed. In calcæmia the calcium content of the renal excretion varies considerably; it depends

on the elimination of water. Only the diffusible non-ionised form is excreted. Of the serum-sodium 10% is in a colloidal form. With increasing glycolysis the colloidal fraction of the dextrose diminishes.

A. A. ELDRIDGE.

Use of copper and iron salts for the deproteinisation of blood. M. SOMOGYI (J. Biol. Chem., 1931, **90**, 725—729).—Proteins and non-sugar reducing substances are precipitated from laked blood by treatment with (*a*) copper sulphate and sodium tungstate, or (*b*) ferric sulphate and sodium hydroxide. The filtrates give true sugar values. Copper is superior to zinc (A., 1930, 801) for the precipitation of plasma- and serum-proteins. A. COHEN.

Distribution of blood-sugar. M. SOMOGYI (J. Biol. Chem., 1931, **90**, 731—735).—The ratio corpuscle-sugar : plasma-sugar, calculated from determinations on protein-free filtrates (cf. preceding abstract), is the same in non-diabetic (0·70—0·84) as in diabetic persons (0·75—0·84). The higher ratio observed in diabetes by Folin and Svedberg (this vol., 110) is due to the use of total reducing substance values for plasma. A. COHEN.

Blood-choline and -choline esters. H. BOHN (Klin. Woch., 1930, **9**, 2147—2148; Chem. Zentr., 1931, i, 957).—Highly active choline esters may be present in circulating blood. A. A. ELDRIDGE.

Determination of uric acid in small quantities of blood. S. A. POVORINSKAJA (Russ. J. Physiol., 1930, **13**, 664—666).—A method for preparing a stable coloured solution suitable for use in the wedge of the Autenrieth colorimeter is given. W. O. KERMACK.

Gravimetric determination of cholesterol in blood and serum. O. MUHLBOCK and C. KAUFMANN (Biochem. Z., 1931, **233**, 222—235).—A gravimetric method for the determination of pure cholesterol and its esters by means of digitonin is described and adapted to determinations in blood and serum. The values obtained by Bloor's colorimetric methods are as much as 76% and by Meyer's method 38% too high.

P. W. CLUTTERBUCK.

Bromine and iodine contents of blood. L. BALDAUF and L. PINCUSSEN (Klin. Woch., 1930, **9**, 1505; Chem. Zentr., 1930, ii, 2399).—The bromine content of blood is practically 100 times that of iodine, which in normal metabolism averages $10·9 \times 10^{-6}$ g. per 100 c.c.; in syphilis it is about 50% greater. Two children with nephritis showed an iodine content of $31·7—32·9 \times 10^{-6}$ per 100 c.c. of blood.

L. S. THEOBALD.

Determination of iodine in blood. H. A. A. AITKEN (Biochem. J., 1931, **25**, 446—448; cf. A., 1930, 1463).—An improvement in the measurement of the thiosulphate is introduced. A micro-burette is described in which the standard solution floats on a thread of mercury, the position of the latter being adjusted by means of a fine screw projecting into a mercury reservoir. Conditions for more complete extraction of the potassium iodide are also described.

S. S. ZILVA.

Determination of blood-sulphur. CHATRON (J. Pharm. Chim., 1931, **13**, 425—435, and Bull. Soc. Chim. biol., 1931, **13**, 300—325).—For total sulphur determinations on whole or protein-free serum ashing with nitro-perchloric acid is recommended. Normal sera contain 0·8—2·2 mg. of inorganic sulphate, 2—4 mg. of total sulphate, and 3·2—5·6 mg. of non-protein sulphur per 100 c.c. C. C. N. VASS.

Effect of human and guinea-pig serum on quinine and saponin hæmolysis. G. P. CUCCO (Giorn. Batt. Immunol., 1929, **4**, No. 5, 6 pp.; Chem. Zentr., 1931, i, 957).—Unheated human serum favours the hæmolysis of small doses of quinine; otherwise it has an inhibiting effect. Inhibition of saponin hæmolysis by human serum is not exhibited by sera of cancer and tuberculosis. A. A. ELDRIDGE.

Digestive enzymes of the human fœtus. M. F. L. KEENE and E. E. HEWER (Lancet, 1929, **216**, 767—769).—The following enzymes have been detected in the human fœtus at the ages given: proteolytic, 16 weeks; rennin, hydrochloric acid, 19 weeks; and pancreatic lipase, 32 weeks. Carbohydrate-splitting enzymes were found rarely at 24 weeks and not invariably at full time.

L. S. THEOBALD.

Chemistry of the adrenals of mammals. Comparative study of the medulla and the cortex. A. LEULIER and L. REVOL (Bull. Soc. Chim. biol., 1931, **13**, 211—253).—After extraction of the fresh tissue for ½ hr., the adrenaline content is determined by Bailly's method (cf. A., 1925, ii, 248), which gives more consistent results than the iodometric method of Abelous, Soula, and Ivujan if the concentrations of the acid in the extract and in the standards are identical. For tissue extracts the colour reaches a maximum intensity after 25 min., whereas for the vacuum-dried powder and pure adrenaline solutions a maximum intensity is reached in 3—5 min. In the sheep, goat, ox, calf, pig, and horse very little if any adrenaline is found in the cortex, whilst the medulla contains considerable quantities of both free and "virtual" adrenaline, which vary from individual to individual in the same species. The "virtual" adrenaline is set free on keeping the tissue over sulphuric acid in a vacuum for 24 hrs. The amount of free cholesterol varies within narrow limits, whereas the combined cholesterol shows wide individual variations. The cortex contains rather more lipin and less total phosphorus than the medulla. Potassium is distributed equally in the organ, whilst the cortex contains the larger amount of total sulphur. Except for the horse, the cortex appears to be richer in nitrogen and to contain rather less water than the medulla.

C. C. N. VASS.

Occurrence of ether-insoluble lecithins in brain. W. MERZ (Z. physiol. Chem., 1931, **196**, 10—18).—An ether-insoluble lecithin was isolated from the "protagon" fraction of brain and hydrolysed with methyl-alcoholic barium hydroxide. Palmitic, very little stearic, and 21% of oleic acid were obtained. Since less than 50% of unsaturated acid was found, the occurrence of natural lecithins containing only saturated acids is demonstrated. Of the glycerophosphoric acid obtained 58% was present as the β-acid. J. H. BIRKINSHAW.

Block staining of nervous tissue with silver. II. Trichloroacetic acid, sulphosalicylic acid, Hofker's and Carnoy's fluids as fixatives. H. A.

DAVENPORT (Stain Tech., 1931, 6, 37—40).—Alcoholic solutions of trichloroacetic acid and sulphosalicylic acid, and Hofker's solution fix mammalian spinal chord with less shrinkage than is caused by ammoniacal alcohol, but during alkalisation, washing, and silvering the acid-fixed specimens shrink more than the alkali-fixed. Carnoy's fluid causes the greatest shrinkage.

H. W. DUDLEY.

Cytochrome. R. BIERICH and A. ROSENBOHM (Z. physiol. Chem., 1931, **196**, 87—88; cf. A., 1929, 1340).—The authors' measurements of the reduction time of cytochrome were performed on testes poisoned with hydrocyanic acid. Shibata's differing results (cf. A., 1930, 949) are explained by the fact that he used plant cytochrome.

J. H. BIRKINSHAW.

Total carbohydrate content of isolated frog muscle. M. KERLY (Biochem. J., 1931, **25**, 671—690).—The resting value of the total carbohydrate of isolated frog muscles as determined by a modified method in which the whole muscle is hydrolysed was much greater than the sum of the glycogen and alcohol-soluble carbohydrate. During incubation in a phosphate buffer (p_H 8) this excess carbohydrate is removed from the muscle, but does not appear as lactic acid. The lactic acid increase is in general somewhat greater than the decrease of the sum of glycogen and alcohol-soluble carbohydrate. The excess carbohydrate is not removed during incubation in 2% sodium hydrogen carbonate buffer. In muscles poisoned with mono-iodoacetic acid during anaerobiosis and fatigue the total carbohydrate content does not change significantly, whilst the glycogen content falls. The lactic acid content rises very slightly on the average. The alcohol-soluble carbohydrate rises, but not sufficiently to account for the fall in glycogen. When the total carbohydrate of muscle is determined by this method there is left in the muscle a small residual amount of glycogen, on the average 50 mg. per 100 g. of muscle. This glycogen does not change significantly in amount during incubation in phosphate buffer. Approximately the same amount of glycogen is found remaining after incubation when the whole glycogen content of the muscle is determined by Pfluger's method. It is suggested that this glycogen may be of a different nature from the main bulk of that present in muscle.

S. S. ZILVA.

Creatine in human muscle. M. BODANSKY (J. Biol. Chem., 1931, **91**, 147—149).—The total creatine+creatinine contents of various human muscles have been determined soon after death. The values obtained range from 0·220% (as creatine) for cardiac muscle to 0·485% for the psoas muscle.

F. O. HOWITT.

"Bound potassium" in muscle. W. E. CALLISON (J. Biol. Chem., 1931, **90**, 665—668).—The decrease in potassium content of muscle tissue (rabbit's gastrocnemius) kept in isotonic salt solution varies with the amount of solution, the frequency of its change, and the subdivision of the tissue. Diffusion of potassium into the solution is not influenced by autolysis. The existence of bound potassium in muscle is not verified.

A. COHEN.

Spectrographic analysis of animal tissues. H. M. FOX and H. RAMAGE (Proc. Roy. Soc., 1931, B, **108**, 157—173).—By means of the spectrographic method described (A., 1927, 527), the amount of many elements in animal tissues can be determined. The washed tissues are dried at 100°, powdered, and 50 mg. burnt in an ashless filter paper in front of the slit of a quartz spectrograph. Results are expressed in percentages of the dried tissues. Iron and copper were found in all the tissues examined, and are apparently essential constituents of protoplasm, whilst nickel (0·004—0·01%), cobalt (0·002—0·006%), lead, silver (0·005%), cadmium (0·05—0·20%), strontium (0·0008—0·008%), rubidium (0·0008—0·002%), lithium (0·0002—0·005%), and manganese (0·0008—0·002%) were found in some, but not all, tissues. The last two metals were found widely distributed. Calcium fluoride was detected in one instance only. Barium and cæsium were not found.

B. LEVIN.

Lead in the animal organism. G. BERTRAND and V. CIUREA (Compt. rend., 1931, **192**, 990—992).—Lead occurs only in traces in the skeletal muscle of ox, horse, and sheep. The highest content is in the tongue, the epithelial mucosa containing more than the muscular tissue (for ox 2·33 and 0·82 mg. per kg., respectively). In other organs of the ox 0·05—0·74 mg. per kg. has been detected.

F. O. HOWITT.

Copper content of livers and liver extracts. G. N. QUAM (Proc. Iowa Acad. Sci., 1929, **36**, 267—268).—Adult ox liver contains 16—30 mg. of copper per kg. Adult hog's liver contains 50 mg. (average), human fœtal liver 69 mg., liver of a still-born child 28 mg., and an adult liver (cirrhosis) 20 mg. per kg. The copper contents of Armour's liver extract (liquid) and Abbot's liver extract (dry) corresponded, respectively, with 0·5 and 25 mg. per kg. of the equivalent amount of raw liver.

CHEMICAL ABSTRACTS.

Distribution of molybdenum in nature. H. TER MEULEN (Rec. trav. chim., 1931, **50**, 491—504).—A colorimetric method, based on that of ter Meulen (A., 1925, ii, 330), for the determination of traces of molybdenum is described. Organic material may be destroyed by incineration in iron vessels and subsequent treatment with aqua regia without loss of molybdenum, providing the heating is not too intense. Molybdenum is very widely distributed in nature. It is present in most soils and plants, especially in seeds and bulbous roots. In animal organisms it accumulates in the liver, but appreciable traces are present in the blood, bile, and milk, and any excess is eliminated in the fæces and urine. Its presence could not be detected in sea- or river-water, but the presence of considerable quantity in the mineral water of La Bourboule suggests that it has a therapeutic value.

J. W. BAKER.

Combined Gram–Pappenheim stain for formalin-fixed tissues. S. A. SCUDDER and J. A. LISA (Stain Tech., 1931, **6**, 51—52).—Sections of tissue fixed in 10% formalin are covered with a solution of crystal-violet in phosphate buffer for 3—5 min. and then with aqueous iodine solution. They are decolorised by treatment with acetone for 10 sec. and then counterstained with a mixture of methyl-green and pyronin-yellowish. After washing

they are immersed for less than 1 min. in origanum oil, cleared in bergamot oil, and mounted in balsam.

H. W. Dudley.

Effect of hyperglycæmia on the amylolytic power of saliva and blood. T. Gayda (Arch. Sci. biol., 1930, **15**, 147—161; Chem. Zentr., 1931, i, 799).—Hyperglycæmia in rabbits is accompanied by an increase in the amylolytic power of the saliva, but that of the blood-serum is unchanged. The effect is probably due to insulinæmia. A. A. Eldridge.

Digestive glands of ruminants. II. Physiology of the secretory nerve apparatus of the parotid gland of the goat. G. A. Babitschev, N. S. Perstnev, and I. I. Kulesko (Russ. J. Physiol., 1930, **13**, 636—647).—Pilocarpine and physostigmine raise the p_H of the saliva, whilst atropine has the opposite effect. The specific gravity and dry residue vary inversely with the rate of secretion.

W. O. Kermack.

Gastric secretion. I. Gastric juice of constant acidity. F. Hollander and G. R. Cowgill (J. Biol. Chem., 1931, **91**, 151—182).—Dogs with stomach pouches (Pavlov and Heidenhain), the mouths of which were brought out through the oblique muscles so that natural sphincter action took place, were used. The gastric juices were collected both periodically and continuously and the acidities determined by the quinhydrone electrode. With continuous collection and either histamine or food as a stimulus the reaction ran parallel to the rate of secretion when this is low, but for high rates of secretion under histamine stimulus such a correlation disappears. With discontinuous collection the post-prandial acidity is much higher than that for the corresponding continuous experiment and practically the same as for low secretion experiments using histamine. The maximum acidity in absence of catheter irritation, which causes a lowering of the acidity by mucous secretion, was p_H 0·91±0·02, and this value is constant for discontinuous withdrawal of gastric juice. F. O. Howitt.

Determination of calcium, magnesium, and acid-soluble phosphorus of milk by means of trichloroacetic acid filtrates. G. P. Sanders (J. Biol. Chem., 1931, **90**, 747—756).—The proteins in milk are precipitated by 4 parts of 10% trichloroacetic acid, and analyses of the filtrates give accurate results for calcium and magnesium. Of the total phosphorus, 68·4—81·9% is acid-soluble. The distribution of inorganic, lipoid, and caseinogen-phosphorus is discussed. A. Cohen.

Residual nitrogen of cow's milk. F. Kieferle and J. Gloetzl (Milchwirt. Forsch., 1930, **11**, 62—117; Chem. Zentr., 1931, i, 702).—The total non-protein-nitrogen (R_1) and the total residual nitrogen (R_2=R_1 less albumose- and peptone-nitrogen) are distinguished. For the determination of R_1 diluted (1 : 10) milk is heated in presence of acetic acid; for ordinary (mixed) milk R_1=66·3, for special milk mg. per 100 c.c. R_2 is determined in sodium tungstate–trichloroacetic acid serum, hexone-base-nitrogen also being precipitated; R_2=22·9, 28·4 mg., the constituents (as nitrogen) being: albumose 27·2, 30·7; peptone 18·7, 24·2; amino-acids 4·6, 3·9; ammonia 1·1, 1·3; carbamide 10·1, 13·4; creatinine 1·7, 2·3; creatine 2·2, 3·1; uric acid 1·5, 2·1 mg. By souring, the casein- and especially the albumin-nitrogen diminishes; that of the fission products (chiefly complexes of a polypeptide nature) increases, and is followed by an increase in that of simpler nitrogenous units. The fall in albumin-nitrogen in long pasteurisation is 5·3%, and on boiling 81·6%; it is hydrolysed as well as coagulated. Corresponding values for increase in R_2 are 10·4 and 18·6%.

A. A. Eldridge.

Glyceride structure of butter-fats. T. P. Hilditch and J. J. Sleightholme (Biochem. J., 1931, **25**, 507—522; cf. A., 1930, 1308).—Four English butter-fats from members of the same herd of cows fed on pasture, on pasture and winter diet, on winter diet with added coconut cake, and on winter diet with added soya-bean cake, and a New Zealand pasture-fed (December) butter-fat have been oxidised and their content of fully-saturated glycerides has been determined. The fatty acids of the latter have also been analysed. In all the butters, as with other animal fats, the content of fully-saturated glycerides is a function of the proportion of the total saturated acids present in the mixed acids of the whole fat. In the butters from the "normal" (usually pasture-fed) cows the component acids of the fully-saturated parts are present in approximately the same quantitative amounts, the composition of the fully-saturated glycerides tending to be the same whatever the original unsaturation of the butter as a whole. Similar concordance is revealed in the combined butyric–lauric acid contents and in the combined myristic–palmitic acid contents of the whole fats and of their two divisions fully- and non-fully-saturated glycerides, whilst the content of unsaturated acids in the non-fully-saturated glycerides increases steadily and slowly with increase of unsaturation in the fats as a whole. When coconut fat is offered in the diet, the fully-saturated part of the butter shows a marked increase in butyric–lauric acid content, but for the most part the composition of the non-fully-saturated glycerides is normal. With a soya-bean oil diet the fully-saturated components of the butter are not far removed from the normal in composition, but the lower acids of the non-fully-saturated portion were present in excess of the usual proportion. S. S. Zilva.

Examination of the urine and blood of *Octopus vulgaris* for trimethylamine oxide and betaine. F. A. Hoppe-Seyler and W. Linneweh (Z. physiol. Chem., 1931, **196**, 47—63).—Betaine is present in the urine and blood of the octopus. Trimethylamine is absent from the urine and the oxide from the blood and urine. Previous observations on the occurrence of hypoxanthine in, and the absence of carbamide from, the urine are confirmed. J. H. Birkinshaw.

Nature of the porphyrin appearing in urine following ingestion of chlorophyll. Y. Nakamura (J. Biochem., Japan, 1930, **12**, 475—485).—Urinary porphyrin following ingestion of chlorophyll is isomeric with blood-porphyrin. After ingestion of chlorophyll the urobilin output is increased.

Chemical Abstracts.

Determination of the nitrogen of the so-called oxyproteic acid fraction of urine. B. WEISSBERG (Biochem. Z., 1931, **233**, 113—117).—The following method for isolation of the fraction is adopted. After removal of the carbamide by fermentation with urease, the solution is acidified with sulphuric acid, evaporated to small bulk, and the inorganic salts are precipitated by the addition of alcohol. Ammonia is then completely removed by boiling with excess of baryta, the excess of baryta removed with carbon dioxide, and the oxyproteic acid fraction precipitated in alkaline solution with mercuric acetate.
P. W. CLUTTERBUCK.

A urine containing true mucin. P. FLEURY and E. DUFAU (J. Pharm. Chim., 1931, [viii], **13**, 417—422).—The high viscosity of the urine was due to the presence of 0·024% of a mucin containing traces of a phosphoprotein. C. C. N. VASS.

Blood-urea clearances and diuresis in normal and nephritic animals. R. L. JOHNSTON (J. Lab. Clin. Med., 1930, **15**, 943—952).—The ability of the kidneys of the normal and nephritic fasting animal to clear the blood of urea is correlated with the water-diuresis curve. CHEMICAL ABSTRACTS.

Incidence of lipins in urine. A. T. BRICE, jun. (J. Lab. Clin. Med., 1930, **15**, 953—960).—Lipins were detected in 13·3% of the pathological urines examined. CHEMICAL ABSTRACTS.

Glycogen as a normal and pathological constituent of urine. H. CAPPENBERG (Arch. Pharm., 1931, **269**, 164—166).—Glycogen may form 0·1% of normal and 1% or more of pathological urines. It may be accompanied by protein or dextrose and tests by which the three substances may be distinguished are described. The iodine colour test may be applied to the acidified and decolorised (charcoal) urine.
H. E. F. NOTTON.

Micro-distillation apparatus for the detection of acetone in urine. H. KAISER and E. WETZEL (Pharm. Monatsh., 1930, **11**, 228—229; Chem. Zentr., 1931, i, 821).—The urine (3 c.c.) is heated at 40° in a vessel from the cover of which is suspended a drop of *p*-nitrophenylhydrazine reagent in a ring of vaseline. The formation of the crystalline *p*-nitrophenylhydrazone will detect 0·1 mg. of acetone in 2 c.c. of urine. A. A. ELDRIDGE.

Influence of bulk in diet on fæcal calcium and phosphorus. L. ASCHAM (J. Nutrition, 1931, **3**, 411—420).—The excretion of calcium and phosphorus was greatest when a high proportion of roughage or agar was fed to dogs. No special function in the intestine can be assigned to calcium.
CHEMICAL ABSTRACTS.

Effect of variations in respiratory rate on excretion of chloride and water. R. S. HUBBARD and C. B. ALLISON (J. Biol. Chem., 1930, **89**, 627—630).—Experiments on human achlorhydric subjects showed that conditions favouring the excretion of an alkaline urine cause an increased excretion of chloride and water. G. F. MARRIAN.

Congo-red test with special reference to excretion of the dye in the urine. N. W. BAKER and A. M. SNELL (J. Lab. Clin. Med., 1930, **16**, 262—270).—The disappearance in 1 hr. of more than 60% of intravenously injected Congo-red from the blood stream is a specific test for amyloidosis. Urinary excretion is not observed in absence of albuminuria.
CHEMICAL ABSTRACTS.

Oxidation by potassium ferricyanide of certain constituents of serum in anæmia. G. P. WRIGHT and B. ARTHUR (J. Biol. Chem., 1931, **90**, 757—769). —Anæmia in rabbits is accompanied by parallel increases in the iodine value of the serum-lipins and the oxidisability of the serum by potassium ferricyanide. After oxidation by the latter the iodine value is considerably decreased. It is therefore concluded that unsaturated fatty acids are responsible for interference with the use of the Haldane apparatus for blood-oxygen determination in anæmia. The oxidation of oleic acid under similar conditions is discussed. A. COHEN.

Inability of metals other than copper to supplement iron in curing the nutritional anæmia of rats. F. A. UNDERHILL, J. M. ORTEN, and R. C. LEWIS (J. Biol. Chem., 1931, **91**, 13—25).— Rats kept in glass cages were fed a basal diet of whole milk until anæmia and loss of weight developed. The addition of iron alone was ineffective, but supplemented by copper was effective in restoring normal growth and blood count. Copper cannot be replaced by cobalt, nickel, zinc, or manganese (cf. Titus and others, A., 1929, 206). F. O. HOWITT.

Behaviour of blood-water during asphyxia. T. SASO (J. Biochem., Japan, 1930, **12**, 281—315).— In acute asphyxia the blood-plasma volume decreases by 14·8%, and the density of the serum rises by 0·3%. Dehydration is slight. In prolonged asphyxia the water content of the blood or serum increases.
CHEMICAL ABSTRACTS.

Thiol compounds of normal and pathological human blood. M. LABBE and F. NEPVEUX (Compt. rend., 1931, **192**, 1061—1062).—The thiol content of venous blood as determined by the method of Tunnicliffe (A., 1925, i, 752) is lower than the normal in disturbances of nutrition such as those due to obesity, diabetes, cirrhosis, and gout. F. O. HOWITT.

True sugar content of skin and muscle in diabetic and non-diabetic persons. H. C. TRIMBLE and B. W. CAREY, jun. (J. Biol. Chem., 1931, **90**, 655—663).—In a non-diabetic group of patients the average true sugar contents of skin and muscle were 56 and 28 mg. per 100 g., respectively, and the corresponding values in diabetes were 144 and 51 mg., whilst for whole blood it was 226 mg. per 100 g. Approximately the same muscle-sugar values are observed in diabetes whether a long or short period had elapsed since the last administration of insulin.
A. COHEN.

Determining factors of hypoglycæmia in diabetic children. P. B. LANDABURE (Semana med., 1931, I, 160—164).—In 50% of diabetic children subjected to diet and insulin treatment hypoglycæmic symptoms develop at a blood-sugar level of 0·07—0·024%. CHEMICAL ABSTRACTS.

Initial hypoglycæmia after complete extirpation of the pancreas. F. MEYTALER and H. REIN-

WEIN (Arch. exp. Path. Pharm., 1931, **159**, 583—588).—The hypoglycæmia which may be observed in dogs within a few hours after pancreatectomy is apparently caused by the liberation of insulin from the pancreas as the result of manipulation during the operation. The hypoglycæmia is more marked in dogs which have fasted and less marked in those which have been fed on a carbohydrate diet, presumably in consequence of differences in the amounts of stored insulin. W. O. KERMACK.

Carbohydrate metabolism and soluble sulphur compounds in erythrocytes and tissues. D. CAMPANACCI (Klin. Woch., 1930, **9**, 1212—1213; Chem. Zentr., 1930, ii, 2401).—In diabetes, the glutathione of venous blood decreases independently of blood-sugar and acidosis. The decrease is affected by administration of insulin or sulphur preparations in small amounts. L. S. THEOBALD.

Clinical investigation of carbohydrate metabolism by means of *d*-sorbitol. S. DONHOFFER and M. DONHOFFER (Deut. Arch. klin. Med., 1930, **167**, 257—272; Chem. Zentr., 1930, ii, 2401).—*d*-Sorbitol produces an increase of blood-sugar in normal metabolism and in diabetes. The sorbitol curve differs in character from that of dextrose, and in diabetes the sorbitol sensitivity increases to an extent greater than that of dextrose.
L. S. THEOBALD.

Proteins in articular exudates. C. ACHARD and M. PIETTRE (Compt. rend., 1931, **192**, 996—998).—Mucous fluid from articular synovitis was freed from proteins originating from the serum and analysed. Mucin was present (3—5%) when there was little inflammation, but absent in presence of a strongly marked inflammatory process, which also caused an increased lipin content. Both types of exudate contained fibrin. F. O. HOWITT.

Clear fluid test meals (water, caffeine solution, alcohol) in fractional gastric analysis. A. L. GARBAT (Arch. Int. Med., 1931, **47**, 601—611).—Meals of water, caffeine solution, and alcohol are compared and discussed in relation to the Ewald meal of tea and toast as gastric stimulants. In 65% of the cases the same results of gastric analysis are obtained with the three meals. A. COHEN.

Frequency of goitre and presence of iodine. T. IVERSEN, G. LUNDE, and K. WULFERT (Norsk Mag. Laegev., 1930, 12 pp.; Chem. Zentr., 1931, i, 640).—Endemic goitre unaccompanied by lack of iodine is recorded. A. A. ELDRIDGE.

Closed intestinal loop. II. Jejunal and ileal loops. Chemical analyses of the blood. G. E. BURGET, K. H. MARTZLOFF, R. C. B. THORNTON, and G. R. SUCKOW (Arch. Int. Med., 1931, **47**, 593—600).—Dogs with closed loops of the ileum or jejunum survive if distension is prevented by aspiration of the loop. The loops of recovered dogs absorb and digest food normally, and their blood chemistry is normal. Distension or rupture of the loop causes a fall in blood-chloride and a rise in non-protein-nitrogen. A. COHEN.

Serum in lipin nephrosis. M. A. MACHEBŒUF and R. WAHL (Compt. rend., 1931, **192**, 1059—1060).—Precipitation of serum-globulins by half-saturation with ammonium sulphate results in partial precipitation of the lipins. In presence of high concentrations of neutral salts and at 3·7 the albumins are precipitated together with the lipins. For each 100 g. of albumin thus precipitated there occur normally 10—15 g. of lipins, in lipin nephrosis more than 70 g., and in cirrhosis, tuberculosis, cardiac œdema, cancer, and nephritis less than 25 g. This amount of lipin corresponding with 100 g. of albumin is designated the "lipoalbumin index."
F. O. HOWITT.

Colloid-osmotic pressure of the blood in normal and pathological conditions. III. Hypotension and hypertension. F. NAKAZAWA and J. IZUMI. **IV. Experimental kidney damage.** K. KIMURA and F. NAKAZAWA (Tohoku J. Exp. Med., 1930, **16**, 341—351, 352—360). CHEMICAL ABSTRACTS.

Urease and its therapeutic use in carbonyl chloride poisoning. S. E. SVENSSON [in part with A. ANDERSSON] (Svensk farm. Tidskr., 1930, **34**, 493—495, 509—514, 545—549, 565—567; Chem. Zentr., 1931, i, 799).—The preparation and standardisation of urease from soya-bean flour are described. Unless treated with a small quantity of toluene, aqueous extracts of the flour rapidly lose their activity. Injection (into rabbits) of urease as an antidote is preferably preceded by injection of urea.
A. A. ELDRIDGE.

Composition of bone. X. Mechanism of healing in low-phosphorus rickets. B. KRAMER, M. J. SHEAR, and J. SIEGEL. **XI. Binding of calcium ions by serum.** M. J. SHEAR and M. M. OFFNER (J. Biol. Chem., 1931, **91**, 271—290, 291—305).—X. Rickets accompanied by a low inorganic serum-phosphate was induced in rats by diets of varying calcium and phosphorus contents. Healing, as shown by staining with silver nitrate, occurred within 3 days by means of cod-liver oil or vitamin-*D* preparation, within 24 hrs. by fasting, and within 12 hrs. by addition of phosphate to the diet. In all three cases the product of serum-calcium and -inorganic phosphate increased before the appearance of new calcification.

XI. Human serum was dialysed against 3% sodium chloride solution in order to remove most of the serum-calcium, against 15% urea solution, and finally against water to remove urea and part of the sodium chloride. The residual liquid was concentrated by evaporation at the ordinary temperature and both dialysate and residual fluid were analysed for calcium, total and non-protein-nitrogen, and titrated conductometrically. The serum solutions, which were almost calcium-free, gave titrimetric values below the calculated minimum values, indicating a binding of calcium ions by serum.
F. O. HOWITT.

Induction of tetany in rachitic rats by a normal diet. A. F. HESS, M. WEINSTOCK, H. R. BENJAMIN, and J. GROSS (J. Biol. Chem., 1931, **90**, 737—746).—Tetany, accompanied by a fall in serum-calcium, can be induced and maintained for a few days in rachitic rats by a sudden replacement of the rachitogenic diet (Ca : P=4 : 1) by a normal adequate diet with a

Ca : P ratio of 1—1·5 : 1. The reaction is not induced by an absolute or relative increase in phosphorus in the diet, but is ascribed to the sharp change in the Ca : P ratio. The influence of a diet may therefore be determined not only by its adequacy, but also by its relation to a previous diet. A. COHEN.

Diffusible calcium of the blood in tetany. L. GUNTHER and D. M. GREENBERG (Arch. Int. Med., 1931, **47**, 660—673).—The total serum-calcium is not necessarily an index of the clinical condition in juvenile and parathyroid tetany, which are shown to be associated with a fall of the diffusible calcium to about 3·5 mg. per 100 c.c. No fall in ionic calcium is observed in tetany due to hyperventilation and increased blood-hydrogen carbonate. A. COHEN.

Metabolism in scurvy. III. Absorption and retention of calcium and phosphorus by guinea-pigs. F. E. HUMPHREYS and S. S. ZILVA (Biochem. J., 1931, **25**, 579—593).—There is no deviation from the normal in the absorption or retention of calcium or of phosphorus before or during the development of scurvy in guinea-pigs. Disturbances in the calcium and phosphorus balances are noted only in the last stages, when all the functions of the animal organism become deranged by the disease. The calcium and phosphorus content of the blood of protected and scorbutic guinea-pigs varies within wide limits, and no difference can be established in this respect between the two groups. S. S. ZILVA.

Experimental scurvy. X. Adrenaline content of the suprarenals and the amount of adrenaline-like substance in the serum of guinea-pigs fed on a diet free from vitamin-*C*. S. OHATA (J. Biochem., Japan, 1930, **12**, 419—427).—The amounts of adrenaline-like substance in the serum, and of adrenaline in the suprarenals, of scorbutic guinea-pigs are low. CHEMICAL ABSTRACTS.

Ergotamine. IV. Effect of ergotamine on basal metabolism, circulation, and blood-sugar of normal persons and of patients with thyrotoxicosis. J. B. YOUMANS and W. H. TRIMBLE (Arch. Int. Med., 1931, **47**, 612—632).—A subcutaneous dose of 0·5 mg. of ergotamine had little effect on the basal metabolism and fasting blood-sugar of normal persons. It raised the blood-pressure slightly, and lowered the pulse rate, but did not prevent the higher pulse rate caused by atropine. Similar results were observed in cases of thyrotoxicosis, but the blood-pressure and pulse rate effects were greater. A. COHEN.

Chemotherapy of tuberculosis. III. E. HESSE and G. MEISNER. **IV.** G. MEISNER and E. HESSE (Arch. exp. Path. Pharm., 1931, **159**, 676—686, 687—697).—III. By means of the capillary blood-fibrin method of Wright the bacteriostatic actions of a number of pyridine, quinoline, acridine, and azine derivatives have been investigated. Some compounds including certain benzene-azo- and -hydrazo-derivatives of pyridine and quinoline show considerable activity.

IV. A number of the compounds showing activity by the capillary method have been investigated as to their action on experimental tuberculosis in guinea-pigs; some appear to exert a therapeutic effect (cf. A., 1928, 1286; 1930, 376). W. O. KERMACK.

Effect of arginine on the body-weight of mice injected with thyroxine and bearing the tumour M 63. E. GILROY (Biochem. J., 1931, **25**, 414—417; cf. A., 1930, 1309).—Arginine prevents a loss of weight in rats which thyroxine would otherwise have induced. S. S. ZILVA.

Hydrogen-ion concentration and acid–base equilibrium in normal pregnancy. D. M. KYDD (J. Biol. Chem., 1931, **91**, 63—68).—In normal pregnancy the alkali reserve decreases without any change occurring in the hydrogen-ion concentration, the decrease in base being balanced by decrease in acid. The serum-albumin is decreased, whereas the serum-globulin, -chloride, and -phosphorus are unchanged. F. O. HOWITT.

Metabolism of trioctoin and trilaurin. M. POWELL (J. Biol. Chem., 1930, **89**, 547—552).—Trilaurin and trioctoin were fed to rats after a preliminary period of starvation. The depot fat of the rats fed on trioctoin showed a decrease in iodine value from that of control animals, whilst the saponification value was practically unchanged. Determination of volatile fatty acids present showed that the amount of octoic acid deposited was small. The decrease in iodine value, being unaccompanied by a rise in saponification value, was not due to the deposition of octoic acid, but to an increase in the proportion of higher saturated fatty acids. After feeding trilaurin, 25% of the acids in the depot were shown to consist of lauric acid. G. F. MARRIAN.

Feeding tests on calves with skim milk and cod-liver oil emulsion as a substitute for milk. W. LIEBSCHER (Tierernahr., 1930, **2**, 11—26; Chem. Zentr., 1930, ii, 2400).—Skim milk and cod-liver oil emulsion have the smaller nutritive value. L. S. THEOBALD.

Pasteurised and raw milk. R. A. FISHER and S. BARTLETT (Nature, 1931, **127**, 591—592).—Pasteurised milk has the smaller nutritive value. L. S. THEOBALD.

Influence of iodised milk and potassium iodide on the size and iodine content of the thyroid gland of the rat. W. E. KRAUSS and C. F. MONROE (J. Biol. Chem., 1930, **89**, 581—588).—Potassium iodide and milk from cows fed with iodides were administered to rats over periods of several weeks. In each case the weight of the thyroid gland was decreased and the iodine content of the gland increased compared with control rats fed on iodine-free normal milk. Both sources of iodine were effective in decreasing the weight and increasing the iodine content of the thyroids of rats having enlarged thyroids as a result of receiving a Steenbock rachitic diet. G. F. MARRIAN.

Metabolism of iodine. IV. Distribution of iodine in normal and iodised hyperthyreotic thyroids. G. LUNDE and K. WÜLFERT (Endokrinol., 1930, **7**, 327—363; Chem. Zentr., 1931, i, 637—638).—The glands were exhausted with water and the solution was precipitated with acetone. The distribution of

iodine between the residue and the two fractions is practically unaltered by iodine treatment.

A. A. ELDRIDGE.

Metabolism of iodine. V. Metabolism in the surviving thyroid. I, II. A. STURM (Z. ges. exp. Med., 1930, 74, 514—554, 555—574; Chem. Zentr., 1931, i, 637).—In perfusion experiments inorganic iodine was retained by the dog's thyroid. Moderate doses of iodoprotein and thyroxine had no effect. Addition of iodine in quantities of the order of that present naturally caused a fall in the oxygen quotient and often an increase in anaerobic and aerobic glycolysis. These and other metabolic changes are attributed to a catalytic fermentative action of iodine.

A. A. ELDRIDGE.

Dependence of gaseous metabolism and action of iodine on hydrogen-ion concentration. L. WISLICKI (Klin. Woch., 1930, 9, 2354; Chem. Zentr., 1931, i, 809).—Manometric measurements of the gaseous metabolism of the diaphragm and muscles of the rat were carried out at high and low carbon dioxide tensions. The effect of iodine on the gaseous metabolism of the isolated muscle varies with changes in the carbon dioxide tension and the sodium hydrogen carbonate content. Thyroxine appeared not to affect the respiration of muscle. A. A. ELDRIDGE.

Ovarian function and iodine economy. I. DAVANZO (Giorn. Batt. Immunol., 1930, 5, No. 6, 19 pp.; Chem. Zentr., 1931, i, 956—957).—During the intermenstrual period the venous blood of normal women contains $8 \cdot 5 \times 10^{-6}$ g. I per 100 c.c.; the quantity increases during menstruation, pregnancy, functional menorrhagia, and the menopause. Low values are sometimes observed in pubertal and preclimacteric bleeding. A. A. ELDRIDGE.

Effect of manganese on the growth of rats. V. E. NELSON, J. M. EVVARD, and W. E. SEWELL (Proc. Iowa Acad. Sci., 1929, 36, 267).—With 100 parts of manganous sulphate tetrahydrate in 10^6 of ration an increase, and with 100 parts an inhibition, of growth were observed. CHEMICAL ABSTRACTS.

Use of cotton-seed meal in the diet of the rat. W. D. GALLUP (J. Biol. Chem., 1931, 91, 387—394).—Ill-health and retarded growth in rats fed with a diet containing 40% of cotton-seed meal are due to the presence of gossypol, the deleterious action of which can be greatly reduced by supplementing the diet with inorganic iron salts or by autoclaving the meal at high temperatures, whereby the gossypol is inactivated.

F. O. HOWITT.

Self-selection of food constituents by the rat. S. K. KON (Biochem. J., 1931, 25, 473—481).—Young rats receiving equal vitamin supplies by hand do not grow as well and consume only about 6·5% of protein when sucrose or rice starch, caseinogen, and a salt mixture are offered *ad libitum* separately, as when the same constituents are incorporated in one diet with a 20% protein content. S. S. ZILVA.

Does the feeding of maize silage to dairy cows lead to acidosis? A. E. PERKINS, C. C. HAYDEN, and C. F. MONROE (Ohio Agric. Exp. Sta. Bimonthly Bull., 1931, No. 148, 8—11).—Maize silage fed at the rate of 50 lb. daily did not produce acidosis in milch cows. Organic acids present in the silage are fully metabolised and do not appear as acids or related compounds in the urine. A G. POLLARD.

Factors which determine renal weight. VII. Protein intake and age. VIII. Protein intake and sex. E. M. MACKAY and L. L. MACKAY (J. Nutrition, 1931, 3, 375—385).

CHEMICAL ABSTRACTS.

Bile salt metabolism. V. Certain proteins as diet factors. VI. Proline, tryptophan, and glycine in diet. VII. Indene, hydrindene, and isatin. VIII. Liver injury and liver stimulation. IX. Effects of Eck fistula. H. P. SMITH and G. H. WHIPPLE (J. Biol. Chem., 1930, 89, 689—704, 705—717, 719—725, 727—738, 739—751).—V. The effect of feeding various proteins to dogs with biliary fistulæ on the production of bile salts was studied. Bile salts were determined by determining the increase in amino-nitrogen after alkaline hydrolysis of the bile. Comparisons were made with control animals fed on "salmon bread." Caseinogen, liver, kidney, beef muscle, and beef blood + salmon bread caused an increased bile salt output, egg yolk a slight increase. "Sweetbreads" gave variable results, but no marked increase was observed. Red blood-cells caused a slight increase, and egg-albumin a large increase, even when fed with the control diet.

VI. The addition of proline to a diet of "salmon bread," egg-albumin, or gelatin considerably increased the bile salt output. Tryptophan similarly supplemented a diet of gelatin, but not of egg-albumin. A diet of proline, tryptophan, and sugar alone caused no increase. Marked cholagogue effects were observed with both substances, which were independent of the effects on the bile salt production. Glycine added to an egg-albumin diet increased bile salt production, but showed no cholagogue effect.

VII. Indene caused no increase in bile salt output, but a strong cholagogue effect. Hydrindenedicarboxylic acid gave negative results in both respects. Isatin alone or isatin indigo slightly increased bile salt output. Isatin had a powerful cholagogue action.

VIII. Chloroform injury of the liver caused a large but transient fall in the bile salt output. Liver extracts effective in pernicious anæmia or ferric citrate added to the control diet had no effect on bile salt production. Daily feeding of the bile secreted by dogs on the control or on a meat diet raised the bile salt output to a high level. A bile surplus in the body is not excreted in the urine.

IX. The effects on bile and bile salt output observed in the previous papers were considerably modified when an Eck fistula was combined with the simple closed sterile bile fistula. G. F. MARRIAN.

Effect of heat on the biological value of cereal proteins and caseinogen. A. F. MORGAN (J. Biol. Chem., 1931, 90, 771—792).—The protein of toasted cereals does not support growth in rats as well as that of raw cereals, and its biological value (percentage of food nitrogen retained) is lower. This defect is not caused by water-cooking or caramel formation, and is corrected by the addition of 5% of caseinogen to toasted diets. Maximum growth rate is observed when the protein content of raw or toasted diets is

18%. Toasting does not affect digestibility, and the decreased biological value is accounted for by loss of nitrogen in the urine. A. COHEN.

Effect of desiccation on the nutritive properties of egg-white. II. M. A. B. FIXSEN (Biochem. J., 1931, **25**, 596—605).—Pure ovalbumin, ovoglobulin, and the total albumin and ovomucoid fraction form nutritionally satisfactory proteins for young rats, and desiccation does not alter their nutritive properties as in the case with crude egg-white (cf. A., 1927, 797). A toxic substance is probably formed from some non-protein constituent in the process of desiccation. It is possible to prepare from dried egg-white a protein fraction uncontaminated by the toxic substance. The protective factor *X*, which is capable of neutralising the toxic substance, is present in raw liver, in a dried preparation of the total albumin and ovomucoid fraction of egg-white, but not in raw beef steak. It is only partly extracted from yeast by boiling dilute acetic acid and is not removed from caseinogen by washing with dilute acetic acid and extraction with alcohol. Rats suffering from the effects of the dried egg-white can become spontaneously refected. This condition can be transmitted from one rat to another by ingestion of the fæces. Refection can also be induced in rats receiving the dried egg-white diet by feeding the fæces of refected rats on diets deprived of vitamin-*B*. S. S. ZILVA.

Determination of the digestibility of crude protein by animal experiments and artificially. II. W. WÖHLBIER (Tierernähr., 1930, **1**, 467—501; Chem. Zentr., 1930, ii, 2400—2401).

Effect of ingested urea on nitrogen metabolism. D. D. MOORE, P. H. LAVIETES, A. M. WAKEMAN, and J. P. PETERS (J. Biol. Chem., 1931, **91**, 373—385).—Urea was fed in daily doses of 35—52 g. to three normal human subjects and the nitrogen metabolism and blood-non-protein-nitrogen were determined before, during, and after the administration. The sum of the urinary and fæcal nitrogen did not account for a considerable amount of the administered nitrogen. Retention of this nitrogen as protein or urea or its excretion in sweat appeared unlikely.

F. O. HOWITT.

Metabolism of amines. II. Dimethylamine. W. D. LANGLEY and R. J. WEBER (J. Biol. Chem., 1930, **89**, 567—574).—After feeding dimethylamine hydrochloride plus one equivalent of sodium hydrogen carbonate to rabbits, 1—30% of the free base was recovered from the urine. When fed with two equivalents of hydrogen carbonate approximately 50% of the base was not metabolised. No significant excretion of trimethylamine or monomethylamine was observed. The administration of the amine was accompanied by an increased urea excretion. No relationship between the amounts of ammonia excreted and base ingested were recorded. G. F. MARRIAN.

Effect of diet and nephrectomy on the creatine and nitrogen content of the rat. A. CHANUTIN (J. Biol. Chem., 1930, **89**, 765—774).—The total nitrogen and creatine content of the eviscerated bodies of adult rats was not affected by previous feeding on high- and low-protein diets in which caseinogen, edestin, gelatin, and dried beef served as sources of protein. Feeding the animals on diets containing 10% of creatine caused a slight immediate rise in body-creatine, which did not increase after the first day. Rats fed on high-protein diets during their whole lifetime gave normal figures. No change in total nitrogen or creatine was observed 48 hrs. after nephrectomy. The values were calculated on the basis of dry, fat- and ash-free tissue. The results do not support the theory of exogenous formation of creatine from ingested protein. G. F. MARRIAN.

Arginine. I. Catabolism of arginine in rats. Determination of arginine in biological material. V. C. KIECH, J. M. LUCK, and A. E. SMITH (J. Biol. Chem., 1931, **90**, 677—695).—Arginine in protein-free tissue extracts is converted by arginase into ornithine and urea, the latter is converted into dixanthhydrylcarbamide, which is determined volumetrically by oxidation with potassium dichromate. The average arginine content of fasting rats is 26·1 and 27·5 mg. per 100 g. of muscle and carcass, respectively.

Rapid degradation of arginine occurs when it is injected subcutaneously into fasting rats. Ornithine is apparently formed and destroyed almost as rapidly as arginine, since, apart from arginine and urea, less than 12% of the injected nitrogen is found in the liver-free carcass 1 hr. after injection. A. COHEN.

Specific dynamic action of alanine; role of pyruvic and lactic acids. E. F. TERROINE, R. BONNET, and V. ZAGAMI (Bull. Soc. Chim. biol., 1931, **13**, 326—342).—In the rabbit, intraperitoneal injections of sodium pyruvate (1 g. per kg.) or sodium lactate (3 g. of kg.) dissolved in Ringer's solution produce no change in the respiratory quotient, or liberation of heat, and these substances are not excreted in the urine. The specific dynamic effect of alanine cannot be explained on the basis of a loss of energy caused by the metabolism of these acids.

C. C. N. VASS.

Role of ternary acids in the specific dynamic effect of amino-acids and the intermediate metabolism of sugars. V. ZAGAMI (Bull. Soc. Chim. biol., 1931, **13**, 354—366).—In the rabbit, intraperitoneal injections of sodium succinate produce an increase in the gaseous exchange which is not parallel to the metabolism of the salt. Administration *per os* of sodium malate or citrate causes no appreciable liberation of heat. C. C. N. VASS.

Intermediate metabolism of sugars. Do dihydroxyacetone and glycerol produce a specific dynamic effect? V. ZAGAMI (Bull. Soc. Chim. biol., 1931, **13**, 343—353).—Neither dihydroxyacetone nor glycerol, injected intraperitoneally, causes a liberation of heat or an increased gaseous exchange following absorption. C. C. N. VASS.

Animal calorimetry. Metabolism of dextrose administered to the fasting dog. M. DANN and W. H. CHAMBERS (J. Biol. Chem., 1930, **89**, 675—688).—Hyperglycæmia, glycosuria, and loss of power to oxidise ingested dextrose were observed in dogs starved for 19—31 days. Daily administration of

dextrose resulted in a recovery of the normal degree of utilisation of carbohydrate. The administration of 60 units of insulin together with the dextrose caused an improvement but not total recovery of the normal dextrose utilisation. G. F. MARRIAN.

Urinary galactose after ingestion of galactose. V. J. HARDING and O. MOBERLEY (J. Biol. Chem., 1930, **89**, 535—545).—When galactose in amounts from 10 to 50 g. was fed to normal men and women, no statistically significant sex difference in the amounts excreted was observed. Positive Benedict tests were given after the ingestion of smaller amounts of galactose in men than in women. This was not due to a sex difference in the amounts of non-fermentable reducing substances excreted, but rather to a slightly greater degree of diuresis in women following ingestion of the galactose solution. G. F. MARRIAN.

The recovery process after exercise in the mammal. I. Glycogen resynthesis in the fasted rat. C. N. H. LONG and R. GRANT (J. Biol. Chem., 1930, **89**, 553—565).—A method is described for exercising rats by administering a series of induction shocks of known frequency. Determinations of liver- and muscle-glycogen, blood-sugar, blood- and carcass-lactic acid were made on controls, on animals after varying amounts of exercise, and on exercised animals after recovery periods of 1—24 hrs. The muscle-glycogen could not be reduced by more than about 70% by exercise alone. The blood-lactic acid and total lactic acid returned to the normal level 1—2 hrs. after exercise. Considerably longer recovery periods (2—15 hrs.) were required for the muscle-glycogen to regain its normal value. No significant changes in liver-glycogen were observed. A fall of 30% was observed in the blood-sugar immediately after exercise. Within 1 hr. it was normal again.

G. F. MARRIAN.

Heat and osmotic change in muscular contraction without lactic acid formation. A. V. HILL and J. L. PARKINSON (Proc. Roy. Soc., 1931, B, **108**, 148—156).—When frogs' sartorius muscle poisoned by iodoacetic acid is stimulated to complete exhaustion in the absence of oxygen, 0·367 g.-cal. per g. is evolved, and an increase of osmotic pressure equivalent to the addition of 0·147% NaCl to Ringer's fluid is found. This increase is twice that calculated on the assumption that the whole of the phosphagen and pyrophosphate is broken down. The heat evolved in the poisoned muscle together with the heat produced in lactic acid formation and neutralisation are sufficient to account for the whole of the heat produced in anaerobic stimulation of the normal muscle. B. LEVIN.

Ammonia content of frog's muscle and reversibility of ammonia formation in isolated frog's muscle. G. EMBDEN (Z. physiol. Chem., 1931, **196**, 23—46).—Polemical against Parnas (cf. this vol., 255). A defence of the author's method and results. J. H. BIRKINSHAW.

Action of various materials on carbohydrate metabolism. G. L. PIOTROWSKI (Rev. Med. Suisse rom., 1930, 34—45; Chem. Zentr., 1931, i, 642).

Significance of bile acids in carbohydrate metabolism. IX. Effect on sugar assimilation. S. FUZITA (J. Biochem., Japan, 1930, **12**, 383—391).—The capacity of the fasting rabbit's liver to form glycogen from monoses decreases in the order: *d*-lævulose, dextrose, *d*-mannose, and *d*-galactose. The capacity is increased by 42—52% by administration of cholic acid. CHEMICAL ABSTRACTS.

Influence of arsenicals and crystalline glutathione on the oxygen consumption of tissues. C. VOEGTLIN, S. M. ROSENTHAL, and J. M. JOHNSON (U.S. Publ. Health Service Reprint, 1931, No. 1449, 1—16).—Addition of crystalline reduced or oxidised glutathione to suspensions of liver, kidney, or testis of the rat, Jensen's rat sarcoma, and of yeast cells in Ringer–Locke solution does not increase the rate of oxygen consumption. Arsenious oxides (RAsO) and neoarsphenamine, due to its rapid oxidation, reduce the rate of oxygen consumption, whereas quinquevalent arsenicals ($R·AsO_3H_2$) and sulpharsphenamine have no effect. Reduced glutathione in the ratio of 10 mols. to 1 mol. of arsenoxide prevents the reduction in oxygen consumption due to the arsenoxide, whilst oxidised glutathione is ineffective.

C. C. N. VASS.

Properties, irritant and toxic actions of ethylene glycol. P. J. HANZLIK, M. A. SEIDENFELD, and C. C. JOHNSON (J. Pharm. Exp. Ther., 1931, **41**, 387—406).—The slight and temporary irritation to mucosæ, motor nerve fibres, and muscle caused by glycol is weaker than that due to glycerol. Its intramuscular injection is followed by rapid absorption, irritation being absent. The toxic intravenous doses of glycol are 2·3 and 3·3 g. per kg. of body-weight for rat and rabbit, respectively, the intramuscular values being 4·4 and 6·6 g. Daily drinking of more than 4 g. per kg. of rat is rapidly fatal. Rats drinking 0·7 g. per kg. daily showed stunted growth without oxaluria or renal calculi, but these were observed on 2·2 g. per kg. daily. Most patients receiving 2—10 g. of a preparation largely glycol showed no oxaluria. The use of glycol as a medicinal vehicle is discussed. A. COHEN.

Antiseptic and trypanocidal action of certain styryl- and anil-benzthiazole derivatives. C. H. BROWNING, J. B. COHEN, S. ELLINGWORTH, and R. GULBRANSEN (Proc. Roy. Soc., 1931, B, **108**, 119—129).—The antiseptic power of a large number of substituted anil- and styryl-benzthiazole compounds against *Staphylococcus aureus* or *B. coli* has been determined. The anilbenzthiazoles were less active than the corresponding anilquinolines previously investigated (cf. A., 1929, 1109), whilst the styryls possessed the same order of activity as the anilbenzthiazoles. The trypanocidal action of these substances was also tested on mice infected with *T. brucei*. The maximum effect was produced when one nucleus contained a basic and the other an acetamido-group. The styryls were much more powerful than the anils. The following compounds were prepared: *nitro-2-methylbenzthiazole*, m. p. 165—166°; *amino-2-methylbenzthiazole*, m. p. 124—125° (*acetyl* derivative, m. p. 149—150°); *acetamido-2-methylbenzthiazole methosul-*

phate; *dimethylamino-2-methylbenzthiazole methiodide.* The styryls were prepared from the benzthiazole quaternary compound and the appropriate aldehyde, using piperidine as condensing agent, whilst the anils were prepared from the quaternary compound and the appropriate nitroso-compound in alcoholic or aqueous alcoholic solution. The following are described: 2-(p-*acetamidostyryl*)*aminobenzthiazole methochloride*; 2-(p-*acetamidostyryl*)*dimethylaminobenzthiazole methiodide.* B. LEVIN.

Colloid-chemical union of germanin with protein complexes. II. Effect of Bayer 205 on the protein components of the hæmolytic system. V. A. NOVESSELSKY (Z. Immunität., 1930, **68**, 328—341; Chem. Zentr., 1931, i, 957—958).

Toxicity of certain benzene derivatives and related compounds. H. F. SMYTH (J. Ind. Hygiene, 1931, **13**, 87—96).—The toxicities of technical samples of guanidine and derivatives, aniline and derivatives, diphenyl and derivatives, phenylnaphthylamines, and various condensation products on white rats, guinea-pigs, and rabbits are tabulated. C. C. N. VASS.

Relation of chemical constitution and biological action. Amyostatic poisons. T. SASAKI and I. OTSUKA (J. Biochem., Japan, 1930, **12**, 429—458).—The amyostatic action of 3-aminohydrocarbostyril, novocaine, tutocaine, and acoine is discussed. CHEMICAL ABSTRACTS.

Chemical constitution and physiological action. Behaviour of the [stereoisomeric] α-bromo*iso*hexoyl-*l*-asparagines. M. FURIA (Boll. Chim.-farm., 1931, **70**, 137—139).—The *d*-form of α-bromo*iso*hexoyl-*l*-asparagine is more active than the *l*-form in producing successive excitation and hypnosis in gold-fish, and the water–oil partition coefficient of the former is slightly higher. The behaviour is like that of the bromo*iso*valeryl compounds (A., 1930, 111). R. K. CALLOW.

Pharmacological detection of poisons. H. FÜHNER (Arch. Pharm., 1931, **269**, 176—182).—A review. The mouse/frog index, *i.e.*, the ratio of the minimum lethal doses for animals of equal weight, is useful in the identification of traces of poisons. It is greater than unity for glucosides and equal to or less than unity for alkaloids, excepting cytisine. H. E. F. NOTTON.

Toxicity of *Corydalis caseana*. M. R. MILLER (J. Agric. Res., 1931, **42**, 239—243).—Assays of the air-dried plant gave crude alkaloid contents of 1·10 and 1·90%. Physiological tests on rats showed that the lethal dose for a 200-g. rat is 0·0076 g. of the crude alkaloids, corresponding with 24·4 g. of the fresh plant per kg. body-weight. The toxicity appears to be diminished by the action of light and heat. H. J. DOWDEN.

Blood-lipase in children under the influence of pilocarpine with an acid or alkaline diet. S. A. POVORINSKAJA (Russ. J. Physiol., 1930, **13**, 745—749).—The blood-lipase content does not change under the action of pilocarpine, but differs much from individual to individual, and the same child exhibits marked variations. W. O. KERMACK.

Effect of the administration of pilocarpine and sugar on blood-amylase. E. T. MINKER-BOGDANOVA (Russ. J. Physiol., 1930, **13**, 750—759).—The blood-amylase varies much from individual to individual, and even in the same person may change markedly within 3 hrs. On an unusually acid or alkaline diet there is occasionally an inverse relationship between the amylase and sugar content. Pilocarpine has no specific effect on the amylase content. After the administration of sugar by mouth a relationship is usually but not always observed between the blood-amylase and -sugar. W. O. KERMACK.

Alteration of the non-protein-nitrogen of blood by the action of subcutaneous administration of pilocarpine. S. A. POVORINSKAJA (Russ. J. Physiol., 1930, **13**, 627—635).—Subcutaneous administration of pilocarpine in therapeutic doses does not affect the blood-uric acid, but brings about a decrease in the amino-nitrogen and an increase in the residual nitrogen, the latter being more marked on a basic and less marked on an acid diet. When the amino-nitrogen rises the residual nitrogen tends to fall and *vice versa.* W. O. KERMACK.

Santonin. II. Effect of santonin on the excretion of uric acid. H. SEEL (Arch. exp. Path. Pharm., 1931, **159**, 589—605).—Administration of santonin to rabbits brought about an increase in the excretion of uric acid; the action is presumably dependent on the presence of the lactone ring. In rabbits to which large doses of irradiated ergosterol had been given (which itself caused a slight increase in uric acid excretion) santonin has the same action. In man, both when normal or when suffering from gout, administration of santonin brought about an increase in the excretion of uric acid. Observations on the blood confirm the view that santonin acts on the uric acid metabolism by increasing its rate of elimination through the kidneys and not by increasing production or decreasing oxidation. W. O. KERMACK.

Physiological action of co-zymase. S. GARD (Z. physiol. Chem., 1931, **196**, 65—70).—Both active and inactivated co-zymase when injected into the jugular vein of the rabbit depress the blood-pressure considerably. The action is probably due to adenylic acid or its derivatives, since yeast-adenylic acid and adenylthiopentose produce a similar effect, which has also been demonstrated for muscle-adenylic acid. In the surviving perfused heart the activity is increased. J. H. BIRKINSHAW.

Effect of camphor on the adrenaline output and blood-sugar in non-anæsthetised, non-fasted dogs. K. OIKAWA and T. INABA (Tohoku J. Exp. Med., 1930, **16**, 298—310).—When injected subcutaneously in quantities greater than 1·75 g. per kg., camphor caused increased secretion of adrenaline and hyperglycæmia. CHEMICAL ABSTRACTS.

Effect of starvation, phloridzin, thyroid, adrenaline, insulin, and pituitrin on the distribution of glycogen in the rat. R. D. LAWRENCE and R. A. MCCANCE (Biochem. J., 1931, **25**, 570—578).—Starvation does not reduce the glycogen of the heart, kidney, or stomach. Phloridzin reduces the glycogen of the liver and muscles slightly below

starvation level, but has no effect on that of the heart, stomach, or kidney. Thyroid extract by mouth reduces very greatly the glycogen of the heart. The hyperthyroid heart is unable to replenish its glycogen stores even after high carbohydrate feeding. After starvation for 24 hrs. the hyperthyroid liver contains only slightly less glycogen than the control, but has completely lost the normal ability to store glycogen after carbohydrate food. The hyperthyroid 24 hrs.' starved muscle contains slightly less glycogen than the normal, but storage is normal after carbohydrate ingestion. The heart-glycogen is the first to be depleted by thyroid. Adrenaline increases the liver-glycogen and decreases the muscle-glycogen of starved animals. It has no effect on the glycogen of other organs. Insulin has no effect on the glycogen of heart, stomach, or kidney. It reduces liver- and muscle-glycogen slightly. Pituitrin has no effect on the glycogen of the fasting rat. S. S. ZILVA.

Influence of calcium on the rate of diffusion of sugars through surviving intestine. H. E. MAGEE and K. C. SEN (Biochem. J., 1931, **25**, 643—646).—Dextrose diffuses more slowly from the lumen of the rabbit's intestine into calcium-free than into calcium-containing outer fluids, the process in the former case being a physical one but in the latter partly of the nature of a selective action. The presence of calcium ions in the environment is indispensable for the manifestation of selective action of the intestinal wall towards sugars placed in the lumen.

S. S. ZILVA.

Biological action of *X*-rays on blood and spleen. I. Changes in blood-picture following *X*-irradiation of the spleen. II. Changes in blood viscosity and serum-protein following irradiation of the spleen. S. KATSURA (Tohoku J. Exp. Med., 1930, **16**, 241—259, 260—276).—Strong irradiation leads to a decrease in serum-protein, whilst weak irradiation effects no change. In both cases the globulin fraction is relatively increased.

CHEMICAL ABSTRACTS.

Influence of radium on the nitrification of ammonium sulphate. J. GUERILLOT (Bull. Soc. Chim. biol., 1931, **13**, 367—368).—Radium exerts no influence on the progress of nitrification.

C. C. N. VASS.

Action of dyes on enzymes. I. Dyes and oxidations. J. H. QUASTEL and A. H. M. WHEATLEY (Biochem. J., 1931, **25**, 629—638).—The effect of 29 dyes on the oxidation of dextrose, lactate, succinate, and formate by *B. coli* has been studied. Basic dyes have a vigorous toxic action, acidic have little or no action. There is a specificity of behaviour towards the dehydrogenases. The toxicity of the basic dyes is greatly dependent on the nature of the buffering agent present. The action of dyes on the oxidation of succinate by muscle-tissue is similar to that found with bacteria. In the case of methylene-blue or toluidine-blue there is a toxic action leading to inhibition and a catalytic action leading to an increased rate of oxidation due to the reversible nature of the dye. As in the case of bacteria, the presence or absence of phosphate influences considerably the toxicity of the dyes. The dyes appear to have no inhibitory action on the oxidation of succinate by brain-tissue. S. S. ZILVA.

Specific action of tyrosinase. E. ABDERHALDEN and W. SCHAIRER (Fermentforsch., 1931, **12**, 329—332).—It has been previously stated (A., 1926, 1276) that *m*-tyrosine does not show the characteristic colour change with tyrosinase given by *p*-tyrosine. This was confirmed for some preparations of the enzyme, but a reaction was obtained from *Russula delica* extracts in water, salt solution, or glycerol. Various tyrosine dipeptides and other substances give the reaction.

J. H. BIRKINSHAW.

Synthetic action of emulsin on dextrose in allyl alcohol solution. M. OLIVE (Bull. Soc. Chim. biol., 1931, **13**, 254—271).—The optimum conditions for the synthesis of allyl-β-glucoside are obtained in 90% allyl alcohol containing 8 g. of dextrose and 0·4 g. of emulsin per 100 c.c. of alcohol at 50°; smaller concentrations of the alcohol have a lower optimum temperature. C. C. N. VASS.

Temperature of destruction of emulsin in allyl alcohol of varying strengths. M. OLIVE (Bull. Soc. Chim. biol., 1931, **13**, 272—275).—The temperature at which emulsin begins to become inactive in allyl alcohol solutions varies from 60° to 20° for liquids containing 10—90% of alcohol. Total destruction of activity occurs at temperatures ranging from 50° to 70°. C. C. N. VASS.

Optimum hydrogen-ion concentration and temperature of the style enzyme of *Pecten maximus*. A. GRAHAM (Proc. Roy. Soc., 1931, **B**, **108**, 84—95).—The effect of time on the p_H optimum, of p_H on the temperature optimum, and of time and temperature on the p_H optimum of the diastase of the crystalline style of *P. maximus* has been studied, using 1% starch as substrate. There is no variation of the p_H optimum (6·5) with variation in time of the experiment. There is a fall in the optimum temperature accompanying a fall in the p_H of the medium. When two of the three factors, time, p_H, and temperature, are made equal to those in natural conditions, the optimum of the third is found to be the natural condition of the living animal. B. LEVIN.

Model for the separation of enzyme–substrate (diastase–starch) in the cell. M. MUHLBAUER (Fermentforsch., 1931, **12**, 273—294).—The separation of enzyme and substrate in the living cell is imitated *in vitro* by a diastase–starch "model" in which inhibition of hydrolysis is produced by the addition of surface-active substances such as sodium oleate, lecithin, bile-acid salts, and cholesterol. In the case of the soap, enzyme and substrate particles are each surrounded by a micellar envelope carrying a positive charge; thus normal enzyme action is prevented. This inhibition by surface-active substances is reversible. Small changes of hydrogen-ion concentration towards the acid side lower the separation, whilst increase of p_H produces a stabilising effect. The addition of other surface-active substances, *e.g.*, alcohols, in isocapillary amounts also decreases the separation effect. J. H. BIRKINSHAW.

Lactic acid fermentation of warm-blooded tissue. IV. Relationship between extra-fer-

mentation and sugar fermentation in the liver. O. ROSENTHAL (Biochem. Z., 1931, **233**, 62—85).—The amount of fermentation of added sugar with the liver tissue of fed rats when asphyxiated immediately after removal is compared with that when asphyxiation occurs some time later (*i.e.*, including extra-fermentation). The intensity of both processes is conditioned by the presence of an activator which is formed under aerobic conditions and disappears during anaerobiosis (cf. A., 1929, 722, 1337; this vol., 123).
P. W. CLUTTERBUCK.

Relation between amylase and lactic acid formation in muscle. E. M. CASE (Biochem. J., 1931, **25**, 561—569; cf. McCullagh, A., 1928, 550; Case and McCullagh, A., 1928, 1049; Harrison and Mellanby, A., 1930, 365).—In the inhibition of lactic acid formation in muscle caused by amylase, an enzyme–substrate compound is formed prior to the hydrolysis of starch or glycogen by amylase. The amylase of muscle is concerned in the process of formation of lactic acid from carbohydrate. S. S. ZILVA.

Intermediary carbohydrate metabolism. Effect of sodium iodoacetate on glyoxalase. H. W. DUDLEY (Biochem. J., 1931, **25**, 439—445).—Sodium iodoacetate is a powerful inhibitor of the enzyme glyoxalase which converts methylglyoxal into lactic acid (cf. Lundsgaard, A., 1930, 368). Iodoacetate may owe its power of interfering with normal glycolysis to this fact, which supports the view that methylglyoxal is the immediate precursor of lactic acid. The inhibitory actions of sodium iodoacetate and pancreatic antiglyoxalase on glyoxalase are similar in character. S. S. ZILVA.

Rate of hydrolysis of α- and β-glycerophosphates by enzymes. H. D. KAY and E. R. LEE (J. Biol. Chem., 1931, **91**, 135—146).—Animal and vegetable phosphatases hydrolyse *dl*-α- and -β-glycerophosphoric acids at different rates, the β-isomeride being more actively attacked. With kidney-phosphatase the magnitude of this difference depends on the p_H and is increased by presence of magnesium ions. With taka-phosphatase magnesium ions partly inhibit the hydrolysis of the β- but accelerate that of the *dl*-α-ester, whereas with dialysed kidney-phosphatase the hydrolysis of both isomerides is accelerated. The identification of an unknown glycerophosphate preparation by comparison of its rate of hydrolysis by a phosphatase with those of authentic α- and β-glycerophosphates is suggested.
F. O. HOWITT.

Pepsin. H. HOLTER (Z. physiol. Chem., 1931, **196**, 1—9).—The change of viscosity during the earlier stages of peptic digestion of caseinogen was followed. After a shallow minimum there is a rapid rise to a maximum, representing coagulation. Crystallised pepsin and that from dog's gastric juice follow the "normal" curve, from which human pepsin deviates in a characteristic manner. If pepsin is fractionated by adsorption on aluminium hydroxide, the residual solution shows a deviation similar to, but more marked than, that of human pepsin, whereas the eluted adsorbate yields a curve deviating in the opposite sense. J. H. BIRKINSHAW.

Physico-chemical method of measuring the activity of pepsin. I. E. R. THEIS (J. Amer. Pharm. Assoc., 1931, **20**, 355—357).—A method for the determination of the activity of peptic enzymes is based on the measurement of hydration of proteins caused by the addition of such enzymes to suspensions of proteins contained in an improved dilatometer. The amount of peptic digestion is determined from the graph of the volume changes. E. H. SHARPLES.

Spreading method for the evaluation of trypsin and pepsin preparations. F. GRENDEL (Pharm. Weekblad, 1931, **68**, 387—395).—By measurement of the unimolecular layer formed by a protein on 0·1*N*-hydrochloric acid solution at various intervals after addition of an enzyme the rate of proteolysis may be determined. Comparison of the results obtained by this and by the nephelometric method for the hydrolysis of caseinogen by trypsin and pepsin shows that the new method gives a truer insight into the mechanism of the process. Under conditions such that, according to the nephelometric method, 75% hydrolysis has taken place, the spreading method shows that some 30% of the protein is still present in a complex form. The influence of ageing on the proteolytic activity of an enzyme solution has been studied; a steady value is attained after about 24 hrs. at 0° with trypsin, but with pepsin ageing has but little influence. H. F. GILLBE.

Homogeneity of trypsin solutions prepared by the method of Waldschmidt-Leitz. E. ABDERHALDEN and E. VON EHRENWALL (Fermentforsch., 1931, **12**, 411—420).—Trypsin solutions which, when freshly prepared with addition of glycerol, are unable to hydrolyse *dl*-leucylglycine (test for absence of erepsin), on keeping develop this power. Absence of glycerol, or storage at 1° instead of 37° prevents the change. The change is favoured by p_H 7 and is accompanied by an increase in amino-nitrogen. Addition of fresh trypsin solution, either in the active condition or inactivated by heating, to a solution which has become active to leucylglycine prevents hydrolysis for a time, but the power is regained on keeping. Addition of amino-acids activates trypsin solutions, which alone are inactive to leucylglycine. Chloroacetyl-*d*-alanine, which is attacked by erepsin, is not hydrolysed by "aged" trypsin solutions.
J. H. BIRKINSHAW.

Effect of fission products on fermentative proteolysis. P. RONA and H. KLEINMANN (Klin. Woch., 1930, **9**, 1360—1361; Chem. Zentr., 1930, ii, 2392).—With diminution of the quantity of enzyme the effect of the fission products vanishes.
A. A. ELDRIDGE.

Inactivation of trypsin-kinase by heat and the effect of added protein thereon. J. PACE (Biochem. J., 1931, **25**, 422—429).—The heat-inactivation of trypsin-kinase obtained by the interaction of trypsin and enterokinase for 30 min. at 30° proceeds as a unimolecular reaction. The critical increment of the heat-inactivation as determined at five values between p_H 4 and 9 is of the order of 40,000 g.-cal. per "molar unit" of enzyme. The initial addition of caseinogen to solutions of trypsin-kinase undergoing heat-inactivation at p_H 8·5 slows the reaction, but at

p_H 4·7 there is no marked stabilisation. The stabilising effect is relatively reduced when caseinogen is added initially at p_H 8·5, but at a temperature 10° higher. Products of hydrolysis of caseinogen probably stabilise the enzyme. S. S. ZILVA.

Behaviour of polypeptides containing proline towards the erepsin and trypsin-kinase complex. E. ABDERHALDEN and O. ZUMSTEIN (Fermentforsch., 1931, **12**, 341—349; cf. A., 1930, 1475).—Various polypeptides were prepared containing proline linked by its carboxyl group: dl-*prolylglycine* (I), m. p. 222—223° (sinters and becomes brown), dl-*prolyl*-d-*alanine* (II), dl-*prolyl*-dl-*leucine* (III), m. p. 225—226°, dl-*prolylglycylglycine* (IV), dl-*prolyl*-dl-*leucylglycine* (V), m. p. 245° (decomp.), dl-*leucyl*-dl-*prolyl*-dl-*leucine* (VI), m. p. 255—256° (decomp.). Erepsin did not hydrolyse I and attacked II and IV only slightly. III and V were rapidly hydrolysed; VI was not attacked. Trypsin-kinase did not attack any of the polypeptides. III and VI were resistant to *N*-alkali hydroxide, whilst I and II were hydrolysed. It is evident that enzymes do not merely stimulate reactions already in progress. J. H. BIRKINSHAW.

Behaviour of polypeptides containing lysine substituted in the α- and ε-position towards *N*-alkali hydroxide, erepsin, and trypsin. E. ABDERHALDEN and F. SCHWEITZER (Fermentforsch., 1931, **12**, 350—375).—The following lysine polypeptides and precursors substituted in the α-position (starting from ε-benzoyl-*dl*-lysine) or in the ε-position (starting from α-methyl-*dl*-lysine) were obtained: ε-N-*benzoyl*-α-dl-*alanyl*-dl-*lysine* (I), m. p. 240° (uncorr.), turns brown, from ε-N-*benzoyl*-α-(dl-α-*bromopropionyl*)-dl-*lysine*, m. p. 129—130° (uncorr.); ε-*benzoyl*-α-dl-*alanyl*-dl-*lysine*, m. p. 145—146°; ε-N-*benzoyl*-α-dl-*leucyl*-dl-*lysine*, m. p. 232—233° (uncorr.), turns brown, from ε-N-*benzoyl*-α-(dl-α-*bromoisohexoyl*)-dl-*lysine*, sinters 145°, m. p. 148—150°; ε-N-*benzoyl*-α-(N-*benzoyl*-dl-*leucyl*)-dl-*lysine*, m. p. 155—156°; ε-N-*benzoyl*-α-(N-*benzyl*-dl-*leucyl*)-dl-*lysine*, m. p. 190—191°; ε-N-*benzoyl*-α-dl-*norleucyl*-dl-*lysine*, m. p. 251—252°, turns brown, from ε-N-*benzoyl*-α-(dl-α-*bromohexoyl*)-dl-*lysine*, m. p. about 140° after sintering; ε-N-*benzoyl*-α-(dl-*leucyl*-dl-*alanyl*)-dl-*lysine* (II), decomp. about 90°, from ε-N-*benzoyl*-α-(dl-α-*bromoisohexoyl*-dl-*alanyl*)-dl-*lysine*, m. p. 154—155°; (dl-αε-dibenzoyl-lysine [which, contrary to earlier literature (A., 1909, i, 229), on partial debenzoylation with hydrochloric acid yields ε-benzoyl-*dl*-lysine]; *dl*-α-N-methyl-lysine (*hydrochloride*, m. p. 244—245° (uncorr.); *hydriodide*, m. p. 239—241° (decomp.); ε-dl-*alanyl*-α-N-*methyl*-dl-*lysine*, m. p. about 115°, from ε-(dl-α-*bromopropionyl*)-α-N-*methyl*-dl-*lysine*; ε-dl-*leucyl*-α-N-*methyl*-dl-*lysine*, decomp. 120°, from ε-(dl-α-*bromoisohexoyl*)-α-N-*methyl*-dl-*lysine*.

dl-Lysine [*monohydrochloride*, m. p. 235—236° (uncorr.)] furnished the αε-substituted lysines: dl-αε-*di*-dl-*alanyl*-dl-*lysine* (III), by way of dl-αε-*dibromopropionyl*-dl-*lysine* and dl-αε-*dileucyl*-dl-*lysine* (IV), m. p. about 130°, by way of dl-αε-*dibromoisohexoyl*-dl-*lysine*, m. p. 93—94°. An attempt to couple ε-N-*benzamido*-α-*bromohexoyl chloride* with *d*-alanine was unsuccessful.

Of these compounds, erepsin attacked I, II, and III. Trypsin-kinase hydrolysed II and IV to a small extent. In the latter case only the leucyl group in the α-position was eliminated. With dilute alkali hydroxide the compounds were all hydrolysed, the velocity of reaction depending on the constitution. In no case was the group introduced into the ε-position of lysine removed by enzyme action, making it probable that in protein lysine is attached only by its α-amino-group. J. H. BIRKINSHAW.

Behaviour of polypeptides built up of glycine and alanine towards polypeptidases and *N*-alkali hydroxide. E. ABDERHALDEN and E. VON EHRENWALL (Fermentforsch., 1931, **12**, 376—410).—The following polypeptides and precursors were prepared: glycyl-*d*-alanine (*copper* salt, $[\alpha]_{Hg}^{20}$ −211°), from chloroacetyl-*d*-alanine (*ammonium* salt, m. p. 197° (decomp.), $[\alpha]_D^{20}$ −60°; double *salt* of ammonium chloride and glycyl-*d*-alanine, loses ammonium chloride by sublimation at 183°, decomp. 233°, $[\alpha]_D^{20}$ −9·4°); d-*alanylglycyl*-d-*alanine*, m. p. (decomp.) above 268°, $[\alpha]_D$ −47° (*copper* salt, $[\alpha]_{Hg}^{20}$ +98°), from d-α-*bromopropionylglycyl*-d-*alanine*, darkens at 186°, decomp. 192°; *glycyl*-d-*alanylglycyl*-d-*alanine* (*copper* salt, $[\alpha]_{Hg}^{0}$ −183°), browns at 231°, from *chloroacetyl*-d-*alanylglycyl*-d-*alanine*, sinters at 191°, $[\alpha]^{20}$ −119°; *dl*-alanylglycine; *glycyl*-dl-*alanylglycine*, m. p. 243°, from *chloroacetyl*-dl-*alanylglycine*, sinters at 163°, decomp. 186—187°; dl-*alanylglycyl*-dl-*alanylglycine*, decomp. about 260°, from dl-α-*bromopropionylglycyl*-dl-*alanylglycine*, decomp. 183°; *glycylglycyl*-dl-*alanine*, browns at 215°, from *chloroacetylglycyl*-d-*alanine*, m. p. 157° (browns); dl-*alanylglycylglycyl*-d-*alanine*, browns at 185°, m. p. about 203°, from dl-α-*bromopropionylglycylglycyl*-d-*alanine*, m. p. 166—169° (decomp.); *chloroacetyl*-d-*alanyl chloride*, $[\alpha]_D^{20}$ +12°. The following derivatives were obtained: *benzoylglycyl*-d-*alanylglycyl*-d-*alanine*, decomp. 174°; *phenylcarbimidoglycyl*-d-*alanine*, m. p. 151°; *phenylcarbimido*-d-*alanylglycyl*-d-*alanine*, m. p. 148°, -*glycyl*-d-*alanylglycyl*-d-*alanine*, m. p. (decomp.) 178°, -dl-*alanylglycine*, m. p. 203°, -*glycyl*-dl-*alanylglycine*, decomp. 181°, -dl-*alanylglycyl*-dl-*alanylglycine*, m. p. 144°, -*glycylglycyl*-d-*alanine*, m. p. (decomp.) 176°, -dl-*alanylglycylglycyl*-d-*alanine*, m. p. 162°; 2-naphthalenesulphonylglycyl-*d*-alanine; *di-2-naphthalenesulphonylglycyl*-d-*alanine*, sinters 228°, decomp. 250°; 2-*naphthalenesulphonyl*-d-*alanylglycyl*-d-*alanine*, m. p. 182° (decomp.), -*glycyl*-d-*alanylglycyl*-d-*alanine*, browns at 192°, decomp. 215°, -dl-*alanylglycine*, m. p. 175°, -*glycyl*-dl-*alanylglycine*, m. p. 213° (decomp.), -dl-*alanylglycyl*-dl-*alanylglycine*, sinters at 202°, -*glycylglycyl*-d-*alanine*, sinters and darkens at 222°, -dl-*alanylglycylglycyl*-d-*alanine*, decomp. above 257°.

Differences were noted in the rate of hydrolysis of the tri- and tetra-peptides by *N*-alkali hydroxide. The benzoyl and phenylcarbimido-compounds were in general more easily hydrolysed than the corresponding free polypeptides; inhibition occurred with phenylcarbimido-*dl*-alanylglycylglycyl-*d*-alanine. Inhibition was also found with the 2-naphthalenesulphonyl derivatives, but all the halogenoacyl compounds were hydrolysed. Erepsin hydrolysed all the polypeptides and some of the halogenoacyl compounds, but did not attack the benzoyl, phenylcarbimido-, or 2-naphthalenesulphonyl derivatives. Trypsin-kinase hydrolysed *dl*-alanylglycyl-*dl*-alanylglycine and *dl*-alanyl-

glycylglycyl-*d*-alanine, but had no action on glycyl-*d*-alanylglycyl-*d*-alanine or the di- and tri-peptides. A trypsin-kinase preparation of Waldschmidt-Leitz did not attack any of the phenylcarbimido- or 2-naphthalenesulphonyl derivatives, although other preparations were active in some cases. The halogenoacyl compounds were all hydrolysed with the exception of chloroacetyl-*dl*-alanylglycine. J. H. BIRKINSHAW.

Behaviour of dipeptides containing *m*- or *o*-, or *p*-nitro-tyrosine or phenyl-β-alanine towards *N*-alkali hydroxide, erepsin, and trypsin-kinase. E. ABDERHALDEN and W. SCHAIRER (Fermentforsch., 1931, **12**, 295—312).—The following dipeptides and precursors were prepared: *glycyl*-l-p-*tyrosine*, froths at 130°, from chloroacetyl-*l*-tyrosine; dl-*leucyl*-l-p-*tyrosine* from *dl*-α-bromo*iso*hexoyl-*l*-*p*-tyrosine; *glycyl*-dl-o-*tyrosine*, begins to froth at 120°, from *chloroacetyl*-dl-o-*tyrosine*, begins to sinter at 120°; dl-*leucyl*-dl-o-*tyrosine*, decomp. 170°, from dl-α-*bromo*iso*hexoyl*-dl-o-*tyrosine*, begins to sinter at 94°; *glycyl*-dl-m-*tyrosine*, m. p. 120—130° (decomp.), from *chloroacetyl*-dl-m-*tyrosine*, m. p. 136°; dl-*leucyl*-dl-m-*tyrosine*, m. p. 120—130° (decomp.), from dl-α-*bromo*iso*hexoyl*-dl-m-*tyrosine*, begins to sinter at 127°; *glycyl*-l-2-*nitro*-p-*tyrosine*, decomp. 220°, from *chloroacetyl*-l-p-*nitrotyrosine*, begins to sinter at 165—166° (*ethyl* ester, sinters at 92°); dl-*leucyl*-l-p-*nitrotyrosine*, decomp. 210—220°, from dl-α-*bromo*iso*hexoyl*-l-p-*nitrotyrosine*, sinters at 170° (*ethyl* ester, sinters at 72°); *glycyl*-dl-*phenyl*-β-*alanine*, m. p. 222° (decomp.), from *chloroacetyl*-dl-*phenyl*-β-*alanine*, m. p. 141°; dl-*leucyl*-dl-*phenyl*-β-*alanine*, m. p. 200° (decomp.), from dl-α-*bromo*iso*hexoyl*-dl-*phenyl*-β-*alanine*, m. p. 132°. The dipeptides glycyl- and *dl*-leucyl-*dl*-phenyl-β-alanine and glycyl- and *dl*-leucyl-*dl*-*m*-tyrosine were practically unchanged by erepsin and *N*-alkali hydroxide; chloroacetylnitrotyrosine was readily hydrolysed by the latter. Both erepsin and trypsin-kinase attacked glycyl- and *dl*-leucyl-*l*-*p*-tyrosine, although to different extents, depending on the age of the enzyme preparation. Trypsin-kinase hydrolysed chloroacetyl-*dl*-*o*-tyrosine and, to a small extent, *dl*-α-bromo*iso*hexoyl-*dl*-*o*-tyrosine. The remaining halogenoacyl substances and the corresponding dipeptides were not attacked.

J. H. BIRKINSHAW.

Specificity of the polypeptidases. E. ABDERHALDEN and E. SCHWAB (Fermentforsch., 1931, **12**, 432—461).—Trypsin-kinase did not decompose the ethyl or *iso*amyl ester of glycyl-*dl*-leucylglycyl-*dl*-leucine, but a hydrolysis of the CO·NH linking occurred. The isolation of the anhydride of glycylleucine by way of the diketopiperazide showed that the amino-acid chain had been broken in the middle. The action of trypsin-kinase was studied on a number of amino-acids, polypeptides, and their derivatives, constituted of glycine, leucine, and tyrosine. These included: esters of *l*-tyrosine, n-*propyl*, m. p. 125° (*hydrochloride*, m. p. 148°), iso*butyl*, m. p. 146—147° (*hydrochloride*, m. p. 172°), and iso*amyl*, m. p. 88° (*hydrochloride*, m. p. 158°); ester hydrochlorides of *dl*-leucine, iso*butyl*, m. p. 106°, and iso*amyl*, m. p. 98°; ester hydrochlorides of *dl*-leucylglycyl-*l*-tyrosine, *ethyl*, iso*butyl*; iso*butyl* ester hydrochloride of *dl*-leucyl-*dl*-leucylglycyl-*l*-tyrosine, m. p. 181°; *ethyl* ester hydrochloride of *dl*-leucylglycyl-*l*-leucine, m. p. 183°, iso*butyl* ester hydrochloride of glycyl-*dl*-leucylglycyl-*dl*-leucine, iso*amyl* ester hydrochloride of glycyl-*dl*-leucylglycyl-*d*-leucine, iso*butyl* ester hydrochloride of *dl*-leucylglycyl-*dl*-leucylglycyl-*l*-leucine, *ethyl* ester of chloroacetyl-*dl*-leucine, m. p. 51°, *ethyl* ester of phenylcarbimido-*dl*-leucylglycine.

Hydrolysis occurred only in the case of the esters of those polypeptides which themselves were hydrolysed by the enzyme. It is probable that the enzyme which is responsible for hydrolysis also produces polypeptide fission. J. H. BIRKINSHAW.

Intermediate products formed during the hydrolysis of carbamide by urease. J. B. SUMNER, D. B. HAND, and R. G. HOLLOWAY (J. Biol. Chem., 1931, **91**, 333—341).—Contrary to the finding of Fearon (A., 1927, 76) no cyanate is formed during the hydrolysis of carbamide by crystalline urease. The formation of ammonium carbamate as stated by Yamasaki (A., 1920, i, 577) is confirmed. A method for the determination of carbamate, depending on the fact that when a solution of ammonium carbamate is nesslerised only the nitrogen of the ammonium group reacts, was devised and by its use it was shown that the decomposition of carbamate is accelerated by the presence of buffers and delayed by carbonic acid. F. O. HOWITT.

Involution cultures of yeast. II. A. T. HENLEY (J. Inst. Brew., 1931, **37**, 239—240; cf. A., 1930, 1218).—When *S. intermedius* is inoculated on the surface of a 0·75% Irish moss–wort gel, the strength of which is 17—24, it grows as a circular spot with a smooth surface until the diameter reaches 0·5 in., when the centre becomes convoluted and the rim, which is smooth at first, is traversed by radial ridges.

C. RANKEN.

Comparative biochemistry. VII. Sake yeast. J. I. SAGARA (J. Biochem., Japan, 1930, **12**, 459—471).—A di- or tri-aminomonophosphatide, but not lecithin, is present. A pentose and a substance related to bioses are also present. Arginine, histidine, lysine, phenylalanine, proline, and valine were identified; amylase, esterase, glycerophosphatase, pepsin, and trypsin are present. The nucleic acid is distinguished (in two strains) by low nitrogen and phosphorus contents. CHEMICAL ABSTRACTS.

Yeast trehalose. G. TANRET (Compt. rend., 1931, **192**, 1056—1058).—Trehalose, $[\alpha]_D$ +180°, has been isolated from fresh or dried top yeast, the yield being 2%. The disaccharide could not be found in bottom yeast. The glycogen content of top yeast was 3·8%, whilst that of bottom yeast was 1·5%. Ergothioneine could not be detected. F. O. HOWITT.

Gram reaction in crushed yeasts. H. A. KEMP (Stain Tech., 1931, **6**, 53—56).—Thick smears of yeasts are dried, crushed, and stained with aniline crystal-violet for 1·5 min., Lugol's iodine solution for 2 min., decolorised in aniline, and counterstained with 1% aqueous safranine. The crushed yeasts then display a Gram-positive outer layer and a Gram-negative inner substance. H. W. DUDLEY.

Changes of reaction observed during the growth of fungi. Influence of the nature of the

source of nitrogen. F. LABROUSSE (Compt. rend., 1931, **192**, 980—982).—In gelatin-media containing equimolecular equivalents of calcium nitrite, ammonium nitrate, or ammonium sulphate as the sole source of nitrogen, *Cladosporium cucumerinum* and *Verticillium dahliæ* produce in the calcium nitrite medium an immediate alkaline reaction, in the others an immediate acid reaction; with *Sclerotinia libertiana* and *S. minor* the reactions of the media become progressively acid as growth proceeds. C. C. N. VASS.

Influence of hydrogen-ion concentration and of sodium carbonate and related substances on *Penicillium italicum* and *P. digitatum*. R. H. MARLOTH (Phytopath., 1931, **21**, 169—198).—The treatment of citrus fruits with sodium hydrogen carbonate prior to packing is examined. The p_H growth tolerance of the fungi is 2·9—6·5 for *P. italicum* and 3·0—6·0 for *P. digitatum*. The sodium ion is more toxic than the potassium ion when the citrates are compared. The toxic effect of potassium and sodium chlorides is probably due mainly to the chlorine ion. No constant differences in the toxic action of sodium and potassium salts were observed. Borax was relatively more toxic to spores of *P. digitatum* and the hydrogen carbonates were more toxic to *P. italicum*. The hydrogen carbonate ion, as such, is probably toxic to the fungi. When the hydroxyl-ion concentration of a solution is sufficient to produce $p_H > 10$, the toxic property of the solution lies in the hydroxyl ion. A. G. POLLARD.

Dependence of oxidising fermentations on the oxidation–reduction potential of the medium. S. J. KUSNETZOV (Zentr. Bakt. Par., 1931, II, **83**, 37—52).—In cultures of *Aspergillus niger* in Winogradsky flasks anaerobic conditions develop below the layer of mycelium, the r_H falling to 15. When r_H becomes <17, formation of citric acid occurs. When cultures are grown in an atmosphere of nitrogen an r_H range of 12·8—14·0 is reached and alcohol formation begins. In an atmosphere of hydrogen (r_H 2) citric acid production ceases. A. G. POLLARD.

Bacterial lipins. M. GUNDEL and W. WAGNER (Z. Immunitat., 1930, **69**, 63—76; Chem. Zentr., 1931, i, 801).—Extracts of *B. pyocyaneus* in alcohol or acetone have a highly bactericidal action which is not affected by heat. The effect is attributed to the presence of fatty acids. The antigenic and bactericidal properties of the bacterial lipins are not associated. A. A. ELDRIDGE.

Acetic acid bacteria. S. HERMANN and P. NEUSCHUL (Biochem. Z., 1931, **233**, 129—216).—The metabolic products of 14 strains of acetic acid bacteria when grown on a variety of substrates for 3—4 months are investigated. The reactions of this group are shown to be essentially oxidative and only occasionally hydrolytic. All the strains oxidise ethyl and propyl alcohols. Dextrose is oxidised primarily to gluconic acid by all strains except *B. ascendens*, Henneburg, and arabinose and galactose to arabonic and galactonic acids by all but *B. aceti*, Henneburg, *B. Kützingianum*, and *B. ascendens*, Henneburg. Lævulose is attacked only by *B. gluconicum* and gives ketogluconic acid. Sucrose is inverted by 8 strains, whilst maltose and lactose are not attacked by any of the bacteria. Raffinose is hydrolysed only by *B. gluconicum*, *B. aceti*, Hansen, and *B. vini acetati*. Glycerol is oxidised to dihydroxyacetone by 5 strains (yields up to 90%), erythritol by the same 5 strains to erythritose, mannitol by 7 strains to lævulose and by 1 strain to mannose, sorbitol by 4 strains to sorbose, dulcitol only very slowly by *B. gluconicum*. Gluconic acid and its calcium salt are next converted into 5-ketogluconic acid. On the basis of their biochemical behaviour, the organisms are grouped into ketogenic bacteria (*B. gluconicum*, *B. xylinum*, *B. xylinoides*, *B. orleanense*, *B. aceti*, Hansen) and aketogenic bacteria (*B. aceti*, Henneburg, *B. Pasteurianum*, *B. acetosum*, *B. rancens*, *B. ascendens*, Berlin, *B. vini acetati*, *B. Kützingianum*, and *B. ascendens*, Henneburg). P. W. CLUTTERBUCK.

Nitrifying bacteria. S. VINOGRADSKI (Compt. rend., 1931, **192**, 1000—1004).—Nitrifying bacteria are grown in a silica gel containing ammonium chloride and covered by a crust of insoluble carbonate to eliminate mobility of the bacteria. Counts are given for various soils and characteristics of some types are described. F. O. HOWITT.

I. Nitrogen cycle in forest soils. II. Seasonal changes in microbiological activity in forest soils. D. FEHER (Arch. Mikrobiol., 1930, **1**, [3]; Proc. Internat. Soc. Soil Sci., 1931, **6**, 17—19, 19—21).—The various factors affecting the nature, quantity, and seasonal variations of the nitrogen compounds, and the formation of humus in two types of forest soils are examined. A. G. POLLARD.

Factors which affect the decomposition of carbamide in soil. T. GIBSON (Zentr. Bakt. Par., 1930, II, **81**, 45—60; Chem. Zentr., 1930, ii, 2929).—The microflora which decompose carbamide in active soils are markedly affected by a difference in temperature. Carbamide quickly decomposes at 1—2°; the decomposition in anaerobic soil is 70% of that in aerobic. Humus and humus-forming substances, and lime increase decomposition, but phosphate is without marked effect. L. S. THEOBALD.

Effect of hydrogen-ion concentration in some oxidations by *B. coli communis*. R. P. COOK and R. S. ALCOCK (Biochem. J., 1931, **25**, 523—533).—The anaerobic oxidations in the presence of methylene-blue give p_H–activity curves which rise steadily from the acid region to a plateau which starts at about p_H 7·0 with formate, 7·4 with lactate, and 8·5 with succinate. There is a steady drop from the plateau at about p_H 9·5 in all cases. The p_H–activity curves obtained in the aerobic oxidation of the three substrates resemble in general shape the curves for the dehydrogenases, but the optima have been shifted to the acid side. Exposure to solutions of low p_H inactivates the dehydrogenases in the order succinate, lactate, and formate. The aerobic mechanism is affected about equally in each instance. The effect is not so marked in the alkaline region. The oxidation of succinate both anaerobically and aerobically and the aerobic oxidation of formate are the mechanisms most affected. S. S. ZILVA.

Relationship between the respiratory catalysts of *B. coli*. R. P. COOK, J. B. S. HALDANE, and

L. W. Mapson (Biochem. J., 1931, **25**, 534—550).—The reduction of methylene-blue by the system succinate, lactate, or formate and toluene-treated *B. coli* is little affected by potassium cyanide or carbon monoxide, but 8-hydroxyquinolinesulphonic acid and 8-amino-α-naphthol-5-sulphonic acid, which unite with copper, inhibit the action of formic dehydrogenase. The former compound has no effect on oxygen reduction by this substrate. Oxidation by molecular oxygen of the above substances through the catalytic agency of the toluene-treated organism is inhibited by potassium cyanide and carbon monoxide. The activators of oxygen concerned in the three catalyses differ in their susceptibilities to these poisons. Phenylurethane has little or no effect on these catalysts, but it makes them more sensitive to potassium cyanide and carbon monoxide. Oxalate renders the oxidation of lactic acid far less sensitive to carbon monoxide. In presence of cyanide methylene-blue can replace the activators of oxygen. Its action, like theirs, is inhibited by carbon monoxide.

S. S. Zilva.

Nature of the proteins and lipins synthesised by the colon bacillus. H. C. Eckstein and M. H. Soule (J. Biol. Chem., 1931, **91**, 395—404).—Analysis of the proteins formed by *B. coli*, Jordan, aerobically cultured on media containing inorganic salts, carbohydrate, and either *d*-alanine or *l*-cystine shows a synthesis of arginine, histidine, lysine, tyrosine, and tryptophan. No cystine synthesis occurred with the alanine culture. Lipins, characterised by low iodine values and by absence of common sterols and fatty acids more highly unsaturated than oleic acid, were synthesised, and, whilst the alanine culture produced considerable amounts of phospholipins, the cystine culture produced only traces.

F. O. Howitt.

Chemical study of bacteria. *d*-Mannose and *d*-arabinose in carbohydrate from culture medium after growth of tubercle bacilli. A. G. Renfrew (J. Biol. Chem., 1930, **89**, 619—626).—Human tubercle bacilli were grown on synthetic medium. The medium was filtered, concentrated, and precipitated with neutral lead acetate. The filtrate yielded with basic lead acetate a precipitate which was then decomposed with hydrogen sulphide. The lead-free filtrate after concentration and treatment with ethyl alcohol yielded a powder containing 2·2% N, 1% P, and 11% of ash. Fractional precipitation with alcohol from aqueous solution yielded a substance of $[\alpha]_D$ +32·0° and containing 1·20—1·35% N, 3% of ash, and some phosphorus. Acid hydrolysis yielded 41% of reducing sugars (19% of pentose). *d*-Mannose was isolated as the phenylhydrazone, and *d*-arabinose as the phenylbenzylhydrazone. The residue of the hydrolysate after removal of *d*-mannose and *d*-arabinose contained traces of two unidentified hydrazine derivatives and inositol.

G. F. Marrian.

Lipins of tubercle bacilli. XIX. Composition of phosphatide fraction from bovine tubercle bacilli. XX. Occurrence of mannose and inositol in phosphatide fraction of human, avian, and bovine tubercle bacilli. R. J. Anderson and E. G. Roberts (J. Biol. Chem., 1930, **89**, 599—610, 611—617).—XIX. 11·28 G. of phosphatide, m. p. 205—208° (N 1·00, P 1·87%), prepared as previously described (A., 1927, 1114), were hydrolysed with dilute alcoholic hydrochloric acid, diluted with water after partial removal of the alcohol, and extracted with light petroleum. The dried extract after saponification yielded 0·55 g. of "unsaponifiable wax," m. p. 57—58°, and 5·9 g. of fatty acids. The latter by the lead soap process yielded 3 g. of palmitic acid and 2·9 g. of liquid acid of iodine value 12·1. Stearic acid and a liquid saturated acid (C 75·88, H 12·75%, mol. wt. 306) resembling tuberculostearic acid were isolated from the liquid fraction after catalytic reduction. Treatment of the aqueous fraction from the initial hydrolysis with phenylhydrazine yielded mannosephenylhydrazone. After removal of the excess of phenylhydrazine with benzaldehyde, the barium salt of an organic phosphoric acid (probably glycerophosphoric acid) and inositol were isolated.

XX. The water-soluble fraction of the phosphatide isolated from human tubercle bacilli, after removal of the glycerophosphoric acid consisted mainly of inositol, mannose, and another reducing sugar which yielded glucosazone, the latter being probably a mixture of dextrose and lævulose. Mannosephenylhydrazone and inositol were also isolated from similar fractions obtained from avian and bovine tubercle bacilli.

G. F. Marrian.

Fat-splitting enzyme from the guinea-pig's lung and its action on the tubercle bacillus. D. Kanócz (Z. Tuberkulose, 1929, **53**, 124—128; Chem. Zentr., 1930, ii, 2393).—A fat-splitting enzyme from the guinea-pig's lung removes the fatty coating of the bacillus. L. S. Theobald.

Effect of high dilutions of quinine on the growth of the bacterial flora of hay infusions. M. Feiler (Zentr. Bakt. Par., 1931, II, **83**, 63—68).—Growth of *B. subtilis* and *B. proteus* was stimulated by the presence of quinine in concentrations $10^{-25}M$ to $10^{-8}M$ with a maximum effect at approx. $10^{-10}M$. With concentrations $>10^{-8}M$ quinine became toxic. Similar but less regular effects on *Paramecium* are recorded and discussed. A. G. Pollard.

Feulgen's reaction applied to protozoa and worms mounted in Venetian turpentine. L. A. Margolena (Stain Tech., 1931, **6**, 47—49).—Feulgen's stain, a solution of basic fuchsin decolorised with sulphurous acid, detects aldehydes produced when nucleic acids are partly hydrolysed; it therefore stains chromatin. A method for applying the stain to the protoplasts of small organisms is described.

H. W. Dudley.

Non-toxic dyes and dye-resistant bacteria. J. W. Churchman (Stain Tech., 1931, **6**, 57—63).—Three typical organisms—*B. prodigiosus*, *B. anthracis*, and *S. aureus*—were not killed by 48 hrs.' exposure to saturated aqueous neutral-red; *B. prodigiosus* survived 9 days' exposure. *B. anthracis* was not killed by 40 days' exposure to saturated aqueous Bismarck-brown, and the other two organisms survived 24 hrs.' exposure. *B. prodigiosus* was alive after 26·5 months' exposure to 1 in 15,000 gentian-violet solution. The bactericidal action of gentian-violet and acid fuchsin is greatly increased by slight rise of temperature.

H. W. Dudley.

Staining of bacterial flagella. C. E. SAFFORD and M. S. FLEISHER (Stain Tech., 1931, 6, 43—45).—The smear is covered with a fixative consisting of 25 c.c. of saturated aqueous picric acid solution, 5 g. of tannic acid, and 7·5 g. of ferrous sulphate in 100 c.c. of water. The slide is heated, and after 2 min. is washed with water, dried, and covered with a stain (Fontana spirochæte stain) prepared by adding dilute ammonia to 25 c.c. of 2% silver nitrate until the precipitate formed just redissolves, when silver nitrate solution is added until a faint turbidity persists. This stain is allowed to act warm for 1—2 min.

H. W. DUDLEY.

Effect of the anterior pituitary hormone. M. REISS and K. LANGENDORF (Endokrinol., 1929, 3, 161—174; Chem. Zentr., 1931, i, 636).—The blood-cholesterol of rabbits and dogs is increased.

A. A. ELDRIDGE.

Perfusion and the hydrology of the vasomotor system. M. VILLARET, L. JUSTIN-BESANÇON, and J. CAMUS (Compt. rend., 1931, 192, 1046—1047).—Perfusion experiments of the blood-vessels of the frog and guinea-pig show that a physiological antagonism exists between adrenaline (1 in 100,000) and a sulphuretted mineral water.

F. O. HOWITT.

Appearance of proteases in the blood or urine after parenteral administration of thyroxine, adrenaline, and insulin. E. ABDERHALDEN and E. WERTHEIMER (Fermentforsch., 1931, 12, 421—431).—After parenteral administration of thyroxine, adrenaline, and insulin to rabbits or dogs, enzymes appear in the urine, capable of hydrolysing organ-substrates. When the amount of hormone injected is small, the action is quite specific, only that substrate being hydrolysed which is prepared from the organ elaborating the hormone in question. This applies even when the organ has been extirpated from the experimental animal. With larger doses the action becomes unspecific in the case of adrenaline and thyroxine, and substrates of other organs are attacked. This excretion of specific proteases persists for some weeks after the administration of the hormone has ceased.

J. H. BIRKINSHAW.

Extraction of insulin. P. G. MARSHALL and B. P. WIESNER (Nature, 1931, 127, 630).—A method for the extraction of insulin from pancreas by means of 20% sulphosalicylic acid is described.

L. S. THEOBALD.

Effect of insulin on the amino-acid content of blood. A. C. DANIELS and J. M. LUCK (J. Biol. Chem., 1931, 91, 119—126).—The finding of Luck, Morrison, and Wilbur (A., 1928, 676) that administration of insulin is followed by a decrease in blood-amino-nitrogen was confirmed in human subjects. The theory that insulin increases amino-acid catabolism without a compensatory increase in regeneration of amino-acid from tissue proteins is advanced.

F. O. HOWITT.

Influence of insulin on glycogen distribution in marine fishes. R. W. ROOT, F. G. HALL, and I. E. GRAY (J. Biol. Chem., 1931, 91, 27—35).—Large doses of insulin intraperitoneally injected into the scup (*Stenotomus chrysops*, L.) produce a steady fall in the liver-glycogen and, following a transient hyperglycæmia, a pronounced hypoglycæmia. The muscle-glycogen increases until convulsions intervene, when it falls rapidly. The transient hyperglycæmia is due to the initial strong glycogenolysis from a glycogen-rich liver. The use of poikilothermic animals for the study of insulin is recommended.

F. O. HOWITT.

Metabolism of animals on a carbohydrate-free diet. II. Variations in the sensitivity towards insulin of different species of animals on carbohydrate-free diets. A. HYND and D. L. ROTTER (Biochem. J., 1931, 25, 457—464).—Mice fed on a carbohydrate-free diet are more resistant to the effects of insulin than are those receiving carbohydrates. A carbohydrate-free diet consisting exclusively of either fat or protein is not so satisfactory as one in which both protein and fat are present. Rabbits on green food are less resistant than when fed on oats. There is no significant difference in the reducing power of the blood-plasma and corpuscles of the two groups of rabbits. There is a much earlier onset of symptoms in kittens on a carbohydrate-free than on carbohydrate-containing diet.

S. S. ZILVA.

Increased effect of insulin in presence of lipins. L. SURANYI and F. SZALAI (Klin. Woch., 1930, 9, 2159; Chem. Zentr., 1931, i, 957).—When administered with a 2% aqueous emulsion of lecithin (3. c.c.) to rabbits (2000 g.), insulin (10 units) caused a 6 hr.-hypoglycæmia without symptoms.

A. A. ELDRIDGE.

Proteolytic enzymes of the tissues as inactivators of insulin. A. A. SCHMIDT (Z. ges. exp. Med., 1930, 70, 27—39; Chem. Zentr., 1930, ii, 2398).—Liver extracts have an inactivating effect even stronger than that of kidney extracts.

L. S. THEOBALD.

Milk secretion and menformone. S. E. DE JONGH and E. LAQUEUR (Klin. Woch., 1930, 9, 2344—2346; Chem. Zentr., 1931, i, 805).—A sudden fall in the amount of menformone injected into male or female guinea-pigs caused the secretion of milk.

A. A. ELDRIDGE.

Follicular hormone. B. SKARŻYŃSKI (Z. physiol. Chem., 1931, 196, 19—22).—Small amounts of crystalline hormone isolated by Marrian's method from urine of pregnancy corresponded in m. p. and absorption curve with Butenandt's product. The change in the ultra-violet spectrum of the hormone in alcoholic potassium hydroxide on keeping suggests that it undergoes deep-seated changes in alkaline solution.

J. H. BIRKINSHAW.

Mol. wt. of vitamin-*A*. H. R. BRUINS, J. OVERHOFF, and L. K. WOLFF (Biochem. J., 1931, 25, 430—438).—The diffusion constant of carotene in xylene at 20° is 0·455 cm.^{2} per 24 hrs., that of vitamin *A* as determined colorimetrically is 0·578 cm.^{2} per 24 hrs. A mol. wt. of about 330 has been deduced for vitamin-*A*. It is improbable that there is a simple chemical relation between vitamin-*A* and carotene.

S. S. ZILVA.

Vitamins-*A* and -*D*. VIII. Relation of the chromogen of fish-liver oil to cholesterol, ergosterol, and vitamins-*A* and -*D*. W. KERPPOLA (Skand. Arch. Physiol., 1930, 60, 311—319; Chem. Zentr., 1931, i, 641).—Colour reactions obtained

with crystalline substances extracted by means of ether from saponified fish-liver oil, unsaponifiable residue, or cholesterol are described. It is possible that vitamin-*A* is identical with a certain chromogen.
A. A. ELDRIDGE.

Association of vitamin-*A* with greenness in plant tissue. III. Vitamin-*A* content of asparagus grown under light of various qualities. J. W. CRIST and M. DYE (J. Biol. Chem., 1931, **91**, 127—134).—A quantitative relationship exists between the development of chlorophyll and the elaboration of vitamin-*A* in the plant (cf. A., 1927, 904; 1929, 610). Parallel with the increase in chlorophyll there is an increase in water-soluble nitrogen and calcium content but a decrease in that of potassium. F. O. HOWITT.

Antimony trichloride colour reaction for vitamin-*A*. IV. Vitamin-*B* in the biological assay of vitamin-*A* and the stability of the vitamin-*A* and the chromogen in diluting oils. E. R. NORRIS and A. E. CHURCH (J. Biol. Chem., 1930, **89**, 589—598).—The premature flattening of the growth curves of rats fed on vitamin-*A*-free diets supplemented with some source of vitamin-*A* was prevented by increasing the amount of vitamin-*B* (dried yeast) in the basal diet. The vitamin-*A* growth-promoting value and the antimony trichloride chromogen of cod-liver oil unsaponifiable matter underwent destruction when dissolved in olive oil or peanut oil; the greater destruction occurring in the latter. The stability of the chromogen in coconut oil varied for different samples of the latter. The destruction of the chromogen in these media was prevented by the addition of 0·05% of quinol.
G. F. MARRIAN.

Behaviour of vitamin-*A* from primary sources. E. J. QUINN, J. C. HARTLEY, and M. A. DEROW (J. Biol. Chem., 1930, **89**, 657—663).—Dried spinach lost approximately 70% of its vitamin-*A* activity when stored in sealed jars exposed to diffuse daylight for 15 months. The addition of 20% of rancid butter-fat to the spinach increased the degree of destruction of the vitamin. The vitamin-*A* present in dried tomato pulp, dried carrots, and dried broccoli was readily extracted by peanut oil. Exposure of a light petroleum extract of dried carrots to ultra-violet light resulted in the complete destruction of vitamin-*A*.
G. F. MARRIAN.

Effect of use of mineral oil on absorption of vitamin-*A*. J. I. ROWNTREE (J. Nutrition, 1931, **3**, 345—351).—The effect depends on the vitamin-*A* content of the diet. CHEMICAL ABSTRACTS.

Effect of adding vitamin-*A* to a rachitogenic diet. A. L. BACHARACH, E. ALLCHORNE, and V. HAZLEY (Biochem. J., 1931, **25**, 639—642).—Addition of 1 g. of fresh carrot daily to Steenbock's diet 2965 does not significantly affect growth rate in the absence or presence of vitamin-*D*. There is no correlation between severity of rickets and rate of growth.
S. S. ZILVA.

Caseinogen for vitamin tests. K. H. COWARD, K. M. KEY, F. J. DYER, and B. G. E. MORGAN (Biochem. J., 1931, **25**, 551—560).—" Light white casein " may be safely used without extraction for vitamin-*A* tests. Extraction of this casein does not remove the growth factor described by Coward, Key, and Morgan (A., 1929, 1203). Heating under certain conditions partly destroys this factor. Male rats require more vitamin-*A* to prevent death than do females. S. S. ZILVA.

Vitamin-petent foods. I. Caseinogen as vitamin-*A*-petent. H. SELYE (Z. ges. exp. Med., 1930, **74**, 320—323; Chem. Zentr., 1931, i, 641).—A caseinogen, but not a carbohydrate, diet causes xerophthalmia in guinea-pigs; hence vitamin-*A* is necessary for the utilisation of caseinogen, which is " vitamin-*A*-petent." A. A. ELDRIDGE.

Serum-calcium, -proteins, and -inorganic phosphorus in vitamin-*B* deficiency and inanition. V. SCHELLING (J. Biol. Chem., 1930, **89**, 575—580).—No significant changes in serum-calcium, -protein, and -inorganic phosphorus were observed in dogs fed on a vitamin-*B*-deficient ration during the period when they consumed the ration. In the later period when no food was consumed and the loss of body-weight exceeded 20%, a fall in serum-calcium and a slight rise in inorganic phosphorus was observed.
G. F. MARRIAN.

Dietary requirements for fertility and lactation. XXIII. Specific effect of vitamin-*B* on lactation. B. SURE and D. J. WALKER (J. Biol. Chem., 1931, **91**, 69—75).—Vitamin-*B*, in addition to its effect on nutrition, has a specific action in lactation. F. O. HOWITT.

Biological significance of milk peroxidase. T. ARAKAWA (Tohoku J. Exp. Med., 1930, **16**, 118—122).—The milk of pregnant rabbits on a diet free from vitamin-*B* contains no peroxidase.
CHEMICAL ABSTRACTS.

"Aperoxidatic" milk as a possible early symptom of avitaminosis-*B*. K. SUZUKI and T. ARAKAWA (Tohoku J. Exp. Med., 1930, **16**, 228—231).—The blood leucocytes of rabbits secreting milk free from peroxidase (cf. preceding abstract) give a normal peroxidase reaction. CHEMICAL ABSTRACTS.

Preparation of a concentrated source of heat-labile vitamin-B_1 uncontaminated with the heat-stable factor B_2. H. M. EVANS and S. LEPKOVSKY (J. Nutrition, 1931, **3**, 353—374).—Clay activated by 25% ethyl-alcoholic extract of both vitamins of rice is a good source of vitamin-B_1 free from the heat-stable factor. When the syrup resulting from concentration of the 25% ethyl-alcoholic extract is treated with 95% alcohol to give a 90% alcoholic solution most of the heat-stable factor is removed, but the heat-labile factor suffers large losses. Rice polishings contain so little of the former that fractionation with 80% alcohol yields an extract almost free from the heat-stable factor and very rich in vitamin-B_1.
CHEMICAL ABSTRACTS.

Differentiation of vitamins-B_1 and -B_2. H. C. SHERMAN and M. R. SANDELS (J. Nutrition, 1931, **3**, 395—409).—Dried bakers' yeast affords to 80% ethyl alcohol a much larger proportion of its vitamin-B_1 than of its -B_2; with 95% alcohol no -B_2 is extracted. Vitamin-B_1 is related to the maintenance of appetite and the prevention of polyneuritis in rats; both vitamins are necessary for growth. Lack of vitamin-B_2

produces a pellagra-like disease, but variability of symptoms may be due to the multiple nature of this factor. CHEMICAL ABSTRACTS.

Is avitaminosis-B_1 an intoxication by methylglyoxal? Glyoxalase-co-enzyme ratio in experimental beriberi. P. VOGT-MØLLER (Biochem. J., 1931, **25**, 418—421).—Methylglyoxal is absent in hexosephosphate + liver enzyme systems of starved or normal mice or pigeons or of vitamin-B_1-deficient animals which received vitamin-B_1 concentrates, whilst it is present when the liver enzyme from vitamin-B_1-deficient animals are used. Methylglyoxal is converted into lactic acid only very slowly when added to a system containing the enzyme from livers of vitamin-B_1-deficient animals, but it disappears when the enzymes from normal livers are added. A boiled aqueous extract of a normal animal liver when added to the enzyme system originating from animals suffering from avitaminosis-B_1 brings about dismutation. S. S. ZILVA.

Vitamin-B_2. B. C. GUHA (Nature, 1931, **127**, 594—595).—The effects of various reagents on the vitamin-B_2 of a commercial liver extract are summarised. The stability towards heat shows anomalies. The vitamin is stable towards sulphur dioxide, hydrogen peroxide, ozone, and trypsin; it is probably a neutral substance. L. S. THEOBALD.

Nitrogen balance in vitamin-B_2-deficiency in the rat. S. K. KON (Biochem. J., 1931, **25**, 482—493).—The experiments were inconclusive. Two of the experimental animals stored less and one more nitrogen than the controls. There were indications of a higher biological value of the ingested nitrogen in the case of the control rats. These animals also gained more weight than the experimental rats although they consumed slightly less food. S. S. ZILVA.

Reprecipitation of the antiscorbutic factor from decitrated lemon juice. S. S. ZILVA (Biochem. J., 1931, **25**, 594—595; cf. A., 1930, 119, 380; this vol., 271).—The active fraction precipitated with lead acetate at p_H 7·0—7·2 can be reprecipitated at p_H 6·4—7·4 when the minimum quantity of 10% acetic acid is used to dissolve the first precipitate. No purification is, however, effected. S. S. ZILVA.

Biological detection of irradiated ergosterol. J. WARKANY (Klin. Woch., 1930, **9**, 2152—2153; Chem. Zentr., 1931, i, 959).—48 Hrs. after ingestion of irradiated ergosterol (30—100 mg.) a rabbit, the urine of which contains no phosphate owing to feeding calcium carbonate, excretes large quantities of phosphate. Only highly active preparations can thus be examined, and the method is merely qualitative.
A. A. ELDRIDGE.

Parallelism between the antirachitic and toxic factors in irradiated ergosterol. Standardisation of vitamin-*D*. O. SCHULTZ and W. MEYER (Klin. Woch., 1930, **9**, 1361; Chem. Zentr., 1930, ii, 2399).—Experiments with rabbits showed no parallelism between the antirachitic and toxic factors. The standardisation of vitamin-*D* preparations by the blood-chemical method after administration of large doses to animals does not appear promising.
A. A. ELDRIDGE.

Intoxication and pulmonary calcification provoked in the rabbit by large doses of irradiated ergosterol. H. SIMONNET and G. TANRET (Bull. Soc. Chim. biol., 1931, **13**, 283—299; cf. A., 1930, 822).—The toxicity of large doses of irradiated ergosterol (40 mg. per day) administered, *per os*, in an oil, is retained after oxidation or reduction. Certain animals, irrespective of breed, show a marked resistance. Discontinuous administration of the ergosterol delays death and results in diminished calcification. Simultaneous administration of potassium iodide prolongs the life of the animal and inhibits calcification. Equal quantities given in large doses, in a given period, kill the animals more quickly than the same amounts given in smaller daily doses. Massive daily doses cause early death without noticeable lesions or calcification. Administration of irradiated ergosterol causes a marked increase in the pulmonary calcium of normal rabbits; in rabbits infected with bovine tubercle bacillus no appreciable change is recorded in the pulmonary calcium until the administration of the ergosterol, when a marked calcification occurs. C. C. N. VASS.

Effect of large doses of irradiated ergosterol on the ash content of the femora of young and adult rats. J. H. JONES and G. M. ROBSON (J. Biol. Chem., 1931, **91**, 43—56).—Administration of toxic doses of irradiated ergosterol to adult rats does not lessen the mineral content of the femur, whilst in growing rats the relative but not the absolute content is slightly decreased. F. O. HOWITT.

Source of excess calcium in hypercalcæmia induced by irradiated ergosterol. J. H. JONES, M. RAPOPORT, and H. L. HODES (J. Biol. Chem., 1930, **89**, 647—656).—The daily administration of irradiated ergosterol in doses of 1 mg. per kg. body-weight to dogs fed on diets containing 0·25% or more calcium produced a marked hypercalcæmia within 2 weeks. On calcium-free diets the same dosage of irradiated ergosterol caused only a slight increase in blood-calcium after 3 weeks. The addition of calcium to the diet at the end of this period caused an immediate hypercalcæmia. The source of the excess of blood-calcium is the food and not the body-tissues.
G. F. MARRIAN.

Autoxidation of fats with reference to their destructive effect on vitamin-*E*. M. J. CUMMINGS and H. A. MATTILL (J. Nutrition, 1931, **3**, 421—432).—The autoxidisability of oils increases in the order: cod-liver oil, lard, butter fat, cottonseed oil, stearin, hydrogenated cottonseed oil. The relation between autoxidisability and effect on reproductivity of animals was studied. The possible role of vitamin-*E* as an antioxidant is discussed.
CHEMICAL ABSTRACTS.

Autocatalysis in green and other vegetables in various gases. Effect of temperature. F. SCURTI and A. ZAVANAJU (Ann. Sperim. agrar., 1930, **4**, 39—80; Chem. Zentr., 1931, i, 864).—The production of carbon dioxide by the decomposition of vegetables in air takes place with intermediate formation of alcohol, acetaldehyde, and acetic acid, the whole tissue and carbohydrates taking part. It takes place in air, ozone, carbon dioxide, nitrogen, hydrogen,

methane, or argon. At 1—2° the reaction is arrested; in ozone and oxygen there is preliminary absorption.

A. A. ELDRIDGE.

Effect of petroleum oils on the respiration of bean leaves. J. GREEN and A. H. JOHNSON (Plant Physiol., 1931, 6, 149—159).—The respiration rate of bean leaves was increased by spraying with dark petroleum oils having more than 16% of sulphonatable matter and decreased by light-coloured oils with less than 16% of sulphonatable matter.

A. G. POLLARD.

Function and significance of polyphenol-oxidase in potatoes. A. SZENT-GYÖRGYI and K. VICTORISZ (Biochem. Z., 1931, 233, 236—239).—The rate of utilisation of oxygen by thin strips of potato skin is increased 15 times on chopping to a pulp. It is suggested that not only may this system be of importance in respiration, but that the production of quinones on oxidation may be used as a protection against invading bacteria. P. W. CLUTTERBUCK.

Phenolase activity in relation to seed viability. W. C. DAVIS (Plant Physiol., 1931, 6, 127—138).—A modification of the Nadi phenolase reaction is described. Phenolase activity is high in young seeds of high and low in old seeds of low germinative capacity. Enzymic material heated at 25° for 90 min. did not show increased phenolase activity. Phenolase and catalase activity showed a general parallelism in wheat and cucumber. A. G. POLLARD.

Movement of organic materials in plants. A. S. CRAFTS (Plant Physiol., 1931, 6, 1—41).—Experimental evidence favours the view that the walls of the phloem act as channels for the movement of organic material through plant stems.

A. G. POLLARD.

Ripening of rice grains. T. TADOKORO and M. ABE (J. Fac. Agric. Hokkaido Imp. Univ., 1930, 27, 349—387).—During ripening the ash and phosphorus decreased at first; the total nitrogen was unchanged, but the ratio of protein- to non-protein-nitrogen increased. The water-soluble protein decreased, whilst the sodium chloride- and alcohol-soluble groups increased. The alkali-soluble group was inconstant. The changes are the reverse of those during germination. The formation of higher from lower proteins is indicated. The oryzanin decreased in ash and phosphorus, but increased in nitrogen, sulphur, and amino-nitrogen content; its degradation by ultra-violet light also increased. Arginine at first increased and then decreased, whilst histidine increased continuously. Lysine decreased at the later stage, whilst cystine decreased and then increased. The ash and phosphorus content of the starch decreased, whilst the saponification value increased. The amount of dextrose formed by acid hydrolysis was maximal before complete ripeness; at the same period the rotatory power of the acetylated starch was maximal and its acetyl content minimal.

CHEMICAL ABSTRACTS.

Effect of ethylene on the chemical composition and the respiration of the ripening Japanese persimmon. W. B. DAVIS and C. G. CHURCH (J. Agric. Res., 1931, 42, 165—182).—The Fuyu (non-astringent) variety had a greater quantity of sugar, soluble solids, and moisture, and the Hachiya (astringent) was slightly more acid and developed colour more quickly. Ethylene treatment stimulated softening, colour development, and respiratory activity in both varieties; astringency decreased and moisture increased in the Hachiya, whilst with the Fuyu insoluble solids decreased with increase in soluble solids. The stimulative effect of ethylene on respiration declined and the R.Q. tended to increase as the fruit ripened. Results of storing the less active mature persimmons, untreated, at room temperatures, indicated for most constituents, except astringency in the Hachiya which decreased rapidly, a continuance of the changes already begun on the tree.

E. HOLMES.

Influence of calcium on the physiological function of magnesium [in plants]. O. LOEW (Ernähr. Pflanz., 1931, 27, 97—101, 121—122).—A critical discussion of existing data concerning the effect of the CaO : MgO ratio on plant growth.

A. G. POLLARD.

Radium content of plants. III. E. BURKSER, W. KONDOGURI, W. MILGEWSKA, and K. BRONSTEIN (Biochem. Z., 1931, 233, 58—61).—The radium and thorium contents of a number of plants are tabulated and are of the same order as the content of these elements in sea-water (cf. A., 1929, 1264, 1335).

P. W. CLUTTERBUCK.

Permeability to iodine of some economic plants. R. C. MALHOTRA (Protoplasma, 1931, 12, 1—22).—The intake of iodine by a number of vegetable plants is examined. Of these, carrot showed the highest values and tomato the lowest. Root crops generally had the greatest capacity for absorbing and retaining iodine. Iodine is lost from soils during weathering. The intake of iodine by carrots was roughly proportional to the iodine content of the soils in which they grew. Maximum intake of iodine was observed in soils of p_H 6—7. Iodine had no very marked effect on plant growth, although slight stimulative effects on carrot and slight repressive effects on tomato were observed. A. G. POLLARD.

Permeability to urea of *Spirogyra* cells of varying age. F. WEBER (Protoplasma, 1931, 12, 129—140).—The permeability of cells of *Spirogyra* to hypertonic solutions of urea is examined. Although notable exceptions are recorded, older cells exhibit maximum permeability, that of the younger cells being practically nil. A. G. POLLARD.

Physiological action of homologous ionic series. K. PIRSCHLE (Jahrb. wiss. Bot., 1930, 72, 335—368; Chem. Zentr., 1931, i, 98).—Comparative measurements of the toxic effect on the growth of seedlings of various plants, the production of carbon dioxide in yeast fermentation, and the escape of water from transpiring *Tradescantia* shoots have been made with a number of positive and negative ions, and the results are correlated with the atomic number, the structure, or the size of the ions.

A. A. ELDRIDGE.

Mineral elements in bean sprouts. L. TING (Science, China, 1930, 14, 1631—1646).—Soya- and mung-bean sprouts contain, respectively, 0·1, 0·05% CaO, and 0·3, 0·2% P_2O_5; higher values are obtained

by sprouting in water containing at least 0·5% CaO and 0·2% P_2O_5. CHEMICAL ABSTRACTS.

Percentage of iodine in algæ. S. C. DIXIT (J. Indian Chem. Soc., 1931, 7, 959).—Sea-weeds collected in the Bombay Presidency contained 0·23—0·92% I (air-dried weed). F. L. USHER.

Influence of salts on geotropic reaction [of plants]. T. WARNER (Planta [Z. wiss. Biol.], 1931, **12**, 635—669).—Nitrates of calcium, magnesium, strontium, and barium in concentrations of 0·02—0·005*M* increased the geotropic reaction of seedling roots of *Lepidium sativum*. For each cation a definite concentration effecting maximum reaction is attained. Sodium and potassium nitrates in similar concentration depressed the reaction and lithium and ammonium nitrates increased it. Cations produce maximum reactions in the order of their ability to penetrate the cell wall. A. G. POLLARD.

Action of ammonium salts [on plants] in relation to hydrogen-ion concentration. A. RIBBERT (Planta [Z. wiss. Biol.], 1931, **12**, 604—634).—The precipitation of tannin in the cell-sap of *Spirogyra* produced by additions of ammonium sulphate to culture solutions is examined. For a given concentration of ammonium sulphate the rate of precipitation increases with increasing p_H and at constant p_H precipitation increases with the concentration of ammonium sulphate used. Precipitation is controlled by the ionic product ($NH_4^{\cdot} \times OH'$). Rising temperature increases the rate of precipitation. Growth in the dark for several days prior to the experiment increased the sensitiveness of *Spirogyra* to tannin precipitation. The presence of calcium salts in the nutrient does not affect the precipitating action of ammonium sulphate. Cell injury accompanies tannin precipitation. Injection of ammonium sulphate into certain leaf tissues produces an increased alkalinity of the leaf juices. Solutions of sodium carbonate increase the alkalinity of epidermal cells only after the death of the cell. A. G. POLLARD.

Influence of the hydrogen-ion concentration of nutrient solutions on the reaction of the plant. E. KEYSSNER (Planta [Z. wiss. Biol.], 1931, **12**, 575—587).—Variations are recorded for the reaction of the expressed juice of the leaves and roots of a number of plants grown in nutrient solutions of different p_H. Changes in root-sap reaction were greater than those in the leaf, observed differences averaging from 0·1 to 1·3 p_H for nutrient solutions between p_H 3·6 and 8·0. A. G. POLLARD.

F.-p. depression and specific conductivity of sorghum tissue fluids. J. H. MARTIN, J. A. HARRIS, and I. D. JONES (J. Agric. Res., 1931, **42**, 57—69).—The f.-p. depression and specific conductivity of the juices from various organs of sorghum plants at different stages of growth are recorded and compared with similar data for maize. Varietal differences in f.-p. values were small, but those for conductivity were considerable. Water deficiency does not increase the f.-p. depression or specific conductivity of leaf and stalk juices in sorghum. No evidence was obtained of the presence of "bound" water in sorghum juices. A. G. POLLARD.

Relation of the hydrogen-ion concentration of tissue fluids to the distribution of iron in plants. R. A. INGALLS and J. W. SHIVE (Plant Physiol., 1931, **6**, 103—125).—The hydrogen-ion concentration of plant-tissue fluids varies inversely with the light intensity to which the plants are exposed, variations being wider in fleshy than in thin-leaved plants. Differences between the values for leaf and stem tissues are general, and usually greater in succulent plants. The soluble (filterable) iron content of plant tissues varies directly with the daily change in the hydrogen-ion concentration. Plants in which the tissue fluids have a low hydrogen-ion concentration are characterised by high total and low soluble-iron contents, whereas those having high concentrations in the tissue fluids show low total- and high soluble-iron contents. A. G. POLLARD.

Use of expressed sap in physiological studies of maize. J. D. SAYRE and V. H. MORRIS (Plant Physiol., 1931, **6**, 139—148).—Technique for obtaining samples of the expressed sap of plants is described. The amount and the total solid content of successive portions of expressed plant sap varied with the preliminary treatment of the material, its moisture content, and other factors. The sugar content (sucrose +reducing sugars) of the sap was constant in successive portions expressed after grinding the tissue, but decreased in successive portions after mincing. The sugar content of maize as determined in the expressed sap after grinding the material agreed closely with values obtained by standard methods. The use of 100-g. samples of fresh tissue and a pressure of 5000 lb. per sq. in., followed by pressure-filtration of the sap under standardised conditions, is recommended. A. G. POLLARD.

Titration curves of fruit and vegetable juices and culture media. W. NEWTON and H. I. EDWARDS (Sci. Agric., 1931, **11**, 542—545).—Electrometric titration curves of fruit juices may have some significance in studies of plant disease or of fermentation. The total acid content of loganberries decreases as the fruit matures, but there is not a corresponding increase in p_H. Titration curves of potato juices differed in shape according to whether the tubers were healthy, infected with mosaic disease, or infected with Witches' Broom. Plum, pear, and apple juices have titration curves of different shapes, and varietal differences in grapes are similarly characterised. Fermentation of fruit juices results in altered titration curves. A. G. POLLARD.

Rhusinic acid. K. TERAUCHI (Tohoku J. Exp. Med., 1930, **16**, 123—156).—The chemical and pharmacological properties of the acid, isolated from the fruit of *Rhus succedanea*, L., are described. CHEMICAL ABSTRACTS.

Non-volatile organic acids of green tobacco leaves. H. B. VICKERY and G. W. PUCHER (J. Biol. Chem., 1931, **90**, 637—653).—The barium salts of organic acids in an aqueous extract of tobacco leaves are precipitated by alcohol. About half of the total acids consist of unknown phenolic acids; the rest are isolated and identified by fractionating the ethyl esters. The isolated acids from mature green leaves comprise *l*-malic 85·5%, citric 2·6%, fumaric 1·6%, oxalic 0·6%, and succinic acid 0·2%. A. COHEN.

Cell-wall constituents of *Laminaria* spp. Mannuronic acid. G. M. BIRD and P. HAAS (Biochem. J., 1931, **25**, 403—411).—Fucoidin (cf. Kylin, A., 1915, i, 931) is an ethereal sulphate which also contains a uronic acid complex. Alginic acid occurs in the free state in the cell-wall and to a limited extent only in the form of a water-soluble calcium magnesium alkali metal salt. On hydrolysis the acid obtained from *Laminaria* yields mannuronic acid (but no sugars), from which the *quinine* salt, m. p. 162—163°, $[\alpha]_D$ −175·3°, has been obtained. After prolonged hydrolysis of alginic acid with sulphuric acid a *cinchonine* salt, m. p. 161°, $[\alpha]_D$ +154°, was obtained. On oxidation with nitric acid alginic acid yields mannosaccharic acid. Fucose obtained by the hydrolysis of the complete weed of *Laminaria* is derivable in part from fucoidin and in part possibly from cell-wall residue remaining after exhaustive extraction with sodium carbonate, but none is produced from alginic acid. S. S. ZILVA.

Hemicellulose in plant cells; distribution in the protoplasm. R. C. MALHOTRA (J. Biochem., Japan, 1930, **12**, 341—349).—Hemicellulose is present as protoplasmic inclusions as well as in the cell-wall. Tomatoes grown in the cold contain more hemicellulose than those grown in a warm atmosphere.

CHEMICAL ABSTRACTS.

Composition and synthesis of plant-cell membranes. M. LÜDTKE (Biochem. Z., 1931, **233**, 1—57).—As a preliminary to studying the susceptibility and resistance of plants to attack by parasites, the chemical, morphological, and physiological changes occurring during the formation of plant membranes are examined. It is shown that the production of the membrane substance takes place in stages and runs parallel with the general development of the organism. The effect of amount and quality of nutritional substances on the carbohydrates of the cell-wall is studied and the intermediate products of each stage of development are isolated with a view of studying the attack on them of enzymes of parasites.

P. W. CLUTTERBUCK.

Physico-chemistry of the carbohydrate occurring in the root of *Arctium lappa*. J. C. KRANTZ, jun., and C. J. CARR (J. Physical Chem., 1931, **35**, 756—763).—The carbohydrate, presumed to be inulin, has $[\alpha]_D$ −34·7°. Data relating to the influence of temperature and of acid concentration on the inversion are recorded; at 50° k is $9{\cdot}07\times10^{-3}$. The mol. wt., determined cryoscopically, is 1550. The elevation of the f. p. of N-sodium hydroxide is a function of the concentration of the dissolved inulin. Compound formation between the inulin and sodium hydroxide (0·1—1N) is indicated by f.-p. measurements. The buffering capacity of this carbohydrate for solutions of sodium hydroxide is negligible.

L. S. THEOBALD.

New sources of inulin. E. YANOVSKY and R. M. KINGSBURY (J. Amer. Chem. Soc., 1931, **53**, 1597—1601).—The isolation of inulin, $[\alpha]_D$ −28° to −33°, from the roots of *Camassia esculenta*, *Allium nuttallii*, and *Balsamorrhiza sagittata* is described.

H. A. PIGGOTT.

Sorbitol content of Norwegian rowan berries. A. JERMSTAD (Arch. Pharm., 1931, **269**, 68—69).—The ripe fruit contains 4·95% of sorbitol or 31% of the total soluble matter. Unripe fruit contains less sorbitol and, unlike the French berries (Tanret, A., 1930, 967), less acid. H. E. F. NOTTON.

Occurrence of a dihydroxyphenyl derivative and of a specific enzyme in apples and other fruits. K. SPITZER (Biochem. Z., 1931, **231**, 309—313).—Apples, pears, and bananas contain a substance the colour reactions of which indicate that it is a dihydroxyphenyl compound, very probably dihydroxyphenylalanine. The cell-substance of apples and pears contains an enzyme which has no action on tyrosine, but reacts specifically with dihydroxyphenylalanine. An explanation of the development of brown colour in exposed sections of fruit is thus provided. W. McCARTNEY.

Ether extractives of white leaves of cabbage. I, II. J. OZAKI (J. Agric. Chem. Soc. Japan, 1930, **6**, 633—642, 688—700).—The leaves contain as much vitamin-*B* as green leaves, but no vitamin-*A*. Ultra-violet irradiation of an ethereal extract produces a substance like vitamin-*D*. The leaves contain an oil, saponif. value 144·06, acid value 21·24, Hehner value 61·59, iodine value 103·44, unsaponif. matter 21·66%, Reichert-Meissl value 2·0. Of the acids, 83·7% was unsaturated; arachidic, palmitic, and a trace of myristic acid were present, together with isomerides of oleic and linoleic acids.

CHEMICAL ABSTRACTS.

Unsaponifiable lipins of lettuce. I. Carotene. H. S. OLCOVICH and H. A. MATTILL (J. Biol. Chem., 1931, **91**, 105—117).—Carotene, m. p. 180° (corr.), was separated from the unsaponifiable lipins of lettuces in various crystalline forms, all of hexagonal structure. Decolorisation of the crystals occurs in air, oxygen, or carbon dioxide at the same rate, no change in weight being experienced. The decolorised carotene, m. p. 167—168° (uncorr.), is stable towards oxygen and possesses no vitamin-*A* activity. Carotene shows increasing stability in the following series of solvents: ethyl oleate, ethyl laurate, ethyl oleate+quinol, ethyl laurate+quinol. In the last solvent the pigment does not fade in 45 days at the ordinary temperature and exposed to air. Carotene shortens the induction period of autoxidation. Doses of 0·005 mg. daily maintain normal growth in rats deprived of vitamin-*A*.

F. O. HOWITT.

Lipoid material extracted from green leaves (spinach and cabbage). D. L. COLLISON and I. S. MACLEAN (Biochem. J., 1931, **25**, 606—613; cf. A., 1929, 361, 855).—The unsaponifiable matter of spinach leaf contains in addition to carotene and a sterol, $C_{27}H_{46}O$, hentriacontane and ceryl alcohol. Palmitic, cerotic, oleic, and linolenic acids and an isomeride of linoleic acid have been isolated. The identification of nonacosane and dimyristyl ketone in the unsaponifiable matter of the cabbage leaf (cf. Channon and Chibnall, A., 1929, 729) is confirmed. The saturated fatty acids are palmitic and a higher fatty acid, probably behenic. S. S. ZILVA.

Preparation of an active substance from raw coffee. L. VON NOEL and F. DANNMEYER (Strahlenther., 1930, **38**, 583—590; Chem. Zentr., 1931, i, 959).—The only "active," but nearly always in-

effective, substance obtained was crystallised from the ethereal extract of the unsaponifiable fraction of the oil. It contained C 72·32—72·90, H 9·21—8·54; *M* 259—269; α −150° to −220°, and had a variable iodine value. Mineral acids caused a green coloration becoming dark violet or black, with separation of a similarly coloured precipitate. A. A. ELDRIDGE.

Tannin of barley husk. H. LUERS and J. STAUBER (Woch. Brau., 1931, **48**, 93—96, 103—105, 117—120).—The tannin may be prepared by the method of Seyffert (B., 1904, 874), but better from Moufang's "testin" substance (cf. Lüers, B., 1931, 217). It may also be extracted directly by hot water, dilute alcohol, or 0·2—0·3% alkali. It is best purified by suspending the precipitated lead compound in dilute organic solvents and treating with not too great an excess of hydrogen sulphide. For further purification advantage is taken of its solubility in dilute alcohol, acetone, etc. and its insolubility in pure organic solvents. It is uncertain whether all the preparations described are modifications of a single substance; they differ mainly in their solubility, some dissolving in water, one in ether, but all in dilute organic solvents. The tannin is very hygroscopic; intensive drying, especially if with heat, decreases its solubility. Its solutions precipitate gelatin, best at about p_H 5·0; they give no precipitates with quinine, quinoline, or pyridine, and are only incompletely precipitated by brucine and cinchonine. The latter precipitates are not decomposed by acetic acid. Heavy metals give precipitates. Ammonium molybdate, arsenic acid, or potassium dichromate yields no precipitate, but that with vanadic acid is brown. Precipitates are given by bromine and on heating with formaldehyde and hydrochloric acid. Fehling's solution and gold chloride are both reduced. The tannin is soluble in dilute acids to yellow solutions which darken owing to phlobaphen formation; the solutions in alkalis darken rapidly by oxidation. If heated at 100° with a little water an odour resembling that of oil of cloves is produced, and the tannin becomes less soluble and dissolves in alkalis to a dark solution. The tannin contains no free ellagic or gallic acid, nor combined citric or ellagic acid. Hydrolysis with 2% sulphuric acid for 6 hrs. yields 0·3% of dextrose; the product of acid hydrolysis also gives the reactions of phloroglucinol. This derivative is recognisable in the product of alkali fusions, as are also mono- and di-hydroxybenzoic acids, the latter being probably a product of oxidation. Barley-husk tannin must be placed with the unclassified group, which includes the tannins from quebracho, rumex, etc. The bitter resin of Seyffert (*loc. cit.*) is obtained as a syrup by extracting the "testin" substance with ether and the dried product with chloroform. It is readily soluble in 96% alcohol and on hydrolysis yields parasitosterol, and oleic and palmitic acids, but not a recognisable amount of stearic acid. F. E. DAY.

Constituents of "Salpamisri." C. GRIEBEL and G. STEINHOFF (Arch. Pharm., 1931, **269**, 37—49).—This Indian drug probably consists of the dried bulbs of *Allium Macleanii*. It contains water (9·2%), ash (3·7%), free acid (as malic acid, 1%), lævulose (~%), a polysaccharide (as lævulose, 69·6%), a saponin (4%), ether extract (0·6%), containing hydrocarbons and sterols, and insoluble matter (11%). The *saponin*, $C_{50}H_{80}O_{40}$, darkens from 100°, is hydrolysed by dilute acid to a *sapogenin*, $C_{25}H_{40}O_6$ (12%), m. p. above 300°, darkening from 180°, galactose (20%), arabinose (23%), a methylpentose (6%), and galacturonic acid (as lactose, 42%). Distillation of the sapogenin with zinc dust gives a *sesquiterpene* and other products. The *polysaccharide*, $(C_6H_{10}O_5)_3$, decomp. from 105°, yields, on hydrolysis, lævulose to the extent of more than 90%, with a little galacturonic acid, and is probably a trifructosan contaminated by pectins. The hæmolytic index of the saponin is 6700, and its fish index, 13,300. The corresponding values for the drug are 310 and 666, respectively, indicating a saponin content of 4·6%, or 5·0%.
H. E. F. NOTTON.

Sparassol, a constituent of the cortex of *Rhododendron japonicum* root. K. KINOSHITA (Acta Phytochim., 1930, **5**, 157—165; cf. Pfau, A., 1924, i, 512; Spath and Jeschki, *ibid.*, 513).—The product (0·36%) of alcoholic extraction of the cortex is identified as sparassol (methyl evernate). The m. p. of evernic acid is now recorded as 174—175°, and *monobromosparassol*, m. p. 157°, has been prepared. Far smaller quantities of sparassol are present in young roots. A *substance*, m. p. 237—238°, not present in the root, is extracted from the flower. A. COHEN.

Colouring matter of "Awobana." C. KURODA (Proc. Imp. Acad. Tokyo, 1931, **7**, 61—63).—The blue colouring matter of the Japanese flower "Awobana" precipitated from aqueous solution by methyl alcohol gives (14·5—15%) ash. Heating with concentrated hydrochloric acid gives a solution which yields glucosazone on treatment with phenylhydrazine, whilst fusion with alkali under various conditions yields *p*-coumaric acid and *p*-hydroxyacetophenone.
B. LEVIN.

Distribution of glucosides in [vegetable] tissues. A. NIETHAMMER (Biochem. Z., 1931, **233**, 217—221).—The use of the sublimation and bromine methods for detection of glucosides in parts of plants is described. P. W. CLUTTERBUCK.

Distribution of saponins in *Digitalis* plants. R. FISCHER and H. SCHROPP (Arch. Pharm., 1931, **269**, 157—164).—The saponin content of two-year-old leaves of *Digitalis purpurea* and *D. lanata* varies within wide limits. It is larger for young leaves than for older leaves from the same plant. It is the same in leaves dried in the sun, at 60°, or at 100°, but it is diminished when the leaves are kept moist for a long time. Leaves from one-year-old plants contain relatively little saponin. In the flowering plant, the leaf, phloem, and infructescence contain most saponin. The saponin content of the pericarp decreases as ripening proceeds, whilst that of the seed increases rapidly. In the seeds saponin (digitonin) is confined to the innermost layer of the epidermis, in which it occurs very richly. In germinating seedlings saponin does not appear until the cotyledons turn green. Commercial digitonin yields at 250° under the microscope a sublimate of digitogenin, m. p. 250—253°, and at 270—275° a further sublimate of gitogenin, m. p. 270—272°. H. E. F. NOTTON.

Viburnum. II. History, botany, and pharmacognosy of *Viburnum lentago*, L. H. W. Youngken (J. Amer. Pharm. Assoc., 1931, 20, 315—328).—Botanical and histological details. E. H. Sharples.

Isolation of anonaine from *Anona squamosa*, Linn. F. R. Reyes and A. C. Santos (Philippine J. Sci., 1931, 44, 409—410).—Anonaine is obtained (0·0143%) from the bark by the method used for its isolation from *Anona reticulata*, Linn. (cf. A., 1930, 242). B. Levin.

Microchemical detection of alkaloids in plants. XII. Detection of colchicine. G. Klein and G. Pollauf. **XIII. Detection of piperine and its cleavage products, piperidine and piperic acid.** G. Klein and M. Krisch (Osterr. bot. Z., 1929, 78, 251—256, 257—263; Chem. Zentr., 1930, ii, 1104).—XII. Colchicine occurs in large quantities in the following Liliaceæ; *Bulbocodium*, *Tofieldia*, *Veratrum anthericum*, *Hemerocallis*, *Ornithogalum*, and *Tulipa*, and in traces in *Asphodelus*, *Fritillaria*, *Lloydia*, and *Muscari*.

XIII. The best test for piperine and its products consists of microsublimation and treatment of the sublimate with cadmium chloride in strongly acid solution. The base is found only in fruits and seeds. L. S. Theobald.

Detection of choline in plants. G. Klein and A. Zeller (Osterr. bot. Z., 1929, 79, 40—57; Chem. Zentr., 1930, ii, 1104).—Microchemical methods are described. Choline has been detected in all parts of plants of many different species; only in *Evernia prunastri*, *Parmelia sulcata*, and *P. perforata* could none be found. L. S. Theobald.

Choline as poison of diseased barley. G. Schroeter and L. Strassberger (Biochem. Z., 1931, 232, 452—458).—The substance to which part or all of the poisonous effect on pigs of a certain shipload of diseased barley is to be attributed was choline or easily hydrolysable choline salts of aliphatic acids. A method by which choline hydrochloride can be isolated from diseased grain is described. *Chloroethylglucoside* can be prepared from dextrose and ethylene chlorohydrin and from this glucoside by heating with trimethylamine the *glucoside* of choline hydrochloride (*phosphomolybdate*; *carbonate*; *oxalate*; *platinum* salt) obtained. The hydrochloride, which has $[\alpha]_D$ +49·55°, reduces Fehling's solution and gives an osazone only after heating with mineral acid; the glucoside (subcutaneously injected) is physiologically inactive to frogs, pigs, and mice. W. McCartney.

Nature of the virus principle in mosaic disease. W. F. Bewley (Nature, 1931, 127, 442).—Results which suggest that the principle causing mosaic disease in tomato is of the bacteriophage type are described. L. S. Theobald.

Device for evaporating alcohol from plant extracts. F. E. Gardner (Plant Physiol., 1930, 5, 617—619).—Alcoholic extracts are heated to boiling and evaporated by a brisk air current without further heating. 100 C.c. of 95% alcohol may be evaporated in 15—20 min. A. G. Pollard.

Preparation of micro-electrodes for the electrometry of cells and tissues. E. Dejdar (Z. wiss. Mikros., 1929, 46, 361—368; Chem. Zentr., 1930, ii, 948).—A description of the preparation of microelectrodes, containing 0·1*N*-potassium chloride-agar, by Hiklhorn and Umbrath's method.

A. A. Eldridge.

Colorimetric determination of p_H. E. Herzfeld (Biochem. Z., 1931, 232, 72—77).—Details are given for determination of the p_H of any fluid (urine, blood-serum, etc.) from 2·2 to 10·0 using a series of dichroic indicators and a table from which the values are read off. P. W. Clutterbuck.

Determination of urobilin and urobilinogen with the Zeiss step-photometer. L. Heilmeyer and W. Krebs (Biochem. Z., 1931, 231, 393—398).—The substances cannot be determined satisfactorily by colorimetry. A method involving the use of the Zeiss step-photometer is described.

W. McCartney.

Rapid dialysis of large volumes of protein solutions. H. A. Abramson and E. B. Grossman (J. Gen. Physiol., 1931, 14, 487—491).—An apparatus is described which allows 1200 c.c. of protein solution to be dialysed almost free from salts in 12—24 hrs.

W. O. Kermack.

Apparatus for the micro-determination of carbon in blood-serum, urine, and other organic fluids. F. Negri (Biochim. Terap. sperim., 1930, 17, 225—231; Chem. Zentr., 1931, i, 118).—Nicloux's apparatus has been modified. A. A. Eldridge.

Determination of iron in organs and body fluids. H. Horsters (Biochem. Z., 1931, 232, 469—478).—The method of Butterfield (A., 1909, ii, 903) modified as here described gives satisfactory results in the case of material (2—10 g.) containing 2—4 mg. of iron. For material containing up to 0·1% a modification of Lintzel's (A., 1928, 542) adaptation of Willstätter's method (A., 1920, ii, 559) is recommended. W. McCartney.

Detection of traces of metal in organic tissue. W. Schwarzacher (Naturwiss., 1931, 19, 213).—The method of emission spectrum analysis in conjunction with microelectrodialysis can be used for the detection of small amounts of metals.

J. W. Smith.

Effect of nitrites, thiocyanates, and of some organic substances on [the sensitivity of] the starch-iodine reaction. Z. Ernst (Biochem. Z., 1931, 232, 346—351).—The sensitivity of the starch-iodine reaction in an acid solution containing nitrite is much greater when saliva is also present than when it is absent. This increased sensitivity is due to the salivary thiocyanate which suppresses the inhibitory actions of the acid and nitrite. Uric acid, peptone, leucine, trypsin, and serum-albumin act in the same way as does thiocyanate but less effectively.

W. McCartney.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JULY, 1931.

General, Physical, and Inorganic Chemistry.

Continuous spectrum of hydrogen. Interpretation of excitation potential curve. W. FINKELNBURG and W. WEIZEL (Z. Physik, 1931, **68**, 557—584).

Distribution of intensity among the fine-structure components of the series lines of hydrogen and ionised helium according to the electron theory of Dirac. M. SAHA and A. C. BANERJI (Z. Physik, 1931, **68**, 704—720).

Spectra of hydrogen and helium produced by condensed discharge. H. NAGAOKA and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1931, **7**, 54—55).—Using a disruptive discharge in H_2 the Balmer lines become diffuse, and sharp lines of the secondary spectrum can be observed among them. With He the lines become slightly diffuse, but the broadening is very small compared with that in the Balmer lines. With O_2 the lines are as sharp as with an ordinary discharge. E. S. HEDGES.

Boltzmann distribution in the hydrogen arc. L. S. ORNSTEIN, J. G. EYMERS, and J. WOUDA (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 505—507).—The Boltzmann distribution holds for the H_2 arc spectrum. The temp. determined for three arcs are 4900, 5300, and 6300° Abs. E. S. HEDGES.

Spectrum of beryllium. F. PASCHEN and P. G. KRUGER (Ann. Physik, 1931, [v], **8**, 1005—1016).—The spectra Be I and Be II, especially two series of singlets therein, have been experimentally investigated. W. GOOD.

Singlets of the two-electron spectra B II, C III, N IV, and O V. B. EDLÉN (Nature, 1931, **127**, 744).—Data for certain combinations and transitions are recorded. L. S. THEOBALD.

Displacement of certain lines in the spectra of ionised oxygen (O II, O III), neon (Ne II), and argon (A II). W. E. PRETTY (Proc. Physical Soc., 1931, **43**, 279—304; cf. A., 1929, 1205).—Many lines are displaced towards the red. C. W. GIBBY.

Structure and Zeeman effect of the neon spark spectrum, Ne II. T. L. DE BRUIN and C. J. BAKKER (Z. Physik, 1931, **69**, 19—35).—280 Ne II lines are tabulated; the Zeeman effect in 40 of the lines is also given. A. B. D. CASSIE.

Collisions of the second kind and their effect on the field in the positive column of a glow discharge in mixtures of the rare gases. L. B. HEADRICK and O. S. DUFFENDACK (Physical Rev., 1931, [ii], **37**, 736—755).—Measurements of the electric field and spectroscopic observations were made over a range of currents and pressures for mixtures of two of the gases He, Ne, and A, and a mixture of each with Hg vapour. The electrical and spectral characteristics of the uniform positive column can be explained principally in terms of collisions of the second kind between ions or metastable atoms of one gas and neutral atoms of the other. N. M. BLIGH.

Intensity of forbidden transitions in the alkalis. N. WHITELAW and A. F. STEVENSON (Nature, 1931, **127**, 817).—The values of $(1S-3D)/(1S-2P)$ calc. for the alkali metals (A., 1930, 1075) are supported by Prokofiev's experimental values (A., 1929, 1205). L. S. THEOBALD.

Wave-length standards in the extreme ultraviolet aluminium spectrum. J. SODERQVIST and B. EDLEN (Z. Physik, 1931, **69**, 356—365).—Wave-length standards between 312 and 68 Å. were obtained in the spectrum of ionised Al with an accuracy of 0·003—0·01 Å. A. B. D. CASSIE.

Temperature determination from band spectra. II. Rotational energy distribution in the cyanogen and AlO bands, and temperature distribution in the arc. L. S. ORNSTEIN and H. BRINKMAN (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 498—504).—The temp. of the gas in the violet kernel of the C arc has been determined as 6500±300° abs. The value is independent of the length of the arc (3—18 mm.) and of the current (1—12 amp.). E. S. HEDGES.

Perturbations and predissociation in the S_2 band spectrum. A. CHRISTY and S. M. NAUDE (Physical Rev., 1931, [ii], **37**, 903—919).—The S_2 bands were photographed in absorption and emission between λ 3500 and λ 2400. Wave-lengths and quantum analysis are tabulated, and an equation for the unperturbed heads is found. Perturbations found are discussed. Predissociation is discussed in terms of the Franck–Condon principle of transition probabilities. The dissociation energies of the lower and upper states are 4·45 and 2·07 volts. N. M. BLIGH.

Structure of the spectra of sulphur: relations between spectra of the same multiplicities. M. GILLES (Ann. Physique, 1931, [x], **15**, 267—410).—The spectra of S II, S III, and S IV for the range 7634—640 Å., excited in S vapour in a pyrex Geissler tube, were photographed and tabulated. Using an im-

proved form of tube, with a field of 31,700 gauss, the Zeeman effect for 55 lines of S II and 51 lines of S III was investigated. The multiplet systems are interpreted in detail; the triplets, quintuplets, and a singlet of S III, and the quadruplets of S II are recognised and tabulated with their term values. Certain doublets of S II reported by Ingram (cf. A., 1929, 965) are verified. N. M. Bligh.

Hyperfine structure in the spectra of Ca II, Ba II, and Tl I. S. Frisch (Z. Physik, 1931, **68**, 758—763).—A dispersion of 0·7 Å. per mm. failed to reveal hyperfine structure in lines due to Ca II and Ba II and the nuclear angular momentum of these elements is probably zero. A. B. D. Cassie.

Band spectra of calcium hydride. I. B. Grundstrom (Z. Physik, 1931, **69**, 235—248).—The recorded systems of bands in CaH_2 (A., 1927, 185) have been more closely analysed, and new bands near 7500 Å. were obtained with 3—4 atm. H_2. The pronounced pressure effect in the *C*-system is explained as predissociation. A. B. D. Cassie.

Properties of some zinc, cadmium, and mercury bands. J. G. Winans (Physical Rev., 1931, [ii], **37**, 902; cf. A., 1929, 481).—Zn bands at wavelengths 2139, 2064, and 2002 Å. resemble the corresponding bands of Cd and Hg in emission and in absorption. N. M. Bligh.

Zeeman effect and krypton spark spectrum (Kr II). C. J. Bakker and T. L. de Bruin (Z. Physik, 1931, **69**, 36—51).—The Zeeman effect in 90 Kr II lines and some new terms in this spectrum are described. A. B. D. Cassie.

Arc spectrum of zirconium. C. C. Kiess and H. K. Kiess (Bur. Stand. J. Res., 1931, **6**, 621—672).—Nearly 1600 lines have been measured between 2085 and 9300 Å. About 80% have been classified as combinations between terms of the singlet, triplet, and quintuplet systems. The terms, without exception, are those required by Hund's theory, and many have been confirmed by Zeeman effect. The ionisation potential of the neutral Zr atom is 6·92 volts. C. W. Gibby.

Temperature classification of the spectra of europium, gadolinium, terbium, dysprosium, and holmium, 3850—4700 A. A. S. King (Astrophysics J., 1930, **72**, 221—255).—Electric furnace, arc, and spark spectra of these rare earths have been obtained, and examined with regard to the segregation of neutral and enhanced lines, temp. classification, and hyperfine structure. Hyperfine structure occurs regularly in the spectra of rare earths of odd at. no., and is absent in those of even no. L. S. Theobald.

Afterglow period of cadmium vapour fluorescence. W. Kapuściński (Naturwiss., 1931, **19**, 400—401).—A phosphoroscopic method was used. The max. intensity of the visible band fluorescence does not coincide with the moment of excitation, but occurs $2 \cdot 5 \times 10^{-5}$ sec. later. The fluorescence diminishes at a rate rather greater than exponential. A. J. Mee.

Radiation properties of oxidised palladium. W. Zobel (Ann. Physik, 1931, [v], **9**, 519—536).—Pd, when oxidised by heating in air, shows a max. of temp. radiation when heated at 300—600° in vac. This radiation max. is due to a change in the capacity of the element for absorption in consequence of the decomp. of the oxide layer and recrystallisation of the reduced Pd. At the same time there is a min. of reflected radiation. A. J. Mee.

Energy of dissociation of mercury molecules. J. G. Winans (Physical Rev., 1931, [ii], **37**, 897—901).—The absorption spectrum of Hg vapour in the Schumann region showed three continuous bands with max. at 1808, 1849, and 1692 Å. The absorption spectrum in the region 1900—1804 Å. is correlated with a pair of potential energy curves for Hg_2, which give the energy of dissociation of Hg_2 as 0·15 volt. N. M. Bligh.

Emission bands in the mercury spectrum under low excitation. (Lord) Rayleigh (Nature, 1931, **127**, 662).—The diffuse absorption bands from 2943 to 2614 Å. are obtained in emission when Hg vapour fluoresces under the Fe arc; the intensity is increased when the vapour is superheated. Superheating also increases the continuous emission from 2950 to 3600 Å., but extinguishes the green visual fluorescence. L. S. Theobald.

Existence of a two-volt term in the mercury atom. V. Kondrateev (Physikal. Z., 1931, **32**, 288—289).—The existence of a 2-volt term (probably ^3F) in the Hg atom is deduced from considerations of optical and thermochemical data on Hg halides and HgH. W. R. Angus.

Potential drop and ionisation at mercury arc cathode. E. S. Lamar and K. T. Compton (Physical Rev., 1931, [ii], **37**, 1069—1076).—By means of a movable Langmuir collector, the potential, ion concentration, and electron temp. were measured at various distances from a stationary Hg cathode spot at various arc currents. N. M. Bligh.

Theory of the mercury arc. K. T. Compton (Physical Rev., 1931, [ii], **37**, 1077—1090).—The theory of heat balance at the cathode is extended. Expressions are obtained giving the temp. of the cathode spot and the v. p. outside it. The thickness of the cathode fall space is less than the electron mean free path. N. M. Bligh.

Verification of hyperfine structure theory. J. Wulff (Z. Physik, 1931, **69**, 70—77).—Observed hyperfine structure of the doublet ground levels of Tl is consistent with theory. A. B. D. Cassie.

Hyperfine structure in ionised bismuth. R. A. Fisher and S. Goudsmit (Physical Rev., 1931, [ii], **37**, 1057—1068).—Measurements of the hyperfine structure of lines in the spectra of Bi II and Bi III are tabulated with intensities and classifications. Level separations obtained from the analysis are compared with theoretical formulæ (cf. this vol., 664). N. M. Bligh.

Intensity relations in transitions due to inner electric fields. S. Sambursky (Z. Physik, 1931, **68**, 774—781).—The intensities of transitions forbidden by ordinary selection rules were calc. by means of the Kramers–Heisenburg dispersion formula, assuming a disturbing electric field at the atom. A. B. D. Cassie.

Multiplet intensity and arc temperature. L. S. ORNSTEIN and S. SAMBURSKY (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 339—340).—The sum rule for the relative intensities of the multiplet components in at. spectra depends on the terms of the initial state, differing by j, being almost the same in each case. When these differ considerably, deviations from the rule occur. This has been confirmed by measurements with the Au arc. J. W. SMITH.

Duration of metastable states. J. M. ANDERSON (Canad. J. Res., 1931, **4**, 312—321).—Decay curves of the absorption of the line 7635 Å. in A have been obtained at room temp. and at —180°. The half life of the $^3P_0$ state is approx. 2×10^{-4} sec. and is short compared with that of the $^3P_2$ state.

C. W. GIBBY.

Quadratic Stark effect levels. K. F. HERZFELD (Z. Physik, 1931, **69**, 249—252).—Theoretical.

A. B. D. CASSIE.

Theory of complex spectra. II. E. U. CONDON and G. H. SHORTLEY (Physical Rev., 1931, [ii], **37**, 1025—1043; cf. this vol., 2).—Formulæ for the relations between the energies of multiplets arising from the same electron configuration for a number of two- and three-electron configurations are deduced by Slater's method (cf. A., 1930, 126); applications to available data are discussed. N. M. BLIGH.

Total intensities of Fraunhofer lines. M. MINNAERT and C. SLOB (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 542—549).—The method of calculation is described and results are given.

E. S. HEDGES.

Statistical analysis of the spectrum of an ionised atom. E. SEGRE (Nuovo Cim., 1930, **7**, 326—329; Chem. Zentr., 1931, i, 1239).—An extension of Fermi's method. A. A. ELDRIDGE.

Form of the positive column by short periodic excitation. O. BARTELT (Ann. Physik, 1931, [v], **9**, 679—703).—Two forms of the positive column are found in cylindrical rare-gas discharge tubes, (1) luminous cylinder with central dark space, (2) whole cylinder luminous. Only the first form is found with other gases. J. FARQUHARSON.

Influence of slit width on the intensity of spectral lines. II. P. H. VAN CITTERT (Z. Physik, 1931, **69**, 298—308; cf. *ibid.*, 1930, **65**, 547).—The work is extended to include absorption and dispersion of the apparatus, and lines obtained with an absorbing prism are shown to be considerably broadened; a 15° prism can advantageously replace the 60° prism of a quartz spectrometer in the extreme ultra-violet.

A. B. D. CASSIE.

Modes of spectrograph slit irradiation. D. C. STOCKBARGER and L. BURNS (Physical Rev., 1931, [ii], **37**, 920—922).—Photographs of the Hg lines λ3650—63 showed a max. sharpness and resolution for a crit. slit width; multiples of this width produced multiple lines, and narrower widths caused diffraction patterns to appear between the lines.

N. M. BLIGH.

Spectrograph plate shield. J. T. LAY and I. C. CORNOG (Rev. Sci. Instr., 1931, [ii], **2**, 293—296).

More intense X-ray spectra obtained with concave crystals. H. H. JOHANN (Z. Physik, 1931, **69**, 185—206).—The possibilities of X-ray reflexion spectra from concave crystals is discussed theoretically and experimentally. A. B. D. CASSIE.

Theory of Compton effect. S. KIKUCHI (Z. Physik, 1931, **68**, 803—812).—Theoretical. Quantum electrodynamics verifies Compton's classical calculation of the scattering of X-rays. A. B. D. CASSIE.

Structure of X-ray absorption edges of the lighter elements measured by an electron-counting tube. H. NEUFELDT (Z. Physik, 1931, **68**, 659—674).—The measurement, by means of an electron-counting tube, of absorption edges in the long wave-length region of X-rays from 15 to approx. 50 Å. is discussed. Details of the apparatus and technique are given. Thin sheets of celluloid, Cr, and Be were measured. Fine structure edges due to O, N, and C were detected in the results obtained from celluloid. Be sheets could not be prepared free of oxide and the absorption edges of O appear in the absorption curve. A table showing the dependence of the mass absorption coeff. on the wave-length is given for each of the substances investigated.

W. R. ANGUS.

Wave-length and structure of the K absorption edge of cobalt. M. A. VALOUCH (Coll. Czech. Chem. Comm., 1931, **3**, 205—215).—The wave-length of the K absorption edge of Co, deposited electrolytically on Al foil, is 1·6044 Å., that of the Co ion in alcoholic solution is 1·6026 Å., and in aq. solution is 1·6022 Å.

H. F. GILLBE.

Anomalous X-ray diffraction intensities. W. A. WOOD (Nature, 1931, **127**, 703).—Cr-plated wires with a high lustre show variations in the relative intensities of the lines of any X-ray spectrum without a corresponding change in at. arrangement.

L. S. THEOBALD.

Partial absorption of X-rays. O. BERG and W. ERNST (Naturwiss., 1931, **19**, 401).—The partial absorption lines observed by Ray (this vol., 277) can be explained as emission lines of certain rare earths.

A. J. MEE.

Radiation from metals bombarded by low-speed electrons. F. L. MOHLER and C. BOECKNER (Bur. Stand. J. Res., 1931, **6**, 673—681).—A continuous spectrum is emitted by metal surfaces in discharges in Cs and K vapours and in He. Assuming that these spectra are analogous to X-ray spectra, observed limits indicate work functions of 1·95 volts for Cu, 2·1 volts for Ag, and 1·45 volts for W, all in Cs vapour. C. W. GIBBY.

Scattering of X-rays from gases. E. O. WOLLAN (Physical Rev., 1931, [ii], **37**, 862—872).—The intensity of scattering of X-rays for scattering angles from 10° to 90° by H_2, He, O_2, Ne, and A was measured. Calc. values of the structure factors for Ne and A are compared with those found by wave mechanics. N. M. BLIGH.

Interaction of X-rays with bound electrons. A. J. O'LEARY (Physical Rev., 1931, [ii], **37**, 873—883).—Fine structure previously reported for scattered X-rays (cf. A., 1929, 985), and a change in wave-length

reported by Ray (cf. A., 1930, 1334) and by Majumdar (cf. this vol., 288) are not confirmed.
N. M. BLIGH.

Soft X-ray spectra. V. DOLEJSEK (Compt. rend., 1931, **192**, 1088—1089).—By a modification of Osgood's method (cf. A., 1927, 602), using Mg for both cathode and anticathode, a series of lines the most intense of which form a doublet at about 480 Å. and an absorption band at about 500 Å. were obtained.
C. A. SILBERRAD.

Fermi–Dirac statistics applied to the problem of space charge in thermionic emission. R. S. BARTLETT (Physical Rev., 1931, [ii], **37**, 959—969).—Mathematical.
N. M. BLIGH.

Experiments on electron emission by incandescent metals near their melting points. I. AMEISER (Z. Physik, 1931, **69**, 111—140).—Experiments on Ag, Au, and Cu indicate that electron emission diminishes and surface potential remains unchanged as the metal passes to the liquid phase.
A. B. D. CASSIE.

Oxygen films on tungsten. I. Study of stability by electron emission in cæsium vapour. I. LANGMUIR and D. S. VILLARS (J. Amer. Chem. Soc., 1931, **53**, 486—497; cf. A., 1925, ii, 254).—The electron emission from a W wire coated with Cs is about 10^{21}-fold that from bare W at the same temp. (*e.g.*, 590° abs.), and increases with rise of temp. to a max. and then decreases owing to evaporation of Cs. Admission of Cs to a filament coated with O, followed by flashing at 1600—1800° abs., affords an electron emission, at 850° abs., 10^5- to 10^6-fold that observed with Cs alone on the filament. The O retains the Cs with greater tenacity than the bare W. The rate of evaporation of O from W at 2070°, 1978°, and 1856° abs. has been evaluated from the change produced in the electron emission of the surface at 800—1100° abs. in the presence of Cs by each exposure to the evaporation temp. The results indicate a heat of evaporation of O from the adsorbed layer of 162 kg.-cal. per g.-atom.
J. G. A. GRIFFITHS.

Kinetic energy of positive thermions of aluminium phosphate. E. BADAREU (Bul. Fac. Stiinte Cernauti, 1927, **1**, 1—3; Chem. Zentr., 1931, i, 1238).

Sources of positive ions. E. BADAREU (Bul. Fac. Stiinte Cernauti, 1927, **1**, 4—13; Chem. Zentr., 1931, i, 1238).

Action of a crystal as a two-dimensional lattice in diffracting electrons. W. L. BRAGG and F. KIRCHNER (Nature, 1931, **127**, 738—739).—Relations between crystal orientation and electron diffraction are described.
L. S. THEOBALD.

Dynamical problems of field theory and electron constants. M. MATHISSON (Z. Physik, 1931, **69**, 389—408).—Theoretical.
A. B. D. CASSIE.

Electronic velocities in the positive column of high-frequency discharges. E. HIEDEMANN (Physical Rev., 1931, [ii], **37**, 978—982).—Theoretical. Small values of the electric force do not prohibit the production of electrons of sufficient velocity to excite or ionise gas mols.
N. M. BLIGH.

Hertz theory of the motion of slow electrons in gases. V. A. BAILEY (Z. Physik, 1931, **68**, 834—842).—Hertz's diffusion equation is a special case of that given by Maxwell (Phil. Trans., 1867, 73).
A. B. D. CASSIE.

Energy loss and scattering of electrons of medium velocity on passage through a gas (N_2). M. RENNINGER (Ann. Physik, 1931, [v], **9**, 295—337).—The energy loss of electrons of velocity 200—2000 volts in N_2 was determined. The N_2 was at low pressure so that collisions were single.
A. J. MEE.

Angular distribution of electrons scattered by mercury vapour. J. M. PEARSON and W. N. ARNQUIST (Physical Rev., 1931, [ii], **37**, 970—977).

Specific charge of the electron. F. KIRCHNER (Ann. Physik, 1931, [v], **8**, 975—1004).—Direct measurement of the velocity of cathode rays gives $e/m_0=(1\cdot7598\pm0\cdot0025)\times10^7$ electromagnetic units.
W. GOOD.

Diffraction of hydrogen atoms. T. H. JOHNSON (Physical Rev., 1931, [ii], **37**, 847—861; cf. A., 1930, 1232).—Improved photographs of the diffraction patterns produced by reflexion of a beam of H atoms from a LiF crystal were obtained; the positions of intensity distribution max. were in good agreement with theory.
N. M. BLIGH.

Wandering and space charge of air ions. H. GREINACHER (Physikal. Z., 1931, **32**, 406—410).—A simple demonstration experiment is described.
A. J. MEE.

Measurements on the discharge of hydrogen canal rays. J. KOENIGSBERGER (Z. Physik, 1931, **69**, 424—427).—A discussion of possible errors in methods described by Bartels (A., 1930, 1493) and others.
A. B. D. CASSIE.

Mean free path of electrons. J. S. TOWNSEND (Ann. Physik, 1931, [v], **8**, 805—808).—Controversial.
W. GOOD.

Method in the measurement of effective cross-sections. C. RAMSAUER (Ann. Physik, 1931, [v], **8**, 809—810).—A reply to Townsend (above).
W. GOOD.

Effective cross-section of gas molecules towards protons. C. RAMSAUER, R. KOLLATH, and D. LILIENTHAL (Ann. Physik, 1931, [v], **8**, 709—736).—The effective cross-sections of gas mols. towards slowly moving protons have been determined for He, Ne, A, H, and N at proton velocities of 30—2500 volts. The apparatus is described. Each curve of effective cross-section against proton velocity shows, except in the case of He, a min. effective cross-section. Further experiments to study the nature of the action of mols. on moving protons are described. A comparison of the results with existing data for electrons leads to the conclusion that the abs. values of the effective cross-section towards protons and electrons are of the same order of magnitude.
W. GOOD.

Production of protons. C. RAMSAUER, R. KOLLATH, and D. LILIENTHAL (Ann. Physik, 1931, [v], **8**, 702—708).—An experimental method of producing protons is described.
W. GOOD.

Angular distribution of the scattering of slow electrons by gas molecules. C. RAMSAUER and

R. KOLLATH (Ann. Physik, 1931, [v], 9, 756—758).—The scattering of slow electrons by He, A, and H_2 is described. J. FARQUHARSON.

Coefficient of recombination of gaseous ions. O. LUHR and N. E. BRADBURY (Physical Rev., 1931, [ii], **37**, 998—1000).—Previous values, 12% too high, are corrected ($\times 10^6$) to : air $1\cdot23\pm0\cdot1$; O_2, $1\cdot32\pm0\cdot1$; N_2 and A, $1\cdot06\pm0\cdot1$; H_2, $0\cdot28\pm0\cdot05$. N. M. BLIGH.

Proton and electron. H. S. ALLEN (Nature, 1931, **127**, 662—663).—Fürth's relationship (A., 1929, 1123) can be written $2bc/gM_H=16^{32}$, where M_H is the mass of the H atom and $b=h/2\pi$; it also suggests that the ratio mass of proton/mass of electron is 1844·68. It is considered that contrasted with the electron the proton is a space in the ether without electric or magnetic moment. L. S. THEOBALD.

Radiation-less collision processes at small velocity. P. M. MORSE and E. C. G. STUECKELBERG (Ann. Physik, 1931, [v], 9, 579—606).—The theory of inelastic collisions between at. and mol. particles is considered and compared with the experimental facts. A. J. MEE.

First report of the Committee of at. wts. of the International Union of Chemistry. G. P. BAXTER, (MME.) M. CURIE, O. HONIGSCHMID, P. LE BEAU, and R. J. MEYER (J. Amer. Chem. Soc., 1931, **53**, 1627—1639; cf. A., 1930, 269).—The following revised at. wts. are adopted : Re, 186·31; Ta, 181·4; As, 74·93; Ca, 40·08. J. G. A. GRIFFITHS.

Masses of O^{17}. H. C. UREY (Physical Rev., 1931, [ii], **37**, 923—929).—Calc. values of the rest mass of O^{17} are not in agreement with experimental data; various explanations are discussed. N. M. BLIGH.

At. wt. of cæsium : use of the word "mass-spectrograph." F. W. ASTON (Nature, 1931, **127**, 813).—Mass-spectra of Xe and Cs, obtained during the same exposure, give a packing fraction of $-5\cdot0+2\cdot0$ for Cs, and an at.wt. $132\cdot91\pm0\cdot02$. The word "mass-spectrograph" should not be applied to Dempster's apparatus. L. S. THEOBALD.

***X*-Ray search for element 61.** S. TAKVORIAN (Compt. rend., 1931, **192**, 1220—1223).—By fractionation of the double Mg nitrates from monazite sands from India, 500 g. of the mixed Nd–Sm double nitrates was obtained. *X*-Ray examination, both absorption and emission, showed that the amount of element 61 therein could not exceed 1 part in 10^4. C. A. SILBERRAD.

Nuclear impulse rotation of lead isotopes. H. KOPFERMANN (Naturwiss., 1931, **19**, 400).—The spectra of neutral and singly-ionised Pb were investigated for ordinary and U-Pb. Whilst the lines of wave-lengths 4058, 4242, 4245, and 5373 Å. show hyperfine structure in the ordinary Pb spectrum, they are simple for U-Pb. The U-Pb line does not agree with the strongest line in the hyperfine structure, but with the second strongest. There is well-marked isotopic displacement between the lines of Pb^{206} and Pb^{208}. A. J. MEE.

Luminescence due to radioactivity. D. H. KABAKJIAN (Physical Rev., 1931, [ii], **37**, 1120—1128).—General observations and results cannot be explained by any form of Rutherford's active-centre theory, but can be interpreted qualitatively by assuming that α-, β-, and γ-rays produce excited mols., which, returning to their initial state, emit luminous energy. Other aspects of the problem are discussed. N. M. BLIGH.

The recoil phenomenon and conservation of momentum. F. JOLIOT (Compt. rend., 1931, **192**, 1105—1107).—The experiments of Akiyama (cf. A., 1924, ii, 814) on the direction of the recoil atoms of actinon and actinium-*A* have been repeated with an improved apparatus giving recoil tracks up to 7 mm. long. There are no grounds for assuming the emission of γ-rays simultaneously with that of the recoil atom. C. A. SILBERRAD.

Complexity of the α-radiation of radioactinium. (MME.) I. CURIE (Compt. rend., 1931, **192**, 1102—1104).—Measurements of the range of α-particles of radioactinium by means of the Wilson expansion chamber show that these fall in about equal amounts into two groups with ranges in air, at 760 mm. and 15°, of 4·68 and 4·48 cm. Absence of actinium-*X* from the radioactinium used was definitely proved, as also the impossibility of the particles of less range being due to retardation at the source. C. A. SILBERRAD.

Artificial disintegration by α-particles. J. CHADWICK, J. E. R. CONSTABLE, and E. C. POLLARD (Proc. Roy. Soc., 1931, **A**, **130**, 463—489).—An examination has been made of the protons emitted by a number of elements when bombarded by α-particles from a Po source. Definite effects were found for B, N_2, F, Na, Al, and P. Except in the cases of F and Na, the results suggest the presence of distinct groups in the protons released in disintegration, which are explained on the assumption of definite levels for the protons and α-particles in a nucleus. It is assumed that all the α-particles of a stable nucleus are in the same energy level and that not more than two protons can be put into the same proton level. Of the two possible types of disintegration, (1) in which the α-particle is captured by the nucleus, (2) in which a proton is ejected without capture of the α-particle, the first explains the present results. L. L. BIRCUMSHAW.

Structure of the α-particle. O. K. RICE (J. Amer. Chem. Soc., 1931, **53**, 2011—2012; cf. this vol., 544).—Theoretical. J. G. A. GRIFFITHS.

Absorption of β-rays by matter. G. FOURNIER and M. GUILLOT (Compt. rend., 1931, **192**, 1100—1102; cf. this vol., 543).—If the source of β-rays and the absorbent metal are placed so that varying proportions of the radiation reach the ionisation chamber, μ/ρ may be calc. from the slope of the log. curve, provided that the superficial density is sufficient. C. A. SILBERRAD.

Weak lines in the natural β-ray spectrum of radium-*C*. C. D. ELLIS and H. H. ELLIOTT (Proc. Camb. Phil. Soc., 1931, **27**, 277—279; cf. A., 1930, 1339).—To overcome the difficulty of distinguishing very faint lines from defects in the plate several photographs were compared. Eight new lines with their estimated intensities are tabulated, and previously reported lines are eliminated or corrected. N. M. BLIGH.

Elimination of the β-wave-length from the characteristic radiation of iron. W. A. Wood (Proc. Phys. Soc., 1931, **43**, 275—278).—A thin film of Mn, prepared by electrolytic deposition on Al foil, removes the β-wave-length by selective absorption.
C. W. Gibby.

Eve's constant. A. W. Reitz (Z. Physik, 1931, **69**, 259—286).—A study of the secondary electrons emitted by Ra-C γ-radiation from Al, Zn, and Pb has led to a redetermination of Eve's const. for air, which at 0° and 760 mm. is $4{\cdot}3\times10^9$. The significance of the const. in cosmic-ray measurements is discussed.
A. B. D. Cassie.

Existence of anode sputtering. M. Bareiss (Z. Physik, 1931, **68**, 585—590).—Anode sputtering of Ba and Au may occur, but the effect is very small.
R. W. Lunt.

Action of radiation on atomic nuclei. G. I. Pokrovski (Ann. Physik, 1931, [v], **9**, 505—512).—It is deduced generally that exothermic at. disintegration must be accelerated by radiation. The effect observed must always be positive, but its abs. magnitude cannot be calc. without closer knowledge of the nuclear structure. J. W. Smith.

Opacity and stellar structure. D. S. Kothari (Nature, 1931, **127**, 740—741).

Origin of corona lines. E. A. Hylleraas (Z. Physik, 1931, **69**, 361—365).—Theoretical.
A. B. D. Cassie.

Quantum theory of radiation. L. Rosenfeld and J. Solomon (J. Phys. Radium, 1931, [vii], **2**, 139—147).

Application of some thermodynamic laws to the explanation of atomic nuclear processes. G. I. Pokrovski (Physikal. Z., 1931, **32**, 374—377).—The Boltzmann principle is applied to at. nuclear processes with results agreeing satisfactorily with experiment.
A. J. Mee.

Relation concerning atomic nuclei. W. D. Harkins (J. Amer. Chem. Soc., 1931, **53**, 2009—2011).—Concerning the author's and Latimer's theories (this vol., 544). J. G. A. Griffiths.

Quantised rotation of the potassium atom. R. G. Loyarte and R. Grinfeld (Univ. Nac. La Plata, Estud. Cienc., 1929, No. 89, 103—108).
Chemical Abstracts.

Discharge in pure water vapour. S. Franck (Z. Physik, 1931, **69**, 409—417).—Initial and spark discharges in water vapour at atm. pressure were studied with plane, spherical, and pointed electrodes opposed to a plane electrode. A. B. D. Cassie.

Absorption of light by simple ionic crystals and electrical detection of latent images. R. Hilsch and R. W. Pohl (Z. Physik, 1931, **68**, 721—734).—Work on formation of latent images in KBr crystals is summarised and experiments showing that there is no measurable motion of electricity during formation of a latent image are described; a movement of electricity occurs during irreversible bleaching of the image. A. B. D. Cassie.

Crystal structure of nitrates. C. Schaefer (Z. Physik, 1931, **68**, 766—767).—Differences in the reflexion maxima of calcspar and $NaNO_3$, observed by Schaefer and others (A., 1928, 349), could not be detected with a new specimen. A. B. D. Cassie.

Rotational constants of the iodine monochloride molecule. W. E. Curtis and J. Patkowski (Nature, 1931, **127**, 707).—Details of the rotation structure in the region 6482—6837 Å. and the rotational constants obtained are recorded.
L. S. Theobald.

Band spectra of alkaline-earth halides. K. Hedfeld (Z. Physik, 1931, 68, 610—631).—The band spectra of $CaCl_2$, $SrCl_2$, $BaCl_2$, $CaBr_2$, $SrBr_2$, $BaBr_2$, and CaI_2 have been investigated for the visible spectral region. Photographs of the spectra were obtained by incorporating a quantity of the appropriate salt in a C arc and in an oxy-acetylene flame. In practically all the substances the strict isotope separations were obtained. W. R. Angus.

Valency. XV. Absorption spectra of polyhalide ions. F. L. Gilbert, (Mrs.) R. R. Goldstein, and T. M. Lowry (J.C.S., 1931, 1092—1103; cf. A., 1926, 454).—Mol. extinction coeffs. were obtained for 7 aromatic polyhalides of the series $BrC_6H_4{\cdot}NMe_3^+$ in EtOH, for 8 Cs polyhalides in EtOH and in water, and for a series of aq. K polyhalides prepared by adding free halogens to the K halides. The polyhalide ions from I_3' to $BrCl_2'$ gave characteristic absorption spectra not attributable to hydrolysis, dissociation, reduction, or double decomp. Dissociation, especially marked in aq. solutions, diminishes the intensity of the strong selective absorption of the ions, without changing the form of the absorption curves. N. M. Bligh.

Absorption of [light by] acetone vapour in the Schumann region. G. Scheibe and C. F. Linstrom (Z. physikal. Chem., 1931, **B**, **12**, 387—388).—Three narrow bands, separated by the same intervals as in the Me halides, have been observed between λ 1900 and 1860 Å. They are attributed to oscillation of the Me group. F. L. Usher.

Absorption spectra of *o*-chlorophenolindophenol and *o*-cresolindophenol. M. M. Brooks (J. Amer. Chem. Soc., 1931, **53**, 1826—1830).—*o*-Chlorophenolindophenol shows an absorption max. at 625 mμ in solutions (0·00005—0·0002M) of p_H 8·0—9·6; the dye is almost completely dissociated at p_H 9·6. *o*-Cresolindophenol at p_H 8·0 shows a max. at 500 mμ with a slight secondary max. at 610 mμ; increase in p_H causes a rise in the max. (610 mμ).
H. Burton.

Ultra-violet absorption spectra of barbituric acid, veronal, and other hypnotics. N. Gómez (Anal. Fís. Quím., 1931, **29**, 280—283).—The ultra-violet absorption spectra of veronal, luminal, and *iso*propylallylbarbituric acid are similar, and do not show a band; barbituric acid has a band max. about 2500 Å. Benzylidenebarbituric acid has one band at 2500 Å. and another at about 3300 Å., attributed to the presence of conjugate double linkings; reduction by nascent H causes the disappearance of both bands, and the spectrum is like that of veronal.
H. F. Gillbe.

Constitution and spectra of the porphyrins. H. Hellstrom (Z. physikal. Chem., 1931, **B**, **12**,

353—363).—The absorption and fluorescence spectra of different porphyrins have been examined in neutral, acid, and alkaline solution. Certain broad bands are resolvable into groups, the significance of which is discussed. F. L. USHER.

Raman spectrum of solid nitrogen peroxide. A. C. MENZIES and C. O. PRINGLE (Nature, 1931, **127**, 707).—The Raman spectrum of solid NO_2 at approx. $-80°$ consists of one line with a shift of 275 $cm.^{-1}$ L. S. THEOBALD.

Smekal–Raman effect. K. W. F. KOHLRAUSCH (Physikal. Z., 1931, **32**, 385—406).—A review.

Raman effect and molecular constitution. IV. B. TRUMPY (Z. Physik, 1931, **68**, 675—682).—The Raman effects for $SiBr_4$ have been measured and compared with the displacements for $SnBr_4$ (cf. this vol., 284). With an appropriate selection of mol. constants it is found that the displacements calc. on the basis of a tetrahedral mol. configuration agree very well with the observed shifts. Mixtures of $SiCl_4$ and $SiBr_4$ exhibited no new Raman lines, indicating that no mixed mols. are found.

PCl_3 and PBr_3 give four fundamental Raman displacements which are in good agreement with the frequencies expected on the assumption of a pyramidal structure. From these fundamentals certain mol. constants have been evaluated. The Raman spectra of mixtures of PCl_3 and PBr_3 indicate the existence of two new mol. species in the mixture. These are assumed to be PCl_2Br and $PClBr_2$. The alternation of intensities of the Raman displacements according as the ratio $PCl_3 : PBr_3$, is 2 : 1 or 1 : 2 indicates that the mixed halides are in chemical equilibrium with the simplo halides. W. R. ANGUS.

Raman effect of certain sulphur compounds. F. MATOSSI and H. ADERHOLD (Z. Physik, 1931, **68**, 683—695).—The Raman effect has been studied for liquid S_2Cl_2, SO_2, CS_2, $SOCl_2$, SO_2Cl_2, $ClSO_3H$, Me_2SO_3, Et_2SO_3, Me_2S, Et_2S, MeEtS, and cryst. S. Good agreement is found with results of other investigators. Characteristic displacements are satisfactorily assigned to several groups, but there is some doubt as to the justification of assigning a particular displacement to other groups. It is concluded that S_2Cl_2 and $SOCl_2$ are Y-shaped mols. with a S atom at the centre. Binding const. ratios (S—SO)/(S—Cl) and the semi-angle of the Y are calc. The theory of valency and deformation oscillations (A., 1930, 1236) is discussed. W. R. ANGUS.

Raman effect in organic substances and its use in chemical problems. A. DADIEU and K. W. F. KOHLRAUSCH (J. Opt. Soc. Amer., 1931, **21**, 286—322).—A review.

Influence of type of chemical combination on the properties of polar molecules in the state of vapour. K. BUTKOV (Z. physikal. Chem., 1931, **B**, **12**, 369—376).—The determining character of the ionisation potential of the positive constituent of a binary mol. is illustrated by plotting heats of dissociation into atoms, energy of dissociation into ions, the product of the exponents in the expression for nuclear potential energy, and the Rosen–Mecke const. severally against the first-named quantity, for the halides of Cs, Rb, K, Na, Tl^I, Ag, and Cu^I. A systematic change in the order named is observed in each case, tending to the value of the respective property of the non-polar halogen mol. F. L. USHER.

Influence of secondary emission on valve characteristics. H. BITTMANN (Ann. Physik, 1931, [v], **8**, 737—776).—The systematic irregularities appearing in Dynatron characteristics have been experimentally investigated. W. GOOD.

Photo-electric properties of composite surfaces at various temperatures and potentials. D. RAMADANOFF (Physical Rev., 1931, [ii], **37**, 884—896).—The variation of photo-electric current with temp. and plate potential for Ba photo-electric cells with steady and interrupted illumination is plotted. The variation in photo-electric sensitivity with temp. for composite surfaces of Ba and O_2 on Pt can be explained by the diffusion of Ba or O_2 on the surface. N. M. BLIGH.

Photo-electric cells with silver/silver bromide electrodes. I. B. VANSELOW and S. E. SHEPPARD (Z. wiss. Phot., 1931, **30**, 13—39).—The p.d. between AgBr-coated Ag electrodes in KBr solution was measured by a vacuum-tube voltmeter. The small initial negative effect in the illuminated electrode was quickly superseded by an increasing positive effect which reached a max. The voltage increased with the thickness of the AgBr and also with the concentration of KBr. Reproducibility is difficult. Halogen acceptors (*e.g.*, $NaNO_2$, MeCN) decrease the positive effect, and Br increases it. An explanation is advanced on the basis of the discharge of electrons from Br ions on illumination, the positive effect being produced on recombination of Br atoms with Ag. J. LEWKOWITSCH.

Photo-electric effect from a barium oxide-coated platinum filament. K. NEWBURY and F. LEMERY (J. Opt. Soc. Amer., 1931, **21**, 276—281).—The current approaches a saturation value at a plate potential of 13 volts. For const. voltage it passes through a max. at filament temp. of 1000°. The long wave-length limit of the effect is not above 4046 A. C. W. GIBBY.

Conductivity of deformed and tempered rock-salt crystals. F. QUITTNER (Z. Physik, 1931, **68**, 796—802).—The true conductivity of rock salt obeys van 't Hoff's law with constants dependent on the extent of tempering and deformation. A. B. D. CASSIE.

Temperature variation of the conductivity of lead chloride with admixed potassium chloride. Z. GYULAI (Z. Physik, 1931, **67**, 812—816).—Temp. variation of the conductivity of $PbCl_2$ containing 0·005 part of KCl follows a van 't Hoff law, as does pure $PbCl_2$, except for changes in const. parameters. A. B. D. CASSIE.

Conduction of thin glass plates with high field strengths. W. HUBMANN (Ann. Physik, 1931, [v], **9**, 733—755).—The conduction of an ordinary glass and Jena glass using Hg and amalgam electrodes is examined. J. FARQUHARSON.

Electronic conductivity of solid oxides of various valencies. M. LE BLANC and H. SACHSE

(Ber. Sachs. Ges. Wiss., math.-phys. Kl., 1930, **82**, 153—158; Chem. Zentr., 1931, i, 1245—1246).—When UO_3 is heated, O_2 is evolved and above 350° the conductivity markedly increases, U_3O_8 being formed. The conductivity of UO_2 is greater than that of U_3O_8. In_2O_3 is a bad, but InO_2 a better, conductor. The results are interpreted from the electronic point of view; the analogous case of Mn, and the anomalies shown by Pb and Tl, are discussed. The lattice structure is also of significance. A. A. ELDRIDGE.

Increase in conductivity of nickel oxide in absorption of oxygen. M. LE BLANC and H. SACHSE (Ber. Sachs. Ges. Wiss., math.-phys. Kl.,1930, **82**, 133—140; Chem. Zentr., 1931, i, 1245).—Black NiO, containing O, has a higher electrical conductivity than yellow NiO. A. A. ELDRIDGE.

Nuclear moment and nuclear structure. S. FRISCH and R. DE L. KRONIG (Naturwiss., 1931, **19**, 444).—The connexion between impulse moment of the at. nucleus and the structure of the nucleus is discussed. The impulse is a whole no. or a half no. according as the total no. of particles in the nucleus is odd or even. A. J. MEE.

Dependence of molecular polarisation of αβ-dichloroethane on temperature, especially as regards free rotation. R. SÄNGER (Physikal. Z., 1931, **32**, 414—415).—A summary of results in reply to criticism by Meyer (A., 1930, 980, 1331). A. J. MEE.

Molecular association. J. A. WEHRLE (Physical Rev., 1931, [ii], **37**, 1135—1146).—Full data are tabulated for the dielectric const. of mixtures of $PhNO_2$ with C_6H_6 (non-polar solvent) and Et_2O, PhCl, and $COMe_2$ (polar solvents), and for the mol. polarisations of the two polar substances calc. as a function of the concentrations. Taking the dependence of the mol. polarisation of one polar liquid on the concentration of the other as a measure of the association, the larger is the electric moment of the molecule the stronger is the association. Association takes place not only between the mols. of a given substance, but also between two different substances, provided both are polar. N. M. BLIGH.

Polarisation and electric moment of tung oil. A. A. BLESS (Physical Rev., 1931, [ii], **37**, 1149—1154).—The method of mixtures gave the values 360 c.c. and $2{\cdot}29\times10^{-18}$ e.s.u. for the molar polarisation and moment, respectively. Values of the moment of tung oil and of Et_2O determined from the variation of the polarisation with temp. disagree with those from the method of mixtures, due probably to the non-elimination of the internal field. N. M. BLIGH.

Variation of electric moment with temperature. C. P. SMYTH and R. W. DORNTE (J. Amer. Chem. Soc., 1931, **53**, 2005—2006).—The electric moments in heptane are: ethylene dichloride 1·07 (—70°), 1·42 (30°); ethylene chlorobromide 0·92 (—50°), $1{\cdot}19\times10^{-18}$ e.s.u. (30°) (cf. A., 1930, 980). The moment of ethyl succinate in kerosene is 2·01 at 0° and 2·47 at 180° (cf. this vol., 410). J. G. A. GRIFFITHS.

Dielectric constants of solutions of electrolytes. W. ORTHMANN (Ann. Physik, 1931, [v], **9**, 537—569).—New apparatus is described. For $AgNO_3$ and Ag_2SO_4 for concentrations of M and $0{\cdot}02M$ and for frequencies 50—5000 Hertz a progressive decrease in dielectric const. is noted. For $AgNO_3$ there was also a dependence on frequency which could not be ascribed to polarisation. A. J. MEE.

Rules and superposition of optical activity. K. FREUDENBERG and W. KUHN (Ber., 1931, **64**, [*B*], 703—734; cf. A., 1930, 1556).—Considerations of the optical rotation of a series of substances are based on the principles that the activity contribution of a substituent generally increases when it contains strongly absorbing groups near the centre of activity and that this is influenced by the vicinal action of other substituents attached to the same centre. The activity proper to a substituent is very sensitive to chemical alteration within the substituent, whereas changes in proximate substituents have less effect on their vicinal action on the particular group, and this effect decreases with increasing distance from the active centre. When several asymmetric C atoms are present, a steric change in a particular group is regarded as similar to a chemical alteration in estimating its vicinal action towards a selected centre; this is particularly marked when the C atom at which steric change occurs is directly united to the selected group. No case has been observed in which in such proximity the vicinal action remains unchanged, and the principal of optical superposition is therefore fulfilled. Cases in which conclusions based on the principal of optical superposition in the chemistry of the sugars are at variance with chemical evidence are characterised by the unwarranted assumption of independence of vicinal action of neighbouring asymmetric C atoms on configuration. The presence of an uninterrupted sequence of asymmetric C atoms in the sugars and their derivatives excludes a strict application of superposition and an accurate calculation of the activity contributions of individual C atoms or their substituents. Cases in which the principle of superposition appears to be fulfilled are shown to depend on the assumption of independence of configuration on vicinal action when the C atoms in question are separated by a C atom. A limitation of the principle is thus involved which can be regarded only as an approximation in its revised form. In its original form it is so inaccurate and partly directly false that in the case of directly neighbouring asymmetric atoms it is preferable to rely on the investigation of the vicinal actions which the most powerfully absorbing neighbouring substituents experience.

Similarly, the displacement rules have limited applicability in the field of optical activity, but their probable validity can be examined by dissection of vicinal action and resolution of the displacement components into components of individual substituents. In many cases measurements of activity in the region of absorption of the substituents are necessary. H. WREN.

Superposition of optical absorption bands and their recognition by means of optical activity. W. KUHN and H. K. GORE (Z. physikal. Chem., 1931, **B**, **12**, 389—397; cf. A., 1930, 1556).—The absorption band of *d*-camphor at 2900 Å. consists of two partly

superposed bands, that nearer the red being characterised by strong circular dichroism and contributing almost entirely to the optical rotation in the visible. The band of shorter wave-length shows feeble dichroism but stronger absorption. Comparison with the behaviour of other substances indicates that the band in question is the normal ketone band. The factor of anisotropy has an electronic origin and is nearly independent of the thermal energy of the mol.

F. L. USHER.

Optical properties of heterogeneous uniaxial structures. R. GIBRAT (Compt. rend., 1931, **192**, 804—805, 1094—1096).—Mathematical.

C. A. SILBERRAD.

Ordinary and magnetic rotation of fused *l*-menthol, *d*-camphor, and *d*-carvone. C. SALCEANU (Compt. rend., 1931, **192**, 1218—1220).—The sp. ordinary and magnetic rotation of *l*-menthol, *d*-camphor, and *d*-carvone have been determined at 46·5—189°, 179—193°, and 18—100°, respectively (λ=5780). [α] decreases with rise of temp. much more quickly than [ω]. For camphor ordinary dispersion agrees with Lucas' results (A., 1928, 816) for solutions in *cyclo*hexane, magnetic dispersion with those of Darmois (A., 1911, ii, 352) for solutions in hexane or Et_2O, but not with Schonrock's for solution in EtOH. *l*-Menthol does, the others do not, follow Wiedemann's rule of the independence of ω/α of wave-length.

C. A. SILBERRAD.

Magnetic rotation of crystalline and fused quartz. A. COTTON (Compt. rend., 1931, **192**, 1166—1168).—The (double) sp. magnetic rotations of plates 1 mm. thick of fused and cryst. (perpendicular to the axis) quartz for the yellow Hg lines, in a field of 56,000 gauss, are respectively 1·25 and 1·21, a difference in excess of experimental error.

C. A. SILBERRAD.

Combined effect of magnetic rotatory polarisation and magnetic birefringence in a liquid. G. DUPOUY and M. SCHERER (Compt. rend., 1931, **192**, 1089—1091).—A beam of monochromatic polarised light is incident on liquid placed in a uniform field of 43,650 gauss, the angle between the incident beam and the magnetic field varying from $-4°$ to $+11° 30'$. Results are given for 1-bromonaphthalene, $PhNO_2$, and CS_2.

C. A. SILBERRAD.

Optical properties of a liquid in a magnetic field traversed in any direction by polarised light. A. COTTON (Compt. rend., 1931, **192**, 1065—1069).—The apparatus used in the experiments referred to in the preceding abstract is described and the results are discussed.

C. A. SILBERRAD.

Ultra-violet absorption and Raman effect for hydrazine. S. IMANISHI (Nature, 1931, **127**, 782).—For N_2H_4 the frequency shifts with the exciting radiations at 4047 Å. and 4359 Å. are 900, 1120, and 3212, 3289, 3339 cm.$^{-1}$, respectively. The 900 line is attributed to N_2H_4,H_2O, the 1120 line to N—H (single linking) vibration in the N_2H_4 mol., and the remainder to internal vibration frequencies of the N—H or NH_2 group.

L. S. THEOBALD.

Raman spectra of gases. S. BHAGAVANTAM (Nature, 1931, **127**, 817—818).—The following Raman frequencies have been observed: C_2H_2 1974 and 3372, N_2O 1283 and 2226, CO_2 1288 and 1389 cm.$^{-1}$ (intensities 1 : 3). Results for O_2 and N_2 agree with those of Rasetti. With CO_2 and C_2H_2 the strongest lines ascribed to a linear vibration of the mol. are almost completely polarised.

L. S. THEOBALD.

Intensity distribution in Rayleigh lines due to organic liquids. J. WEILER (Z. Physik, 1931, **68**, 782—795).—The intensity distribution in Rayleigh scattering of the lines 5461, 4358, and 4047 Å. by C_6H_6, *cyclo*hexene, and *cyclo*hexane was studied; the broadening of the lines followed molecular anisotropy.

A. B. D. CASSIE.

Magneto-electric rotatory power. J. BECQUEREL and L. MATOUT (Compt. rend., 1931, **192**, 1091—1093).—If plane polarised light is passed through a crystal of xenotime arranged as previously described (cf. this vol., 673), on rotating the plane of polarisation of the incident light, or the crystal, or changing the direction of the magnetic field, effects are obtained indicating that the frequencies of the circular vibration absorbed, and the intensities of the components of the bands depend on the orientation of the binary axes of the crystal relative to the field, and of the orientation of the incident light relative to both. The circular polarisation is therefore caused by the internal electric field of the crystal, which does not distinguish between the directions of the absorbed vibrations (cf. A., 1929, 1134; 1930, 397). These are, however, affected differently according to the direction of the superposed magnetic field. The name "magneto-electric rotatory power" is suggested for the effect.

C. A. SILBERRAD.

Magnetic birefringence of liquid hydrocarbons. M. SCHERER (Compt. rend., 1931, **192**, 1223—1225).—The magnetic birefringence (Cotton–Mouton const.) of $PhNO_2$ being 10, the following are given for Hg λ 5780: C_nH_{2n+2}, n=8, $-0·6$, 9, $-0·6$, 10, $-0·8$, 11, $-0·9$, 14, $-1·1$; C_nH_{2n}, n=8, $+0·05$, 9, $-0·1$, 10, $-0·3$, 12, $-0·6$; hendeca-$\alpha\alpha$-diene $+0·4$; *cyclo*hexane $-0·5$; *cyclo*hexene $+0·5$; PhEt 19·8; PhBr 18; PhBu 16·5. (Cf. A., 1929, 1128.)

C. A. SILBERRAD.

Concept of a pure substance in organic chemistry. J. TIMMERMANS (Helv. Chim. Acta, 1931, **14**, 445—455).—A lecture, indicating the criteria which should be applied to determinations of physico-chemical constants, and describing the work of the International Bureau for Physico-chemical Standards.

H. F. GILLBE.

Lattice energy and state of combination. W. KLEMM (Z. physikal. Chem., 1931, B, **12**, 1—32).—For comparative purposes a co-ordinated lattice, *i.e.*, a lattice consisting of atoms or ions, may be characterised by its "lattice quotient," G, representing the ratio of the lattice energy calc. by the Born cycle to the energy of a standard lattice consisting of ions which have the same magnitude and charge, but have the inert gas configuration. The calc. lattice energy, U, of a halide of an element in one of the principal groups of the periodic classification having the standard lattice may be represented by the empirical equation $U=a'Ne^2/(r^+ + r^-)$, where a' is a const., N the Avogadro no., and e the electronic

charge, and r^+ and r^- are the radii of cation and anion, respectively. As in a given group a' is almost const. for the salts of a given halogen acid the value may be used to calculate the energy which other co-ordinated and non-co-ordinated lattices would possess if they had the standard configuration, and hence the value of G. Such calculations show that the value of G is a useful index to the behaviour and nature of a halide, an oxide, or a sulphide lattice. In respect of energy relationships, the difference between halides of elements in the sub-groups and those of elements in the principal groups is greater in the gaseous than in the solid state. The transition from a co-ordinated to a mol. lattice, or from ionic to at. linking within a single mol., is not accompanied by any abrupt change in the energy relationships. R. Cuthill.

Covalency. G. Dupont (Bull. Soc. chim., 1931, [iv], **49**, 453—495).—A lecture.

Natural classification of chemical compounds. H. G. Grimm (Z. physikal. Chem., 1931, **154**, 478).—Figures given by Schemjakin (this vol., 287) were already published in 1927. F. L. Usher.

Constitution of two copper–nitrogen complexes. M. Auméras and A. Tamisier (Compt. rend., 1931, **192**, 1156—1158).—Spectrophotometric observations on mixtures of $Cu^{\cdot\cdot}$ and NH_2Me and nicotine salts show the existence of the ions $Cu(NH_2Me)_4^{++}$ and $Cu(C_{10}H_{14}N_2)_4^{++}$, only the N of the pyridine ring being active in the latter case. Dissociation constants are, respectively, $1{\cdot}6\times10^{-8}$ and $2{\cdot}2\times10^{-3}$ (cf. A., 1930, 1120). C. A. Silberrad.

Influence of magnetic field on chemical reactions. S. Kaneko (J. Soc. Chem. Ind. Japan, 1931, **34**, 133—134B).—Equations are given for the free energy and equilibrium const. in a magnetic field, and for the influence of the field on chemical affinity. H. F. Gillbe.

Deformation of electron shells. III. Magnetic susceptibility of neodymium nitrate [at 20°]. P. W. Selwood (J. Amer. Chem. Soc., 1931, **53**, 1799—1805; cf. this vol., 143).—The prep. of the anhyd. *salt* is described. The susceptibility of the Nd ion decreases from 4980 to 4880×10^{-6} per g.-ion as the concentration of the nitrate in water is increased from 0·3 to 3·0N. J. G. A. Griffiths.

Magnetic behaviour of phosphorus. H. Buchner, W. Gerlach, and E. Rupp (Ann. Physik, 1931, [v], **8**, 874—876).—The method used by Rupp to determine the sp. magnetic susceptibility of P is shown to have a possible error of 10—30%. W. Good.

Magnetism and molecular structure. III. Influence of geometric isomerism on the diamagnetic susceptibility. S. S. Bhatnagar, R. N. Mathur, M. B. Nevgi (Z. Physik, 1930, **69**, 373—379).—The *cis*-isomerides of maleic acid, fumaric acid, and some of their derivatives are more diamagnetic than the *trans*-isomerides. J. Farquharson.

Magnetic susceptibility of oxygen at low pressure. E. C. Wiersma, W. J. de Haas, and W. H. Capel (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 494—497).—Measurements of the magnetic susceptibility of O_2 at low pressures reveal deviations from Curie's law, which agree with those obtained by Woltjer and others (A., 1930, 282) for gaseous O_2 at high densities, but not with the results of Perrier and Onnes (A., 1914, ii, 334) for liquid O_2. E. S. Hedges.

Anomalous magnetic properties of anhydrous copper chloride and copper sulphate at low temperatures; the field-dependency of paramagnetism. W. J. de Haas and C. J. Gortner (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 317—324).—The magnetic susceptibilities of $CuCl_2$ and $CuSO_4$ have been investigated down to 14·42° abs. J. W. Smith.

Surface tension of mercury. (Miss) M. Kernaghan (Physical Rev., 1931, [ii], **37**, 990—997).—39 values for the temp. range 12·5—67° are tabulated. N. M. Bligh.

Calculation of surface tension from rise of liquids in capillary tubes. A. W. Porter (Trans. Faraday Soc., 1931, **27**, 205—210; cf. A., 1930, 1014).—Rayleigh's modification of Poisson's equation is given in a more rapidly convergent form, and is extended to include the case of a finite angle of contact. F. L. Usher.

Graphical methods of evaluating the quadratic form of X-ray powder method photographs. T. Bjurstrom (Z. Physik, 1931, **69**, 346—355).—Graphical methods are described that use all observed lines and eliminate effects due to foreign substances. A. B. D. Cassie.

Application of X-rays to chemical problems. M. L. Huggins (J. Physical Chem., 1931, **35**, 1216—1225).—A review. L. S. Theobald.

Interferometer measurements on the chloromethanes. L. Bewilogua (Physikal. Z., 1931, **32**, 265—282).—The X-ray interference effects produced by gaseous CCl_4, $CHCl_3$, CH_2Cl_2, and CH_3Cl are recorded and from them the Cl–Cl separations are calc., and the angles of the C–Cl linkings evaluated. The phenomena can be explained by the Debye theory of X-ray scattering in amorphous substances. W. R. Angus.

Vicinal faces on octahedra of aluminium alums. A. Schubnikov and B. Brunowsky (Z. Krist., 1931, **77**, 337—345).—The vicinal faces on the octahedra of K alum are true faces, but whether with rational indices or not is undecided (cf. A., 1903, ii, 472). The mass absorption coeff. of K alum for Mo-$K\alpha$ radiation is 3·60. C. A. Silberrad.

X-Ray investigations in the system S–Se. III. Space lattice of mixed crystals of the type γ-sulphur (Groth's Type A). F. Halla, E. Mehl, and F. X. Bosch (Z. physikal. Chem., 1931, B, **12**, 377—386; cf. this vol., 414).—The unit cell of mixed crystals with 33·4 at.-% Se has a' 8·48, b' 13·34, c' 8·33 Å., β' 67° 30′, and contains 32 atoms. There is a simple crystallographic relation between γ-S and monoclinic Se II. F. L. Usher.

Structures of modifications of a substance. H. Shoji (Z. Krist., 1931, **77**, 381—410).—All cases of lattice transformation can be represented as combinations of relative gliding and shearing of certain planes, at. or mol. groups of greatest cohesion usually

continuing as such in all modifications. Relations between the nature of the transformations and their velocity of occurrence are traced. These principles are illustrated in detail with reference to the transformations of Fe ($\alpha-\gamma$), Co, Sn, C (diamond–graphite), NH_4Cl, ZnS (transition temp. $1020°\pm5°$), TiO_2 (anatase–rutile), $CaCO_3$, carborundum, HgS, SiO_2 (α- and β-quartz–β-tridymite–β-cristobalite)

C. A. SILBERRAD.

Structure of alkali cyanides and their isomorphism with the halides. G. NATTA and L. PASSERINI (Gazzetta, 1931, **61**, 191—215).—NaCN, KCN, RbCN, and CsCN were examined by the *X*-ray powder method. The first three are isomorphous, face-centred, cubic, unit cell 4 mols. NaCN: a $5{\cdot}83\pm0{\cdot}005$ Å., $d_{calc.}$ 1·624. KCN: a $6{\cdot}51\pm0{\cdot}005$ Å., $d_{calc.}$ 1·56. RbCN: a $6{\cdot}82\pm0{\cdot}005$ Å., $d_{calc.}$ 2·32. CsCN: unit cell cubic 1 mol., a $4{\cdot}25\pm0{\cdot}005$ Å. $d_{calc.}$ 2·93. NaCN, KCN, and RbCN probably belong to the space-group T^1 or T_d^1; for CsCN T^3, T_d^1, T_d, and T^5 are possible.

The systems NaCN–NaCl and NaCN–NaBr form continuous series of solid solutions; lattice const. following Vegard's law. The system NaCN–NaI does not show formation of mixed crystals. The CN ion has a radius of 1·92 Å. in all alkali cyanides. In the cyanide lattice the distance between the N and the C atom is less than the sum of the radii of the neutral atoms. It is supposed that in the CN ion the N and C atoms are associated in such a way that two C electrons and three N electrons are shared by the two atoms so as to complete the octets.

O. F. LUBATTI.

Crystal structure of argentite and acantite. J. PALACIOS and R. SALVIA (Anal. Fís. Quím., 1931, **29**, 269—279).—Argentite and acantite yield the same Debye–Scherrer diagram, and below 180° consist of a mixture of crystals of the cubic and rhombic systems. The cubic form is metastable below 180°, and has a 4·90 Å., with 2 mols. in the unit cell. The rhombic form has a 4·77, b 6·92, and c 6·88 Å., with 4 mols. in the unit cell. H. F. GILLBE.

Unit cell of titanium carbide. L. R. BRANTLEY (Z. Krist., 1931, **77**, 505—506).—The unit cell of TiC_2 has a $4{\cdot}31\pm0{\cdot}02$ Å. C. A. SILBERRAD.

Structure of carbonyl sulphide at temperature of liquid air. L. VEGARD (Z. Krist., 1931, **77**, 411—423).—COS has d 1·52; the unit cell, rhombohedral, a 4·08 Å., ω 98° 58′, contains 1 mol.; space-group C_{3v}^5 (perhaps C_3^4). The atoms in a mol. are in a line, the mols. in chains parallel to the trigonal axis; C–O 1·10, C–S 1·96, O–S 2·78 Å. These distances and those between atoms of different chains indicate that the atoms in a chain are bound by their chemical valencies, and those in different chains by the van der Waals force. C. A. SILBERRAD.

Lattice of lead chromate. R. BRILL (Z. Krist., 1931, **77**, 506).—The unit cell has a 7·10, b 7·40, c 6·80 Å., and contains 4 mols.; space-group C_{2h}^5. The CrO_4 group has no intrinsic symmetry.

C. A. SILBERRAD.

[Crystal] structure of hexahydrated barium and calcium iodides. Structure of the alkaline-earth halide hexahydrates; strontium chloride type. Z. HERRMANN (Z. anorg. Chem., 1931, **197**, 339—349).—The hexagonal cells of $CaI_2,6H_2O$ and $BaI_2,6H_2O$ have a 9·4, 8·9, c 4·25, 4·60 Å., $d_{calc.}$ 2·55, 2·61, respectively; 1 mol. in the unit cells; space-group C_{3i}^1. The complete structure of the alkaline-earth halides has been developed, and details are given for $SrCl_2,6H_2O$. The 6 mols. of H_2O form a highly deformed octahedron, of which the z co-ordinate is only 0·4% of the axial length.

H. F. GILLBE.

Structure of β-alumina. W. L. BRAGG, C. GOTTFRIED, and J. WEST (Z. Krist., 1931, **77**, 255—274; cf. A., 1928, 112).—β-Alumina probably has the composition $Na_2Al_{23}O_{35}$ (perhaps $Na_2Al_{22}O_{34}$; cf. A., 1927, 8); d $3{\cdot}30\pm0{\cdot}01$; unit cell has a 5·56, c 22·55 Å., and contains 1 mol. as above; space-group approx. D_{6h}^4. The linear absorption coeff. μ, for Rh-$K\alpha$ radiation is 5·6. C. A. SILBERRAD.

Orientation of crystals, especially quartz, by means of etch-figures. C. GAUDEFROY (Compt. rend., 1931, **192**, 1113—1116).—The method, by which it is possible to orientate any fragment of quartz devoid even of any crystal face, and determine the position of its axis with an accuracy of 1°, depends on a consideration of the relative positions of the faculæ and luminous lines produced by the reflexion of a point source of light from the etch-figures.

C. A. SILBERRAD.

Crystal structure of chromium trioxide. W. A. WOOSTER and N. WOOSTER (Nature, 1931, **127**, 782).—Thin red needles of CrO_3 obtained by adding conc. H_2SO_4 to a conc. solution of $K_2Cr_2O_7$ have a 8·50, b 4·73, and c 5·72 Å. with 4 mols. per cell, and probable space-group Q_h^{17}–*Ccmm*. Specimens so far examined are mimetic twins on (110) simulating hexagonal symmetry. L. S. THEOBALD.

Structure of silicates. W. L. BRAGG (J. Soc. Glass Tech., 1930, **14**, 295—305T).—A lecture.

Crystallographic investigation of chlorites. G. R. LEVI and A. SCHERILLO (Z. Krist., 1931, **76**, 431—452).—NH_4ClO_2, d 1·85, is tetragonal (C_{4v}^2), $a:c=1:0{\cdot}420$, mols. in a unit cell (z) 4, a 8·95 Å., lattice base-centred. The Na, K, Rb, and Cs salts are anhydrous, and afford no definite crystals. $Ca(ClO_2)_2$, d 2·71, pseudocubic; z 2, a 5·80 Å. $Zn(ClO_2)_2,2H_2O$, d 2·77, monoclinic, C_{2h}, $a:b:c=1{\cdot}261:1:1{\cdot}364$, $\beta=90°\ 20'$, z 4, b 6·88 Å.; or $a:b:c=0{\cdot}9260:1:0{\cdot}9326$, $\beta=85°\ 28'$, z 2. $Cd(ClO_2)_2,2H_2O$, isomorphous with the zinc salt. $AgClO_2$, d 4·30, pseudotetragonal, $a:c=1:0{\cdot}55$, z 16, a 12·17 Å. $Pb(ClO_2)_2$, d 5·10, rhombic pseudotetragonal.

C. A. SILBERRAD.

Structure of analcime. I. F. KASTNER (Z. Krist., 1931, **77**, 353—380).—The cubic structure (cf. A., 1928, 1314) for analcime is disproved in favour of a tetragonal structure, space-group D_{4h}^{20}. The water is constitutional with definite positions in the lattice. Etched figures give no useful indications.

C. A. SILBERRAD.

Chabazite. J. WYART (Compt. rend., 1931, **192**, 1244—1246).—The unit cell has a 13·75, c 14·94 Å., and contains 2 mols. $CaAl_2(SiO_3)_4,6H_2O$; space-group D_{3d}, the Si and Al atoms playing the same part in the lattice. When heated at 350° in dry

air, the water is driven off, but slight change in the lattice occurs. When an anhyd. crystal is placed in Hg vapour at 340°, it turns black, and on cooling shows an increase in wt. of 60%, giving an X-ray diagram practically identical with that of the ordinary hydrated crystal. C. A. SILBERRAD.

Crystal structure of methane. H. H. MOOY (Nature, 1931, **127**, 707).—X-Ray examination at 21·1° and 18·5° Abs. reveals no difference of crystal structure at these two temp. L. S. THEOBALD.

Crystal structure of methane. H. H. MOOY (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 550—553; cf. this vol., 150).—X-Ray analysis indicates a face-centred cubic translation lattice, a 5·89±0·01 Å. With 4 mols. to the unit cube, $d_{calc.}$ 0·517±0·006. The observed intensities disagree slightly with those to be expected from a close-packed structure of atoms, indicating that the mol. structure of CH_4 must be considered. E. S. HEDGES.

Chloro- and bromo-stannates of toluidines and substituted anilines. P. MAIER (Z. Krist., 1931, **76**, 529—541).—Measurements are given of 11 chloro- and bromo-stannates of aniline, chloro- and bromo-anilines, 5 toluidines, and of *p*-toluidine chlorotellurate. *p*-Chloroaniline chlorostannate exists in two forms, d^{20} 1·799 and 1·649; *p*-toluidine chlorostannate in two, d^{20} 1·696 and d^{17} 1·251; and *p*-bromoaniline bromostannate in three, d^{20} 2·395, 1·600, and >3. C. A. SILBERRAD.

Structure of glycine. J. HENGSTENBERG and F. V. LENEL (Z. Krist., 1931, **77**, 424—436).—Glycine has d 1·61 (cf. A., 1883, 337). The unit cell has a 5·1, b 11·9, c 5·43 Å., and contains 4 mols., space-group C_{2h}^5. Definite positions for C, N, and O atoms are deduced, agreeing with the accepted constitution. C. A. SILBERRAD.

Crystal structure of some forms of glucose. O. L. SPONSLER and W. H. DORE (J. Amer. Chem. Soc., 1931, **53**, 1639—1643; cf. A., 1930, 983).—Data for β-*d*-glucose are given. The unit cell of α-*d*-glucose contains 4 mols.; a 10·45, b 14·85, c 4·97 Å. The unit cell of α-glucose monohydrate contains 2 mols.; a 8·72, b 5·03, c 9·59 Å., β 97° 59′: space-group C_2^2. J. G. A. GRIFFITHS.

X-Ray interferometer measurements of inter-atomic distances in benzene and carbon tetra-bromide. E. RUMPF (Ann. Physik, 1931, [v], **9**, 704—714).—X-Ray measurements on liquid C_6H_6 and a solution of CBr_4 show the interat. distances to be, in C_6H_6 C–C 1·36 Å., and in CBr_4 Br–Br 3·53 and C–Br, 2·16 Å. J. FARQUHARSON.

Crystallographic description of theelol. C. B. SLAWSON (J. Biol. Chem., 1931, **91**, 667—669; cf. this vol., 879).—Theelol forms monoclinic rectangular parallelepipeds, angles 109·5° and 70·5°. They are optically negative: n_α 1·533, n_β 1·642, n_γ 1·686, extinction angle 5·5°, and $2V$ 60°. Theelin (cf. A., 1930, 1110) has extinction angle 12°. R. S. CAHN.

X-Ray examination of cellulose derivatives. VIII. Alkali celluloses. K. HESS and C. TROGUS (Z. physikal. Chem., 1931, **B**, **11**, 381—408; cf. A., 1930, 750).—No alteration in the X-ray diagram of cellulose is produced until the concentration of NaOH exceeds 9%. Between 12 and 20% a new pattern (I) completely displaces that of the original cellulose, whilst between 21 and 45% a substance (II) giving a different pattern is formed. The period of identity along the axis of the fibre is 10·4–0·2 Å. for I and 15·1±0·2 Å. for II. On drying, II remains unchanged, but I gives rise to a still different pattern which belongs to a substance (III) differing from II probably in respect of water content. It is shown that water is essential to the production of the two alkali celluloses. Similar results were obtained with LiOH and KOH. F. L. USHER.

Fine structure of gelatin micelles. O. GERNGROSS and J. R. KATZ (Biochem. Z., 1931, **233**, 246).—The equal share of the two authors in their joint work is stated (cf. A., 1930, 1250). P. W. CLUTTERBUCK.

Electron theory of metals. I, II. L. NORDHEIM (Ann. Physik, 1931, [v], **9**, 607—640, 641—683).—Theoretical. A. J. MEE.

Dependence of the electrical discharge in crystals on orientation. J. LASS (Z. Physik, 1931, **69**, 313—331).—Point-to-plate discharges through rock salt, fluorite, and calcite showed paths dependent on the crystallographic structure. A. B. D. CASSIE.

Electric and mechanical effects in metal wires of heat, magnetic, and acoustic disturbance of structure. A. VON HIPPEL and O. STIERSTADT (Z. Physik, 1931, **69**, 52—55).—An electric current is shown to be associated with transition points due to heat, magnetic, and acoustic disturbance of metal crystals. A. B. D. CASSIE.

Thomson effect in cadmium and zinc single crystals. H. VERLEGER (Ann. Physik, 1931, [v], **9**, 366—384).—The Thomson effect for differently oriented single crystals of Cd and Zn has been measured directly by Cermak's method. A. J. MEE.

Magnetic disturbance of the superconductivity of single-crystal wires of tin. W. J. DE HAAS and J. VOOGD (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 63—69; cf. A., 1928, 695).—The disturbance of single-crystal wires of Sn produced in magnetic fields parallel with and perpendicular to the axis of the wires has been investigated. J. W. SMITH.

Permeability of iron, nickel, and cobalt in the frequency range 10^3—10^4 kc. M. J. O. STRUTT (Z. Physik, 1931, **68**, 632—658).—The permeability of Fe, Ni, and Co in the frequency range 10^3—10^4 kc. has been determined. The results obtained at room temp. and with liquid air do not confirm the anomalies found by workers of the Russian school, but gradual diminution of the permeability was observed as the frequency increased. R. W. LUNT.

Reason for the high permeability of air-cooled permalloy. K. HONDA (Z. Physik, 1931, **67**, 808—811).—High permeability is caused by the deformation of the atoms in the sample, the deformation caused by heating being retained at room temp. with the correct quenching. J. FARQUHARSON.

Magnetisation-temperature curves of iron, cobalt, and nickel. F. TYLER (Phil. Mag., 1931, **11**, 596—602).—The "corresponding state" magnetisation curves for Fe, Co, and Ni are closely

coincident, and over the greater part of the range are practically coincident with the quantum curve for $j=\frac{1}{2}$. The electron spin is the fundamental magnetic element operative in ferromagnetic metals. The spin is associated with a bound electron and interaction between spins of neighbouring ions produces the ferromagnetic effects. The spontaneous magnetisation curve for $j=\frac{1}{2}$ is as applicable to Fe and Co, which have more than one interacting electron per atom, as to Ni, which has less than one. The value $j=\frac{1}{2}$ indicates that the electron spins are independent, a conclusion confirmed by the change of sp. heat at the Curie point. E. S. HEDGES.

Magnetic properties of crystals. Measurement of magnetic field. G. DUPOUY (Ann. Physique, 1931, [x], **15**, 495—591).—The principal coeff. of magnetisation (χ_1, χ_2) of chalybite (73·79% $FeCO_3$, 6·22% $MnCO_3$), hæmatite, and rhodochrosite at 288—400° T. are deduced from $(\chi_1+\chi_2)/2$ determined from the powdered crystal, and $(\chi_1-\chi_2)$ by measuring the couple, due to its anisotropy, exerted on a crystal in a magnetic field. A gaussmeter depending on the latter effect is described. $(\chi_1-\chi_2)\times10^6$ has respectively the values at 290° T., 47·89, 8·09, 0·107; and at 390—400° T. 26·2, 9·45, 0·072. Weiss' law is followed by chalybite and rhodochrosite, not by hæmatite. C. A. SILBERRAD.

Influence of the field on the magnetic state of platinum. (MLLE.) P. COLLET and G. FOEX (Compt. rend., 1931, **192**, 1213—1215).—Curves relating $1/\chi$ to temp. for one sample (cf. this vol., 673) for fields of 6000, 9300, and 14,000 gauss, and temp. from −180° to +400° show marked variations in magnetic moment, but appear to indicate a limit of 8 magnetons as the field increases. Similar curves for fields of less than 3000 gauss show a series of steps, χ remaining constant over considerable intervals of temp.

C. A. SILBERRAD.

Ferromagnetic saturation of elements other than iron, nickel, and cobalt, and the periodic system. C SADRON (Compt. rend., 1931, **192**, 1311—1313).—(Magnetic saturation)-(at. percentage of second metal) curves for a series of alloys with Ni (cf. this vol., 28) show that the at. moments of Cr, Mo, and W are all 19 experimental magnetons, their atoms in the alloys lying antiparallel to those of Ni. The moments of Pd (in Ni) and of Pt (in Co) are 3 magnetons, with atoms parallel. C. A. SILBERRAD.

Ferromagnetism. W. HEISENBERG (Z. Physik, 1931, **68**, 720).—A disclaimer (cf. Tunazima, this vol., 551). R. W. LUNT.

Ferromagnetism. R. H. FOWLER and F. C. POWELL (Proc. Camb. Phil. Soc., 1931, **27**, 280—289). —Mathematical. N. M. BLIGH.

Ferromagnetism and electrical properties. II. Significance of magnetic resistance increase of ferromagnetic electron conductors. W. GERLACH (Ann. Physik, 1931, [v], **8**, 649—662).—Consideration of the magnetic resistance change in Fe crystals, electrolytic Fe, Ni, and Ni alloys leads to the conclusion that the increase of resistance is, above a critical value J_0, proportional to the square of the magnetisation J. J_0 is the magnetisation above which the spontaneous magnetisation is altered by the external field. W. GOOD.

Theory of fine structure of magnetisation curve for single crystals. N. AKULOV (Z. Physik, 1931, **69**, 78—99; cf. this vol., 551).—A second method for computing the magnetisation curve of single crystals is described. The magnetostriction is shown to be a function of the magnetisation. The theory explains the fine structure of the magnetisation curve.

J. FARQUHARSON.

Theory of magnetostriction and the magnetisation curve. W. HEISENBERG (Z. Physik, 1931, **69**, 287—297).

Propagation of large Barkhausen discontinuities. K. J. SIXTUS and L. TONKS (Physical Rev., 1931, [ii], **37**, 930—958).—The discontinuities in Ni and Ni–Fe wires occur as a propagation starting at a nucleus; the velocity was found as a function of the applied field, and appears to depend on surface phenomena. N. M. BLIGH.

Tensile strength of rock salt and sylvine after water treatment. U. HEINE (Z. Physik, 1931, **68**, 591—609).—Experiments are described relating to the mechanical properties of rock salt and sylvine in relation to the mechanical treatment and water treatment of the crystals. R. W. LUNT.

Compressibility of alkali metals. D. S. KOTHARI and R. C. MAJUMDAR (Naturwiss., 1931, **19**, 443—444).—The compressibilities are calc. and compared with the results of Bridgeman, with which there is qual. agreement. A. J. MEE.

Empirical law of atomic repulsion in relation to cohesion. G. A. TOMLINSON (Phil. Mag., 1931, [vii], **11**, 1009—1052).—Theoretical. The results support the exponential law of repulsion and show that cohesional properties are directly dependent on the properties of the fundamental forces of attraction and repulsion. F. L. USHER.

Mode of deformation of a single crystal of silver. H. J. GOUGH and H. L. COX (Inst. Metals, 1931, advance copy).—A single crystal of Ag has been tested under alternating torsional stresses, with and without annealing, but no definite twin markings were observed, although the surface of the specimen was covered by a complete system of slip-bands in good agreement with the max. resolved shear stress law.

O. J. WALKER.

Allotropism of rhodium and some phenomena observed in the *X*-ray analysis of heated metal wires. F. M. JAEGER and J. E. ZANSTRA (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 15—32).—*X*-Ray analysis of finely-divided Rh shows not only the lines to be anticipated from a face-centred cubic lattice, but also 39 lines more attributed to another modification which is the more stable at low temp., and is a simple cubic lattice, edge 9·211 Å., with 48 atoms in the unit cell. This form co-exists with the normal form up to at least 1000°, but its proportion decreases with rise of temp. The *X*-ray spectrograms of Rh and of Pt and Pd show the existence of a special kind of thermal hysteresis connected with the process of recrystallisation. J. W. SMITH.

Physico-chemical methods of determination of mol. wt. by gaseous densities. A. Boutaric (J. Chim. phys., 1931, **28**, 174—180).—It is shown mathematically that Berthelot's limiting-density method, Guye's corresponding-density method, and Leduc's mol.-vol. method are identical in principle.

E. S. Hedges.

Conduction of heat of lead and tin at low temperatures. W. J. de Haas and H. Bremmer (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 325—338). —The thermal conductivity of Pb and Sn and the influence of a magnetic field thereon have been examined down to about 2° abs. J. W. Smith.

Velocity of sound in gaseous helium at temperatures obtained with liquid helium. I. W. H. Keesom and A. van Itterbeek (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 204—209).—The velocity of sound in He has been measured at 4·245° and 3·873° abs. and at various pressures. The ratio of the sp. heats c_p/c_v for zero pressure at these temps. is 1·669 and 1·682 respectively. These slight deviations from the value 1·667 are attributed to inaccuracy in temp. measurement. J. W. Smith.

Steepness of the transition curve of superconductors. W. J. de Haas and J. Voogd (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 192—203).—The range of temp. within which the resistance vanishes for a superconducting material is the shorter the better is the cryst. state. J. W. Smith.

Electrical conductivity of thin metal films. G. Braunsfurth (Ann. Physik, 1931, [v], **9**, 385—418).—A function is derived for the variation of the resistance of thin metallic films with thickness and the thickness of the film below which there is no conductivity has been determined for several metals. The temp. coeff. of the resistance, and ageing phenomena in sputtered metals have also been investigated.

J. W. Smith.

Specific resistance of thin metallic layers, especially silver and tungsten. L. Hamburger and W. Reinders (Rec. trav. chim., 1931, **50**, 441—474; cf. A., 1919, ii, 136).—A method is described for measuring the sp. resistance of thin metallic layers, formed on glass surfaces by condensing the metal vapour in vac., at $-185°$ and at room temp. The thinnest layers obtained are 1 atom (W) and 16 atoms (Ag) thick at $-185°$, and 2 atoms thick for both metals at room temp. The variation of the sp. resistance with the thickness of the layer has been studied under varying conditions. Thin films of the two metals are readily attacked by moist O_2. O. J. Walker.

Structure of thin metallic layers, especially of tungsten, and its influence on the specific conductivity. W. Reinders and L. Hamburger (Rec. trav. chim., 1931, **50**, 475—490; cf. preceding abstract).—Probability calculations are made of the distribution of metallic atoms condensed on a glass surface. Thin W layers have a structure which agrees with the probability expression obtained. The high sp. resistance of thin metallic films is due mainly to the large distance between the atoms. Small amounts of non-metallic impurities reduce the conductivity considerably. O. J. Walker.

Density and conductivity of bismuth single crystals grown in magnetic fields with relation to their mosaic structure. A. Goetz and A. B. Focke (Physical Rev., 1931, [ii], **37**, 1044—1056; cf. this vol., 292).—The density and sp. resistance of different sections of halves of a Bi single crystal formed within and outside of a strong magnetic field were measured, and the variations of these quantities are discussed. N. M. Bligh.

Role of protons in electrical conductivity of metals. D. P. Smith (Z. Physik, 1931, **69**, 253—258).—Diminution in the electrical resistance of Pd with occlusion of H (A., 1930, 836) was verified, but the effect is ascribed to the influence of the protons on their surroundings rather than to their own conductivity. A. B. D. Cassie.

Two modifications of liquid nitrobenzene. M. Wolfke and J. Mazur (Nature, 1931, **127**, 741—742; cf. this vol., 148).—Heating curves show a transition temp. at 9·5°. L. S. Theobald.

Apparent value of C_v for water vapour, ammonia, methane, and higher paraffins. M. Trautz (Ann. Physik, 1931, [v], **9**, 465—485).—When $(C_v-3R/2)z/bM^{2/3}$ is plotted against bM_bT_k (b—valency of central atom, M=mol. wt., M_b=mol. wt. OH, NH, CH resp., z=1, 1·5, 3 resp.), all the experimental data for the sp. heats of H_2O, NH_3, and CH_4 fall on the same curve. The relation of these data to those determined spectroscopically is discussed. From the value observed in the case of CH_4, the values of C_v for other paraffins can be deduced and are tabulated.

J. W. Smith.

Specific heat of solid substances at the temperatures obtainable with the aid of liquid helium. III. Measurements of the atomic heats of lead and bismuth. W. H. Keesom and J. N. van den Ende (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 210—211; cf. A., 1930, 677).—An error was made in the calculation of the figures quoted previously. The revised at. heat figures are a little lower and the θ values a little higher than those given originally. J. W. Smith.

Physical properties of the *n*-paraffin hydrocarbons, pentane to dodecane. A. F. Shepard, A. L. Henne, and T. Midgley, jun. (J. Amer. Chem. Soc., 1931, **53**, 1948—1958).—Pentane, b. p. 36·0°, m. p. $-129·93°$, hexane, b. p. 68·71°, m. p. $-95·39°$, heptane, b. p. 98·38°, m. p. $-90·65°$, octane, b. p. 125·59°, m. p. $-56·9°$, nonane, b. p. 150·71°, m. p. $-53·68°$, decane, b. p. 174·06°, m. p. $-29·76°$, undecane, b. p. 195·84°, m. p. $-25·65°$, and dodecane, b. p. 216·23°, m. p. $-9·73°$, have been isolated from petroleum by the method previously described (B., 1930, 803). Numerous physical data are recorded.

H. Burton.

Equation of state of gases and liquids with reference to the change of *a* and *b* with *T* and *v*. I. Hydrogen. I, II. J. J. van Laar (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 227—238, 348—360).—I. The extent to which the "constants" *a* and *b* in van der Waals' equation of state vary with temp. and pressure is discussed, and a mode of calculating them for any values of *T* and *v* in the case of H_2 is deduced.

II. The equation derived is applied to the behaviour of H_2 at high pressures, the theoretically deduced relations being compared with those observed by Amagat and Bridgman. J. W. SMITH.

General equations of energy and entropy of gases. T. C. HUANG (Physical Rev., 1931, [ii], **37**, 1171—1174).—Mathematical. Equations are deduced, and, applied to a perfect gas and to gases obeying the ordinary equations of state, give results in agreement with those of thermodynamics. N. M. BLIGH.

Vapour-pressure relationship. V. KIREJEV (Z. anorg. Chem., 1931, **197**, 350—352).—From the Clausius–Clapeyron equation the isothermal relationship $\log p_a = Q \log p_b + c$, is derived, where p_a and p_b are the v. p. of two substances of similar chemical nature and not widely differing b. p., and Q and c are constants which may be evaluated from thermal data. It is applicable to the v. p. of pure liquids and solids, total and partial pressures of solutions and mixtures, adsorbed gases, and the decomp. pressure of hydrates etc. H. F. GILLBE.

Intensity of molecular beams. A. ELLETT and R. M. ZABEL (Physical Rev., 1931, [ii], **37**, 1112—1119).—The intensity of mol. beams was measured by a Pirani gauge sensitive to 10^{-8} mm. changes. The gauge is shown to be applicable to the measurement of mean free paths. N. M. BLIGH.

Calculation of vapour pressures of solids from their solubilities. L. FRANK (Z. Physik, 1931, **69**, 418—420).—A method is indicated for calculating v. p. from solubilities, and is applied to C_6H_6 and to $C_{10}H_8$. A. B. D. CASSIE.

Compressibility isotherms of helium at temperatures from −70° to 200° and at pressures to 1000 atm. R. WIEBE, V. L. GADDY, and C. HEINS, jun. (J. Amer. Chem. Soc., 1931, **53**, 1721—1725).—Values of pv at −70°, −35°, 0°, 50°, 100°, and 200° are recorded (cf. A., 1925, ii, 851). J. G. A. GRIFFITHS.

Viscous friction. P. MERCIER (J. Phys. Radium, 1931, [vii], **2**, 114—132).—The theory of the movement of surfaces in a viscous fluid is discussed, and a method for the determination of the coeff. of friction, within wide limits, is described. H. F. GILLBE.

Viscosity, heat conductivity, and diffusion in gas mixtures. XIV. M. TRAUTZ (Ann. Physik, 1931, [v], **8**, 797—804).—The pressure coeff. of viscosity of gases at moderate pressures is theoretically deduced and extended to the case of binary mixtures of unideal gases. W. GOOD.

Propagation velocity of diffusion and its determination. K. SITTE (Physikal. Z., 1931, **32**, 410—414).—Experiments described to test the theory of Frank show very good agreement. A. J. MEE.

Dielectric constants of H_2O_2–Et_2O and H_2O_2–H_2O–Et_2O mixtures. E. P. LINTON and O. MAASS (Canad. J. Res., 1931, **4**, 322—329).—Over a wide range the dielectric const. of H_2O_2 in Et_2O is proportional to the concentration. The dielectric const. of pure H_2O_2 at 0° is 93·7. The densities of H_2O_2–Et_2O mixtures show a max. deviation from linearity in a 50—50 mixture. C. W. GIBBY.

Possibilities of application of refractometry to mixtures and solutions. O. MERZ (Farbenchem., 1931, **2**, 259—261).—The connexion between n and the composition of binary mixtures is discussed. C. W. GIBBY.

State of formaldehyde in aqueous solutions. F. WALKER (J. Physical Chem., 1931, **35**, 1104—1113).—Mainly a discussion of previous work. In CH_2O solutions up to 38% concentration methylene glycol is in equilibrium with the polymeride $(CH_2O)_3,H_2O$, and a rise in temp. or decrease in concentration favours the methylene glycol. For solutions up to 34%, the partial pressure of the aldehyde is proportional to the concentration of solute in the glycol form. Formaldehyde in the vapour in equilibrium with an aq. solution is probably CH_2O. L. S. THEOBALD.

Solubilities of gases in liquids at high pressure. P. K. FROLICH, E. J. TAUCH, J. J. HOGAN, and A. A. PEER (Ind. Eng. Chem., 1931, **23**, 548—550).—Measurements have been made at high pressures and 25° of the solubilities of CH_4, H_2, and N_2 in H_2O, the lower alcohols and a number of hydrocarbon solvents. The values for C_3H_8, C_3H_6, H_2S, C_2H_4, and O_2 up to pressures of 7, 7, 15, 60, and 100 atm., respectively, have been measured in one or more of the following solvents: gas oil, CCl_4, EtOH, heavy naphtha, H_2O, HCO_2H, and C_5H_{12}. If the gas does not form a chemical compound with the solvent, Henry's law is obeyed over a wide range of pressure within the limits of error allowed in engineering calculations. The solubility of H_2, N_2, O_2, and CH_4 is approx. a linear function of the pressure. The validity of this relation holds at much higher pressures if corrections for deviations from the gas laws are applied. H. INGLESON.

System n-butyl alcohol–methyl alcohol–water. A. J. MUELLER, L. I. PUGSLEY, and J. B. FERGUSON (J. Physical Chem., 1931, **35**, 1314—1327).—The binodal curves, tie lines, and plait points have been determined for temp. between 0° and 105°. L. S. THEOBALD.

Influence of pressure on solubility of sodium chloride in water. Measurement of solubilities of electrolytes under pressure. L. H. ADAMS and R. E. HALL (J. Wash. Acad. Sci., 1931, **21**, 183—194).—By means of a new apparatus for the determination of solubilities under pressure the solubility of NaCl in H_2O at 30° under pressures up to 4000 bars has been measured. R. CUTHILL.

Solubilities of slightly soluble organic compounds in water. P. M. GROSS and J. H. SAYLOR (J. Amer. Chem. Soc., 1931, **53**, 1744—1751).—Solubility data at 15° and 30° for 20 org. compounds are recorded. The interferometer method affords evidence of the hitherto undetected hydrolysis of several substances in water. J. G. A. GRIFFITHS.

Solvent power of alcohols for cellulose nitrate. BARBIERE and DESMAROUX (Compt. rend., 1931, **192**, 1231—1233).—The order of the alcohol (or phenol) radical in the alcohol constituent of an equimol. Et_2O–ROH mixture as regards decreasing solvent

power for cellulose nitrate is: Me, Et, allyl, CH_2Ph, *cyclo*hexyl, Pr^α, C_2H_4Ph, Bu^α, Pr^β, *iso*amyl, heptyl, *tert.*-Bu, *tert.*-amyl, *sec.*-octyl, Ph. This order is, so far as these have been determined, substantially that of decreasing heat of reaction with MgEtI (cf. A., 1924, ii, 929). C. A. SILBERRAD.

Solubility of picric acid in mixed solvents. I. Water–alcohol and water–acetone mixtures. J. C. DUFF and E. J. BILLS (J.C.S., 1931, 1196—1201).—The solubility of picric acid in aq. EtOH, PrOH, and $Pr^\beta OH$ is a max. when the alcohol content of the solvent is 80%, 75%, and 80%, respectively, *i.e.*, when the dielectric consts. are approx. equal; the position of the max. is almost independent of temp. between 0° and 50°. The solubilities in the anhyd. alcohols agree with the order of the dielectric consts. of the solvents and with the conductivities of the dil. solutions. The degree of association of the alcohols influences the solubility markedly, and the dissociating influence of H_2O also is apparent. In $COMe_2$ the solubility is much greater than in the alcohols, but the degree of ionisation of the acid is very small. The solubility curve is approx. linear for binary mixtures of the alcohols. H. F. GILLBE.

Solubility of gold in mercury. III. A. A. SUNIER and L. G. WEINER (J. Amer. Chem. Soc., 1931, **53**, 1714—1721).—The data have been determined between 200° and 300° in an atm. of H_2 with a modified solubility tube. At the higher temp., the results differ from those of Britton and McBain (A., 1926, 474). J. G. A. GRIFFITHS.

Solubility of copper in silver. N. AGEEV and G. SACHS (Mitt. deut. Materialprüf. Berlin-Dahlem, 1930, No. 13, 50—55; Chem. Zentr., 1931, i, 1065).—*X*-Ray determinations of lattice const. show that the solubility of Cu in Ag falls from 14% at 700° to 0·1% at 0°. A. A. ELDRIDGE.

Influence of particle size of carbon on adsorption in solutions. F. KRCZIL (Kolloid-Z., 1931, **55**, 143—148).—Diminution of the particle size of activated C does not increase its adsorptive capacity for I_2, $HgCl_2$, PhOH, BzOH, and indigo. The adsorption of the colouring matter in molasses is greater with more finely divided C, but the difference is not great enough to justify an alteration of the present technical methods. E. S. HEDGES.

Vapour-pressure isotherms and submicroscopic structure of active carbon. P. KUBELKA (Kolloid-Z., 1931, **55**, 129—143).—The capillary condensation isotherms at 20° for CO_2, H_2, and the vapours of C_6H_6, Et_2O, and chloropicrin on 10 different kinds of C are in accordance with Zsigmondy's theory (A., 1911, ii, 880). Using Thomson's relation (Phil Mag., 1871, **42**, 448) between the equilibrium partial pressure and the capillary diameter, information relating to the submicroscopic structure of the adsorbents has been obtained. The structure curves are typical probability curves. Condensation of gas in the capillaries of C is possible at temp. above the crit. temp. of the gas. E. S. HEDGES.

Adsorption of certain vapours by activated charcoal. III. J. N. PEARCE and A. L. TAYLOR (J. Physical Chem., 1931, **35**, 1091—1103; cf. A., 1930, 989).—The adsorption of the vapours of EtCl, PrCl, $Pr^\beta Cl$, BuCl, and *tert.*-butyl chloride by charcoal has been determined from 0° to the decomp. temp. in contact with charcoal. Stability towards heat decreases with an increase in mol. complexity and the *iso-* and *tert.*-compounds decompose at lower temp. than do the normal compounds. At low pressures the vol. of vapour adsorbed in the normal series increases with mol. wt., but at 0° and higher pressures the order is reversed. Above 100°, adsorption at all pressures increases with the length of the C chain. Branched-chain compounds are less adsorbed than normal compounds at all temp. and pressures. The heats of adsorption calc. from the isosteres are less than those obtained experimentally. The distribution of the potential and of the density of the vapours in the adsorption space has been calc. by Pólányi's method. L. S. THEOBALD.

Asymmetric adsorption. H. FISCHGOLD and R. AMMON (Biochem. Z., 1931, **234**, 39—45).—When animal charcoal is shaken with an aq. solution containing *r*-mandelic acid and alkaloid salts (quinine hydrochloride, quinidine hydrochloride, etc.) the non-adsorbed mandelic acid is optically active due probably to differences in the adsorption of the alkaloid *d*- and *l*-mandelates. P. W. CLUTTERBUCK.

Adsorption of water from ethyl alcohol–water mixtures by silica gel. H. M. DAVIS and L. E. SWEARINGEN (J. Physical Chem., 1931, **35**, 1308—1313).—SiO_2 gel prepared by Patrick's method and activated by heating at 130°/25—28 mm. preferentially adsorbs H_2O from EtOH–H_2O mixtures. Adsorption is greatest from the vapour phase at 78°. The fraction of the total H_2O removed decreases with a decrease in H_2O content of the mixture. Adsorption increases with an increase in amount of adsorbent. A fraction (20%) of the condensate from the true azeotrope contained 99·11% EtOH. L. S. THEOBALD.

Determination of adsorption in ternary solutions. J. A. V. BUTLER (Nature, 1931, **127**, 778—779).—Theoretical. L. S. THEOBALD.

Water adsorption on silica gel. P. KOETS (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 420—426).—The adsorption of water from solutions of sucrose, KCl, KCNS, LiCl, and EtOH by SiO_2 gel has been investigated, and the results are discussed on the basis of the formation of a hydration layer on the surface of the gel. J. W. SMITH.

Absorptive power of cellulose for ions. K. KANAMARU (J. Cellulose Inst., Tokyo, 1931, **7**, 101—118).—The theoretical aspects of ionic effects at cellulose–water interfaces are discussed for normal, oxy-, hydro-, and acetyl-cellulose and a theory is advanced to explain the ionic behaviour of these materials in water or in solutions of electrolytes. Depending on its previous history, cellulose contains electrolytes of various kinds and amounts and therefore shows different values of the ζ potential against water and varies in its absorptive power for ions. Oxycellulose behaves as an acid to an extent which increases with increasing oxidation, whilst hydrocellulose behaves somewhat as a base and has great affinity for multivalent anions. Swelling effects in

cellulose, caused by beating or by the action of NaOH, $ZnCl_2$, etc., comprise (1) a loosening of the gel structure, indicated by enhanced water or dye absorption, and (2) intramicellar changes. The second effect persists in cellulose hydrate even after drying, whilst the first is partly lost on drying. The ζ-potential is related to the second effect and is indicative of intramicellar changes. B. P. RIDGE.

Inner adsorption in crystalline salts. II. D. BALAREV [with N. LUKOVA] (Kolloidchem. Beih., 1931, **32**, 304—319).—Several recently reported mixed crystal systems are explained in terms of the inner adsorption theory (A., 1930, 684). Freshly-precipitated $BaSO_4$, coloured red by the presence of $KMnO_4$, may contain more than 100 mol.-% of adsorbed H_2O, which is in bivariant equilibrium with H_2O vapour, resembling the state in hydrophilic colloids. The inclusion of $NaNO_3$ in $CaCO_3$ ppts. is related to the formation of the polar adsorption compound $CaCO_3,H_2O,Na_2CO_3$, and this compound plays a part in the crystallisation of $NaNO_3$ from its saturated solution on a surface of cryst. $CaCO_3$. E. S. HEDGES.

Desorption of gases from the walls of a closed system in which the pressure is independently changing. G. E. PRINGLE and G. VAN PRAAGH (Proc. Camb. Phil. Soc., 1931, **27**, 250—254).—Mainly mathematical. The reaction between Pt and I vapour at low pressures in a glass bulb has been examined, pressures being corrected for the gas desorbed from the walls of the bulb. N. M. BLIGH.

Comparison of commercial "getters." M. R. ANDREWS and J. S. BACON (J. Amer. Chem. Soc., 1931, **53**, 1674—1681).—Films of partly degassed Mg, Ca, Na, and P absorb residual gas from evacuated vessels more slowly and afford higher equilibrium pressures than the elements which have been more completely degassed. These pressures are independent of temp. between 0° and 90°. J. G. A. GRIFFITHS.

Heat of wetting of charcoal as a measure of its activity. R. MACY (J. Physical Chem., 1931, **35**, 1397—1409).—The heat of wetting in C_6H_6 is shown to be a good rapid test of the gas adsorbent qualities of different charcoals. Heat of wetting, however, is more a function of retentivity than of adsorption capacity. Heat of wetting and retentivity are probably a measure of surface area. L. S. THEOBALD.

Interfacial forces at the interface dielectric–aqueous solution. K. LARK-HOROVITZ (Naturwiss., 1931, **19**, 397).—The dielectrics used were quartz glass and paraffin. Quartz in acid solution behaves as a H electrode, and in NaOH or NaCl solution as a Na electrode. The potential at the boundary is obtained. A. J. MEE.

Size of pores of ultra-filters. H. BECHHOLD, M. SCHLESINGER, and K. SILBEREISEN [with L. MAIER and W. NÜRNBERGER] (Kolloid-Z., 1931, **55**, 172—198).—The measurement of the diameter of pores in ultrafilters by the air-bubble pressure method requires heavy pressures, which deform the membrane and may break the porcelain or other support. Experiments also show that the nature of the support influences the results obtained. By replacing the air–liquid interface, having a high surface tension, by a liquid–liquid interface of very low surface tension the pressures required to displace one liquid by the other are less and a porcelain support for the membrane is not essential. The method recommended is to measure the pressure required to force H_2O through the ultrafilter membrane impregnated with *iso*-BuOH. An apparatus for this purpose is described, together with some experiments with membranes of collodion from glacial AcOH. The diameter of the relatively wide pores can be calc. from the formula $d=4\sigma/p$, where σ is the surface tension and p the pressure, but the simple formula is invalidated for very fine pores by the increased frictional resistance, especially when σ is low. The modified formula $d=(4\sigma/p)[1+(2l/\sigma)\sqrt{A(\eta_1+\eta_2)/2}]$ is developed, where η_1 and η_2 are the viscosities of the liquids, l is the length of the capillary channel, and $A=dp/dt$. Experiments are described on the preparation of ultrafilter membranes of reproducible permeability. E. S. HEDGES.

Osmosis in systems containing liquids of constant composition. III. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 341—347; cf. A., 1930, 992; this vol., 680).—Mathematical. J. W. SMITH.

Osmosis in systems containing liquids of constant composition. IV. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 524—530).—Mathematical. E. S. HEDGES.

Membrane phenomena produced by insulated metal plates. M. J. LOISELEUR (Bull. Soc. Chim. biol., 1931, **13**, 276—282).—If an insulated metal plate is brought into contact with the membrane of a dialyser containing a solution of an electrolyte a p.d. is set up instantaneously between the solutions on either side of the membrane; the difference varies widely with the nature of the metal, the concentration of the solution, and, to a smaller extent, with the nature of the ions present, and falls rapidly with time. The effect is ascribed to a preferential deposition of ions on the plate, which produces polarisation of the membrane; the p.d. represents the work of combination of the metallic ions with negative ions which are provided, not by the solution, but by the membrane. A secondary diffusion effect corresponding with the re-establishment of equilibrium has been observed. The results are discussed in relation to biological phenomena such as oligodynamic action. H. F. GILLBE.

Electrokinetic potentials. IX. Electric field of force at liquid–liquid interfaces. H. B. BULL and R. A. GORTNER (Proc. Nat. Acad. Sci., 1931, **17**, 288—294).—An apparatus is described for determination of the potential at a liquid–liquid interface, and by varying the distance between the electrodes, a position of max. streaming potential is obtained. The temp. coeff. and the potentials for solutions of NaCl, $CaCl_2$, $ThCl_4$, and sodium stearate against nujol are recorded. The potential curves at an oil–aq. solution interface closely resemble those at cellulose- and glass–aq. solution interfaces. P. W. CLUTTERBUCK.

Deviations from Helmholtz's theory of electrokinetic effects. H. REICHARDT (Z. physikal. Chem.,

1931, **154**, 337—357).—The theory of electro-osmotic flow and of streaming potential in capillary tubes is developed from modern conceptions of the nature of the double layer. The equations derived agree with those given by Helmholtz only when the thickness of the double layer is negligibly small. In very narrow capillaries the electro-osmotic flow is diminished by the factor $(1-d/r)$, where d is the thickness of the double layer and r the radius of the capillary. Experiments on streaming potential with distilled water in very narrow tubes give $d=1{\cdot}2\times10^{-7}$ cm., the calculation being based on the electro-osmotic counter-effect. F. L. USHER.

Molecular depression of the f. p. for bornyl chloride; the constant for camphor. R. J. W. LE FÈVRE and W. H. A. WEBB (J.C.S., 1931, 1211—1216).—Rast's micro-method for the cryoscopic determination of mol. wt. has been modified by taking as the m. p. the temp. at which a solid cryst. structure first appears, provided that on reheating it disappears at the same temp. The mol. depression for bornyl chloride is approx. 525, and is thus the largest known for an org. compound. Rast's value for camphor (400) is based on incorrect m.-p. data for the system salol–camphor; new measurements yield a markedly different curve, which shows evidence of compound formation and indicates a value of about 600 for the const. Jouniaux' value (498) appears to be preferable to that of Rast. H. F. GILLBE.

Optical activity of electrolytes. N. CAMPBELL (J. Physical Chem., 1931, **35**, 1143—1155).—The mol. rotation of ammonium α-bromocamphor-π-sulphonate increases slightly with increase in concentration from 0·10 to 0·30M; this can be explained either by variation in the degree of dissociation or by Darmois' deformation theory. The increased rotations caused by adding optically inactive salts and non-electrolytes are smaller than those observed previously and are without the same regularities; the effects are not conditioned solely by the ionic nature of the added substance. The rotations in aq. alcohols have also been determined. L. S. THEOBALD.

Determination of size and form of submicroscopic crystals by X-rays. R BRILL (Kolloid-Z., 1931, **55**, 164—169).—The method described differs from others in being not confined to the cubic crystal system, but of general applicability. E. S. HEDGES.

Particle size determination with technical adsorbents. II. F. KRCZIL (Kolloid-Z., 1931, **55**, 148—150).—Further details are given of the distribution of particles of different size in German and American kieselguhr (cf. this vol., 678). E. S. HEDGES.

Chemical activity and particle size. Rate of dissolution of anhydrite below 70 µ. P. S. ROLLER (J. Physical Chem., 1931, **35**, 1133—1142).—The dissolution curves of anhydrite, determined electrometrically at 20° for six fractions of mean diameter 1·96—66·9 µ, show an initial induction period of 0·1 min., followed by a rapid rise during the next 3—4 min. to a slow continuous rate of dissolution. The dissolution factor, *i.e.*, the relative rate of dissolution per unit surface, is 1 for particles larger than 25 µ; it increases to a maximum of 17·6 at 2·8 µ and then decreases to 11·6 at 1·96 µ. The solubility of natural cryst. anhydrite in water is 0·298 g. per 100 c.c. at 20°. L. S. THEOBALD.

Relation between obscuring power, particle number, and size of screening smokes. P. D. WATSON and A. L. KIBLER (J. Physical Chem., 1931, **35**, 1074—1090).—Smokes made from NH_4Cl, $TiCl_4$, $ZnCl_2$, white P, oleum, and chlorosulphonic acid have been examined at 60 and 90% R.H. Obscuring power is greater the higher is the humidity of the air. For smokes consisting of spherical particles of diameters within the range of visible light the average screening ratio, *i.e.*, the ratio of the total cross-sectional areas of the smoke particles to the area of the target, is 1·27; the correct value is probably 1·35 approx. The screening power is independent of the composition of the particles and, within limits, of their size. P smoke at 90% R.H. has a screening ratio of 3·86 and consists of particles larger than the wave-lengths of visible light and probably screens according to a different law. The precipitation of all the smokes follows an exponential law, the log. of the amount remaining in the air being proportional to the time. L. S. THEOBALD.

Colloidal carbon. H. R. KRUYT and G. S. DE KADT (Kolloidchem. Beih., 1931, **32**, 249—303).—A distinction is made between C which is activated at low temp. and contains surface complexes which give CO_2 on heating, and C activated at 800—900°, which contains surface complexes giving CO when heated. The low-temp. product contains CO_2H groups and is negatively charged, whilst the high-temp. product has a sp. adsorption capacity for H ions and therefore becomes positively charged in H_2O. The peptising and coagulating effects of NaOH on colloidal C under different conditions and the existence of an irregular series are discussed. When C is heated in vac. at 1000° and then exposed to O_2 at room temp. a part of the O_2 is bound irreversibly and on heating is expelled partly as CO_2, but mainly as CO. The C is positively charged and does not adsorb alkali. The product obtained by heating C in H_2 at 1000° is negatively charged, adsorbs alkalis, and forms surface compounds of hydrocarbons. The sols of C are coagulated most strongly by ions which are least adsorbed, contrary to usual experience. It seems, therefore, that two different mechanisms are involved. E. S. HEDGES.

Lyophilic colloids. IX. Viscosity and sol concentration. I. H. R. KRUYT and K. C. WINKLER (Kolloidchem. Beih., 1931, **32**, 374—381).—For sols of starch and of gum arabic the values of $(\eta_s-\eta_0)/c\eta_0$, where is the viscosity of the sol, η_0 that of the dispersion medium, and c the concentration of the sol, fall to a min. and subsequently rise. When a standard sol is diluted, not only is the concentration of the colloid altered but also that of the electrolyte, and with it the magnitude of the electro-viscous effect. If sufficient electrolyte is added to the sol to repress the electro-viscous effect, the initial fall does not occur when the sol is diluted. Deviations from Einstein's formula should not be attributed, therefore, to changes in hydration with the varying concentration of the sol. E. S. HEDGES.

Surface development and surface change in sols and gels of thorium and iron [hydroxides]. G. GRAUE (Kolloidchem. Beih., 1931, **32**, 403—462).—The surface development of ppts. may be studied in the presence of a suitable radioactive substance, which is adsorbed at the surface, by measuring the emanating power of the ppt. Gels of $Th(OH)_4$, obtained by precipitating Th salts with aq. NH_3, have a high emanating power and are highly disperse, the crystallites having a low orientation tendency. $Fe(OH)_3$ gels, prepared from $FeCl_3$ by adding aq. NH_3, have an equally high emanating power only when precipitated in the cold. The orientation tendency is greater in $Fe(OH)_3$ than in $Th(OH)_4$, and gels prepared from hot solutions have less sp. surface. $Fe(OH)_3$ gels made by coagulating the sol have low emanating power and are relatively coarsely disperse. The emanating power of $Th(OH)_4$ gels falls to about 5% in 1 year. $Fe(OH)_3$ gels age more rapidly, but the rate of ageing is reduced by exhaustive washing. The ageing is accelerated by the addition of impurities. Sols of $Th(OH)_4$ and of $Fe(OH)_3$ increase in dispersity on keeping or on heating for some time, but eventually the dispersity decreases. When heated in boiling water, gels of $Th(OH)_4$ and $Fe(OH)_3$ undergo an irreversible diminution of surface, marked by reduction in emanating power; a similar result is brought about by drying the gels over conc. H_2SO_4. The spontaneous crystallisation of $Fe(OH)_3$ gels above 300° is marked by a striking reduction of emanating power.

E. S. HEDGES.

Electrolyte coagulation of colloids. IX. Potentiometric investigation of adsorption of silver ions by tungstic acid sols. A. J. RABINOVITSCH and E. S. AVTONOMOVA (Kolloid-Z., 1931, **55**, 207—212).—The coagulation of WO_3 sols by $AgNO_3$ solutions has been shown to take place through exchange adsorption by potentiometric titration of $Ag^{\cdot}$ with a Ag electrode and simultaneous measurement of $[H^{\cdot}]$ by means of a glass electrode. The amount of $H^{\cdot}$ displaced is less than the amount of $Ag^{\cdot}$ adsorbed. Complete adsorption of $Ag^{\cdot}$ occurs from dil. solutions of $AgNO_3$, but with higher concentrations of $AgNO_3$ the Ag ions are distributed between the colloid particles and the intermicellar liquid.

E. S. HEDGES.

Stabilisers of colloidal ferric hydroxide. K. JABŁCZYNSKI, S. ZALC, and I. EJBESZYC (Rocz. Chem., 1931, **11**, 259—268).—The velocity of flocculation of undialysed $Fe(OH)_3$ sols produced by KCl or KBr increases progressively with the concentration of H_2SO_4 added, whilst with dialysed sols the velocity coeff. at first falls to a min. and then rises abruptly. These effects are ascribed to excess of stabilising power of $H^{\cdot}$ over SO_4'' ions at low concentrations of acid, and to the reversal of these conditions in more conc. acid, when conditions are the same as for undialysed sols. When HCl is taken in place of H_2SO_4, a stabilising effect only is observed, the feeble coagulative properties of Cl' ions being at all concentrations inferior to the stabilising effect of $H^{\cdot}$ ions; similar results are obtained with AcOH.

R. TRUSZKOWSKI.

Oxide hydrates and active oxides. XXXIX. Peptisability and solubility of various oxides and oxide hydrates of aluminium. G. F. HÜTTIG and A. SCHAUFEL (Kolloid-Z., 1931, **55**, 199—207).—The degree of peptisation of Al_2O_3 and $Al(OH)_3$ prepared in numerous different ways in HCl and NaOH solutions varies considerably, but tends to a const. value with increasing crystallinity of the material. Freshly-precipitated gels of $Al(OH)_3$ are not so readily peptised as slightly aged gels, but with further increasing age the peptisability decreases greatly. Diaspore and corundum show a relatively acid character, whilst hydrargillite, bohmite, and γ-Al_2O_3 are relatively basic.

E. S. HEDGES.

Ageing of colloidal solutions. K. JABŁCZYNSKI and S. ZALC (Rocz. Chem., 1931, **11**, 254—258).—The velocity of flocculation of a dialysed $Fe(OH)_3$ sol on adding KCl falls during 10 days to about half the original value, but no change in the dimensions of the particles takes place. This effect is ascribed to gradual diffusion of Cl ions from the interior of the micelles to the pericellular fluid, from which these ions have been largely removed by dialysis. As a consequence, the negative charge of the particles progressively increases, producing greater stability with respect to KCl.

R. TRUSZKOWSKI.

Relation between the plasticity of a two-component solid–liquid system and the degree of wetting of the solid by the liquid. F. E. BARTELL and A. HERSHBERGER (J. Rheology, 1931, **2**, 177—204).—Plastometric measurements afforded by observations on the rates of flow under different pressures through capillary tubes of known dimensions are suggested as a basis for the classification of plastic materials.

J. GRANT.

Thixotropy of pseudo-plastic systems. A. DE WAELE (J. Rheology, 1931, **2**, 141—159).—Pseudo-plastic systems, which exhibit a type of heterogeneous dispersion based on the continuous charge of the stress–shear relationship, have a sp. shear thioxotropy (*i.e.*, a transient change in consistency on agitating; cf. A., 1929, 137). For the lower values of shear a discontinuity was observed which is attributed to a progressive increase in the sp. surface of the primary particles or unit cells. "Negative plasticity" was observed in sols of cellulose nitrate, celluloid, india-rubber, and mineral oil emulsions, and is probably masked in the case of gelatin sol and petroleum jelly by the effect of progressive desolvation or removal of the lyosorbed layer on shear. Plastometric examination of pseudo-plastic fluids provides an indication of colloidal structure, but must be supplemented by knowledge of the rate of shear in order to determine consistency. The absence of thixotropy in coarse emulsions (*e.g.*, oil in water) is due to the smallness or absence of a lyosorbed layer.

J. GRANT.

Scattering of light in sols of casein. B. J. HOLWERDA (Rec. trav. chim., 1931, **50**, 601—609).—The increase in the amount of light scattered by casein sols when NaCl is added is due to a dehydration action on the particles of sol which increases n.

E. S. HEDGES.

Protein systems. I. Non-solvent space, hydration space, and combination with non-electrolytes in ovalbumin solutions. H. H.

WEBER and H. VERSMOLD (Biochem.-Z., 1931, **234**, 62—83).—The magnitude of the non-solvent space in a given protein–crystalloid system is determined by the amounts of hydration space and of crystalloid combined with protein. The hydration space is defined as the non-solvent space when no crystalloid is bound with the protein and gives therefore a maximal value. A method is critically discussed for determining simultaneously the hydration space and the crystalloid combined with albumin. Formulæ are given for calculating the non-solvent space from the measured lowering of f. p. of protein-containing and protein-free crystalloid solutions. The methods for determining hydration- and non-solvent space are experimentally tested. The hydration space of 1 g. of albumin is 1·075 c.c. The non-solvent space–C_e curves are given for glycerol, dextrose, and carbamide. The hydration space for albumin does not change between 3·11 and 10·25 and decreases on heat-coagulation to 0·1 c.c. per g. of albumin. P. W. CLUTTERBUCK.

Effect of preheating on the dispersity of calcium caseinate in skim milk. J. B. NICHOLS, E. D. BAILEY, G. E. HOLM, G. R. GREENBANK, and E. F. DEYSHER (J. Physical Chem., 1931, **35**, 1303—1307).—Preheating of skim milk to 95° has only a small effect on the size distribution of the particles determined by centrifuging. Calcium caseinate particles in milk are less than 200 mμ in diameter and average 90 mμ; a small amount of coarser material, probably colloidal calcium phosphate and some caseinate, is also present. L. S. THEOBALD.

Precipitation of proteins by neutral salts. C. ARTOM (Arch. Sci. biol., 1930, **14**, 391—420; Chem. Zentr., 1931, i, 1458).—In systems containing protein in various concentrations the threshold concentration of salt for precipitation at constant p_H increases with the protein concentration. At various protein concentrations or const. salt concentration the p_H threshold falls with increase in protein concentration. A. A. ELDRIDGE.

Peptisation of iron oxide by proteins. H. FREUNDLICH and G. LINDAU (Biochem. Z., 1931, **234**, 170—185).—The peptisation of roasted Fe_2O_3 by albumin has a null value at the isoelectric point, increases rapidly on both sides of this point, and on the acid side reaches a max. and then completely falls away. The peptising action of gelatin on Fe_2O_3 is much smaller than that of albumin. The peptisability of Fe_2O_3 varies with its physical condition. The sedimentation volumes of powdered quartz and Fe_2O_3 in albumin and gelatin solutions at different p_H are investigated. Using quartz, the volume with both proteins attains a max. at the isoelectric point and sedimentation is accelerated. With powdered Fe_2O_3, the behaviour with gelatin is analogous, but the differences in sedimentation volumes at different p_H are less. With albumin, on the other hand, the differences in sedimentation volume disappear completely. The quartz sedimentation volume method is recommended as a means of determination of the isoelectric point of proteins. P. W. CLUTTERBUCK.

Alteration by neutral salts of the free charge on pure proteins. T. ITO (Biochem. Z., 1931, **233**, 441—448; cf. A., 1929, 1474).—In solutions of pure serum-albumin and ovalbumin the direction of migration of the proteins is reversed by the addition of hexamminocobaltic chloride at concentrations of about 0·0125*N*. This result accords with the view that within the isoelectric zone pure proteins behave towards the ions of neutral salts as multivalent pseudo-ions, but not with the supposition that, in this zone, the CO_2H groups are present in undissociated form. W. MCCARTNEY.

Effect of gelatin and salts on Congo-red. H. L. DAVIS and J. W. ACKERMAN (J. Physical Chem., 1931, **35**, 972—987).—Congo-red, which behaves as a sol intermediate between lyophilic and lyophobic types, is precipitated by NaCl, KCl, NaI, KI, and $BaCl_2$. The presence of gelatin diminishes or prevents this precipitation, and this apparent protection is due to decreased stability and dispersion of the dye by virtue of which it is more strongly adsorbed by the gelatin. In the absence of salts adsorption is too slight for ordinary protection. Salts which peptise gelatin or precipitate it have different effects on the dyeing of cotton as compared with mixed sols of gelatin and Congo-red; both types increase adsorption of the dye, the former being more effective. L. S. THEOBALD.

Ammonia gelatin. W. BILTZ and O. RAHLFS (Z. anorg. Chem., 1931, **197**, 313—320).—Liquid NH_3 exerts a swelling action on gelatin essentially similar to that of water. The NH_3 does not, however, completely dehydrate the gelatin, which suggests the presence of combined water. The swelling curves for egg-albumin and ramie fibre are also of the usual type. R. CUTHILL.

Ebullioscopic determinations of molecular equilibrium of pyrocatechol in lithium chloride solutions. F. BOURION and (MLLE.) O. HUN (Compt. rend., 1931, **192**, 1233—1235).—At low concentrations of LiCl (0·5*M*) pyrocatechol gives rise to equilibria between single and triple molecules, and at higher (1·225*M*) between single and quadruple. The increase of association and of ebullioscopic const. with decrease of mol. wt. already noted in the case of KCl–NaCl (cf. A., 1930, 689) is also shown by LiCl. C. A. SILBERRAD.

Relation of the ratio of reactants to the extent of conversion of benzaldehyde and furfuraldehyde into their acetals. H. ADKINS, J. SEMB, and L. M. BOLANDER (J. Amer. Chem. Soc., 1931, **53**, 1853—1858; cf. A., 1925, i, 785; 1927, 1172; 1928, 274).—The equilibrium const. for the reaction between PhCHO (1 mol.) and EtOH (2—10 mols.) in presence of a little HCl is identical with that for PhCHO and BuOH provided that concentrations are expressed as mol.-fractions; in both cases the const. diminishes slightly when the ratio of alcohol to aldehyde is increased. The const. for the reaction of PhCHO with Pr^βOH and of furfuraldehyde with EtOH are independent of the concentration of the reactants. The percentage conversion of aldehyde into its acetal increases in all cases with increase of the alcohol ratio.

Furfuraldehyde diethylacetal, b. p. 184—185°/740 mm., 77—79°/16 mm., is obtained in 24% yield when a mixture of furfuraldehyde, EtOH, and a little HCl is kept for 1 day, the product treated with Na_2CO_3,

and then fractionally distilled. Slight modifications in the method for determining PhCHO (A., 1925, i, 784) are described. H. BURTON.

Electrolytic dissociation and the deviations from the dilution law. K. FREDENHAGEN (Z. Elektrochem., 1931, **37**, 257—271).—A summary and amplification of the author's views on the nature of electrolytic dissociation (cf. this vol., 430). It is considered that the electrostatic theory is unsound. R. CUTHILL.

Theory of association of strong electrolytes. J. ZIRKLER (Z. Elektrochem., 1931, **37**, 252—254).—Calculations are made on Nernst's theory (A., 1928, 127, 708) of the degree of association of a uni-univalent electrolyte from cryoscopic and conductivity data. R. CUTHILL.

Degree of dissociation and the ions of cadmium iodide in aqueous solution. J. W. McBAIN, P. J. VAN RYSSELBERGE, and W. A. SQUANCE (J. Physical Chem., 1931, **35**, 999—1010).—E.m.f. measurements of cells containing CdI_2 (0·001—0·4M) have been combined with those of other cells to deduce the concentration of the simple ions. The concentrations and mobilities of the complex cations and anions have also been evaluated. The sum of the concentrations of the simple ions is equal to the activity coeff. and for CdI_2 the total dissociation is only slightly greater than the Arrhenius conductivity ratio. A more accurate value for the degree of dissociation of 0·005M-CdI_2 has been deduced from diffusion coeff. for solutions of 0·005—0·5M-CdI_2 [by T. H. LIU]. The diffusion coeff. calc. from the concentrations of the different mol. species present in solutions of CdI_2 agree fairly well with the experimental values. With respect to dissociation and complex formation, CdI_2 differs from other salts containing bivalent ions only in degree. L. S. THEOBALD.

Hydrolysis of the fluosilicate ion. P. KUBELKA and V. PRISTOUPIL (Z. anorg. Chem., 1931, **197**, 391—394).—The p_H of a solution containing NaOH and H_2SiF_6 at a mol. ratio of 2 : 1 lies between 6 and 7, and does not exceed 7 if the ratio is increased to 6 : 1. The hydrolysis const. of the SiF_6'' ion, $[H^{\cdot}]^4[F']^6/[SiF_6^{\cdot\cdot}]$, is 2×10^{-27}. H. F. GILLBE.

Interaction between polybasic acids and neutral salts. I. Orthophosphoric acid. S. K. MAJUMDAR (J. Indian Chem. Soc., 1931, **8**, 87—93).—Measurements of the p_H of solutions of H_3PO_4 containing KCl, KBr, or KI have been used to calculate the first dissociation const. of the acid; the value obtained varies considerably with the salt concentration. R. CUTHILL.

Stabilisation of boric acid buffers by aeration. E. H. FAWCETT and S. F. ACREE (Bur. Stand. J. Res., 1931, **6**, 757—763).—H_3BO_3–KCl–NaOH buffers may be stabilised by aeration; for equilibrium with atm. CO_2 2—6 days are required. C. W. GIBBY.

Effect of the addition of salts on the p_H of solutions of ampholytes. W. GIEDROYC and S. J. PRZYŁECKI (Biochem. J., 1931, **25**, 465—472).—The addition of various mineral salts changes the p_H of solutions of gelatin, ovalbumin, and peptone. The depression of p_H shows a max. on the alkaline side of the isoelectric point. The action of salts is a function not only of their concentration but also of the valency of their ions. The effect produced by unit concentration of salts is greater at very low than at higher concentrations. S. S. ZILVA.

Influence of intensive drying on the establishment of inner equilibrium. II. A. SMITS, E. L. SWART, P. BRUIN, and W. M. MAZEE (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 438—449; cf. this vol., 430).—A method for freeing a liquid from dissolved air is described (cf. A., 1930, 185). After intensive drying for 11 months, C_6H_6, C_6H_{12}, and Br treated in this way still behave in a unary manner. In some cases the attainment of inner equilibrium is very slow at low temp., without chemical drying, and in others the inner equilibrium can be studied only by reference to the fine structure of the rotation bands and the Raman effect. Modern views on allotropy are discussed. J. W. SMITH.

Equilibria in the iron–nitrogen system. S. BRUNAUER, M. E. JEFFERSON, P. H. EMMETT, and S. B. HENDRICKS (J. Amer. Chem. Soc., 1931, **53**, 1178—1186).—The equilibrium data (A., 1930, 699) have been extended to 400° and 575°. A NH_3–H_2 mixture at 1 atm. must contain 37 and 14·5±1% NH_3 at 400° and 575°, respectively, in order to convert Fe into Fe_4N, and 77, 70, and 57±1·5% NH_3 to convert Fe_4N into the ε-phase at 400°, 444°, and 500°, respectively (cf. A., 1930, 996, 1121). X-Ray data for the ε-phase differ slightly from previous results. J. G. A. GRIFFITHS.

Sodium thiosulphate as a standard in thermometry. J. S. N. CRAMER (Chem. Weekblad, 1931, **28**, 316—318).—$Na_2SO_3,5H_2O$, dried over a saturated solution of $CaCl_2$, is recommended as a standard in thermometry in place of $NaBr,2H_2O$ (50·76°); the transition temp. to the dihydrate is 48·45°. Details are given of the purification and testing of the salt. H. F. GILLBE.

System lithium bromate–water. J. P. SIMMONS and W. F. WALDECK (J. Amer. Chem. Soc., 1931, **53**, 1725—1727).—The solubility data refer to the range 5—100°. $LiBrO_3,H_2O$ is stable below 50·8—52°, and the anhyd. salt has m. p. 248° (decomp.). J. G. A. GRIFFITHS.

Oxide hydrates and active oxides. XL. System plumbic oxide–water. G. F. HÜTTIG and B. STEINER (Z. anorg. Chem., 1931, **197**, 257—269; cf. this vol., 797).—Isobaric dehydration and X-ray examination have shown that the only solid phases are the yellow and red forms of lead oxide and the hydrate $PbO,0{\cdot}5H_2O$. The dehydration curve of the hydrate is partly zeolitic in character. R. CUTHILL.

Equilibrium in systems of sulphur dioxide and ammonium or an alkali iodide. H. W. FOOTE and J. FLEISCHER (J. Amer. Chem. Soc., 1931, **53**, 1752—1763; cf. A., 1916, ii, 614; 1919, ii, 366).—V.-p data for the two-component systems between −25° and 25° are recorded. The transition points $RbI,3SO_2 \longrightarrow RbI$, $NaI,4SO_2 \longrightarrow 3NaI,8SO_2$, and $NH_4I,3SO_2 \longrightarrow NH_4I$ are 21·3°, 1·4°, and −8·8°, respectively. Previously reported K and Cs compounds other than $KI,4SO_2$ and $CsI,3SO_2$, in the range −25° to 25°, are not confirmed. J. G. A. GRIFFITHS.

Thermal dissociation of calcium hydride. C. B. HURD and K. E. WALKER (J. Amer. Chem. Soc., 1931, **53**, 1681—1689).—The pressure of H_2 in equilibrium with that inside a Ni vessel containing Ca and CaH_2 at 990—1210° abs. has been determined. There is no evidence for the equilibrium $2CaH_2 \leftarrow 2CaH + H_2$ (cf. A., 1930, 718). The heat of dissociation of calcium hydride at 1100° abs., is 51,100 g.-cal.
J. G. A. GRIFFITHS.

Thermal dissociation of calcium carbonate in an atmosphere of carbon dioxide. M. MATSUI and K. BITO (J. Soc. Chem. Ind. Japan, 1931, **34**, 145—148B).—The dissociation pressure of $CaCO_3$ is equal to 1 atm. at 920—921°; this temp. is appreciably higher than reported by earlier workers. The magnitude of the error caused by inaccurate measurement of temp., especially of larger samples, is emphasised. H. F. GILLBE.

Decomposition pressure and rate of decomposition of calcium carbonate. G. H. WHITING and W. E. S. TURNER (J. Soc. Glass Tech., 1930, **14**, 409—424T).—Grain size influences the dissociation of $CaCO_3$; for precipitated material 0·02 mm. diam. the pressure reaches 760 mm. at about 902°, other grades ranging from 886° to 915°. Dissociation definitely begins below 500°, but is too small to be measured with certainty. With finely ground calcite (0·065 mm. diam.) and precipitated carbonate repeated evacuation at 600° followed by rise of temp. at the rate of 1° per min. gave a close approach to equilibrium conditions, and results so obtained agree with those previously recorded (A., 1923, ii, 490). Heating in air to 610° is sufficient to decompose completely all grain sizes and forms of $CaCO_3$, but at 500° decomp. does not proceed far. Calcite of diam. < 0·063 mm. needs 85 hr. at 610°, 2½ hr. at 750°, and 1 hr. at 800° for complete decomp. The rate is greatly influenced by grain size, falling with increasing size. There is some evidence that difference in form of the carbonate apart from grain size also influences the rate of decomp.
M. PARKIN.

Decomposition of sodium carbonate by heat. J. T. HOWARTH and W. E. S. TURNER (J. Soc. Glass Tech., 1930, **14**, 394—401T).—When heated in a Pt crucible in air Na_2CO_3 suffers no loss in wt. up to 700°, 0·1—0·2% at 800°, 0·9% at 850°, and 3·35% at 1100°. At low pressures there is evidence of slow volatilisation of the carbonate at temp. considerably below 800°. The dissociation pressures obtained by heating in an exhausted Pt tube at const. temp. until equilibrium is attained increase from 1·5±0·5 mm. at 1000° to 77 mm. at 1405°. Plotting $\log p$ against $\log T_{(abs.)}$ gave a straight-line graph from which by extrapolation p=760 mm. at 1750°. M. PARKIN.

Reaction between sodium carbonate and silica as measured by decomposition pressure. J. T. HOWARTH and W. E. S. TURNER (J. Soc. Glass Tech., 1930, **14**, 402—409T).—Using 100—150-mesh quartz and 300-mesh Na_2CO_3, well-marked reaction occurs at temp. below 400°. For the mixture $Na_2CO_3 : 4SiO_2$ pressure development in the evacuated system occurs at 395°, for $NaCO_3 : SiO_2$ at 348°, and for $2Na_2CO_3 : SiO_2$ below 375°. The pressures registered are not true reversible values, the apparent equilibrium depending on the rate of penetration by the gases of the layer of reaction product on the surface of the grains. The reabsorption of CO_2 on cooling tends to become slower after successive reheatings. Some volatilisation of Na_2CO_3 was noted even below 500°. M. PARKIN.

Double decomposition in the absence of a solvent. I. Reciprocal system AgCl+KBr AgBr + KCl. II. AgBr + KI AgI + KBr. A. P. PALKIN (Acta Univ. Asiæ Med., 1930, [vi], No. 4, 3—17, 18—40). CHEMICAL ABSTRACTS.

Ternary system water–sodium nitrate–sodium iodate. E. CORNEC and A. SPACK (Bull. Soc. chim., 1931, [iv], **49**, 582—594).—The isotherm at 0° and certain data between 0° and 100° have been determined, the results being in agreement with those of Foote and Vance (A., 1930, 36). R. CUTHILL.

System ferric oxide–cupric oxide–sulphur trioxide–water. G. TUNELL and E. POSNJAK (J. Physical Chem., 1931, **35**, 929—946).—The systems examined at 50° contain not less than 93·5% of H_2O, and not more than 6·5% of Fe_2O_3, 6·5% of CuO, and 6·5% of SO_3. The crystallographic habits and states of aggregation of the solid phases, viz., Fe_2O_3,H_2O, $3Fe_2O_3,4SO_3,9H_2O$, CuO, $4CuO,SO_3,3H_2O$, and $3CuO,SO_3,2H_2O$, are described. *X*-Ray patterns are given for the first two compounds. The saturation surface is illustrated by a model and is discussed with special reference to its geological significance.
L. S. THEOBALD.

Solubility of chlorine in aqueous solutions of chlorides [at 25°] and free energy of trichloride ion. M. S. SHERRILL and E. F. IZARD (J. Amer. Chem. Soc., 1931, **53**, 1667—1674).—The solubility of $Cl_2(g)$ at 1 atm. in 0—5M aq. H_2SO_4, NaCl, KCl, and $BaCl_2$ decreases with increasing concentration, but passes through a min. in aq. HCl. The salting-out effects of the electrolytes and the extent of trichloride formation are computed. The equilibrium const. for the reaction $Cl_2(g)+Cl'=Cl_3'$ is 0·01 and the decrease of free energy is 2730 g.-cal. J. G. A. GRIFFITHS.

Thermodynamic properties of fused solutions of sodium bromide in silver bromide. E. J. SALSTROM (J. Amer. Chem. Soc., 1931, **53**, 1794—1799; cf. this vol., 309).—The density of the 50 mol.-% solution between 600° and 620° is given by d^t=4·311—0·0009t. From the e.m.f. of the cell $Ag(s)|AgBr(l)$ 0·0—0·487 mol. fraction $NaBr(l)|Br_2(g)$, graphite, between 442° and 622°, the free energy and heat of dilution, entropy, and activity coeff. at 550° and 600° are computed. There is a positive deviation of the activity from Raoult's law. J. G. A. GRIFFITHS.

Entropy of polyatomic molecules. D. S. VILLARS (J. Amer. Chem. Soc., 1931, **53**, 2006—2007).—The entropies of NH_3 and CH_4 computed, on certain assumptions, from spectroscopic data are in accord with accepted values. J. G. A. GRIFFITHS.

Thermodynamic investigation of potassium chloride. F. L. E. SHIBATA, S. ODA, and S. FURUKAWA (J. Sci. Hiroshima Univ., 1931, **1**, 55—63).—By measurement of the e.m.f. of K–Hg in contact with saturated KCl solution the free energy change of the reaction $K+0·5Cl_2 \longrightarrow KCl$ has been determined as —97,551 g.-cal., and the heat of formation of KCl

as $-104{,}169$ g.-cal.; the heat of formation of Hg_2Cl_2 is $-30{,}887$ g.-cal. The fictitious heat of dissolution of KCl at 25° is -3297 g.-cal., the total heat of dissolution is -8025 g.-cal., and the first heat of dilution is -412 g.-cal. H. F. GILLBE.

Heat of formation of calcium nitride. H. H. FRANCK and C. BODEA (Z. angew. Chem., 1931, **44**, 382—383).—The heat of formation of Ca_3N_2 (95—98·5%), determined directly by a bomb method, is 102·6±1 kg.-cal. Earlier values are critically compared. H. F. GILLBE.

Heat of combustion of *dl*-glyceraldehyde. C. NEUBERG, E. HOFMANN, and M. KOBEL (Biochem. Z., 1931, **234**, 341—344).—The heat of combustion of bimolecular glyceraldehyde is 3754·3 g.-cal., the corresponding values for dextrose and lævulose being 3742·8 and 3744·5 g.-cal. P. W. CLUTTERBUCK.

Influence of temperature on the saturation current and conductivity at high voltages of liquid dielectrics. A. NIKURADSE and R. RUSSISCHWILI (Ann. Physik, 1931, [v], **8**, 811—820).—Experimental. W. GOOD.

Application of the Barett method to electrolytic measurements. O. NEESE (Ann. Physik, 1931, [v], **8**, 929—955).—A Barett method is described by which simultaneous measurement of resistance and capacity changes can be made. Sources of error are discussed. Results for NaCl, $MgSO_4$, and $Ba_2Fe(CN)_6$ in aq. solution and for $MgSO_4$ and $Ba_2Fe(CN)_6$ in 50% sucrose solution are given ($\omega=4{\cdot}35\times10^7$). The error for conductivity is 0·5%, for capacity 0·3%. W. GOOD.

Dissociation constants of organic acids. III. Routine preparation of "equilibrium" water and of moderate-grade conductivity water. A. I. VOGEL [with G. H. JEFFERY] (J.C.S., 1931, 1201—1207).—Ordinary distilled H_2O is distilled from an alkaline $KMnO_4$ solution in a current of air free from NH_3 and CO_2, and the steam is fractionally condensed. An all-metal still is described which delivers simultaneously 1·5—2 litres per day of equilibrium H_2O and 4—5 litres per day of second-grade conductivity H_2O; the latter is suitable for the recrystallisation of salts and for similar purposes. H. F. GILLBE.

Bipolar conduction in solid electrolytes. C. TUBANDT, H. REINHOLD, and G. LIEBOLD (Z. anorg. Chem., 1931, **197**, 225—253).—In solid BaF_2, $BaCl_2$, and $BaBr_2$ up to 650° and $PbCl_2$ and $PbBr_2$ up to near the m. p. the current is carried by the anions. In NaF, NaCl, and KCl at 400—450° the current is carried solely by the cations, but at higher temp. the anions also participate in the conduction, and their transport nos. rise with the temp. Over the temp. range 250—290° both the ions of PbI_2 are mobile, the transport no. of the cation increasing as the temp. rises. R. CUTHILL.

The capillary electrometer and the electrocapillary curve. I. Assumptions and consequences of two thermodynamic rules. II. Experimental test of questions of method depending on the theory. F. O. KOENIG (Z. physikal. Chem., 1931, **154**, 421—453; 454—477).—I. Theoretical. The conditions for the validity of the Lippmann–Helmholtz equation of the electrocapillary curve are examined in detail. The curve is theoretically correct only when (1) the potential drop in the capillary occurs practically entirely in the double layer at the Hg–solution interface, and (2) the changes in concentration arising from the polarising e.m.f. are confined to the Hg salt, and all the other constituents external to the double layer remain unchanged. These conditions are fulfilled in practice when the total concentration of all anions present exceeds that of the $Hg_2^{\cdot\cdot}$ ions. Formation of amalgams when alkali salts constitute the foreign electrolyte is unimportant.

II. Apparatus for the study of electrocapillary effects with controlled temp. is described. It is immaterial whether glass or quartz is used for the capillary. The concentration of the ions which determine the potential of the anode must exceed 10^{-4} in order that the latter may be unpolarisable. The conclusions reached theoretically have been confirmed by experiments in which the proportions of $Hg_2(NO_3)_2$ and KNO_3 were varied. Irregularities observed when the proper conditions are not fulfilled are due to a fall of potential in the polarisation layer. Only a small fraction of the depolarisation current is carried by $Hg_2^{\cdot\cdot}$ ions. F. L. USHER.

Temperature coefficients of normal electrode potentials of copper and silver. R. BURIAN (Z. Elektrochem., 1931, **37**, 238—251).—E.m.f. measurements with the electrodes $Cu|Cu^{\cdot\cdot}$ and $Ag|Ag^{\cdot}$ give the values $6{\cdot}6\times10^{-4}$ and $-2{\cdot}45\times10^{-4}$ volt for the temp. coeffs. of the normal electrode potentials of Cu and Ag, respectively, over the range 40—60°, and from these figures the ionic entropies of $Ag^{\cdot}$, $Cu^{\cdot\cdot}$, and $H^{\cdot}$ are calc., and the value $6{\cdot}78\times10^{-4}$ volt is deduced for the temp. coeff. of the normal electrode potential of H. The temp. coeff. of the potential of the N-Hg_2Cl_2 electrode is $5{\cdot}7\times10^{-4}$ volt over the range 20—48°. R. CUTHILL.

Measurement of glass electrode potentials. G. D. GREVILLE and N. F. MACLAGAN (Trans. Faraday Soc., 1931, **27**, 210—222; cf. A., 1929, 782).—A modification of Harrison's method (A., 1930, 1151), involving the use of a more sensitive galvanometer and a special switch, enables glass electrode potentials to be determined with an accuracy of 0·1 mv. A method has been devised for forming the liquid junction in a tube of suitable size connected with a vessel of small capacity containing blood or other fluid in which the partial pressure of CO_2 is of paramount importance. F. L. USHER.

Solution tension of sodium in solvents other than water. F. K. V. KOCH (J.C.S., 1931, 1138—1143).—The solution tension and normal potential of Na in 8 org. liquids of various types have been determined by the method previously described (A., 1928, 370), and found to be dependent, not only on the dielectric const., but also on specific ionic-molecular forces; the sequence obtained when the solvents are arranged in order of decreasing solution tension differs from that observed with the Ag ion. Calculation of the free energy of complex formation resulting from the operation of ionic-molecular covalencies indicates that the Na ion resembles the Ag ion in its affinity for the pyridine mol., but on the contrary has a greater

affinity for ketonic and hydroxylic solvents than for those containing the CN group. H. F. GILLBE.

Oxidation–reduction potentials. IV. Determination from equilibrium data. B. Ferric–ferrous [iron] electrode, S. POPOV, V. B. FLEHARTY, and E. L. HANSON (J. Amer. Chem. Soc., 1931, **53**, 1643—1651).—The equilibrium const. for the reversible reaction $2Fe^{\cdot\cdot\cdot}+2Hg \leftarrow 2Fe^{\cdot\cdot}+Hg_2^{\cdot\cdot}$ is found to be 0.0180 ± 0.0005 at 25° from the data for 0·02—0·002*M*-$HClO_4$ solutions. The oxidation–reduction potential of the $Fe^{\cdot\cdot\cdot}$–$Fe^{\cdot\cdot}$ electrode is −0·7473 volt (cf. A., 1929, 513). J. G. A. GRIFFITHS.

Origin of potential at graphite electrodes. B. VON LENGYEL (Z. physikal. Chem., 1931, **154**, 371—378).—The potential of graphite electrodes in aq. solutions is reproducible within 10 mv., and is determined mainly by the p_H of the solution. Near the "neutral" point small salt effects are observed, due chiefly to the cation, but in the presence of 0·01*N*-acid salts have no detectable influence. The potential is not appreciably affected by the presence of air or H_2. Graphite electrodes in quinhydrone solutions give potentials which strictly correspond with the existing p_H. F. L. USHER.

Photo-voltaic effects in Grignard solutions. II. Nature of the effects. R. T. DUFFORD (J. Physical Chem., 1931, **35**, 988—998; cf. A., 1930, 1126).—An extension of previous work under improved experimental conditions. With Pt–Al electrodes in pure Et_2O a photo-voltaic effect is obtained. With the Grignard solutions the voltage response is approx. proportional to the log. of the intensity of illumination and the sensitivity does not vary greatly with temp. The addition of MeI, EtBr, and BzCl produces a large increase in current and a certain decrease in the photo-voltaic effect. With MgPhBr cells illuminated Mg, Al, Cu, Zn, Pb, and Fe electrodes are more positive than the unilluminated electrode; Pt electrodes may give at least two types of response. Grignard reagents obtained from *o*-, *m*-, and *p*-bromotoluene and from ethylene bromide also show a strong photo-voltaic effect. L. S. THEOBALD.

Calculating and averaging rate constants. W. E. ROSEVEARE (J. Amer. Chem. Soc., 1931. **53**, 1651—1661).—Mathematical. Methods for computing, from the data, the most probable values of the velocity coeff., *k*, of unimol. and bimol. reactions are examined critically. Whilst the graphical method is applicable to all cases where each point represents independent data, other methods (*e.g.*, "least squares") must be used with caution. If the rate law holds within experimental error, further values of *k* should be determined from independent data for the optimum change of concentration. The initial concentration determined directly has less probable error than that calc. analytically. J. G. A. GRIFFITHS.

Kinetics of chlorine bleaching and [decomposition of] hypochlorite solutions. J. J. WEISS (Z. Elektrochem., 1931, **37**, 271).—A correction (cf. this vol., 572). R. CUTHILL.

Oxidation of iodide ion by persulphate ion. IV. Kinetics of reaction in highly dilute aqueous solution [at 25°]. C. V. KING and M. B. JACOBS (J. Amer. Chem. Soc., 1931, **53**, 1704—1714).—The velocity of the reaction between 0·000125—0·012*M*-$K_2S_2O_8$ and 0·000125—0·024*M*-KI in presence of 1.7×10^{-7} to 3×10^{-4}*M*-$Na_2S_2O_3$, 0—0·024*M*-KCl, and 0—0·004*M*-$MgSO_4$ has been determined by observing the time of first appearance of free I ($<10^{-7}$ mol. of I per litre) with the aid of a photo-electric cell. With solutions containing the min. of ions of valency greater than unity, the velocity coeff. conform to the equation $\log k=-1.076+2\sqrt{\mu}$, up to $\mu=0.025$, from which the velocity coeff. at zero ionic strength is 0·0841. With a large proportion of bivalent ions, $\log k_0=-1.06$. J. G. A. GRIFFITHS.

Neutral salt effect of the ferric–iodide ionic reaction. II. Concentrated solutions of salts. A. VON KISS [with I. BOSSANYI] (Z. anorg. Chem., 1931, **198**, 102—115).—The order of the reaction, with respect to the I ions, in conc. salt solutions (cf. A., 1930, 1256) is depressed only by the Cl ion; NO_3 and ClO_4 ions are without influence. With increase of salt concentration above 0·5*N* the influence of concentration ceases to be evident and the classical kinetic laws become valid. The observed neutral salt effect, including the change of sign, is fully in accordance with Bronsted's theory. The specific effect of the ions in conc. solutions is very evident. H. F. GILLBE.

Velocity of hydrolysis of various sodium silicates. L. WASILEWSKI and W. BĄDZYŃSKI (Przemysł Chem., 1931, **15**, 185—188).—The velocity of hydrolysis of Na silicates used for road-surfacing is determined by heating 8 c.c. of their solutions for 60 min. at 100° in presence of powdered limestone, and centrifuging the supernatant fluid in 10-c.c. graduated tubes. When the height of the column of SiO_2 gel formed by hydrolysis exceeds 1 cm., the given sample of water-glass is not suitable as a road surface binder. Generally, amongst other unknown factors, the greater is the ratio $SiO_2 : Na_2O$ and the higher is the temp. at which the water-glass was prepared the greater is the velocity of hydrolysis. R. TRUSZKOWSKI.

Order of the reaction between halogens and organic hydroxy-acids and their salts. W. V. BHAGWAT and N. R. DHAR (Z. anorg. Chem., 1931, **197**, 383—390).—In contradiction to the conclusions of Purkayastha and Ghosh (A., 1930, 717) the reaction between phenyl-lactic acid or mandelic acid and Br, in the dark, is unimol. with respect to Br if a correction is made for the retarding action of the HBr produced. In photochemical reactions between org. compounds and halogens both atoms and activated mols. of the latter may take part. H. F. GILLBE.

Hydrolysis of sucrose by strong acids in presence of their salts. H. COLIN and (MLLE.) A. CHAUDUN (Compt. rend., 1931, **192**, 1229—1231).—*k'* and *k* being the hydrolysis constants of a 5% solution of sucrose, 0·1*N* in HCl, with and without addition of varying amounts of KCl, *k'*/*k* for concentrations of KCl of *N*/50, *N*/20, *N*/10, *N*/2, and *N* is respectively 0·892, 0·978, 1·012, 1·256, and 1·614; similar results are obtained with HNO_3 and KNO_3. On replacing KCl or KNO_3 by KBr *k'*/*k* is always >1. The ratio also increases with increasing concentration

of sucrose. The effect is attributed to the electronegative ions. (Cf. A., 1928, 598.)

C. A. SILBERRAD.

Kinetics of the oxidation of benzoate by permanganate. P. KUBELKA and E. SOVEGJARTÓ (Z. physikal. Chem., 1931, **154**, 379—384).—The reaction has a bimol. velocity coeff. and is but little influenced by excess of alkali or by Na_2SO_4. F. L. USHER.

Nitric acid. VII. Velocity of absorption of oxygen in the highly concentrated system HNO_3–NO_2–H_2O. A. KLEMENC and J. RUPP (Z. anorg. Chem., 1931, **198**, 57—68).—Precise measurements of the velocity of absorption of O_2 are difficult to obtain, since even with highly efficient stirring apparatus the velocity increases with the rate of stirring. With increase of the HNO_3 content of the system above 63% the velocity at 0° diminishes rapidly, and becomes zero at 79% HNO_3. Whereas the diffusion coeff. of O_2 into the system approx. doubles between 0° and 10°, the oxidation velocity increases tenfold. H. F. GILLBE.

Kinetics of decomposition of ammonia on copper. J. K. DIXON (J. Amer. Chem. Soc., 1931, **53**, 1763—1773; cf. A., 1927, 118).—The decomp. of NH_3 in presence of H_2 and N_2 on Cu sintered at 700° has been investigated by a dynamic method in the range 495—620°. The rate of decomp. varies directly as the partial pressure of NH_3 (4—50 cm.) and inversely as that of H_2 (10—60 cm.). The velocity coeff. increases with total rate of flow. The energy of activation is computed to be 46,000±2000 g.-cal. from the temp. coeff. Static experiments confirm that the rate of reaction is independent of the pressure of N_2 and varies as the reciprocal of the pressure of H_2. Formation of copper nitride could not be detected. Traces of CO retarded the decomp., but further quantities had smaller effects. Objections to the use of heats of adsorption in calculating true heats of activation of heterogeneous reactions are discussed.

J. G. A. GRIFFITHS.

Role of ions and crystallographic transformations in reactions in the solid state. J. A. HEDVALL, E. GARPING, N. LINDEKRANTZ, and L. NELSON (Z. anorg. Chem., 1931, **197**, 399—421).—The extent of the reaction between BaO and AgCl or AgI increases very slowly with rise of temp. up to about 320°, when it increases abruptly and rapidly; about 66% conversion takes place at 360°. The effect is attributed to the sudden increase of the ionic conductivity of the halides which occurs in this region of temp. The course of the reaction between BaO and AgI, which commences at about 146°, is more complex and is closely related to the transition to the regular form of the AgI. BaO and TlF at 110° react to a small extent (8%), which does not increase until the temp. exceeds about 150°. CaO and $NiCl_2$ react slowly at 70°, and there is a sharp rise in the reactivity–temp. curve at 340°. The part played by ionic deformation in the opening up of a lattice is discussed in the light of these and earlier results. H. F. GILLBE.

Dependence on temperature of catalysed consecutive reactions. H. DOHSE (Z. physikal. Chem., 1931, B, **12**, 364—368; cf. A., 1930, 1003).—Theoretical. Assuming that in a reaction $A \longrightarrow B \longrightarrow C$ which takes place at a solid catalyst A and B are strongly adsorbed compared with C, and that the individual reactions are unimol., Arrhenius' equation can be used to give the relation between velocity of reaction and temp. By combining the straight lines log (rate)–$1/T$ for the separate reactions, a curve similar to that observed in the decomp. of MeOH on ZnO is obtained. F. L. USHER.

Induced oxidation. W. P. JORISSEN (Natuurwetensch. Tijds., 1931, **13**, 137—138).—In presence of Na_2SO_3 as inductor sodium antimonite, indole, mannitol, and pyramidone react in buffered solutions with a quantity of O equal to that taken up by the inductor. With certain other acceptors a greater quantity of O reacts than can be accounted for by the inductor; such are Na_2PO_3, PrOH, glycol, *cis*- and *trans-cyclo*hexanediol, inositol, sodium potassium tartrate, glycerol, erythritol, lævulose, sucrose, and bismuthyl potassium bismuthyltartrate. In these cases the extent of the induced oxidation appears to vary with the [H˙] of the solution, and with glycerol and lævulose the induced oxidation exceeds 100%, an effect which is ascribed to autoxidation.

H. F. GILLBE.

Action of hydrogen cyanide on the catalytic action of manganese. O. WARBURG (Biochem. Z., 1931, **233**, 245).—Cysteine in borate buffer solution (p_H 9·5) is oxidised in air in presence of small amounts of Mn. The catalytic action of Mn, but not that of Fe, is inhibited by cyanide when the molar concentration of the latter is 200 times that of the Fe or Mn. A very large excess of cyanide (above 20,000 times) inhibits the catalysis by Mn. P. W. CLUTTERBUCK.

Reciprocal action of alcohol and some chloroplatinates. C. G. MAKRIS (J. Pharm. Chim., 1931, [viii], **13**, 569—570).—Reduction of Na_2PtCl_6 is initiated by the presence of traces of actaldehyde present in EtOH and Pt is formed. EtOH is oxidised by Na_2PtCl_6 producing more acetaldehyde, and decomp. is accelerated until all the Pt is liberated as metal. E. H. SHARPLES.

Preparation of copper–chromium oxide catalysts for hydrogenation. R. CONNOR, K. FOLKERS, and H. ADKINS (J. Amer. Chem. Soc., 1931, **53**, 2012; cf. this vol., 598).—Inactivation of the catalyst in the hydrogenation of ethyl phenylacetate is prevented by replacing 10% of the Cu in the catalyst with Ba.

J. G. A. GRIFFITHS.

Decomposition of hydrogen peroxide in presence of active carbon and other adsorbents. K. SKUMBURDIS (Kolloid-Z., 1931, **55**, 156—164).—Experiments on the decomp. of H_2O_2 and on the adsorption of *iso*amyl alcohol in H_2O by active and inactive C fail to show any general relation between catalytic activity and adsorptive capacity. The alkalinity or acidity of adsorbents has little influence on the decomp. of H_2O_2, but dehydration of the adsorbent causes a rapid decomp. of H_2O_2 through the heat of wetting. The decomp. is inhibited by adding capillary-active substances, such as *iso*amyl alcohol, but there is no general relation between this effect and the degree of adsorption of the capillary-active substance. The addition of *iso*amyl alcohol above a certain concentration has no further effect, suggesting

the formation of a unimol. adsorption layer. Hydrophilic colloids and catalyst poisons inhibit the catalytic decomp., an exception in the case of KCN being due to the decomp. effect of KOH. Solutions of dyes have a stabilising effect on H_2O_2. The simultaneous addition of H_2O_2 and charcoal to raw sugar solutions effects a more rapid and complete decolorisation than is obtained by H_2O_2 or C alone, and without measurable loss of sucrose. E. S. HEDGES.

Decomposition of water vapour on carbon containing activating substances. B. NEUMANN, C. KROGER, and E. FINGAS (Z. anorg. Chem., 1931, **197**, 321—338).—The production of water-gas from graphite and steam is catalysed strongly by CuO; the reaction commences at 420° and proceeds to completion at 871°. In presence of oxides of Cr, U, Al, and K the reaction commences at 579°, 623°, 632°, and 550°, respectively; with Cr_2O_3 only one half the quantity of CH_4 is produced compared with that obtained with other catalysts. The percentage conversion in presence of K_2O (added as K_2CO_3) rises very rapidly with the temp., and the reaction is almost complete at 774°; the CO_2 content of the mixture attains a max. (44%) at 685°, and falls to 3% at 774°, whilst the CH_4 content is almost const. from 674° to 774°. Whereas in presence of CuO and U_3O_8 the ratio $CO_2:CO$ changes rapidly with rise of temp., in presence of Al_2O_3, Fe_2O_3, and Cr_2O_3 the ratio is almost const., although much greater than in absence of a catalyst. The theoretical aspect of the results is discussed. The activity of Fe_2O_3 and CuO depends on the production and removal of lower oxides and that of U_3O_8 on the dissociation of the oxide and subsequent formation of U_2C_3. Since a similar explanation cannot apply to Cr_2O_3 and Al_2O_3, it is suggested that the reaction in these cases takes place between the C and the H_2O adsorbed on the surface of the catalyst. The activity of K_2CO_3 at lower temp. is ascribed to the formation of K_2O by the action of H_2O, the reaction taking place between the C and adsorbed H_2O, whilst at higher temp. the lowering of the dissociation pressure of the K_2CO_3 by graphite becomes important.

H. F. GILLBE.

Production of nitric acid by the oxidation of ammonia. J. FAUSER.—See B., 1931, 535.

Catalytic reduction of carbon monoxide to methane in mixtures of carbon monoxide and hydrogen and in illuminating gas in presence of nickel-asbestos. H. A. J. PIETERS.—See B., 1931, 523.

Oxide hydrates and active oxides. XLI. Relation between the previous history of zinc oxide and its catalytic activity in the decomposition of methane. G. F. HÜTTIG, O. KOSTELITZ, and I. FEHÈR. **XLII. Relation between the previous history of zinc oxide and its power of adsorption for organic dyes.** G. F. HÜTTIG and W. NEUSCHUL (Z. anorg. Chem., 1931, **198**, 206—218, 219—232).—XLI. The normal catalytic activity, ϕ (cf. this vol., 692), of specimens of ZnO, prepared and treated by a variety of methods, has been determined. Samples formed by thermal decomp. of, *e.g.*, $ZnCO_3$ yield a relatively high val. of ϕ (>0·9). With rise of the temp. of prep. ϕ falls, and the introduction of impurities or compression of the material into pellets produces the same effect. Three principal types of ZnO are recognised: the cryst. forms, of which the activity characteristics are most clearly defined in the freshly-prepared material, and which on ageing all tend to the stable cryst. form; forms prepared by decomp. of amorphous compounds, which initially show no mol. orientation; and forms produced by direct oxidation. Specimens of ZnO which exhibit selective catalytic activity belong principally to the first type, whereas those of high but general activity are of the two latter types.

XLII. The selectivity of the adsorptive activity of various specimens of ZnO has been determined by measuring the adsorption from solution of a number of dyes. All specimens prepared thermally from $ZnCO_3$ at temp. below 300° exhibit the same type of selectivity as basic $ZnCO_3$, but with specimens prepared at 400° the influence of accelerated ageing becomes evident and the adsorption characteristics tend towards those of the completely aged cryst. form. The selective behaviour of ZnO prepared by precipitation from hot and cold solutions is described. The results demonstrate that the adsorption characteristics of a substance are determined by factors other than those responsible for its behaviour as a catalyst, and suggest that catalytic reactions are not confined to the surface of the catalyst. Details are given of the adsorption characteristics of a number of metallic oxides and minerals and of the variations of the adsorptive power of $Al_2O_3,4H_2O$ on progressive ageing (dehydration). The freshly-prepared material adsorbs acidic dyes very strongly, and basic dyes inappreciably, but when its composition corresponds with that of bayerite the adsorption is almost completely non-selective; when the composition approaches that of hydrargillite the nature of the adsorption is determined mainly by purely chemical constitutional factors. H. F. GILLBE.

Synthesis of methyl alcohol, using copper, zinc oxide, and chromic oxide as catalysts. V. A. PLOTNIKOV, K. N. IVANOV, and D. A. POSPECHOV.—See B., 1931, 530.

Determination of the course of heterogeneous catalyses by measurement of the resistance to direct current of metal powders during the process. (FRL.) L. REICHARDT (Z. Elektrochem., 1931, **37**, 289—306).—When powdered Ni, Cu, or Ag is used to catalyse the reduction of $PhNO_2$ vapour to aniline by H_2 its resistance increases considerably during the reaction, whereas in the reduction of C_6H_6 to *cyclo*hexane the resistance of the Ni catalyst rises only slightly. The resistance of Ni powder is scarcely altered by aniline or *cyclo*hexane vapour, but is greatly increased by slight oxidation. It is therefore concluded that in the reduction of $PhNO_2$ oxidation of the metal according to such a scheme as $PhNO_2+H_2=PhNOH+OH$, $PhNOH+H_2=PhNH_2+OH$, followed by reaction of OH with the metal, or $PhNO_2+H_2+Cu=PhNHOH+CuO$, $PhNHOH+H_2=PhNH_2+H_2O$ is involved, whereas the reduction of C_6H_6 is dependent on adsorption and capillary condensation. This accounts for the

relative readiness with which catalysts for the hydrogenation of hydrocarbons are poisoned.
R. CUTHILL.

Activation by charcoal. W. D. BANCROFT and S. F. WHEARTY, jun. (Proc. Nat. Acad. Sci., 1931, **17**, 181—183).—Purified activated charcoal can cause the formation of ring substitution products from C_6H_6 and toluene and Cl_2. Certain wave-lengths in the ultraviolet produce similar results. C. W. GIBBY.

Liquid partial oxidation. II. R. D. SNOW and D. B. KEYES (Ind. Eng. Chem., 1931, **23**, 561—562; cf. A., 1930, 170).—Experiments were made on the oxidation, by O_2, of liquid EtOH at atm. pressure at 72° in presence of a number of catalysts. In one case only (with cerium oxide in presence of alkali) the oxidation proceeded as far as AcOH. The experiments at 100° and 170 lb. per sq. in. yielded AcOH as well as MeCHO. H. INGLESON.

Conversion of cyanide solution into potassium ferrocyanide and the oxidation of the latter by compressed air and electrolysis. W. GLUUD and others.—See B., 1931, 586.

Electrodeposition of cobalt–nickel alloys. II. S. GLASSTONE and J. C. SPEAKMAN.—See B., 1931, 592.

Electrolysis of phosphate melts. I. Electrolytic preparation of α- and β-tungsten. H. HARTMANN, F. EBERT, and O. BRETSCHNEIDER (Z. anorg. Chem., 1931, **198**, 116—140).—Pure W cannot be obtained by electrolysis of a solution of WO_3 in molten alkali metaphosphates, but by addition of pyrophosphate to the bath, or by using a solution of WO_3 in $Na_4P_2O_7$, pure W separates at 650—700°. The *X*-ray diagram of the product indicates the presence of a new cubic modification of W; *a* 5·04 Å., 8 at. in the unit cell; the existence of this β-form has been confirmed by chemical and thermal methods. The β-W is slowly and irreversibly converted into α by heating at 650°; it has $d_{calc.}$ 19·0, $d_{obs.}$ 12·3, the discrepancy being attributed to the extreme smallness of the particle size. The mechanism of the electrolysis is discussed. H. F. GILLBE.

Lassieur's method of rapid electrolysis. J. GILLIS (Natuurwetensch. Tijds., 1931, **13**, 113—117).—A description of the method, with details of suitable apparatus. H. F. GILLBE.

Rare earths. XXXVII. Electrolytic preparation of rare-earth amalgams. I. Lanthanum and neodymium. L. F. AUDRIETH, E. E. JUKKOLA, and R. E. MEINTS [with B. S. HOPKINS] (J. Amer. Chem. Soc., 1931, **53**, 1805—1809).—Electrolysis, with a mercury cathode, of the anhyd. halides or the monohydrates in alcoholic solution affords better results than in aq. solutions. The amalgams are very reactive and afford free Nd and La when heated in a vac. Amalgam formation did not occur with the *compound* $Nd(NO_3)_3,NH_4NO_3$ as solute.
J. G. A. GRIFFITHS.

Processes in the solution and the gas space in electrolysis by the glow discharge. A. KLEMENC and H. F. HOHN (Z. physikal. Chem., 1931, **154**, 385—420; cf. A., 1928, 30).—The action of a glow discharge on various electrolyte solutions has been studied, using a Wehnelt cathode, and with the anode either in the solution or in the gas space. The observed effects are separable into apolar and polar, the latter conforming with Faraday's laws and the former being operative both in the liquid and the gas space. The total chemical effect is in excess of the Faraday equiv. and is produced in part by radiation of short wave-length. The chemical changes brought about by the apolar process are often different from those effected by ordinary electrolysis. Electrolytic gas is formed in the gas space, whilst in the solution either oxidation or reduction may occur. $HClO_4$ is reduced with ease, $Fe_2(SO_4)_3$ with difficulty. Reducible metals are precipitated as oxides of indefinite composition. The radiation responsible for the apolar effects is deflectable by a magnet. F. L. USHER.

Triatomic hydrogen. J. L. BINDER, E. A. FILBY, and A. C. GRUBB (Canad. J. Res., 1931, **4**, 330—343; cf. A., 1930, 1085).—H_2 free from O_2 may be activated by a vac. discharge if the walls of the vessel are poisoned by stearic acid. H_2 containing 1% O_2 is activated by the corona discharge at 1 atm. and by a vac. discharge at 20—80 mm. Fatigue is related to the O content and to the surface condition of the tube. Plastic S is a better reagent than flowers of S for detecting activation. An explanation of discrepancies in previous work is suggested.
C. W. GIBBY.

Formation of hydrocyanic acid in the electric discharge. K. PETERS and H. KÜSTER.—See B., 1931, 536.

Electrical cyanogen synthesis. K. PETERS (Naturwiss., 1931, **19**, 402—403).—It is possible to convert a mixture of 4 parts of CO and 1 part of N_2 quantitatively into C_2N_2 by an electrical method.
A. J. MEE.

Cathodic projection of elements, and some applications. I. F. JOLIOT (Ann. Physique, 1931, [x], **15**, 418—436; cf. A., 1930, 531).—A *resume* of methods used for the production of thin films by cathodic sputtering. The application of the method to the prep. of photographic plates without emulsion, and to the construction of a bolometer of high sensitivity and low inertia, is given. A. J. MEE.

Photosensitivity and the periodic system. T. PAVOLINI (Ind. Chimica, 1930, **5**, 1107—1115; Chem. Zentr., 1931, i, 1243).—The distribution of elements affording photosensitive compounds is discussed.
A. A. ELDRIDGE.

Energy-emission data of light sources for photochemical reactions. C. E. GREIDER (Ind. Eng. Chem., 1931, **23**, 508—511).—Curves for the spectral energy distribution are given for a number of types of C arc. These include Ce, Ca, Co, and Sr cored as well as plain C arcs. The spectral distribution of the energy emitted from the centre of a 13·6-mm. arc burning 125 amp. at 80 volt. d.c. closely resembles that from the sun; the chief difference between these sources is the radiation shorter than 2900 Å. which is present in the arc but absent from sunlight at the earth's surface. Various applications of the arcs are discussed. H. INGLESON.

Photosensitised explosion of hydrogen–oxygen mixtures in the presence of chlorine. R. G. W.

NORRISH (Nature, 1931, **127**, 853—854).—At 300° there is a sharp limiting pressure of Cl_2 above which an almost instantaneous and quant. explosion of H_2 and O_2 occurs when the mixed gases ($2H_2+O_2$) are exposed to light from a Hg lamp. Below the limit H_2 and Cl_2 unite rapidly with the formation of only a trace of H_2O. The H_2-O_2 explosion can be sensitised to room temp. by increasing the pressure of Cl_2 which is approx. proportional to the total pressure of the system. The explosions, which appear to be connected with a Draper effect, are not complete at the lower temp. L. S. THEOBALD.

Photochemical interactions of hydrogen with chlorine and bromine. D. L. CHAPMAN and F. B. GIBBS (Nature, 1931, **127**, 854).—A brief discussion. L. S. THEOBALD.

Absorption spectrum and photochemical decomposition of hydrogen iodide. G. K. ROLLEFSON and J. E. BOOHER (J. Amer. Chem. Soc., 1931, **53**, 1728—1732).—Continuous absorption extends to 4000 Å. Dissociation by light of wave-lengths greater than 3120 Å. affords normal atoms, whilst with shorter wave-lengths the I atom is excited. The mechanism of the decomp. is essentially the same at all effective wave-lengths. J. G. A. GRIFFITHS.

Influence of wave-length on the photochemical reaction between ethylene iodide and iodine. H. J. SCHUMACHER and I. STIEGER (Z. physikal. Chem., 1931, **B**, **12**, 348—352; cf. this vol., 180).—The quantum yield in the above reaction in the band region at wave-lengths 546 and 578 $m\mu$ is about 1/6 of that in the continuous region at 436 $m\mu$. F. L. USHER.

Physical and chemical action of ultra-violet light on sublimed sulphur. Action of sulphur on *Oidium*. FONZES-DIACON (Bull. Soc. chim., 1931, [iv], **49**, 530—533).—The formation of SO_2 from S under the influence of the ultra-violet rays of sunlight occurs so slowly that it appears probable that the fungicidal action of S towards *Oidium* is due rather to S vapour than to SO_2 or $H_2S_5O_6$. R. CUTHILL.

Separate [processes in] ripening. II. LUPPO-CRAMER (Z. wiss. Phot., 1931, **30**, 7—12; cf. this vol., 579).—The production of a fine-grain emulsion by increase of the gelatin concentration at emulsification is illustrated by photomicrographs; large excess of bromide prevents the effects of the gelatin. Previous work is confirmed. A pure bromide emulsion possesses large well-formed crystals; the presence of iodide checks the growth of the grains. The courses of ripening of emulsions with and without iodide are compared. J. LEWKOWITSCH.

Theory of the latent image. W. GRAMSE (Z. wiss. Phot., 1931, **30**, 40—44).—Experiments are detailed of the action in the dark of gaseous Br on gelatin films, alone or containing KI, P, Ag_2S, or Sb_2O_3 as catalyst. The hardening action is accelerated if Na_2CO_3 or $CaCO_3$ is also added in the film. Cl_2 has no action on such films in the dark. The bearing on the theory of halogen acceptance is discussed. J. LEWKOWITSCH.

Nature of the latent image for physical development. I. H. ARENS (Z. wiss. Phot., 1931, **30**, 49—64; cf. Tollert, A., 1929, 522).—The free Ag (primary, latent image, or developed), grain distribution, and hence grain wt. have been determined in fixed undeveloped and physically developed plates. The results are plotted against exposure and discussed in detail with regard to theories of the latent image in relation to developability. J. LEWKOWITSCH.

Photochemical colour reaction between cyanamide and ferrocyanide. G. H. BUCHANAN and G. BARSKY (Z. angew. Chem., 1931, **44**, 383—385).—The reversible photochemical colour reaction observed in alkaline solutions containing ferrocyanide and cyanamide involves the formation of a complex ion, $[Fe(CN)_5,H_2CN_2]'''$, from the $Fe(CN)_5'''$ ion, produced photochemically and reversibly, and the cyanamide mol. The coloration is not produced by the decomp. products of cyanamide or by related compounds, and in presence of H_2O_2 or CH_2O it does not fade in the dark, although it is not formed without exposure to light. H. F. GILLBE.

Fastness to light of azo-colours. J. S. P. BLUMBERGER (Chem. Weekblad, 1931, **28**, 310—313).—A survey. Examples are given of the increased stability to light effected by the acetylation of active groups, such as NH_2 and OH, and by the introduction of electronegative groups; the role of complex formation in the protection of OMe groups by treatment of the dye with $CuSO_4$ is discussed. H. F. GILLBE.

Photographic effects of vitamins-*A* and -*B*. S. BOTCHARSKY and A. FOEHRINGER (Nature, 1931, **127**, 856).—Extracts of these vitamins give clear images when painted on a photographic plate. Differences in strength are made apparent. L. S. THEOBALD.

Antirachitic activation of ergosterol by soft *X*-rays. E. SHELOW and J. R. LOVFBOUROW (Bull. Basic Sci. Res., 1931, **3**, 47—64).—Ergosterol was activated by irradiation with soft *X*-rays; absorption spectra and animal experiments are described. The effect of irradiation of the solvent, and the possibility of glass containers affording ultra-violet fluorescence radiations, are considered. CHEMICAL ABSTRACTS.

Radiochemical decomposition and synthesis of hydrogen bromide. R. GILLEROT (Bull. Soc. chim. Belg., 1930, **39**, 503—517).—The relationship between the number of HBr mols. formed per ion pair produced in the gas mixture by the radiation (M/I) and the composition of the reactant gas has been studied. The M/I-composition curve passes through a max. value of 2·9 at a H concentration of about 15%. In the radiochemical decomp. of HBr the number of HBr mols. decomposed per ion pair is independent of the intensity of the radiation. The decomp. is also uninfluenced by a small quantity of Br. J. W. SMITH.

Sodium oxide. E. ZINTL and H. H. VON BAUMBACH (Z. anorg. Chem., 1931, **198**, 88—101).—Pure Na_2O free from Ni, $NaNO_3$ and peroxide, may be prepared by heating NaN_3 with $NaNO_2$ or, preferably, $NaNO_3$, in a Ni vessel; the reaction is smooth and is easy to control by regulating the temp. The method is not applicable to K_2O, as the eutectic mixture of KN_3 and KNO_3 is relatively stable and attacks the

vessel. Na_2O forms cubic face-centred crystals, with 4 mols. in unit cell; *a* 5·55 Å, $d_{calc.}$ 2·39. In O_2 at 150 mm. pressure Na_2O does not react below 150°, and several weeks are necessary for the complete formation of Na_2O_2 at 250°; at 12 atm. the reaction is rapid at 200°. Cl_2 reacts very slowly at room temp., but at 120—160° a rapid reaction takes place, with formation of NaCl and Na_2O; NaOCl is formed, if at all, only as an intermediate product. NO does not react at room temp., but at 100° a vigorous and intensely exothermic reaction occurs, with the production, probably by thermal decomp. of Na_2NO_2, of $NaNO_2$ and $Na_2N_2O_2$. Details are given of the prep. of $Na_2N_2O_2$ of 99% purity. H. F. GILLBE.

Polysulphides of the alkali metals. III. Potassium. T. G. PEARSON and P. L. ROBINSON (J.C.S., 1931, 1304—1314; cf. this vol., 443).—A re-examination and extension of previous investigations (cf. J.C.S., 1914, **105**, 2821; 1917, **111**, 1071). From solutions of S in aq. or aq.-alcoholic solutions of K_2S there separate $K_2S_2,3H_2O$, K_2S_3, $K_2S,2H_2O$, $K_2S_4,3H_2O$, and K_2S_5,H_2O, but from abs. EtOH solution only K_2S_3 or K_2S_5 crystallises. Reaction of S with molten K yields K_2S_4. Measurements of the rate of desulphurisation of the polysulphides in N indicate the existence of K_2S_5, K_2S_4, K_2S_2, and possibly K_2S_3. R. CUTHILL.

Decomposition of alkali chlorides at high temperatures. F. C. GUTHRIE and J. T. NANCE (Trans. Faraday Soc., 1931, **27**, 228—233).—Alkali chlorides can be dried without decomp. in a slow current of dry or moist air below their m. p. Above the m. p. the salts become alkaline, the effect being greatest with Li and least with Cs. At high temp. the predominant factor is the concentration of H_2O in the gas used, but some decomp. occurs even in air or O_2 which has been intensively dried. F. L. USHER.

Complex ammonium, potassium, and sodium cuprothiosulphates. III. G. SPACU and I. G. MURGULESCU (Bul. Soc. Stiinte Cluj, 1930, **5**, 344—370; Chem. Zentr., 1931, i, 1426).—The course of the titration of $Cu(NO_3)_2$ solutions with $Na_2S_2O_3$ was followed potentiometrically. In solutions up to *M*, tetrathionate is formed. The salts $Na_5[Cu_7(S_2O_3)_6],8H_2O$ and $Na[Cu(S_2O_3)],1·5H_2O$ were obtained. Further titration of $NaCuS_2O_3$ at various temp. with $Na_2S_2O_3$ indicated the formation of $Na_2[Cu_2(S_2O_3)_3],xH_2O$ and $Na_5[Cu(S_2O_3)_3],xH_2O$, but neither substance was obtained cryst. Titration of a solution containing 1 mol. of $NaCuS_2O_3,1·5H_2O$ and 2 mols. of $NaNO_3$ with $3M$-$Na_2S_2O_3$ indicated the formation of $Na_3[Cu(S_2O_3)_3]$, and the compound $Na_3[Cu(S_2O_3)_3],2NaNO_3$ was isolated. Cl′ or Br′ may substitute NO_3'. A. A. ELDRIDGE.

Calcium sulphate hydrates. F. KRAUSS and G. JORNS (Tonind.-Ztg., 1930, **54**, 1467—1468, 1483—1484; Chem. Zentr., 1931, i, 1257).—The hemihydrate is formed from gypsum at a lower temp. than is the anhyd. salt from the hemihydrate. In the prep. of the hemihydrate the material should be heated to the decomp. temp. of the gypsum and then rapidly cooled to the transition temp. of the hemi- and di-hydrates. A. A. ELDRIDGE.

Nitride theory of the formation of calcium cyanamide from calcium carbide. H. H. FRANCK and C. BODEA (Z. angew. Chem., 1931, **44**, 379—382).—Commercial electrolytic Ca exhibits a max. in the N_2 absorption–temp. curve at about 440°, and a second, much higher, max. at 910°, *i.e.*, in the neighbourhood of the m. p.; after remelting, the metal yields only a sharp max. at about 460°, and after redistillation only the max. at 910°. At all temp. above and below the peaks the absorption is in all cases practically zero. It is suggested that neither α-Ca nor β-Ca reacts readily with N_2, but that reaction occurs during the transition, for which the optimum temp. is 400°; this view is supported by the observed influence of Na and Li (present in the commercial metal) in increasing the reactivity by virtue of their favouring the opening up of the Ca lattice. The primary reaction between Ca_3N_2, C, and N_2 at 800—1100° yields CaC_2, which then reacts with N_2 to form $CaCN_2$; when Ca_3N_2 is heated with C in a vacuum at 900° the pressure at first rises and then falls to its initial value, and the product contains CaC_2 56·9, $CaCN_2$ 31·1, Ca_3N_2 4·3%. The theory that Ca_3N_2 is an intermediate product of the commercial manufacture of $CaCN_2$ from CaC_2 is thus untenable. H. F. GILLBE.

Formation of dicyanogen from calcium cyanamide. H. HEIMANN (Z. angew. Chem., 1931, **44**, 378—379).—By assuming, from analogy with the halogens, a val. of 3·8 for the chemical const. of C_2N_2, the val. of log K_p for the reaction $CaO+(CN)_2 \longrightarrow CaCN_2+CO$ at 1100° abs. is −6·1, corresponding with a C_2N_2 concentration of only 10^{-4} vol.-%. If, however, a mixture of CS_2 vapour and N be passed over pure $CaCN_2$ at 700—850°, C_2N_2 is liberated according to the reaction $CaCN_2+CS_2 \longrightarrow CaS+S+C_2N_2$; the heat effect of the reaction is −21·3 g.-cal. If commercial $CaCN_2$, containing CaO, is employed, COS and CO_2 are evolved. H. F. GILLBE.

Preparation of pure calcium and magnesium cyanamides, and the equilibria $CaO(MgO)+2HCN \rightleftharpoons CaCN_2(MgCN_2)+CO+H_2$. H. H. FRANCK and H. HEIMANN (Z. angew. Chem., 1931, **44**, 372—378).—CaO and HCN react slightly at room temp., whilst at 350° the product contains 35% $Ca(CN)_2$; at higher temp. the cyanide-N content diminishes, owing to decomp. of the $Ca(CN)_2$ into $CaCN_2$. Pure $CaCN_2$ may be prepared by heating $Ca(CN)_2$ at 600° in N_2; by heating the product with C at 1050° in vac. a white CaC_2 of 95% purity may be prepared, the impurities being only $CaCN_2$ (2—3%) and CaO. The equilibrium of the reaction between CaO and HCN has been investigated at temp. between 983° and 1143°; log K_p falls from −3·1 at 900° to −1·8 at 1170°. Extreme variations of the composition of the solid phase cause a considerable change in the isothermal K_p values. The heat effect of the reaction is about 19·1 g.-cal., and the chemical const. of HCN is 3·5, in accordance with the values for the halogens; earlier determinations (2·79—4·2) are apparently not applicable to the temp. range concerned. For the reaction between MgO and HCN log K_p rises from 0·5 at 900° to 0·9 at 1100°, and is in moderate agreement with the calc. chemical const. of

HCN. The mechanism of the reactions involved are discussed in detail. H. F. GILLBE.

Nitrogenation of [formation of calcium cyanamide from] calcium carbide. A. COCHET (Z. angew. Chem., 1931, **44**, 367—372).—A compensation balance method and apparatus for the investigation of heterogeneous reactions at high temp. are described; the results are obtained with greater rapidity and are of higher accuracy than those derived from v.-p. measurements. Equilibrium in the system CaC_2–N_2–C–$CaCN_2$ at temp. from 1220° to 1390° is bivariant. The third phase, *i.e.*, in addition to C and N, must be a solution of CaC_2 in $CaCN_2$; this solution is the true reactant, and its concentration is a determining factor of the equilibrium. The reaction up to at least 1325° is completely reversible and is $CaC_2+N_2 \rightleftharpoons CaCN_2+C$, but at 1400° the $CaCN_2$ decomposes with loss of Ca and N : $CaCN_2+C \longrightarrow Ca+N_2+2C$; at 1600° the whole of the Ca present as $CaCN_2$ volatilises. This second reaction takes place to a certain extent in the technical process, and oxidation of retained Ca provides the large quantity of CaO found in commercial $CaCN_2$. The curve showing the relation between the equilibrium temp. and the N content of the $CaCN_2$ formed, at 1 atm., has been determined for the interval 1050—1500°. At 1120—1130° $CaCN_2$ containing 29% N is stable, but with rise of temp. to 1200° the N content falls rapidly to about 21%; at higher temp. it falls relatively slowly, and at 1500° is 17·5%. H. F. GILLBE.

Calcium meta-arsenite. A. N. KRESTOVNIKOV and G. F. LUTRINGSGAUSER (Min. Ssyrje, 1930, **5**, 870—872; Chem. Zentr., 1931, i, 1257).—The interaction of As_2O_3, finely divided $Ca(OH)_2$, and H_2O is effected at 100° with vigorous stirring. The product is amorphous; solubility in H_2O at 15°, 0·04—0·05%. A. A. ELDRIDGE.

Millon's reagent. M. T. KOKS (Pharm. Weekblad, 1931, **68**, 557—570).—Various official methods of preparing the reagent, which differ very considerably, are described and criticised, and the reactions which take place on dissolution of the Hg are discussed. The prep. of a solution which consists principally of $Hg(NO_3)_2$, but gives also a strong reaction for NO_2', is described; this reagent gives definite reactions with tyrosine (1 : 100,000), carbamide, and peptone, and a red coloration with urine, which is ascribed to the presence of compounds such as phenols and aromatic hydroxy-acids. An account is given of various other applications of the reagent. H. F. GILLBE.

Behaviour of Millon's base. A. BERNARDI and M. A. SCHWARZ (Gazzetta, 1931, **61**, 178—188).—Moist Millon's base prepared according to Proust's method was treated with various reagents. (*a*) Trichloroacetic acid caused the breakage of the mol. structure with formation of $HgCl_2$, HgCl, HgO, and NH_4Cl. The compound $5Hg_2NCl,NH_4Cl$ was formed as intermediate. (*b*) With Ac_2O it forms $Hg(OAc)_2$. The formation of NH_2Ac is probable, but in presence of moisture it is converted into NH_4OAc. (*c*) AcCl reacts vigorously with the base suspended in EtOH, giving $HgCl_2$ and $3HgCl_2,2NH_4Cl$. (*d*) BzCl forms $HgCl_2$, NH_4Cl, and a compound HgNCl. (*e*) Benzyl chloride reacts with the base suspended in EtOH. The compound $3HgO,HgCl_2$, NH_3, and dibenzylethylamine are formed. (*f*) Equimol. quantities of the base and various phenols were heated at a temp. corresponding with the m. p. of the phenol and stable additive *compounds*, $X,Hg_2O_2NH_3$, were obtained. Phenol gives a yellow compound; *o*- and *p*-nitro- and 2 : 4-dinitro-phenol produce compounds ranging in colour from yellow to orange and brown. The difference in colour does not indicate a change in composition. (*g*) NH_2Ac fused in the same manner gave a pale yellow additive *compound*, $Ph{\cdot}NHAc,Hg_2O_2NH_3$. O. F. LUBATTI.

Reaction between hydrogen sulphide and mercury. A. L. ROBERTS (J. Amer. Chem. Soc., 1931, **53**, 1810—1811).—Pure H_2S does not react with Hg until a trace of moist air is added (cf. A., 1930, 556). P_2O_5 free from lower oxides does not react with H_2S. J. G. A. GRIFFITHS.

Homogeneous and heterogeneous complex salts in solution. II. G. SPACU and P. SPACU (Bul. Soc. Stiinte Cluj, 1930, **5**, 387—420; Chem. Zentr., 1931, i, 1425—1426).—The following *compounds* were prepared: $[HgI_3SCN]Cu\ en_2$, $[Hg(CN)_2(SCN)_2]Ni\ en_2$, $[Hg(CN)_2CNO]_2Cu\ en_2$, $[HgBr_4]Ni\ en_3$, $HgBr_4[Co\ en_3]Br$, $[HgBr_3]_2Zn\ en_3$, $[HgCl_3]_3Co\ en_3$, $[HgCl_4]_3[Co\ en_3]_2$, $HgI_3[Co\ en_2\ Cl_2]_6$, $HgI_3[Co\ en_2\ Cl_2]_2$, $[HgI_3]_2Hg\ en_2$, $HgI_4[Cr\ en_3]I$, $[HgI(CN)_2]_2Cu\ en_2$, $[CdClI_3]Cu\ en_2$, $[CdBrI_3]Cu\ en_2$, $[CdI_4]Cd\ en_2$, $[CdI_4]Zn\ en_2$, $[CdI_4]Hg\ en_3$, $[CdI_4][Cr\ en_3]I$, $[CdBr_4]Cu\ en_2$, $[CdBr_4]Ni\ en_3$, $[CdBr_4]Cd\ en_2$, $[CdCl_4]Ni\ en_3$, $[CdCl_4]Cd\ en_2$, $[CdI_3SCN]Cu\ en_2$, $[CdI_3SCN]Ni\ en_3$, $[AgI_2]_2Cu\ en_2$, $[AgI_2]_2Ni\ en_3$, $[AgI_2]_2[Co\ en_3]I$, $[AgI_2]_2Zn\ en_3$, $[AgI_2]_2Cd\ en_2$, $[BiI_4]_2[Cr\ en_3]Cl$, $[CuCl_4]Cu\ en_2$, $[CuBr_4]Cu\ en_2$, $[CuI_4]Cu\ en_2$. The complexes $[HgCl_4]Hg$ and $[CdI_4]Cd$ are considered to be present in the mercurichloride and cadmium iodide solutions. A. A. ELDRIDGE.

New class of ammines. Double selenocyanatoammines. G. SPACU and V. ARMEANU (Bul. Soc. Stiinte Cluj, 1930, **5**, 294—318; Chem. Zentr., 1931, i, 1425).—The following *compounds* were prepared: $[Hg(SeCN)_4][Cu\ en_2]$, $[Hg(SeCN)_4][Ni(Cd,Zn)\ en_3]$, $[Hg(SeCN)_3][Co\ en_3]SeCN$, $[Ag(SeCN)_2]_2[Cu\ en_2]$, $[Ag(SeCN)_2]_2[Ni\ en_2]$, $[Ag(SeCN)_2]_2[Cd\ en_2]$, $[Ag(SeCN)_2]_2[Zn\ en_2]$, $[Ag(SeCN)_2]_3[Co\ en_3]$. Selenocyanatoammines are more labile and less sol. in H_2O than the corresponding thiocyanato-compounds. A. A. ELDRIDGE.

Composition of cyanide complex radical of metals. III. Zinc cyanide complex radical. K. MASAKI (Bull. Chem. Soc. Japan, 1931, **6**, 89—94).—The titration method previously used (this vol., 581) shows the complex ions formed when excess of NaCN is added to a solution of a Zn salt to be $Zn(CN)_3'$ and $Zn(CN)_4''$, the stability constants of which, as evaluated by the e.m.f. method, are $2{\cdot}1\times10^{17}$ and $1{\cdot}5\times10^{19}$, respectively. R. CUTHILL.

Alkali metaplumbates. E. R. SBIERA (Bul. Fac. Stiinte Cernauti, 1927, **1**, 59—61; Chem. Zentr., 1931, i, 1262).—$Cs_2Pb(OH)_6$ separates as a microcryst. powder (rhombic, doubly refracting, colourless) when a paste of PbO_2 and H_2O is added to a mixture of CsOH and H_2O at 100°. It is decomp. by CO_2; in

H_2, decomp. begins at 120° and is complete at 280°. $Rb_2Pb(OH)_6$ (prismatic needles or doubly-refracting rhombohedra) is prepared similarly.

A. A. ELDRIDGE.

Lead double halides. E. R. SBIERA (Bul. Fac. Stiinte Cernauti, 1928, 2, 205—206; Chem. Zentr., 1931, i, 1587).—The *salts* $Be[PbCl_4]$, $PbI_2,LiCl$, and $3PbBr_2,LiCl,H_2O$ have been prepared.

A. A. ELDRIDGE.

Compound of lead halides with carbamide. E. R. SBIERA (Bul. Fac. Stiinte Cernauti, 1928, **2**, 207; Chem. Zentr., 1931, i, 1587).—The *compounds* $PbX_2,CO(NH_2)_2$, where X=Cl, Br, or I, were prepared.

A. A. ELDRIDGE.

Preparation and properties of some phosphides and arsenides. E. HEINERTH and W. BILTZ (Z. anorg. Chem., 1931, **198**, 168—177).—NbP results from heating together the elements at 500°; it forms a black powder which reacts vigorously with conc. HNO_3 and burns readily when heated in air. $NbAs_2$ may be prepared by the analogous reaction, but Ta reacts only incompletely with As, and to only a small extent with P. Electrolytic Cr does not react with P, but forms CrAs when heated with As. $MoAs_2$ is formed by heating powdered Mo with As at 570° and removing by sublimation the excess of As; it forms a black powder readily sol. in HNO_3 or H_2SO_4. WP_2 cannot be prepared by direct union, but is formed by heating WO_3 with P at 500°. W and As unite at 620° to form WAs_2. The following values of d_4^{25} have been determined: MoP_2 5·30, $MoAs_2$ 8·07, WP_2 8·60, $WAs_{1·95}$ 10·93, $NbP_{0·98}$ 5·91, $NbAs_{1·80}$ 7·28.

H. F. GILLBE.

Gas reactions with atomic oxygen. P. HARTECK and U. KOPSCH (Z. physikal. Chem., 1931, B, 12, 327—347; cf. A., 1930, 1388).—A further account of work previously published. F. L. USHER.

Removal of traces of oxygen from nitrogen. E. C. KENDALL (Science, 1931, **73**, 394—397).—A pyrex tube containing as heating unit a nichrome spiral surrounded by mica and a cylinder of Cu gauze completely removes traces of O_2 and H_2 from N_2. Water vapour can be passed through the tube without the formation of a trace of H_2. Regeneration of the Cu by H_2 requires only a few min. The new furnace arranged with the modified electrode cells and movable burettes described ensures complete removal of O_2 in determining oxidation–reduction potentials of cysteine. L. S. THEOBALD.

Isomeric thiosulphuric acids. P. RAY (Nature, 1931, **127**, 856).—Isomeric thiosulphatopentacyanocobaltic acids, $H_4[(CN)_5CoS_2O_3]$ and their salts have been obtained. Hydrolysis yields two varieties of $H_2S_2O_3$, the one decomp. into SO_2 and S and the other into H_2S and H_2SO_4. The constitutions of the acids are best represented by $S:SO(OH)_2$ and $O_2S(OH)(SH)$. L. S. THEOBALD.

Theory of the lead-chamber [sulphuric acid] process. "Blue acid" [SO_5NH_2]. E. BERL and H. H. SAENGER.—See B., 1931, 585.

Selenides. I. Formation of copper selenides by reduction of the selenites in solution. W. GEILMANN and F. W. WRIGGE (Z. anorg. Chem., 1931, **197**, 375—382).—The composition of the ppt. formed when a solution of $CuSeO_3$ is reduced with $NaHSO_3$ varies with the p_H of the solution. In alkaline solution Cu_2O is formed, the Se remaining in solution as an alkali selenite; in neutral or slightly acid solution (p_H 4—1) CuSe is quantitatively precipitated, whilst with increasing acidity at first mixtures of CuSe and Se, and finally pure Se, are formed. Solutions containing an excess of $Cu^{••}$, such as are obtained by dissolving basic natural selenites in acid, yield in alkaline solution Cu_2O, and in solutions at p_H 7·5—7 pure Cu_2Se; with increase of acidity mixtures of Cu_2Se and CuSe, then pure CuSe, and finally Se or mixtures of CuSe and Se, are produced. A great excess of $Cu^{••}$ gives rise to a ppt. containing an excess of Cu. Cu_2Se cannot be formed in other than neutral or slightly acid solution, and Clark's results (A., 1928, 1201) are therefore erroneous; the ppts. in which the ratio Cu : Se is unity, obtained under the conditions described by Clark, consist of pure CuSe.

H. F. GILLBE.

Phosphotungstates and silicotungstates. E. KAHANE and (MME.) KAHANE (Bull. Soc. chim., 1931, [iv], **49**, 557—567).—A more detailed account of work previously published (this vol., 338). R. CUTHILL.

Centrifuging of polonium solutions containing electrolytes. (MLLE.) C. CHAMIE and A. KORVEZEE (Compt. rend., 1931, **192**, 1227—1229).—Pure H_2O and $0·1N$-nitrates of Na, La, Ca, Pb, and Ag to which polonium had been added, after 90 min. centrifuging, had lost, respectively, 40·5, 50·4, 56·7, 82·1, 95·0, and 99·6% of the polonium. A similar solution of Na_2SO_4 lost approx. the same percentage as that of $NaNO_3$.

C. A. SILBERRAD.

Fluorine and ammonia. O. RUFF and E. HANKE (Z. anorg. Chem., 1931, **197**, 395—398).—The action of F on NH_3, under all conditions, yields NF_3, in addition to N_2. Other N fluorides, of unknown composition, are also formed. H. F. GILLBE.

Nitrogen fluorides and their conditions of formation. O. RUFF and (FRL.) L. STAUB (Z. anorg. Chem., 1931, **198**, 32—38).—The products of the electrolysis of anhyd. NH_4F–HF mixtures vary considerably with temp. and with the NH_3 content of the bath. With 31% NH_3 N_2 alone is evolved, whilst with 28·9% (=NH_4F,HF) pure NF_3 is evolved, the current efficiency being about 19%; with 28·9—22% NH_3 increasing quantities of, probably NHF_2, in addition to NH_2F and NF_3, are produced. The exceptionally high current efficiency, viz., 30%, of the formation of NF_3 at 28·6% NH_3 indicates that this compound is formed from NH_2F and NHF_2. On further decreasing the NH_3 content of the bath the quantity of NH_2F formed diminishes, and there is formed a yellow *compound*, probably NF_2, which has b. p. −125° and m. p. below −185°; F also is liberated in increasing quantity, until with 10% NH_3 it is practically the sole product. Electrolysis at 100—140° yields a greater proportion of NF_3, the other F compounds tending to decomp. explosively. NHF_2 has b. p. −65°, m. p. −125° approx., and reacts with Na to form $NaNF_2$ and NaH; it is sol. in H_2O without decomp. NH_2F forms colourless needles; v. p. 760 mm. at −77±0·5°

It is relatively inert, but reduces Fehling's solution immediately to Cu, and with NH_3 solution yields N_2.
H. F. GILLBE.

Possibility of formation of higher oxygen fluorides and the properties of fluorine monoxide. O. RUFF and W. MENZEL (Z. anorg. Chem., 1931, **198**, 39—52).—Pure (99·8%) F_2O, obtained by fractionating the crude material, is without action on dry glass and is not explosive; it is more dangerous physiologically than is F. The v. p. between $-192·2°$ and $-145°$ is given by $\log p=7·3892—578·64/T$; b. p. $-144·8°$, latent heat of evaporation (calc.) 2·650 kg.-cal. per mol., Trouton const. 20·65, crit. temp. $-81°$, $d_{\text{liq.}}$ at m. p. 1·90. Nearly all the metals react readily with F_2O; wood charcoal reacts explosively if it is previously warmed, whilst B and Si at a red heat react violently. P and F_2O combine with formation of POF_3 and PF_3. Powdered S reacts at 150° to form SF_4 and SO_2, and Se and Te readily to form the tetrafluorides. A mixture of Cl_2 and F_2O explodes when heated, forming ClF, but the reaction is never complete. In absence of H_2O, H_2 does not react at room temp., but on sparking the mixture a violent explosion takes place. With aq. solutions the oxidising action of F_2O becomes evident: thus $Co(OH)_2$ and $Ni(OH)_2$, suspended in H_2O, are slowly oxidised to peroxides, and $Cr^{\cdots}$ is oxidised to CrO_4''. F_2O is slightly soluble in H_2O (6·8 c.c. per 100 c.c. at 0°) and the cold solution is fairly stable; when heated at 300° about 28% of the gas is decomp. Higher fluorides of O are not present in the crude material, and attempts to prepare such compounds have been unsuccessful.
H. F. GILLBE.

Preparation of hydriodic acid. T. H. WHITEHEAD (J. Chem. Educ., 1931, 8, 541—542).—In the prep. of HI from H_2S and I, colloidal S is removed before distillation by dialysis for 48 hrs.; formation of I is thereby prevented.
CHEMICAL ABSTRACTS.

Potassium chlororhenate. E. ENK (Ber., 1931, 64, [*B*], 791—797).—K perrhenate is converted by KI and conc. HCl into *potassium chlororhenate*, K_2ReCl_6, d^{15} 3·34, which is stable towards acidified $KMnO_4$, oxidised by H_2O_2 in presence of KOH, unaffected by H_2SO_3 or H_3PO_2, but immediately decolorised by Zn and acid. The corresponding unstable Ag, Cs, and Tl *salts* are described.
H. WREN.

Co-ordinately linked carbon monoxide. Formation of iron carbonyl hydride. W. HIEBER and F. LEUTERT (Naturwiss., 1931, 19, 360—361).—The reaction between $Fe(CO)_5$ and a base proceeds thus: $Fe(CO)_5+2OH'=Fe(CO)_4H_2+CO_3''$. H_2O_2 completely decomposes the carbonyl hydride into $Fe(OH)_3$, H_2O, and CO_2. Mild oxidising agents give $[Fe(CO)_4]_3$; the same compound is produced direct from the pentacarbonyl. Benzoquinone and indigotin are reduced respectively to quinol and indigo-white. $Fe(CO)_4H_2$ plays a definite part in many reactions of $Fe(CO)_5$ and its derivatives. The hydride decomposes spontaneously: $2Fe(CO)_4H_2=Fe(CO)_5+Fe(CO)_3+2H_2$. Its isolation is possible therefore only in high vac. at low temp. At room temp. it is a volatile pale yellow liquid, with a disagreeable odour; f. p. $-68°$ to $-70°$. It oxidises explosively in air. Apart from its reducing qualities it has nothing in common with the solid hydrides of the Fe group. It has a mixed structure similar to those of the iron tetracarbonyl halides, $Fe(CO)_4X_2$ (cf. A., 1930, 875).
W. R. ANGUS.

Synthesis of gas-metal compounds by sputtering. L. R. INGERSOLL (J. Amer. Chem. Soc., 1931, **53**, 2008—2009; cf. A., 1929, 1368; 1930, 1258).—Compounds of Co and Fe with N have been produced. The elimination from the cathode of deep-seated gaseous impurities is discussed.
J. G. A. GRIFFITHS.

Action of arsenious chloride on nickel. G. ARRIVAUT (Compt. rend., 1931, **192**, 1238—1240).—Ni, prepared by reducing at the lowest possible temp. oxide obtained by calcining $Ni(NO_3)_2$, is heated for several days in absence of air and with agitation, with about 500 g. of hot 7% HCl saturated with As_2O_3. The liquid is changed daily and the Ni pulverised until nothing remains but a maroon-coloured powder, which is washed out of contact with the air with H_2O, EtOH, and Et_2O, and dried over H_2SO_4. Analysis corresponds with Ni_3As_2; *d* 7·60. It is not magnetic, and is scarcely attacked by the ordinary acids except HNO_3. The reaction is $6Ni+2AsCl_3=3NiCl_2+Ni_3As_2$, giving a theoretical yield of 92·5% on wt. of Ni, as against 91·6% obtained.
C. A. SILBERRAD.

Complex cyanides of nickel, copper, and chromium. W. GLUUD and W. RIESE.—See B., 1931, 587.

New type of complex compounds of ter- and quinque-valent platinum. III. P. C. RAY and S. C. S. GUPTA (Z. anorg. Chem., 1931, **198**, 53—56).—By the action of benzylamine, *iso*amylamine, and pyridine on $PtCl,Me_2S_2,H_2O$ the *compounds*

$Pt_5Cl,4Me_2S_2,3CH_2Ph·NH_2$,

$Pt_5Cl,4Me_2S_2,3C_5H_{11}·NH_2$,

and $Pt_5Cl,4Me_2S_2,3C_5H_5N$ have been prepared. The first-named yields when treated with a very dil. solution of Br in CCl_4 the *compound* $Pt_5Cl,4Me_2S_2,8Br,CH_2Ph·NH_2$, whilst $PtCl,Me_2S_2,H_2O$ yields $PtBr,Me_2S_2$. An improved method for the prep. of $PtCl,Me_2S_2,H_2O$ is described.
H. F. GILLBE.

Determination of the concentration of colloidal solutions. O. EINSTEIN and H. BORCHERT (Z. anal. Chem., 1931, **83**, 401—410).—The method depends on the fact that on diluting a colloidal solution with further quantities of the solvent a stage is reached when the Tyndall effect or fluorescence of the liquid disappears. The amount of solvent required depends on the original concentration of the solution, so that by constructing a curve for any system the concentration of the colloid in an unknown sol can be readily ascertained by noting the amount of solvent required to cause the disappearance of the fluorescence. The method is illustrated with reference to the systems cholesterol–H_2O and eosin–H_2O and the possible sources of error in the method are discussed.
A. R. POWELL.

Titration of dark-coloured liquids with titration rods. E. ROSSMANN (Chem.-Ztg., 1931, **55**, 403).—A considerable amount of indicator is used and a white rod is dipped into the liquid at intervals

during the titration, the colour of the film of liquid adhering on removal being observed. R. CUTHILL.

Use of Wulff's colorimeter for determining the hydrogen-ion concentration of solutions. E. LARSSON (Svensk Kem. Tidskr., 1931, **43**, 122—130). —A crit. examination of the above colorimeter has been made by comparing the p_H values obtained electrometrically from a series of solutions with those afforded by the colorimeter. The accuracy attainable over the range p_H 1·5—10 was about $\pm 0 \cdot 2$ to 0·3 unit, but above that limit the results were untrustworthy. Errors may also occur through the use of badly buffered solutions, or solutions poor in electrolytes; in both these cases an error up to 1 unit may result, but the addition of 0·03*M*-KCl will sometimes improve the results obtained in the latter case. The instrument can be used satisfactorily with turbid solutions, but with coloured solutions diffusion of the colouring matter into the test slip introduces an error. Good p_H values were obtained for milk, beer, and water, but soil and fertiliser extracts and chrome-tanning solutions gave bad results, and in the case of a Ni-plating solution no value at all could be found. It is concluded that for such technical solutions the method is unsatisfactory. H. F. HARWOOD.

Determination of the p_H of buffer solutions by means of the antimony–antimony oxide electrode. R. J. FOSBINDER (J. Lab. Clin. Med., 1931, **16**, 411—414).—The $Sb-Sb_2O_3$ electrode gives a linear relation between observed e.m.f. and p_H ($\pm 0 \cdot 01$); it is not applicable in determining the p_H of blood-plasma. CHEMICAL ABSTRACTS.

Electrometric and catalytic determination of hydrogen-ion concentration. Mean activity coefficients of the ions of benzoic acid in potassium chloride solutions. M. KILPATRICK, jun., and E. F. CHASE (J. Amer. Chem. Soc., 1931, **53**, 1732—1744).—The [H˙] of benzoic acid–benzoate buffer solutions has been determined from e.m.f. measurements with cells of the type Pt|quinhydrone$+c$HCl $+(m-c)$KCl|KCl(sat.)|$(m-b)$KCl $+b$NaOAc $+$ sat. BzOH$+$quinhydrone|Pt, where $m=0 \cdot 1$—3·0*M* at 25°, and 1—3*M*-KCl or 1—5*M*-NaCl at 20° (cf. A., 1928, 1093). The values of [H˙] agree with those derived from determinations of the catalytic effect on the hydrolysis of diethyl acetal, after correcting for salt effects. The mean activity coeff. of the ions of BzOH are slightly greater in solutions of NaCl than in corresponding solutions of KCl. J. G. A. GRIFFITHS.

Application of acetone to the ebullioscopic method of determination of water content. S. BAKOWSKI (Rocz. Chem., 1931, **11**, 269—288).—The effect of ordinary variations in atm. pressure on the b. p. of different $COMe_2$–H_2O mixtures is negligible and does not influence ebullioscopic determinations. Tables and curves expressing the relation between b. p. and composition of $COMe_2$–H_2O mixtures are given. The above method yields results in good agreement with those obtained by the ordinary oven and xylene extraction methods in those cases where H_2O is in no way combined with the substance under examination, whilst where it is adsorbed on or constitutionally combined with the substrate the results are low. Where the substrate itself is sol. in $COMe_2$ its apparent H_2O content is higher using the ebullioscopic method than using the ordinary methods. R. TRUSZKOWSKI.

Determination of traces of chlorine in bromides. I. E. ORLOV (Z. anal. Chem., 1931, **84**, 185—189).—A mixture containing 30 c.c. of 20% H_2SO_4, 10 c.c. of *N*-HCl, 2 g. of $MnSO_4,5H_2O$, and 3 g. of MnO_2 constitutes an oxidation–reduction buffer; it can be boiled for long periods without loss of Cl_2. Under similar conditions, Br_2 is evolved from bromides, and the method therefore serves as a means of separating and determining Cl in presence of relatively large amounts of Br. Modifications are indicated for the separation of larger quantities of Cl. E. S. HEDGES.

Bromo-iodometric investigations. VIII. J. H. VAN DER MEULEN (Chem. Weekblad, 1931, **28**, 348—350).—Chlorates are reduced to chloride by standardised $FeSO_4$ solution, in presence of HBr and a few drops of OsO_4 solution as catalyst, at 85—90°. The excess of $FeSO_4$ is oxidised by $KBrO_3$ or $KMnO_4$ solution, and the excess of the latter is titrated with KI and $Na_2S_2O_3$; prior to the titration the Fe^{III} salt is rendered inert either by conversion into a complex ferrifluoride by adding HF solution, or by adding 25% H_3PO_4 solution. H. F. GILLBE.

Iodometric determination of the bromide ion. Z. SZABÓ (Z. anal. Chem., 1931, **84**, 24—30).—The solution, containing <20 mg. Br′, is treated with 2 g. $KHCO_3$ and with a solution of at least 300 mg. Cl, whereby Br′ is oxidised to BrO_3'. The mixture is evaporated just to dryness without boiling, the residue dissolved in H_2O, and the BrO_3' determined iodometrically after addition of KI and H_2SO_4. If the original solution contains I′ it is treated first with $NaNO_2$ and H_2SO_4 and the liberated I removed by boiling. A. R. POWELL.

Volumetric determination of hydrofluoric and sulphuric acids. F. H. ZSCHACKE.—See B., 1931, 536.

Determination of traces of oxygen. I. D. F. NOVOTNY and F. TOUL (Coll. Czech. Chem. Comm., 1931, **3**, 241—249).—The method of Binder and Weinland (A., 1913, ii, 239) is unsuitable, even in an improved apparatus, for detecting small traces of O_2, since the pyrocatechol–$Fe(NH_4)_2(SO_4)_2$ solution used is always coloured red by N_2 and H_2 in alkaline medium and the colour cannot be removed with nascent H. The tinge is not caused by either traces of O_2 (absence of O_2 being determined by the Winkler–Romijn and Heyrovsky methods) or by impurities such as SO_2. F. R. SHAW.

Determination of oxygen in aluminium. T. HARADA.—See B., 1931, 544.

Determination of sulphur in pyrites. I. A. LEVIN and G. V. RABOVSKI.—See B., 1931, 537.

Use of buffered ammonia in the iodometric thiocyanate determination. H. A. PAGEL and H. J. KOCH (J. Amer. Chem. Soc., 1931, **53**, 1774—1777).—After the thiocyanate solution has been neutralised and hydroxides of any heavy metals have been precipitated with aq. NH_3, a solution of 1 g. of NH_4Cl, $(NH_4)_2SO_4$, or NH_4NO_3 in 20 c.c. of *N*-aq.

NH_3 is added instead of the $Na_2B_4O_7$ (cf. A., 1930, 1144). Ni, Co, and Mn interfere.
J. G. A. GRIFFITHS.

Measurement of hydroxyl and sulphydrate ions in sodium sulphide solutions. A. W. GOETZ (J. Amer. Leather Chem. Assoc., 1931, 26, 234—249).—The OH′ and SH′ concentrations were measured by Sb and Hg–HgS electrodes, respectively. The Nernst equation $E-RT/F \log [H^{\cdot}]$, was closely approx. for 0·1—1·0N-Na_2S. Less stable and higher e.m.f. values were obtained by plating the Sb electrode in a solution of K thioantimonate than by the use of non-plated electrodes. These electrodes offer a means of controlling depilating liquors. D. WOODROFFE.

Volumetric determination of selenium. B. ORMONT.—See B., 1931, 537.

Electrometric titration of phosphoric acid. A. SANFOURCHE (Compt. rend., 1931, 192, 1225—1227).—Electrometric titration curves for the neutralisation of H_3PO_4 with the (*a*) H and (*b*) quinhydrone electrodes give sharp results for the first equiv. with NaOH, $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$; for the second equiv. NaOH gives a sharp result, $Ba(OH)_2$ the same but with a slight lag, $Ca(OH)_2$ and $Sr(OH)_2$ no or very indefinite indications; for the third equiv. with (*a*) NaOH and $Ba(OH)_2$ give no, $Ca(OH)_2$ and $Sr(OH)_2$ distinct, indications, with (*b*) NaOH (with saturating amount of quinhydrone) gives a visible and $Sr(OH)_2$ (at 0·1325N) a moderately clear indication, $Ca(OH)_2$ and $Ba(OH)_2$ none. Results with phenolphthalein are unsatisfactory. C. A. SILBERRAD.

Volumetric determination and separation of ortho-, pyro-, and meta-phosphoric acids. S. AOYAMA (Z. anal. Chem., 1931, 84, 31—35).—Polemical against Dworzak and Reich-Rohrwig (A., 1929, 667).
A. R. POWELL.

Determination of boric acid. E. SCHULEK and G. VASTAGH (Z. anal. Chem., 1931, 84, 167—184).—An examination of the accuracy of methods of determining H_3BO_3 in dil. solutions (0·01—0·1N), especially in the presence of other acids, indicates that titration of the strong complex acid formed with mannitol is the best procedure. H_3BO_3 may be separated quantitatively from dil. H_2SO_4 solutions of salts of the heavy metals by distillation with MeOH. The experimental conditions described permit the separation of 0·06 mg. of H_3BO_3 from 2 g. of $Al_2(SO_4)_3,18H_2O$. The procedure is not recommended for the determination of borates in silicates, the gelatinous SiO_2 retaining considerable quantities of H_3BO_3. E. S. HEDGES.

Volumetric determination of carbon monoxide with the aid of a suspension of iodine pentoxide in oleum. H. A. J. PIETERS (Chem. Weekblad, 1931, 28, 335—337).—The CO is oxidised by a suspension of I_2O_5 in oleum (10% free SO_3) to CO_2, which is absorbed by KOH solution. The method is applicable in presence of air, H_2, and CH_4, but the results with coal gas are rather lower than those obtained by the use of ammoniacal Cu_2Cl_2 solution. The error is 0·02%. A suspension of I_2O_5 in oleum containing 25% free SO_3 oxidises both H_2 and CH_4, to the extent of about 5—10% within 30 min. H. F. GILLBE.

Potentiometric determination of carbonate. A. RINGBOM (Z. anal. Chem., 1931, 84, 161—166).—CO_3'' may be determined in neutral solution by adding an excess of standard $Pb(NO_3)_2$ solution and 1 c.c. of 0·1M-$K_3Fe(CN)_6$ and titrating the excess of $Pb(NO_3)_2$ with 0·1M-$K_4Fe(CN)_6$, using a Pt-foil indicator electrode. Hot or cold solutions can be used, and stirring is recommended. The solubility product of $Pb_2Fe(CN)_6$ is $10^{-14·9}$. In acid solution the potentiometric titration may be carried out, provided that free CO_2 is previously removed from the solution. At the equiv. point, $[CO_3'']=3\times10^{-9}$. E. S. HEDGES.

Organic substances and the loss on ignition of phosphorites. S. N. ROSANOV (Z. anal. Chem., 1931, 83, 410—421).—Loss on ignition is determined by heating for 3 hr. at 850°; at higher temp. part of the SiO_2 and F is evolved as SiF_4. The true loss on ignition is obtained by applying corrections for the CO_2 evolved from carbonates (difference between the CO_2 content of the original and the ignited material) and for the S oxidised. The content of org. C is determined by collecting the CO_2 evolved during the above ignition and subtracting that due to decomp. of carbonates. A. R. POWELL.

Detection of sodium with the Streng–Kolthoff reagent. R. MONTEQUI and R. DE SADABA (Anal. Fís. Quím., 1931, 29, 255—261).—Kolthoff's zinc uranyl acetate reagent (A., 1927, 436) ppts. K at concentrations which are frequently encountered in practice. The conditions of the reaction and the appearance of the ppt. under the microscope have been examined with the object of establishing a satisfactory technique. The following is recommended: 0·1—0·2 g. of the sample is dissolved in the min. of H_2O and to 1 drop of the solution is added 1 c.c. of the reagent. The ppt. is examined microscopically, and if the characteristic form of the Na salt is not apparent, on account of the quantity of K present, a new ppt. is prepared from 1 drop of the solution diluted with 6—8 drops of H_2O. If the Na ppt. is still obscured by that of K, 0·15 g. of the sample is dissolved in 5 c.c. of H_2O. 1·5—2 c.c. of a solution of $Zn(ClO_4)_2$ are added, and the solution is filtered; to 0·5 c.c. of the filtrate are added 2 c.c. of the reagent, and the ppt., when examined microscopically, then usually exhibits the characteristic form of the pure Na salt. By this procedure 1 part of Na in presence of 1700 parts of K may be detected. The $Zn(ClO_4)_2$ solution is prepared by neutralising the distillate (97 c.c.) obtained from 100 c.c. of 30% $HClO_4$ with basic $ZnCO_3$.
H. F. GILLBE.

Detection of small quantities of calcium [in magnesium salts]. N. EVERS (Analyst, 1931, 56, 293—298).—Hundeshagen's method (cf. A., 1909, ii, 439) gives most accurate results, and slight modifications are recommended. Ca may be determined by opalescence or, more accurately, weighed as sulphate; chlorides do not interfere. T. MCLACHLAN.

Colorimetric detection and determination of small amounts of lead. E. W. KRANS and J. B. FICKLEN (J. Ind. Hygiene, 1931, 13, 140—143).—The Pb is separated as chromate and the ppt. dissolved in HCl and determined colorimetrically with diphenylcarbazide. The method is rapid and accurate

($\pm$0·005 mg.) for quantities of Pb below 0·2 mg., in presence of not more than 0·1 mg. of most other metals, present separately or simultaneously.

H. F. GILLBE.

Volumetric determination of copper by Spacu's reaction. L. CUNY (J. Pharm. Chim., 1931, [viii], 13, 513—518).—The method previously described (B., 1924, 893) has been improved and, by ensuring complete oxidation of the thiocyanate by the $KMnO_4$, accurate results are obtained over a much wider range of Cu content. E. H. SHARPLES.

Analysis of natural selenides. I. Determination of copper selenite in presence of copper selenides. W. GEILMANN and F. W. WRIGGE. **II. Preparation of copper selenides.** W. GEILMANN. **III. Determination of silver selenite in presence of silver selenide.** F. W. WRIGGE (Z. anorg. Chem., 1931, **197**, 353—363, 364—368, 369—374).—I. The action of aq. solutions of NH_3, HCl, and H_2SO_4, in presence and in absence of air, on $CuSeO_3,2H_2O$, Cu_2Se, and CuSe has been investigated. For the determination of $CuSeO_3$ in presence of selenides the finely-powdered sample is digested with 0·5N-aq. NH_3 or H_2SO_4, and after filtration the strongly acidified solution is reduced with SO_2 and the Se is weighed. The dissolved Cu may be determined in the evaporated solution by precipitation as CuS, but the results are high and erratic if Cu_2Se is present; in acid solution Cu_2Se and $CuSeO_3$ react to form CuSe. Analytical data are given for a number of minerals; the error is about 0·1%, but the result for Cu is of little value, since $CuCO_3$ dissolves in both aq. NH_3 and H_2SO_4.

II. The treatment with acid of marble, magnesite, or limestone containing Cu_2Se or CuSe results always in the dissolution of part of the Cu; the effect is especially marked in presence of more than 0·37% of Fe_2O_3. Purely mechanical methods, such as washing, are therefore recommended for the treatment of such minerals. $Fe^{\cdots}$ reacts readily with Cu_2Se, and a method for the approx. determination ($\pm$1%) of Cu_2Se in presence of CuSe is described; the powdered mineral is shaken at room temp. with a solution of ferric ammonium sulphate, and the Cu which dissolves is determined in the filtered solution.

III. Aq. solutions of NH_3, at all concentrations, are without action on AgSe, even in presence of H_2O_2, whereas $2N$ solutions readily dissolve $AgSeO_3$. The solubility of $AgSeO_3$ in H_2SO_4 solutions is less than in NH_3 solutions, and that of AgSe in $2N$-H_2SO_4 is negligible. The determination of selenite in presence of selenide may be effected by extraction of the former with $2N$-aq. NH_3 and determination of Ag in the filtered solution. The method is applicable to the simultaneous determination of $CuSeO_3$ and $AgSeO_3$ in presence of AgSe, but in presence of Cu selenides the results are valueless; the approx. selenite content may nevertheless be obtained by determination of the dissolved Se. H. F. GILLBE.

Use of phenolic acids in the detection, separation, and determination of metals. V. Separation of copper from cadmium and their subsequent determination. P. N. DAS-GUPTA and H. SAHA (J. Indian Chem. Soc., 1931, 8, 19—21; cf. A., 1929, 1412).—The determination of Cu in presence of Cd can be carried out rapidly and accurately by precipitating the Cu from neutral or slightly acid solution by means of gallic acid and NaOAc or NH_4OAc. The voluminous chocolate-brown ppt. is ignited and weighed as CuO. In the filtrate Cd is first precipitated as sulphide and then determined as the sulphate. The method is also suitable for determining small amounts of Cu. O. J. WALKER.

Salicylaldoxime, the copper reagent. F. EPHRAIM (Ber., 1931, 64, [*B*], 1215—1218; cf. A., 1930, 1393, and following abstract).—The precipitation of Cu by salicylaldoxime in presence of $Fe^{\cdots}$ is best effected in very dil. HCl instead of AcOH, since carrying down of Fe is thereby prevented. In the mother-liquors from the Cu ppt. almost all other metals can be readily determined by the usual methods. An exception is presented by $Fe^{\cdots}$, in which case excess of salicylaldoxime is readily destroyed by Br previous to precipitation of Fe as $Fe(OH)_3$. The Ni, Co, Mn, Zn, and Cd *salts* of salicylaldoxime are described. H. WREN.

Group, OH·C·C·C:N·OH, specific for copper. F. EPHRAIM (Ber., 1931, 64, [*B*], 1210—1215; cf. A., 1930, 1393).—The oximes of β-naphthol-1-aldehyde, α-naphthol-2-aldehyde, vanillin, *o*-hydroxyacetophenone, quinacetophenone, resacetophenone, pæonol, quinacetophenone methyl ether, gallacetophenone, and 1-acetyl-β-naphthol are specific reagents for Cu, but not superior to salicylaldoxime (*loc. cit.*). With other metals the sequence of solubility of the salts is almost uniform. The Cu salt is most sparingly sol. and resistant towards AcOH. It is followed by the Ni, Co, Zn, and Cd salts, which are attacked by AcOH or are not precipitated. All other salts are more freely sol. in the sequence Ag, Pb, $Hg^{\cdot\cdot}$, Mg (Ca, Sr, Ba), Na, K. Cr and Al salts give no ppt., whereas $Fe^{\cdots}$ salts give very deeply coloured solutions from which occasionally in the absence of acid black ppts. may separate quantitatively. The exceptional position of Cu may be due to the smallness of the $Cu^{\cdot\cdot}$ ion. The *oximes* of quinacetophenone methyl ether and 1-acetyl-β-naphthol have m. p. 113·5—114° and 85°, respectively. H. WREN.

Determination of mercurous chloride. D. KÖSZEGI (Pharm.-Ztg., 1931, 76, 524).—The sample is shaken with N-NaOH solution until completely decomposed, filtered, and the filtrate titrated with standard acid. Results in excellent agreement with the gravimetric determination of Cl are obtained. Low results are given by the iodometric method of the U.S.P. H. A. PIGGOTT.

Separation of the rare earths by basic precipitation. IX. Preparation of pure erbium oxide. W. PRANDTL (Z. anorg. Chem., 1931, 198, 157—161). —A detailed description of the method used; the final separation from Yt was effected by a modification of the ferrocyanide fractional precipitation method, whereby a coarsely cryst. ppt. was obtained. The product contained no trace of Yt and Ho, and only a faint trace of Tu (X-ray spectroscope).

H. F. GILLBE.

Determination of aluminium oxide in aluminium and its alloys. A. M. SHANDOROV (Tzvet. Met.,

1930, 672—679).—In the Cl volatilisation method, the Cl_2 must be free from O_2 and H_2O. After chlorination, the boat is heated at 1000° to burn the C. Commercial Al contained 0·07—0·10% Al_2O_3, and duralumin contained 0·07—0·21%.

CHEMICAL ABSTRACTS.

Rapid volumetric determination of manganese in ores and alloys. I. MAJDEL.—See B., 1931, 591.

Determination of iron. G. DOMINICI (Folia Clin. Chim. Micros., 1928, 3, 17 pp.; Chem. Zentr., 1931, i, 1648).—Colorimetric determination with KCNS is preferred. A. A. ELDRIDGE.

Titration of iron by Knopp's method. O. ROTHE and A. P. SOBRINHO (Rev. brasil chim., 1929, 1, 129—149).—$K_2Cr_2O_7$ with $NHPh_2$ indicator is preferred to $KMnO_4$. The metals of the second group, especially As and Sb, must be removed with H_2S; small quantities of Cu cause no error. Hg, Sn, or colloidal SiO_2 need not be removed; colloidal Pt arising from fusion of the oxide in a Pt crucible renders the use of $KMnO_4$ necessary. An Ag crucible is preferred. CHEMICAL ABSTRACTS.

Colour reaction for cobalt. M. G. DE CELIS (Anal. Fís. Quím., 1931, 29, 262—263).—To 1 c.c. of the solution to be tested are added 2 c.c. of saturated aq. $Na_2S_2O_3$ and 6 c.c. of EtOH. The appearance of a blue coloration in the lower, oily, layer indicates $Co^{\cdot\cdot}$ (limit, $2·3\times10^{-6}$ g. per c.c.). H. F. GILLBE.

Separation of nickel from cobalt or ferro-cobalt. H. A. KAR (Chemist Analyst, 1931, 20, No. 2, 15).—The HNO_3 solution is treated with aq. NH_3 and $(NH_4)_2S_2O_8$; a large amount of NH_4Cl is added to the filtrate, followed by dimethylglyoxime. The ppt. is dissolved in acid and the treatment repeated.

CHEMICAL ABSTRACTS.

Colorimetry of small quantities of titanium. H. GINSBERG (Z. anorg. Chem., 1931, 198, 162—167).—The depth of colour of a solution containing Ti and H_2O_2 changes on dilution as a result of a disturbance of equilibrium if the Ti concentration is less than 3 mg. per litre; accurate results by the colorimetric method are therefore obtainable only by comparing solutions of identical colour. H. F. GILLBE.

Analytical chemistry of tantalum, niobium, and their mineral associates. XIX. Analytical technique. W. R. SCHOELLER (Analyst, 1931, 56, 304—310; cf. A., 1927, 32; 1930, 184).—Elaborate procedures for the following manipulations are described: hydrogen sulphate fusion, dissolution of melt in oxalate or tartrate solution, tannin precipitations therefrom, and filtration, washing, ignition, and purification of ppts. A micro-test for earth acids depends on destruction of all organic matter, dissolution of the hydrogen sulphate, and fractional precipitation by aq. NH_3. T. McLACHLAN.

Pyrognostic assaying of platinum and palladium. H. CALMON (Rev. brasil. chim., 1929, 1, 84—85).—A sensitive method for the detection of Pd and Pt depends on the incandescence of ignited asbestos threads or filter-paper ash previously impregnated with the salt. CHEMICAL ABSTRACTS.

Potentiometric titration of bivalent platinum in hydrochloric acid solution. O. STELLING (Svensk Kem. Tidskr., 1931, 43, 130—138).—Bivalent Pt in solution can be accurately determined by electrometric titration with $0·1N$-$KBrO_3$; the titration is carried out in 2 to $4N$-HCl, at 70—80°; the end-point is very sharp. Equally good results are obtained by using $0·1N$-$KMnO_4$ in place of the $KBrO_3$; in this case the titration is carried out at room temp., and a correction (usually about two drops) must be made for the consumption of $KMnO_4$ by the HCl. Some preliminary attempts to determine Pt^{IV} by reduction to Pt^{II}, followed by titration as above, proved unsuccessful. H. F. HARWOOD.

Separation and gravimetric determination of osmium. R. GILCHRIST (Bur. Stand. J. Res., 1931, 6, 421—448).—Os, present as halide, is completely precipitated as a hydrated dioxide from a boiling solution of p_H 1·5—6·3; alkali chlorides and sulphates do not interfere, as they may be eliminated by washing. The Munroe crucible or an asbestos filter is suitable for the reduction of OsO_2 by H_2. Errors due to deflagration of OsO_2 on heating, which occur even in H_2, are obviated by impregnating the ppt. with NH_4Cl, and if cooled in an atm. of CO_2 the reduced metal is relatively inert and does not change in wt. in dry air. When originally present as osmate or bromo-osmate Os may be completely removed by distillation as OsO_4 from a solution containing 10 vol.-% of HNO_3; with chloro-osmate this method is less satisfactory, and distillation from conc. H_2SO_4 is recommended. A mixture of H_2SO_4 and HNO_3 is suitable for treating either chloro- or bromo-osmate. Ru is not evolved from boiling 40% HNO_3 nor from H_2SO_4 solution, but is evolved gradually from the mixed acids or from boiling conc. HNO_3. Under the conditions described the remaining metals of the group do not appear in the distillate. For the quantitative recovery of the OsO_4 in the distillate, $6N$-HCl, saturated with SO_2, is recommended as the absorbent, but the solution must be evaporated and digested with HCl, and this procedure repeated several times, to ensure complete decomp. of sulphite compounds of Os. Full details are given of the procedure recommended for the determination of Os, in view of the facts recorded above. The sensitivity of Tschugaev's colorimetric thiocarbamide method for the detection of Os is increased to 1 in 5×10^6 in presence of SO_2, which may be employed also to remove HNO_3.

H. F. GILLBE.

Photo-electric spectrophotometer for measuring the amount of atmospheric ozone. G. M. B. DOBSON (Proc. Phys. Soc., 1931, 43, 324—339).—Two narrow bands in the ultra-violet, one almost outside the O_3 absorption band, and one within it, are isolated by a double quartz spectrograph. A rotating sector allows them to fall alternately upon a photo-electric cell, and the ratio of their intensities is found by reducing that of the brighter to equality with that of the other by means of an optical wedge. C. W. GIBBY.

Excitation of fluorescence by flashlight and photographing of the fluorescent object. PLOTNIKOV (Chem.-Ztg., 1931, 55, 318).—The Mg or Al flashlight powder is enclosed in a small evacuated glass bulb similar to that of a pocket battery lamp and ignited electrically from such a battery. By using an

ultra-violet filter combined with a KNO_2 filter a sharp photograph of fluorescent substances is readily obtained with one of these flash-lamps.

A. R. POWELL.

Spinthariscope for measuring radioactivity. H. A. MANGAN and H. SCHLUNDT (Trans. Amer. Electrochem. Soc., 1931, **59**, 315—321).—An improved spinthariscope for detecting radioactivity in air samples, particularly air exhaled by living persons, is for quantitative purposes still greatly inferior to the electroscope. H. J. T. ELLINGHAM.

Thermostat for temperature range 50—112° abs. W. JUSTI (Ann. Physik, 1931, [v], 9, 570—578).—The construction of a thermostat is described, the lower temp. being reached by adsorption of H_2 on charcoal, and the higher by desorption. A. J. MEE.

Air thermostat for quantitative laboratory work. W. H. J. VERNON (Trans. Faraday Soc., 1931, **27**, 241—247).—The thermostat is capable of maintaining accurate temp. control over comparatively long periods. The spatial temp. variation at 25° is about 0·015° and the time variation about 0·005°.

J. W. SMITH.

Cooling unit for low-temperature thermostats. T. J. B. STEER (Science, 1931, **73**, 288—289).—An arrangement for maintaining temp. between 0° and room temp. to ±0·01° is described.

L. S. THEOBALD.

Precision cryostat with automatic temperature regulation. R. B. SCOTT and F. G. BRICKWEDDE (Bur. Stand. J. Res., 1931, **6**, 401—410).—The cryostat described is suitable for use at any temp. between 0° and —170°, the max. temp. variation being 0·001°. The bath is placed within an intermediate double-walled vessel surrounded with liquid air, H_2, or He. The temp. is adjusted approx. by regulating the pressure between the walls of the intermediate vessel, and is regulated by a photo-electric thermo-regulator which controls the current passing through a heating element wound on the outer surface of the bath. The design affords a large unobstructed const.-temp. space. H. F. GILLBE.

Vacuum-tube method of temperature control. F. O. SCHMITT and O. H. A. SCHMIDT (Science, 1931, **73**, 289—290).—A vac.-tube relay giving a temp. control of 0·001—0·005° is described.

L. S. THEOBALD.

Vacuum oven for temperatures below 300°. G. F. SMITH and V. R. HARDY (J. Chem. Educ., 1931, **8**, 548—555).—A small tube oven, const. to 3°, is described. CHEMICAL ABSTRACTS.

Construction of a flexible glass diaphragm for a clicker gauge. R. NESTER (J. Amer. Chem. Soc., 1931, **53**, 1811—1812).—Just before a thin glass bulb blown at the end of a 3-mm. tube becomes rigid, it is squeezed lightly by a **U**-shaped piece of brass. The resulting flattened sides possess concentric corrugations which improve the clicking of the diaphragm (cf. A., 1924, ii, 748). J. G. A. GRIFFITHS.

Pirani gauge for the measurement of small changes of pressure. A. ELLETT and R. M. ZABEL (Physical Rev., 1931, [ii], **37**, 1102—1111).—Conditions for max. sensitivity of the gauge were investigated. Ni was found to be superior to W wire as a filament. An optimum temp. of the wire for max. sensitivity was established. N. M. BLIGH.

Gas stereometer. L. WHITBY (J. Sci. Instr., 1931, **8**, 117—119).—A compensated Hempel gas burette is adapted for determining the capacities of small vessels. C. W. GIBBY.

Micro-macro-burette. H. LOBER (Chem. Fabr., 1931, 218—219).—The burette described differs from the Bang micro-burette in that absorption of CO_2 by the solution and evaporation are reduced to a min., and in being of more robust construction. It consists of two tubes of equal length but different diameters, either of which may be brought into operation by appropriate manipulation of taps. A titration may be carried nearly to completion with the larger tube, and completed accurately with the smaller.

H. F. GILLBE.

Effect of the method of reading (round mark or point) on the determination of the density [of gases] with the Bunsen–Schilling apparatus. L. ZIPPERER and W. ROTTENGATTER (Gas- u. Wasserfach., 1930, **73**, 1190—1192).—The point method of reading the position of the meniscus in the Bunsen–Schilling apparatus is less liable to personal errors than that in which a circular graduation is used.

A. R. POWELL.

Machine for pulling glass micro-pipettes and needles. D. DU BOIS (Science, 1931, **73**, 344—345).

L. S. THEOBALD.

Absorption of sulphur trioxide in wash-bottles. F. FRIEDRICHS (Chem. Fabr., 1931, 203—204).—The percentage absorption of SO_3 from air containing 20 mg. per litre in washing flasks of various types was studied. The gas velocities were 100 and 400 c.c. per min.; in most cases the nozzle diameters were 2 mm. A marked difference was observed in most cases between the rate of absorption of dry gaseous SO_3 and of clouds of moist SO_3, the absorbent in each case being H_2O, and the rate of absorption of moist gas the greater. Bottles with very narrow nozzles or frits offered an excessive resistance. The best results were obtained with bottles containing spiral screw-shaped gas inlets packed with glass grains of 0·3—0·5 mm. Coarser glass beads etc. are unsuitable, but with the bottles described 100% absorption was obtained at the velocities stated. C. IRWIN.

Liquid atomiser for spectroscopic tests. J. MILBAUER (Chem.-Ztg., 1931, **55**, 323).—A small air-jet atomiser from which the solution to be tested is blown into a Bunsen flame is affixed to the side of the burner; a quartz shield collects any droplets passing through the flame. E. LEWKOWITSCH.

Laboratory evaporator. O. PANKRATH (Chem. Fabr., 1931, 209—210).—An evaporator body suitable for distilling liquids which froth consists of a **U**-tube the upper ends of which connect with a bulb, one in the bottom and the other in the side. The bulb has in addition vac. and filling connexions. The **U**-tube only, or one arm of it, is immersed in a water-bath. A continuous one-way circulation of the liquid is established and superheating is entirely prevented.

C. IRWIN.

Automatic balance. F. J. VEIHMEYER, C. H. HOFMANN, and C. V. GIVAN (Science, 1931, **73**, 424—426). L. S. THEOBALD.

Set of weights for the microchemical balance. W. FELGENTRAEGER (Z. anal. Chem., 1931, **83**, 422—428).—Rules for standardising weights and for converting weighings to vac. are given. A. R. POWELL.

Electromagnetic stirrer. J. REILLY and J. McKENNA (J. Sci. Instr., 1931, **8**, 134).—An electrical make and break is described. C. W. GIBBY.

Nickel-iron alloys and their application to instrument construction. F. E. J. OCKENDEN (J. Sci. Instr., 1931, **8**, 113—117).—A discussion. C. W. GIBBY.

Contact-angle measuring apparatus and technical importance of contact angles. O. HERSTAD (Kolloid-Z., 1931, **55**, 169—171).—The apparatus described enables the contact angle of 1 drop of liquid on a solid surface to be measured without disturbing the surface. The angle differs from 0° in many liquids which wet the solid, and spreading begins when the angle is 3° or 4°. E. S. HEDGES.

Determination of refractive index of solutions by the interferometer principle. W. GEFFCKEN (Z. Elektrochem., 1931, **37**, 233—237).—An interferometric method for the precise determination of n for solutions is described. R. CUTHILL.

Technique of polarographic measurements. P. HERASYMENKO (Trans. Faraday Soc., 1931, **27**, 203—205).—Polemical (cf. Lloyd, A., 1930, 297). F. L. USHER.

Apparatus for potentiometric analysis, using the quinhydrone–calomel electrode. W. SELKE (Chem. Fabr., 1931, 219).—An arrangement of apparatus is described whereby the electrode (B., 1930, 295) may be employed for potentiometric titrations. H. F. GILLBE.

Calibration of [electronic] tube voltmeters to give direct readings of p_H values. W. SELKE (Chem. Fabr., 1931, 210—211).—The anode current of an electronic tube with screen grid is directly proportional to the negative e.m.f. at the grid. Hence a voltmeter of this type can be calibrated to read p_H vals. directly on the galvanometer using a buffer solution and a shunt with variable resistance. It is convenient if the zero can be adjusted by a compensating current. Any suitable solution of known p_H val. can be used for calibrating. C. IRWIN.

Conductometer. A. SCHLEICHER and W. LUDICKE (Chem. Fabr., 1931, 201—203).—This instrument measures comparative conductivities of salt solutions and allows the concentration to be deduced in a manner analogous to the colorimeter. It consists of two similar vertical glass tubes with Pt electrodes of which the upper ones are movable and their position is recorded on a scale. They can be immersed in a thermostat if desired. The zero position in a Wheatstone bridge is first determined using the same solution in both tubes and thus compensating for any errors in the instrument. Concentrations are deduced from a series of curves giving the relation with the scale reading and results are most accurate with great dilution. C. IRWIN.

Quantitative humidification of air. W. H. J. VERNON and L. WHITBY (Trans. Faraday Soc., 1931, **27**, 248—255).—Atm. of any desired degree of humidity can be obtained by admitting the requisite proportions of desiccated and saturated air into an evacuated vessel. Complete saturation of air is best effected by admitting steam to the air current, the excess being condensed out under thermostatic conditions. J. W. SMITH.

Intensive drying [technique]. H. B. BAKER (J. Amer. Chem. Soc., 1931, **53**, 1810; cf. A., 1929, 1160).—Polemical (cf. A., 1928, 1189; this vol., 34). J. G. A. GRIFFITHS.

Geochemistry.

Spectrographic determination of the cations present in natural medicinal waters. I. S. PINA DE RUBIES and C. S. D'ARGENT (Anal. Fís. Quím., 1931, **29**, 235—246).—Various samples of natural H_2O contained, in addition to the usual elements, Pb, Cu, Ag, Sn, Mo, Ga, Ge, and Ti. H. F. GILLBE.

Carbonaceous mineral waters of Gornji Gabernik. S. S. MIHOLIC (Bull. Soc. Chim. Jugoslav., 1931, **2**, 33—56).—Analyses are given. C. W. GIBBY.

Water of Ferrarelle near Riardo. R. NASINI, C. PORLEZZA, and E. BOVALINI (Annali Chim. Appl., 1931, **21**, 182—202).—Except as regards its $CaCO_3$ and CO_2 contents, this water, which, like the gas it emits, exhibits appreciable radioactivity, has remained moderately const. in composition during the past 30 years. T. H. POPE.

Composition of the interior of the earth. A. A. BLESS (Proc. Nat. Acad. Sci., 1931, **17**, 225—229).—The temp. of the core of the earth is about $10^{5\circ}$, at which the energy of thermal agitation of atoms would be sufficient to remove by collision the outer shells of uni-, bi-, and ter-valent atoms. The average density of the ionised atoms is about 10 times that of the non-ionised. A temp. of 40,000° would be sufficient to account for the density of the interior of the earth. C. W. GIBBY.

Composition of volcanic sulphur from Papandajan (West Java). W. GEILMANN and W. BILTZ (Z. anorg. Chem., 1931, **197**, 422—428).—The yellow form contained more than 99·9% S, the residue being chiefly SiO_2; Tl was present as $TlAsS_2$. The grey variety contained 94% S, the chief impurities being SiO_2 and TiO_2, together with $CaSO_4$, $FeSO_4$, alum, and NaCl. H. F. GILLBE.

Mineralogical petrography of Pacific lavas. T. F. W. BARTH (Amer. J. Sci., 1931, [v], **21**, 491—530).—Micrometric analyses were made of 60 lavas,

ranging from basalt to phonolite and to rhyolite, and the chemical composition of the constituent minerals was deduced from their optical characters. The chemical compositions of the rocks calc. from these data agree closely with the results given by chemical analysis. L. J. SPENCER.

Natural silicates and puzzuolana of the Canary Islands. T. GASPAR Y ARNAL (Chim. et Ind., 1931, **25**, 1064—1077).—Analyses are given. C. W. GIBBY.

Nephelitic and leucitic phonolites of Uapu Is. (Marquesas Is.) A. LACROIX (Compt. rend., 1931, **192**, 1161—1166).—The phonolites from all parts of Uapu Is. are green to yellow, and contain the same minerals, but exhibit different structures. Nepheline in phenocrysts, and sanidine predominate with 7—12% of ægyritic augite irregularly distributed. Some of the phonolites are leucitic; they enclose, and consequently are subsequent to, the basaltic lavas. Analyses of a nephelitic (one of four), a nephelitic-leucitic, and a leucitic phonolite, and of two basalts (tephritic and labradoritic) are (figures in this order): SiO_2 54·64, 52·78, 54·08, 48·06, 44·82; Al_2O_3 22·02, 21·86, 21·00, 17·98, 13·06; Fe_2O_3, 2·62, 2·07, 4·20, 3·91, 3·23; FeO 1·44, 2·20, 0·24, 4·61, 8·97; MnO 0·29, 0·22, 0·21, 0·22, 0·16; MgO 0·20, 0·14, 0·15, 2·42, 8·15; CaO, 1·16, 2·56, 2·34, 7·54, 11·74; Na_2O 10·01, 8·57, 7·00, 5·49, 2·17; K_2O 4·85, 5·88, 6·21, 2·84, 1·39; TiO_2 0·10, 0·58, 0·61, 2·74, 3·80; P_2O_5 0·07, 0·07, 0·10, 0·86 0·48; $H_2O(+)$ 1·42, 1·85, 2·19, 2·22, 1·41; $H_2O(-)$ 1·08, 1·00, 1·47, 1·14, 0·87; Cl 0·14, 0·13, 0·19, 0, 0; total 100·04, 99·91, 99·99, 100·03, 100·25%. The phonolites are from a source separate from that of the other lavas of the Marquesas Is. C. A. SILBERRAD.

Chlorite of Bierk. A. GOOSSENS (Natuurwetensch. Tijds., 1931, **13**, 119—122).—The mineral forms optically positive hexagonal plates, d 2·844, n_D 1·618±0·002. A specimen contained SiO_2 25·51, MgO 20·30, Al_2O_3 22·33, FeO 20·76, H_2O 11·05%, and traces of Mn. H. F. GILLBE.

Julienite. A. SCHOEP (Natuurwetensch. Tijds., 1931, **13**, 147—149).—Julienite (A., 1928, 987) may be recryst. by slow evaporation of the aq. solution at room temp.; the tetragonal crystals have d 1·594, ω 1·645, are optically positive, and exhibit feeble pleichroism. Contrary to the previous report, the solution does not contain either Cl′ or NO_3'. H. F. GILLBE.

Pyromorphite–mimetesite–vanadinite group. J. LIETZ (Z. Krist., 1931, **77**, 437—498).—Specially pure crystals gave the following results: pyromorphite (Ems), d^{17} 7·054; Pb 75·53, Ca 0·37, PO_4 21·14, C, 2·63, Fe_2O_3 0·02, Al_2O_3 0·01, H_2O 0·09, total 99·85%. Mimetesite (Tsumeb) d^{19} 7·231—7·243; Pb 69·81, Ca 0·5, PO_4 0·50, AsO_4 27·01, Cl 2·40, total 99·72%. Vanadinite (Obir, Carinthia), Pb 72·52, Ca 0·05, PO_4 0·40, AsO_4 trace, VO_4 24·14, Cl 2·66, total 99·72%. Several other analyses are given. The fact that the order throughout is pyromorphite–mimetesite–vanadinite and not that of the at. wts. is ascribed to V being in the other subdivision of group V. C. A. SILBERRAD.

Gravity separation [of minerals]. R. C. EMMONS (Amer. Min., 1930, **15**, 536).—Evacuation of the separating vessel assists separation when the material, in a fine state of division, contains adhering air bubbles. CHEMICAL ABSTRACTS.

Gallium. IV. Occurrences in zinc minerals. J. PAPISH and C. B. STILSON (Amer. Min., 1930, **15**, 521—527).—Sphalerite, gahnite, hopeite, parahopeite, and adamite, but not calamine, smithsonite, zincite, hydrozincite, goslarite, hodgkinsonite, hardystonite, or clinohedrite, are galliferous. CHEMICAL ABSTRACTS.

Lessingite and cerite from the Kyshtym district. Y. N. KNIPOVICH (Trans. Inst. Econ. Min. Met., Moscow, 1930, No. 44, 46).—Lessingite closely approaches $H_2Ca_2Ce_4Si_3O_{15}$; assuming bastnasite to be present, the composition of the cerite is $4Ce_2O_3,6SiO_2,H_2O$. CHEMICAL ABSTRACTS.

Soda-rich anthophyllite asbestos from Trinity County, California. J. D. LAUDERMILK and A. O. WOODFORD (Amer. Min., 1930, **15**, 259—262).—The material has n^{α} 1·606, n^{β} 1·613, n^{γ} 1·623 and contains SiO_2 55·70, Al_2O_3 2·00, Fe_2O_3 trace, FeO 5·32, MgO 21·12, CaO 5·10, Na_2O 7·40, MnO trace, H_2O+ 1·80, H_2O- 0·30, total 100·74%. CHEMICAL ABSTRACTS.

Arsenoferrite from Jachimov, Czechoslovakia. W. F. FOSHAG and M. N. SHORT (Amer. Min., 1930, **15**, 428—429).—Arsenoferrite, $FeAs_2$, isotropic, has H 5·5, d 6·42; material (with some carbonate gangue) contained Fe 24·88, Cu 1·34, Pb 0·05, $CaCO_3$ 4·00, $MgCO_3$ 1·57, As 66·84, S 1·08, total 99·76%. CHEMICAL ABSTRACTS.

Uraninite from Placer de Guadalupe, Chihuahua. R. C. WELLS (Amer. Min., 1930, **15**, 470—473).—The mineral, d 10·63, which is intimately associated with Au, contains UO_2 70·09, UO_3 22·69 ThO_2 0·20, CeO_2 0·71, La_2O_3 etc. 1·02, Y_2O_3 etc. 3·41, Fe_2O_3 0·10, As_2O_3 0·06, PbO 0·40, CaO 0·30, TiO_2 0·66, Al_2O_3 0·25, H_2O 0·41, total 99·70%. The age, calc. from the Pb : U ratio, is 36×10^6 years. CHEMICAL ABSTRACTS.

Replacement of wolframite by scheelite. Fluorescence of certain tungsten minerals F. R. VAN HORN (Amer. Min., 1930, **15**, 461—469).—A specimen from Camborne is described. The fluorescence of various W minerals was examined: that of some wolframites and hübnerites may be caused by slight alteration to scheelite. CHEMICAL ABSTRACTS.

Seamanite from Iron County, Michigan. E. H. KRAUS, W. A. SEAMAN, and C. B. SLAWSON (Amer. Min., 1930, **15**, 220—225).—The mineral, $a:b:c$ = 0·5195 : 1 : 0·4508, H 4, d 3·128, n^{α} 1·640, n^{β} 1·663, n^{γ} 1·665, contains MnO 56·22, (Mg,Ca)O 1·61, FeO 0·13, B_2O_3 9·95, P_2O_5 16·65, H_2O 14·57%; formula $(3MnO,B_2O_3,3H_2O),(3MnO,P_2O_5,3H_2O)$. CHEMICAL ABSTRACTS.

Psittacinite from Bisbee, Arizona. S. TABER and W. T. SCHALLER (Amer. Min., 1930, **15**, 575—579).—The mineral, associated with higginsite and barite, contains V_2O_5 21·11, As_2O_3 trace, PbO 50·13, CuO, 19·10, loss on ignition (H_2O) 4·79, insol. (MnO_2) 3·06, total 98·19%; formula $2PbO,2CuO,V_2O_5,2H_2O$. CHEMICAL ABSTRACTS.

Minerals of the phosphate nodules from near Fairfield, Utah. E. S. LARSEN and E. V. SHANNON (Amer. Min., 1930, **15**, 307—337).—The following new minerals were isolated and examined :

deltaite, $8CaO,5Al_2O_3,4P_2O_5,14H_2O$;
dennisonite, $6CaO,Al_2O_3,2P_2O_5,5H_2O$;
lewistonite, $15CaO,(K,Na)_2O,4P_2O_5,8H_2O$;
englishite, $4CaO,K_2O,4Al_2O_3,4P_2O_5,14H_2O$;
millisite, $2CaO,Na_2O,6Al_2O_3,4P_2O_5,17H_2O$;
lehite, $5CaO,(Na,K)_2O,4Al_2O_3,4P_2O_5,12H_2O$;
gordonite, $MgO,Al_2O_3,P_2O_5,9H_2O$.

CHEMICAL ABSTRACTS.

Dehrnite and crandallite. E. S. LARSEN and E. V. SHANNON (Amer. Min., 1930, **15**, 303—306).—Dehrnite (from Dehrn), *H* 5, *d* 3·04, contains insol. 0·12, CuO 50·88, P_2O_5 37·12, K_2O 1·20, Na_2O 7·11, H_2O+ 1·52, H_2O- 0·16, CO_2 1·49, total 99·60% ; probably $7CaO,Na_2O,2P_2O_5,H_2O$. Crandallite (from Dehrn, previously "Kalkwavellit"), n^α 1·59, n^γ 1·60, probably orthorhombic, contains SiO_2 4·92, Al_2O_3 37·52, P_2O_5 25·24, CaO 11·04, MgO 0·24, H_2O+ 17·90, H_2O- 1·00, CO_2, 2·52, total 100·40% ; formula $CaO,2Al_2O_3,P_2O_5,6H_2O$.

CHEMICAL ABSTRACTS.

Cenosite from North Burgess Township, Lanark County, Ontario. R. P. D. GRAHAM and H. V. ELLSWORTH (Amer. Min., 1930, **15**, 205—219).—The mineral, orthorhombic prismatic, n^α 1·644, n^β 1·689, n^γ 1·691, *H* 5—6, *d* 3·612, contains SiO_2 34·66, $(Ce,La,Di)_2O_3$ 3·22, $(Y,Er)_2O_3$ 35·46, CaO 16·72, SrO 0·31, Al_2O_3,Fe_2O_3,BeO 0·22, MnO 0·02, Na_2O 0·27, K_2O trace, MgO 0·19, CO_2 6·58, SO_3 0·94, H_2O 2·54, H_2O (110—130°) 0·04, total 100·23%. The formula is $2CaO,(Ce,Y)_2O_3,CO_2,4SiO_2,H_2O$.

CHEMICAL ABSTRACTS.

Franklin minerals. L. H. BAUER and H. BERMAN (Amer. Min., 1930, **15**, 340—348).—Cummingtonite : SiO_2 49·74, Al_2O_3 1·72, FeO 12·80, MgO 8·31, ZnO 10·46, MnO 13·79, CaO 0·49, Na_2O 0·22, H_2O+ 2·16, total 99·69%. Apophyllite : SiO_2 50·90, CaO 24·74, K_2O, 3·70, Na_2O 0·42, MnO 0·47, ZnO 1·79, H_2O 17·71% ; $(Ca,K,Na,Mn,Zn)_2Si_3O_8,3·5H_2O$. Barysilite : SiO_2 16·84, PbO 77·35, MnO 3·33, FeO 0·23, Al_2O_3 0·59, CaO 0·21, MgO 0·78, ZnO 0·30, H_2O 0·07, total 99·70% ; $3PbO,2SiO_2$. Ferroschallerite : SiO_2 31·12, MnO 29·22, FeO 17·12, MgO 0·12, ZnO 3·63, As_2O_3 12·46, H_2O 6·42, total 100·09%. Svabite, *d* 3·542 : insol. 0·29, H_2O 1·32, F 1·41, CO_2 trace, CaO 45·89, ZnO 1·54, MnO 1·23, MgO 0·84, PbO 0·51, As_2O_3 35·24, P_2O_5 12·54, less O for F, total 100·22%. Optical data are recorded, and celestite, chlorophœnicite (clinozosite), datolite, and manganbrucite are mentioned. CHEMICAL ABSTRACTS.

Changes in hornblende at about 800°. V. E. BARNES (Amer. Min., 1930, **15**, 393—417).—When heated in air, green hornblende is converted into brown hornblende with the optical properties of basaltic hornblende. Hornblendes poor in Fe and tremolite are unchanged by heating ; the changes suffered by actinolite are described. Brown hornblende is converted into green hornblende by heating in H CHEMICAL ABSTRACTS.

Pegmatite minerals of Poland, Maine. H. BERMAN and F. A. GONYER (Amer. Min., 1930, **15**, 375—387).—Lithiophilite : FeO 10·96, MnO 31·90, Na_2O 0·30, Li_2O 9·55, H_2O+ 0·40, P_2O_5 46·35, insol. 0·16, total 99·62%. Reddingite : Fe_2O_3, 0·95, FeO 12·68, MnO 38·36, CaO 0·15, Na_2O,K_2O trace, H_2O+ 13·16, P_2O_5 34·52, insol. 0·45, total 100·27% ; $3(Mn,Fe)O,P_2O_5,3H_2O$. Dickinsonite : FeO 12·33, MnO 31·83, MgO 1·67, CaO 2·01, Na_2O 7·41, K_2O 1·73, Li_2O 0·20, H_2O 1·82, P_2O_5 40·78, insol. 1·00, total 100·78% ; $7(Mn,Fe)O,2(Na_2,K_2,Ca),3P_2O_5,H_2O$. Fairfieldite : FeO 4·74, MnO 14·82, CaO 30·85, Na_2O 0·41, K_2O 0, H_2O 9·70, P_2O_5 39·55, insol. 0·50, total 100·58% ; $(Mn,Fe)O,2CaO,P_2O_5,2H_2O$ (Mn : Fe=3 : 1). Landesite : Fe_2O_3+FeO 13·91, Mn_2O_3 2·69, MnO 33·65, MgO 3·07, CaO 1·39, H_2O 13·60, P_2O_5 31·94, insol. 0·13, total 100·38% ; $3Fe_2O_3,20MnO,8P_2O_5,27H_2O$. Optical data for these minerals and for cassiterite and beryl are recorded ; amblygonite, quartz, eosphorite, and apatite are mentioned.

CHEMICAL ABSTRACTS.

Origin of fusain. E. DE OLIVEIRA (Ann. Acad. Brasil Sci., 1930, **2**, 191—193).—A brief survey. Fusain is probably a product of bacterial activity rather than of thermal action. H. F. GILLBE.

Recent and fossil resins. K. A. JURASKY (Brennstoff-Chem., 1931, **12**, 161—163).—Knowledge of the occurrence of resins in plants and in coal is briefly summarised and illustrated by photomicrographs. A. B. MANNING.

Fossil coal resins. H. STEINBRECHER (Brennstoff-Chem., 1931, **12**, 163—165).—Knowledge of the origin and constitution of the fossil resins in coal is briefly summarised. A. B. MANNING.

Microscopic structure and origin of anthracite. A. DUPARQUE (Compt. rend., 1931, **192**, 1257—1260). —Anthracitisation is a process entirely different from that resulting in the formation of vitrain, and there are many varieties of the process. Anthracites usually result from deposits rich in lignin, rarely from such as are rich in cutin, but occasionally metamorphism has obliterated the distinction between the two kinds, even causing anthracitisation of bituminous coals. (Cf. A., 1930, 887.) C. A. SILBERRAD.

Origin of mineral oil. E. KRAUS (Zentr. Min. Geol., 1930, **B**, 488—505 ; Chem. Zentr., 1931, i, 1391).—A discussion. A. A. ELDRIDGE.

Petroleum and α-radiation. S. C. LIND (Nature, 1931, **127**, 813—814).—A discussion.

L. S. THEOBALD.

Dependence of red earth formation on the original rock. A. REIFENBERG (Soil Research, 1931, **2**, 201—203).—A discussion of red earth soils.

A. G. POLLARD.

Chemical composition of Hungarian lowland soils. A. ARANY (Z. Pflanz. Düng., 1931, **20A**, 257—270).—Soils deficient in lime are frequent. The total nutrient contents are, in general, high, but the transition to an assimilable condition is restricted.

A. G. POLLARD.

Organic Chemistry.

Thermal decomposition of organic compounds from the viewpoint of free radicals. I. Saturated hydrocarbons. F. O. RICE (J. Amer. Chem. Soc., 1931, **53**, 1959—1972).—Theoretical. Thermal decomp. of paraffin hydrocarbons is represented as a chain reaction in which free H atoms or radicals combine with H from the surrounding hydrocarbon mol. The resulting hydrocarbon radical then decomposes. The relative probabilities of radical formation from various paraffins are calculated and applied to various examples. H. BURTON.

Electrosynthesis. M. Z. JOVIČIĆ (Rad., 1929, **236**, 233—268; Chem. Zentr., 1931, i, 1235).—The C+H "deficit" of products of the action of the electric discharge on hydrocarbons is due to O, considered to be formed by the action of electrical energy on C and H. A. A. ELDRIDGE.

[Preparation of] *n*-pentane. C. R. NOLLER (Organic Syntheses, 1931, **11**, 84—86).

Dimeride of αβγδ-tetramethyl-$\Delta^{\alpha\gamma}$-butadiene. P. VAN ROMBURGH and G. VAN ROMBURGH (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 224—226; cf. A., 1914, i, 794).—The compound $C_{16}H_{28}$ formed by heating αβγδ-tetramethyl-$\Delta^{\alpha\gamma}$-butadiene with conc. formic acid could not be fully hydrogenated in AcOH solution, using Pt-black as catalyst, but the results indicate the presence of two double linkings in the mol. On ozonisation in CCl_4, MeCHO is formed. On refluxing with S at 180—200°, hexamethylbenzene is produced. It is concluded that the compound is 1 : 2 : 3 : 4 : 5 : 6-*hexamethyl*-4-α-*methyl*-Δ^{α}-*propenyl*-Δ^{1}-cyclo*hexene*. J. W. SMITH.

Detection of traces of acetylene. E. CZAKÓ (Z. angew. Chem., 1931, **44**, 388).—A description of a method, using von Ilosvay's reagent, of which the sensitivity limit is below 0·00025 vol.-%. H. F. GILLBE.

Detection of traces of acetylene. E. PIETSCH and A. KOTOVSKI (Z. angew. Chem., 1931, **44**, 388; cf. preceding abstract).—A reply. H. F. GILLBE.

Action of ultra-violet light on alkyl iodides. G. EMSCHWILLER.—See this vol., 694.

Oxidation of free alkyl groups. Photo-oxidation of gaseous methyl iodide [at 0°]. J. R. BATES and R. SPENCE (J. Amer. Chem. Soc., 1931, **53**, 1689—1704; cf. this vol., 333).—In the light of the Hg arc, MeI exhibits an instantaneous increase of pressure (Budde effect) followed by a slow decrease of pressure due to decomp. Addition of O_2 leads to a 100-fold increase in the rate of pressure decrease; little permanent gas is produced, and the net reaction is $4MeI+2O_2 \longrightarrow$ paraformaldehyde+methylal+H_2O+2I_2. The velocity is directly proportional to the light intensity and about 2 mols. of MeI are oxidised per quantum absorbed. A reaction mechanism involving the intermediate formation of OH rather than a peroxide is more consistent with the kinetics. J. G. A. GRIFFITHS.

[Ready methylation of alcoholic hydroxyls.] J. VON BRAUN (Ber., 1931, **64**, [*B*], 1141).—A reply to von Auwers (this vol., 618). H. WREN.

Action of hydrogen peroxide on simple carbon compounds. I. Methyl alcohol, formaldehyde, and formic acid. II. Mechanism of the reactions. H. S. FRY and J. H. PAYNE (J. Amer. Chem. Soc., 1931, **53**, 1973—1980, 1980—1984).—I. Oxidation of formic acid (1 mol.) to CO_2 by H_2O_2 (1 mol.) in 0·35*N*-H_2SO_4 at 100° occurs to the extent of 76%. The following reactions occur concurrently during the initial oxidation of CH_2O with H_2O_2 at 60°: $2CH_2O+H_2O_2 \longrightarrow 2H{\cdot}CO_2H+H_2$; $CH_2O+H_2O_2 \longrightarrow H{\cdot}CO_2H+H_2O$. The former reaction is favoured by low concentrations of H_2O_2. Oxidation of MeOH to CH_2O is followed by the above-mentioned changes. In all the reactions some H_2O_2 decomposes to H_2O and O_2.

II. The change $H_2CO_3+H_2O_2 \longrightarrow H{\cdot}CO_2H+H_2O+O_2$ probably involves the formation of percarbonic acid which subsequently loses O. The production of H_2 during the oxidation of CH_2O is explained: $2CH_2O \longrightarrow (CHO)_2+H_2$; the glyoxal is then oxidised by H_2O_2 to formic acid. Similar mechanisms are suggested for the oxidation of MeCHO; diacetyl (or pyruvaldehyde) and H_2 (or CH_4) would be produced; further oxidation would give AcOH (or AcOH+formic acid). These predictions are confirmed. The amount of CH_4 formed decreases with increasing concentration of H_2O_2; max. yields of H_2 are obtained with equimol. amounts of aldehyde and H_2O_2. Oxidation of AcOH with H_2O_2 gives no H_2. H. BURTON.

Oxidation of methyl alcohol with air over iron, molybdenum, and iron-molybdenum oxides. H. ADKINS and W. R. PETERSON.—See this vol., 693.

[Preparation of] triethylcarbinol. W. W. MOYER and C. S. MARVEL (Organic Syntheses, 1931, **11**, 98—100).

Reaction of *sec.*-αβ-glycols with thionyl chloride. Z. KITASATO and C. SONE (Ber., 1931, **64**, [*B*], 1142—1145).—Alcohols with two vicinal primary or secondary OH groups yield cyclic sulphites when acted on by $SOCl_2$, whereas those containing a single primary or secondary OH group afford normal sulphites from 2 mol. of the alcohol. Et mucate with boiling $SOCl_2$ or $SOCl_2$ in C_6H_6 and pyridine gives the *disulphite* $(C_{10}H_{14}O_6)S_2O_2$, m. p. 119°. Hydrobenzoin affords the *sulphite* $(C_{14}H_{12}O_2)SO$, m. p. 127—129°, or α-stilbene dichloride, m. p. 191°. Mannitol gives the corresponding *trisulphite*, f. p. 0°. *Cholesteryl sulphite*, m. p. 178°, cyclo*hexyl sulphite*, b. p. 55°/12 mm. (decomp.), and 1 : 2 : 3 : 4-*tetrahydro*-2-*naphthyl sulphite*, b. p. about 220°, are described. H. WREN.

Danger of working with ether containing peroxide. K. W. HETZEL (Z. angew. Chem., 1931, **44**, 388).—An account of the explosion, on drying, of the residue of the evaporation of an ethereal extract. H. F. GILLBE.

Action of magnesium on halogenated ethers. R. PAUL (Compt. rend., 1931, **192**, 964—965).—Phenyl γ-iodopropyl ether reacts with Mg in Bu_2O spontaneously, but in Et_2O only on addition of a trace of $AlCl_3$, the products being trimethylene,

phenol, and a little diphenoxyhexane. Ethyl γ-chloropropyl ether gives a Grignard reagent in ether when catalysed with $AlCl_3$. Condensation of this with chloromethyl amyl ether gave α-ethoxy-δ-amyloxybutane, which gave αδ-dibromobutane on hydrolysis with HBr, whilst condensation with amyloxyacetonitrile gave a 30% yield of *α-(amyloxyacetyl)-γ-ethoxypropane*, b. p. 133°/10 mm. A. A. LEVI.

Preparation of *iso*amyl ether. E. V. ZAPPI and H. DEGIORGI (Anal. Asoc. Quím. Argentina, 1930, **18**, 210—213).—A mixture of ordinary amyl alcohol and 10% of H_2SO_4 (*d* 1·84) is distilled slowly up to 140°. The amyl alcohol distilled is returned to the flask and the heating repeated. The *iso*amyl ether is then distilled in steam and purified by distillation, finally over P_2O_5. R. K. CALLOW.

Occurrence of peroxides in crude dioxan. E. EIGENBERGER (J. pr. Chem., 1931, [ii], **130**, 75—78). —The occurrence of peroxides in technical dioxan is due to the presence of acetal. Pure dioxan, m. p. 12·5—13·0°, prepared from such a product by hydrolysis with *N*-HCl in a stream of air to remove MeCHO, dehydrating successively with NaOH and Na, and distilling, is stable to air and light; acetal under the same conditions readily acquires peroxide characteristics. A modification of the method of hydrolysis may be used to determine the acetal content. H. A. PIGGOTT.

Esters of pyrophosphorous, hypophosphoric, and pyrophoric acids. I. Ethyl esters. A. E. ARBUSOV and B. A. ARBUSOV (J. pr. Chem., 1931, [ii], **130**, 103—132).—Fractionation of the (sol.) product of the action of Br on sodium diethylphosphite in cold ligroin affords diethylphosphorous acid (6·4%), ethyl phosphate (3·9%), *tetraethyl pyrophosphite* (I), $[P(OEt)_2\cdot]_2O$, b. p. 82—83°/2 mm. (1·6%), *tetraethyl hypophosphate* (II), $PO(OEt)_2\cdot O\cdot P(OEt)_2$, b. p. 116—117°/2 mm. (15·8%), and tetraethyl pyrophosphate, $[PO(OEt)_2]_2O$, b. p. 144—145°/3 mm. (8·0%). The pyrophosphite readily reacts with Br or I, ethyl halide being liberated, forms *additive* compounds E,2CuX with Cu_2Cl_2, m. p. 111·5—112·5°, Cu_2Br_2, m. p. 135—136°, and Cu_2I_2, m. p. 119—121°, and with water is exothermally hydrolysed quantitatively to diethylphosphorous acid. With CPh_3Br it yields ethyl triphenylmethyl pyrophosphinate, hydrolysed by HCl at 200° to *triphenylmethylphosphinic acid*, m. p. 277—278° (also+2EtOH). The hypophosphate forms additive compounds with halogens, Cu_2Br_2 (identical with that from the pyrophosphite), and Ag halides, and with S at 160—170° gives a monothiopyrophosphoric *ester*, b. p. 147·5—148·5°/3 mm. With water the hypophosphate reacts exothermally to give Et_2HPO_4 and diethylphosphorous acid, whilst with EtOH 75% reacts according to the equation II+EtOH $\longrightarrow$ $PO(OEt)_2\cdot OH+P(OEt)_3$, and 25% $\longrightarrow$ $PO(OEt)_3+P(OEt)_2\colon O$. Heating with EtI at 100° causes isomerisation of ethyl hypophosphate to a *form*, b. p. 147—147·5°/3 mm., containing two quinquevalent P atoms: II+EtI $\longrightarrow$ $PO(OEt)_2\cdot O\cdot PEtI(OEt)_2 \longrightarrow PO(OEt)_2\cdot O\cdot PEt(OEt)\colon O$ +EtI. In agreement with Balareff (A., 1917, ii, 467) ethyl pyrophosphate is decomposed quantitatively into Et_3PO_4 and $Et_4P_2O_7$ at 218°, but that author's statement that the pyrophosphate is formed by heating these products together is not confirmed. The pyrophosphate is stable towards cuprous halides, and towards H_2O and EtOH at 170°. Previous results are critically summarised. J. W. BAKER.

Mechanism of organic reactions. III. Nature of mechanism of migration of acyl radicals. H. HIBBERT and M. E. GREIG (Canad. J. Res., 1931, **4**, 254—263).—The mechanism first proposed by Fischer (A., 1920, 808) to explain the migration of acyl radicals in the glycerides of the fatty acids receives support by the isolation of a dioxolane derivative of the type postulated by him. Probably the increased polarity of the acyl group increases the tendency to cyclisation to a dioxolane derivative by attracting the mobile H atom to the CO group. In favour of this view, it is shown that whereas benzyl and phenylethyl acetates are relatively stable, the trichloroacetates, when heated, give PhCHO and phenylacetaldehyde, and chloral. β-Hydroxyethyl trichloroacetate appears to be incapable of existence (cf. this vol., 206), all attempts to prepare it leading to *2-hydroxy-2-trichloromethyl-1 : 3-dioxolane*, $\begin{matrix}CH_2\cdot O\\CH_2\cdot O\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\CCl_3\end{matrix}$, b. p 68°/0·025 mm., which decomposes into ethylene carbonate, $CHCl_3$, and unidentified products when heated or with pyridine. The following are described: *2-hydroxy-2-dichloromethyl-*, b. p. 106°/0·08 mm., *2-hydroxy-4-chloromethyl-2-trichloromethyl*, b. p. 99—101°/0·11 mm., and *2-hydroxy-2-trichloromethyl-4-hydroxymethyl-1 : 3-dioxolanes*; *2-hydroxy-2-trichloromethylmetadioxan*, b. p. 90—92°/0·025 mm.; *benzyl*, b. p. 148—149°/15 mm., and *phenylethyl trichloroacetate*, b. p. 167°/17 mm. J. D. A. JOHNSON.

New triglyceride, a palmitostearoazelain, from cacao butter. J. BOUGAULT and G. SCHUSTER (Compt. rend., 1931, **192**, 1240—1241).—Partial hydrolysis of the triglyceride, m. p. 59°, from cacao butter (this vol., 712) affords *glyceryl α-palmitate-γ-stearate* (I), m. p. 34°, converted by stearyl chloride into *α-palmito-βγ-distearin*, m. p. 66°, identical with a specimen prepared from stearyl chloride and glyceryl α-palmitate (Fairbourne, A., 1930, 574), which, in turn, is obtained from palmityl chloride and *iso*propylideneglycerol. Palmityl chloride converts I into αβ-dipalmito-γ-stearin, m. p. 63°, depressed by admixture with αγ-dipalmito-β-stearin, m. p. 62—63°, obtained by the action of silver palmitate on αγ-dichloro*iso*propyl stearate, m. p. 39°, which is prepared from stearyl chloride and epichlorohydrin. In the original triglyceride, m. p. 59°, the azelaic acid residue is, therefore, in the β-position. J. W. BAKER.

Glycerol ethers of nitrophenols. L. DESVERGNES.—See this vol., 722.

Reactions of nitrosyl chloride. V. Action of nitrosyl chloride on mercaptans and mercaptides. Thionitrites. H. RHEINBOLDT, M. DEWALD, and O. DIEPENBRUCK (J. pr. Chem., 1931, [ii], **130**, 133—146).—NOCl reacts with mercaptans and sulphides in Et_2O at 0° to give thionitrites, R·S·R'+NOCl$\longrightarrow$RS·NO+R'Cl, but only the derivatives of tert. radicals are stable. Thus tert.-*butyl*, b. p. 38—39°/55 mm., and tert.-*amyl*, b. p. 78°, *thionitrite*

are obtained from the mercaptans or from *mercuric* tert.-*butyl*, m. p. 159—160°, and tert.-*amyl*, m. p. 157°, *sulphides*, respectively, whilst from triphenylmethyl mercaptan or its Na salt is obtained *triphenylmethyl thionitrite*, m. p. 99·2° with decomp. to NO and $(CPh_3S\cdot)_2$, which can be isolated in a pure state when the thionitrite is heated in boiling $CHCl_3$ or $C_6H_{11}Me$. Similarly, the action of NOCl on 4 : 4′-dithio-diphenyl or -di-*o*-tolyl affords the unstable *diphenyl* and *di-o-tolyl* 4 : 4-*dithionitrite*, respectively.

J. W. BAKER.

Determination of equivalent weight of organic acids in the crystalline state. P. PFEIFFER and R. HANSEN (J. pr. Chem., 1931, [ii], **130**, 1—10).—The solid acid is heated in a current of NH_3 so as to form the salt, and the increase in wt. determined. The method is applicable to aliphatic and aromatic monocarboxylic acids and aromatic dicarboxylic acids.

R. CUTHILL.

Preparation of higher fatty acids from mineral oils and paraffin by oxidation with air at the ordinary or higher pressures and without catalysts. N. DANAILA and M. BOLTUŞ-GORUNEANU (Bul. Chim. pura appl., Bukarest, 1929, **31**, 133—100; Chem. Zentr., 1931, i, 1393).—Oxidation is most efficient when it is carried out successively, and only twice. The chemical removal of olefinic, aromatic, and naphthenic hydrocarbons and paraffinic hydrocarbons with a tert. C atom is desirable in order to diminish the yield of hydroxy-acids.

A. A. ELDRIDGE.

Electrolysis of acetic acid and oxalic acid. E. BAUR (Z. Elektrochem., 1931, **37**, 254—257; cf. this vol., 179).—Small amounts of tartaric acid are formed by the anodic oxidation of AcOH in presence of H_2SO_4. Reduction of oxalic acid in EtOH at a Pb cathode yields a small quantity of tartaric acid and succinic acid, the latter apparently by secondary reduction of the former.

R. CUTHILL.

Walden inversion. XVI. Influence of substituting groups on optical rotation in the series of disubstituted propionic acids containing an ethyl group. P. A. LEVENE and R. E. MARKER (J. Biol. Chem., 1931, **91**, 687—704; cf. this vol., 711).—Synthesis of the series (I) Me·CHRR′, (II) Me·CHR·CH$_2$R′, and (III) Et·CHR·CH$_2$R′, in which R is an alkyl group and R′ is CH_2·OH, CH_2Br, or CO_2H, was effected without Walden inversion. Variation of R′ increases the dextrorotation in series I in the order $CH_2\cdot OH > CH_2Br > CO_2H$, but in series II and III in the order $CO_2H > CH_2\cdot OH > CH_2Br$. The order $CH_2\cdot OH > CH_2Br$ confirms the conclusion (A., 1930, 63) that *d*-aliphatic secondary carbinols are related to *l*-secondary halides. The acids of series I are configuratively related as they rotate in the same direction. β-Methylvaleric acid rotates in the opposite direction to related higher members of series II, *d*-*n*-butan-β-ol leading to *d*-β-methylvaleric acid and *d*-*n*-pentan-β-ol to *l*-β-methylhexoic acid. β-Ethylhexoic acid rotates in the opposite direction to the higher members of series III, because d-β-ethylhexoic acid and *d*-β-propyloctoic acid lead to the same *d*-δ-ethyl-*n*-nonane. The disubstituted acetic and β-disubstituted propionic acids are related because *d*-α-bromo-γ-ethylbutane gives the *d*-γ-methyl-*n*-hexane previously obtained (A., 1904, i, 363) from *d*-α-iodo-β-methylbutane. The series R_1R_2CHBr and $R_1R_2CH\cdot CO_2H$ are related because *d*-pentan-β-ol, *d*-heptan-γ-ol, and *d*-octan-γ-ol lead to *l*-β-disubstituted propionic acids. The exceptional rotation of derivatives of α-methylbutyric and α-ethylvaleric acids is explained by assuming that the rotation is due partly to the radical $R_1R_2CH\cdot$ and partly to the polar group, one or both of which may be lævorotatory. Some radicals may be dextro- or lævo-rotatory, according to the distance from the asymmetric C atom.

Unless otherwise stated, the following substances were prepared by HBr, by Grignard or ethyl malonate syntheses, or by addition of Na in suspension in toluene to an EtOH solution of the ester. Specific rotations are for the homogeneous liquids. α-Bromo-β-methylbutane, $[\alpha]^{29}$ 1·59° (from β-methylbutan-α-ol, $[\alpha]_D^{23}$ −2·72°), gave γ-methylpentan-α-ol, $[\alpha]_D^{27}$ +1·67°, b. p. 80°/47 mm., d_4^{27} 0·822. Pentan-β-ol, $[\alpha]_D^{25}$ +3·28°, gave l-β-*bromopentane*, b. p. 117°, d_4^{25} 1·208, $[\alpha]^{25}$ −5·84°, which afforded l-β-*methylhexoic acid*, b. p. 112°/16 mm., d_4^{26} 0·912, $[\alpha]_D^{25}$ −0·50°. l-γ-*Bromohexane*, b. p. 142°, d_4^{22} 1·166, $[\alpha]^{22}$ −2·03° (from hexan-γ-ol, $[\alpha]_D^{22}$ +1·73°), gave dl-β-*ethylhexoic acid*, the *quinine* salt of which afforded *d*-β-*ethylhexoic acid*, b. p. 106°/5 mm., $[\alpha]_D^{25}$ +2·67° (*Et* ester, b. p. 80°/9 mm., $[\alpha]_D^{30}$ +0·59°). This ester yielded d-γ-*ethylhexan-α-ol*, b. p. 73°/15 mm., $[\alpha]_D^{23}$ +0·49°, which with thionyl chloride gave *α-chloro-γ-ethylhexane*, b. p. 85°/40 mm., $[\alpha]_D^{27}$ +1·15°, and with PBr_3, *α-bromo-γ-ethylhexane*, b. p. 94°/35 mm., $[\alpha]_D^{22}$ +1·02°. l-γ-*Bromoheptane*, b. p. 79°/40 mm., $[\alpha]_D^{22}$ −9·15° (from heptan-γ-ol, $[\alpha]_D^{23}$ +7·37°), gave l-β-*ethyl*-n-*heptoic acid*, b. p. 130°/12 mm., $[\alpha]^{22}$ −1·35° (*Et* ester, b. p. 107°/25 mm., $[\alpha]_D^{22}$ −0·56°). This ester yielded l-γ-*ethylheptan-α-ol*, b. p. 101°/16 mm., $[\alpha]_D^{21}$ −0·66°, which with PBr_3 gave l-*α-bromo-γ-ethylheptane*, b. p. 90°/15 mm., $[\alpha]_D^{23}$ −0·32°. l-γ-*Bromo-octane*, b. p. 85°/25 mm., $[\alpha]_D^{27}$ −11·04° (from octan-γ-ol, $[\alpha]_D$ +6·82°), gave l-β-*ethyloctoic acid*, b. p. 140°/12 mm., $[\alpha]_D^{22}$ −1·67° (*Et* ester, b. p. 104°/12 mm., $[\alpha]_D^{22}$ −0·76°). This ester gave l-γ-*ethylnonan-α-ol*, b. p. 110°/15 mm., $[\alpha]_D^{23}$ −1·15°, which with PBr_3 yielded l-*α-bromo-γ-ethyloctane*, b. p. 99°/14 mm., $[\alpha]_D^{22}$ −0·61°. d-ζ-*Ethylnonan-γ-ol*, b.p. 114°/16 mm., $[\alpha]_D^{25}$ +0·32° (from α-chloro-γ-ethylhexane, $[\alpha]_D^{27}$ +1·15°), with HI gave d-δ-*ethylnonane*, b. p. 77°/20 mm., $[\alpha]_D^{25}$ +0·70°. l-δ-*Ethylnonan-α-ol*, m. p. 127°/15 mm., $[\alpha]^{23}$ 0° (from α-bromo-γ-ethyloctane, $[\alpha]_D^{27}$ −0·69°), with PBr_3 gave l-*α-bromo-δ-ethylnonane*, b. p. 122°/15 mm., $[\alpha]_D^{25}$ +0·29°, which afforded l-δ-*ethylnonane*, b. p. 77°/20 mm.

R. S. CAHN.

[Preparation of] β-methylvaleric acid. E. B. VLIET, C. S. MARVEL, and C. M. HSUEH (Organic Syntheses, 1931, **11**, 76—78).

[Preparation of] α-bromo*iso*valeric acid. C. S. MARVEL and V. DU VIGNEAUD (Organic Syntheses, 1931, **11**, 20—22).

Action of iodine on mesityl oxide in alkaline solution. Dimethylacrylic acid and its salts. V. CUCULESCU (Bul. Fac. Stiinte Cernauti, 1927, **1**, 53—56; Chem. Zentr., 1931, i, 589—590).—The formation of a thick brown oil is avoided by intro-

ducing small portions of mesityl oxide and I solution alternately into the continuously stirred mixture. CHI_3 (80%) and dimethylacrylic acid (75%), m. p. 69° (Ni, Co, and Mn'' salts), are formed.

A. A. ELDRIDGE.

Reliability of methods of Twitchell and of Bertram for separation of fatty acids. A. STEGER and J. VAN LOON (Rec. trav. chim., 1931, **50**, 591—600).—Twitchell's method is best carried out with pure olive oil at 15°, higher temps. giving lower contents of solid acids; the saturated acids separated by Bertram's method have a small I val. Polymerisation of the oil, which is particularly marked with Ni at 200°, and must therefore occur during hydrogenation, leads to a lower I val. (Wijs). Application of Bertram's method to such a product causes partial depolymerisation, but the remaining polymerised acids resist oxidation, and form insol. Mg salts, which are difficultly decomposed by acids; consequently the "saturated" acids are contaminated with them, and are marked by high n and I val. Twitchell's method is even less satisfactory. The Pb salts of the polymerised acids are insol. or almost insol. in EtOH; possibly they also form mixed salts with the saturated acids. Saturated acids are also found in the liquid acids and lead to a low I val.

H. A. PIGGOTT.

Catalytic decomposition of oils and other vegetable products. I. Olive oil. L. BERMEJO and V. G. ARANDA (Anal. Fís. Quím., 1931, **29**, 284—293).—Passage of the vapour of olive oil over a catalyst of Fe_2O_3 and Al_2O_3 at 550° yields a gas containing H_2 50%, C_nH_{2n+2} 23·5%, C_nH_{2n} 8·2%, CO 15·3%, and liquid products, b. p. 40—280°, containing H_2O, unsaturated compounds, free acid, and C. By heating olive oil at 300° with 10% of $ZnCl_2$ a somewhat violent reaction ensues; on distillation, cracking of the products is evidenced by the gradual fall of the distilling temp., after the first fraction has passed over, from about 240° to 85°. The product of the direct distillation (98—240°) separates into an acid aq. layer and an oil (d 0·8273) from which a paraffin-like solid separates at 10°. The cracked product has d 0·7875, I val. (Hübl) 59·7. At the conclusion of the distillation a gas containing H_2+ paraffins 87·8% is evolved. The residue resembles coke, but if the distillation is conducted in a current of air or in vac. the residue is analogous to asphalt.

H. F. GILLBE.

Tetracosoic acid of peanut oil. F. A. TAYLOR (J. Biol. Chem., 1931, **91**, 541—550).—The method of isolation of the higher saturated acids of peanut oil is improved. Fractionation of these yielded n-tetracosoic acid, m. p. 84—85° (Me ester, m. p. 58·5—59·5°; Et ester, m. p. 55—56°), identical with synthetic specimens (A., 1924, i, 828), and fractions of higher and lower mol. wt. Lignoceric acid, m. p. 81°, is probably a mixture.

R. S. CAHN.

Bromides of elæostearic acid. II. Tetrabromide. J. VAN LOON (Rec. trav. chim., 1931, **50**, 638—644; cf. this vol., 335).—Elæostearic acid tetrabromide, m. p. 114·8°, interacts only very slowly with Wijs' solution, 6—8 weeks' contact being needed for the theoretical absorption of Cl; no absorption of Br occurs from Kaufmann's solution. In view of the comparative ease of determination of the unsaturation of elæostearic acid by both these methods it is concluded that the cryst. tetrabromide is a product of rearrangement of the original tetrabromide formed in solution.

H. A. PIGGOTT.

Composition of linseed oil and the designations α- and β-linoleic and α- and β-linolenic acids. H. VAN DER VEEN (Chem. Umschau, 1931, **38**, 117—120).—The bromination and debromination of the unsaturated acids are rejected as a basis for quant. analysis of drying oils. Bromination of a homogeneous $\Delta^{\theta\lambda}$-linolelaidic acid (cf. Diss., Delft, 1928) yielded a mixture of several bromides. Doubt is cast on the validity of thiocyanometric analysis for oils containing linolenic acid.

E. LEWKOWITSCH.

Rate of hydrogenation of acetoacetic ester, dehydracetic acid, benzene, phenol, and aniline over nickel at pressures from 27 to 350 atm. H. ADKINS, H. I. CRAMER, and R. CONNOR.—See this vol., 693.

Condensation of ortho-esters with acetoacetic and malonic esters. P. P. T. SAH (J. Amer. Chem. Soc., 1931, **53**, 1836—1839).—Triethyl orthoacetate (1 mol.) condenses with 1 mol. of ethyl acetoacetate and malonate in boiling Ac_2O (2 mols.) in presence or absence of $ZnCl_2$ forming *ethyl α-ethoxyethylideneacetoacetate*, b. p. 108—123°/3 mm. (*Cu* salt), and *α-ethoxyethylidenemalonate*, b. p. 123—128°/3 mm. (*Cu* salt), respectively. *Ethyl α-ethoxybenzylideneacetoacetate*, b. p. 185—186°/3 mm. (*Cu* salt), and *α-ethoxybenzylidenemalonate*, b. p. 188—190°/3 mm. (*Cu* salt), are prepared similarly from triethyl orthobenzoate, b. p. 240°, 128—130°/3 mm., which is obtained from benzotrichloride and alcoholic NaOEt.

H. BURTON.

[Preparation of] fumaric acid. N. A. MILAS (Organic Syntheses, 1931, **11**, 46—48).

[Preparation of] ethyl pimelate. A. MULLER and E. ROLZ (Organic Syntheses, 1931, **11**, 42—45).

Preparation of esters. F. ADICKES, W. BRUNNERT, and O. LUCKER (J. pr. Chem., 1931, [ii], **130**, 163—176).—Optimal conditions are described for the preparation of ethyl methanetricarboxylate (converted by SO_2Cl_2 at 100° into *ethyl chloromethanetricarboxylate*, b. p. 145—147°/10 mm.) and ethanehexacarboxylate, ethoxalyl chloride, ethyl *cyclo*propane-1 : 1-dicarboxylate and diethoxymalonate, Ph_3PO_4, phenyl formate, acetate, and oxalate.

J. W. BAKER.

Structure of tartaric acids. M. AMADORI (Gazzetta, 1931, **61**, 215—229).—Measurements of the sp. conductivity of the complexes formed by tartaric and boric acids in solution lead to the conclusion that in the active acid mols. the CO_2H groups are on the opposite sides and the OH groups are on the same side, whilst in the inactive acid the pairs of CO_2H and OH groups are on opposite sides. Following the method of Boeseken and Coops, it has been found that in the boric acid complexes two $(\cdot O\cdot CH\cdot CO_2)BOH$ groups are formed and these are disposed on opposite sides in the molecule. It would be convenient, therefore, to adopt the scheme of representing the structure

of these acids by a projection on the plane normal to the axis of the central C atoms. O. F. LUBATTI.

Manganous tartrates. M. AMADORI (Gazzetta, 1931, **61**, 230—241).—Dobbin's work on the formation of the normal Mn tartrate in neutral solutions is confirmed, but in basic solutions other products are formed. Treatment of Mn tartrate with solutions of NaOH and KOH in varying proportions produces $Mn_2C_4H_2O_6,6H_2O$, $MnNa_2C_4H_2O_6,6H_2O$, and $MnK_2C_4H_2O_6,6H_2O$ in addition to the normal $Mn^{\cdot\cdot}$ salt ($2H_2O$). The conditions which determine the formation and stability of these compounds at different concentrations are recorded.

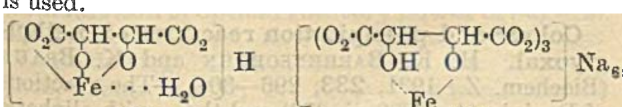
O. F. LUBATTI.

Oxidation products of manganese tartrate in alkaline solutions. M. AMADORI (Gazzetta, 1931, **61**, 241—254).—Mixtures containing $MnCl_2$, alkali tartrate and hydroxide in various proportions and concentrations were treated with a current of air to prevent separation of $Mn^{\cdot\cdot}$ compounds. In some cases the solution is oxidised and becomes green or red. Under other conditions the following products are formed: *manganosomanganic tartrate*, $C_4H_2O_6Mn(MnOH),5H_2O$; sodium manganic tartrate, $MnNa_5(C_4H_2O_6)_2,11H_2O$ (green); manganese and alkali manganites of various composition, dark grey or black. Analogous compounds are obtained with KOH, but potassium manganic tartrate is not formed.

Alkali and manganese manganites separate from more dil. solutions as mixtures of MnO_2, MnO, and Na_2O or K_2O. In these the Mn is oxidised in the ratio $MnO_2:MnO=1:1$ if the solution contains a small amount of hydroxide, but if the hydroxide is in excess oxidation occurs in the ratio 4 : 1. The quantity of the tartrate or the dilution has only a slight effect on the degree of oxidation in the deposit.

The oxidation of $Mn^{\cdot\cdot}$ salts in presence of tartrates is much more rapid than that of $Mn(OH)_2$ in absence of these salts. O. F. LUBATTI.

Complex iron tartrates. W. FRANKE (Annalen, 1931, **486**, 242—284).—The complex ferric tartrate, prepared from $Fe(NO_3)_3$ in presence of NaOH, shows a max. intensity of colour (green) between p_H 4·5 and p_H 6·5. The colour decreases rapidly as p_H increases, and is most intense when the concentrations of tartrate and Fe are equal. From solutions containing Fe^{III}/tartaric acid in the ratio >1, an intensely yellow ppt. (I) is obtained, which forms an easily sol. Na salt. A hot conc. solution of $FeCl_3$ and tartaric acid in mol. proportion loses HCl and, on cooling and removing the precipitated tartaric acid, an intense citron-yellow ppt. of a tribasic acid, $[CO_2H{\cdot}CH(OH){\cdot}CH(OH){\cdot}CO_2FeCl_2](H_2O)_3$, is obtained, which shows the reactions of the Fe^{III} ion. If $Fe(NO_3)_3$ replaces $FeCl_3$, no compound is formed; and, in presence of HNO_3, the tartaric acid is oxidised. For the determination of the concentration of Fe^{III}, the measurement of the reduction potential Fe^{III}/Fe^{II} is used.



(I.) (II.)

Measurements of colour and of p_H of mixtures of Na tartrate, Na ferritartrate, and its higher complex are complicated by reason of dissociation and hydrolysis. When the ratio of $NaOH/Fe^{III}$ is 3, the mixture is green and II is obtained. It is formed from Na tartrate, NaOH, and Na ferritartrate in the ratio 3 : 3 : 1 and is a tritartrate-ferric acid, containing 6-co-ordinated Fe.

If the alkaline solution of the greenish Fe^{III} salt be treated with Fe^{II} salt, an emerald-green colour is obtained. The same colour occurs as an intermediary in the autoxidation of ferrous tartrate solutions. The colours formed when different quantities of $Fe(NO_3)_2$ are added to a standard solution of Na ferritartrate are given. Max. intensity is obtained when the ratio Fe^{II}/Fe^{III} is about 1·25, and may be followed by precipitation of impure green $Fe(OH)_2$, depending on the concentration of $Fe(NO_3)_2$.

By mixing molar solutions of $FeSO_4$ and disodium tartrate in N_2, a light green ferrous tartrate ($2H_2O$) is obtained, which is not readily autoxidised and gives the normal reactions for $Fe^{\cdot\cdot}$ ion. By using excess of Na tartrate $Na_2Fe(C_4H_4O_6)_2,2H_2O$ results as a white, amorphous compound. The aq. solution gives all the reactions of the $Fe^{\cdot\cdot}$ ion; but the salt is decomposed by water to give ferrous tartrate and disodium tartrate, the dissociation const. being approx. invariable. The dissociation of ferrous tartrate is measured; at $M/200$, it is one third dissociated, but this is decreased considerably by the presence of Na tartrate, 6—8 parts entirely suppressing dissociation. Measurements of the dissociation of ferrous hydrogen tartrate alone and in presence of free tartaric acid and of ferrous tartrate in presence of tartaric acid are also described. These results offer an explanation of the conclusions reached by Wieland and Franke (A., 1927, 944; 1928, 965) in the autoxidation of the system Fe^{II}–tartaric acid.

A suspension of ferrous tartrate or disodium ferrous tartrate in alkali develops a feeble green colour which becomes deep green with a trace of O_2 and reacts as a Fe^{II}–Fe^{III} complex. The constitution of the Fe^{II} complex in the light green solution has been determined. By varying the amount of alkali with a const. quantity of neutral ferrous tartrate solution a compound of the type $C_4H_4O_6{<}^{Fe\cdot O\cdot Fe}_{Fe}{>}C_4H_4O_6$ appears to be present and the formation of varying coloured ppts. is described. Precipitation with EtOH of a solution containing equiv. quantities of Na ferrotartrate and NaOH affords the Na salt of the tribasic ferrous ditartaric acid, analogous to I.

The potential of the Fe^{II}–Fe^{III} complex has been measured and is dependent on the p_H value of the solution. The curve closely approaches that of the H electrode in strongly alkaline solution. The time of autoxidation is 10,000 times as rapid at p_H 12·7 as at p_H 1·7. The parallelism between time of autoxidation and potential is clearly shown. The significance of these facts in the activation of autoxidation is discussed. F. R. SHAW.

Electrometric studies of complex formation. II. Tartrates of bismuth. C. MORTON (Quart. J. Pharm., 1931, 4, 1—13).—The existence of the four

sparingly sol. tartrates of Bi described by Corfield and Adams (Yearb. Pharm., 1923, 576; 1924, 594) has been confirmed. When the compounds are dissolved in alkali tartrate solutions and the solutions are titrated with NaOH, the neutralisation curve determined by the glass electrode method (A., 1930, 1009; this vol., 43) indicates that $2\frac{1}{6}$, $1\frac{2}{3}$, $1\frac{1}{6}$, and $\frac{2}{3}$ mols. of tartaric acid have been liberated, respectively, from the compounds in which the ratios $Bi : C_4H_4O_6$ are 1 : 2·5, 1 : 2, 1 : 1·5, and 1 : 1. The compounds are, therefore, not complex acids, but true salts of the weak acid–very weak base type, having the compositions: $Bi_2(C_4H_4O_6)_3,2H_2C_4H_4O_6$; $Bi_2(C_4H_4O_6)_3,H_2C_4H_4O_6$; $Bi_2(C_4H_4O_6)_3$; $Bi(OH)C_4H_4O_6$. These are hydrolysed in solution to the same neutral complex, $2Bi(OH)_3,Bi(OH)C_4H_4O_6$, and tartaric acid.

The "bismuth and sodium tartrates" obtained by dissolving the insol. tartrates in NaOH solutions are equilibrium mixtures of the complex $2Bi(OH)_3,Bi(OH)C_4H_4O_6$ with Na tartrate. There is no evidence of the existence of complex anions in the neutralised solutions. The ppts. produced by EtOH are mixtures.

It is suggested that the method of Corfield and Adams for the prep. of the normal tartrate (1 : 1·5) be adopted as standard, and that "bismuth and sodium tartrate" be prepared by neutralisation of the product and evaporation.

In the absence of complex formation, the precipitation of basic salts of Bi by the addition of alkalis commences at p_H 1·7. It is delayed in the presence of glycerol. R. K. CALLOW.

[Preparation of] citraconic anhydride and acid. R. L. SHRINER, S. G. FORD, and L. J. ROLL (Organic Syntheses, 1931, **11**, 28—29).

[Preparation of] itaconic anhydride and acid. R. L. SHRINER, S. G. FORD, and L. J. ROLL (Organic Syntheses, 1931, **11**, 70—72).

[Preparation of] mesaconic acid. R. L. SHRINER, S. G. FORD, and L. J. ROLL (Organic Syntheses, 1931, **11**, 74—75).

Preparation of gluconic acid. M. PICHON (Bull. Sci. pharmacol., 1930, **37**, 51—53; Chem. Zentr., 1931, i, 924).—Br (150 g.) in small portions is added to a stirred, cold aq. solution of dextrose (100 g. in 500 c.c.); after 30 hrs. at 20° a 5% excess of H_2O_2 (determined on an aliquot portion) is added to oxidise HBr, any HCl being removed with Ag_2O_2. The filtrate is evaporated and the gluconic acid precipitated (yield 70%) as the Ca or Ba salt.

A. A. ELDRIDGE.

[Preparation of] ethyl ethylenetetracarboxylate. B. B. CORSON and W. L. BENSON (Organic Syntheses, 1931, **11**, 36—38).

Decarboxylation of pectins and calcium pectates. C. M. CONRAD (J. Amer. Chem. Soc., 1931, **53**, 1999—2003).—Decarboxylation of apple and lemon pectins occurs appreciably even with boiling 0·1% mineral acid. The rate of decarboxylation of Ca pectate from various sources by boiling 2% H_2SO_4 is approx. the same in each case. H. BURTON.

Sulphonic acids of higher fatty acids. Action of chlorosulphonic acid on Δ^{ι}-undecenoic acid. K. H. BAUER and J. STOCKHAUSEN (J. pr. Chem., 1931, [ii], **130**, 35—44).—*κ-Xanthatoundecoic acid*, m. p. 88°, prepared by interaction of the Na salt of the corresponding κ-bromo-acid and K xanthate in aq. solution, is converted by cold alcoholic NH_3 into *κ-dithiocarbamato-*, m. p. 38°, and *κ-thiol-undecoic acid*, m. p. 94—95°. The last is oxidised by HNO_3 (*d* 1·2) to the corresponding *disulphide*, m. p. 105—106°, unaccompanied by the expected sulphonic acid. The action of $ClSO_3H$ on Δ^{ι}-undecenoic acid and hydrolysis of the product gives the two possible *hydroxysulphoundecoic acids*, m. p. 208—209° (*Ac* derivative, m. p. 199—200°), and m. p. 186—187° (*Ac* derivative, m. p. 211—212°), which are separated by means of Et_2O, in which the former alone is sol. The product of interaction of Δ^{ι}-undecenoic acid with NaOCl, probably *ι-chloro-κ-hydroxyundecoic acid*, m. p. 62°, is only partly sulphonated by $ClSO_3H$, and the oily product is immediately decomposed by water.

H. A. PIGGOTT.

Disulphosuccinic acid. II. H. J. BACKER and J. M. VAN DER ZANDEN (Rec. trav. chim., 1931, **50**, 645—654).—The product obtained by interaction of acetylenedicarboxylic acid and a sulphite (cf. A., 1928, 809) is shown by the resolution of its *distrychnine dihydrogen* salt ($+3H_2O$) to be dl-αβ-*disulphosuccinic acid*, values of $M[\alpha]_D^{15}$ of +25·4°, −26·1° being observed. This acid is also produced by sulphonation of succinic acid or anhydride (cf. A., 1927, 856) and by interaction of $KHSO_3$ with the K salts of sulphomaleic, bromomaleic, and bromofumaric acids in aq. solution at 160°, room temp., and 100°, respectively. In the case of sulphomaleic acid partial conversion into sulphofumaric acid seems to occur. In no case was the expected *meso*-compound isolated. The *dipotassium dihydrogen*, *dibrucine dihydrogen*, *tribrucine hydrogen*, *tetrabrucine*, and *quinine trihydrogen* salts are described.

Bromofumaric acid is conveniently prepared by exposing bromomaleic acid in aq. solution containing a little Br to sunlight. H. A. PIGGOTT.

[Preparation of] β-chloropropaldehyde acetal. E. J. WITZEMANN, W. L. EVANS, H. HASS, and E. F. SCHROEDER (Organic Syntheses, 1931, **11**, 26—27).

[Preparation of] acraldehyde acetal. E. J. WITZEMANN, W. L. EVANS, H. HASS, and E. F. SCHROEDER (Organic Syntheses, 1931, **11**, 1—2).

[Preparation of] *dl*-glyceraldehyde and its acetal. E. J. WITZEMANN, W. L. EVANS, H. HASS, and E. F. SCHROEDER (Organic Syntheses, 1931, **11**, 50—51, 52—53).

(+)ε-Hydroxy-γ-methylhexaldehyde, an ε-hydroxyaldehyde. B. HELFERICH and G. SPARMBERG (Ber., 1931, **64**, [*B*], 1151; cf. this vol., 336).—The 2 : 4-*dinitrophenylhydrazone* of (+)ε-hydroxy-γ-methylhexaldehyde has m. p. 82·5—83·5° (corr.), $[\alpha]_D$ +34° in EtOH. By means of it the fission of the corresponding methyl-lactolide by *N*-HCl is established. H. WREN.

Colour and precipitation reactions of methylglyoxal. H. K. BARRENSCHEEN and K. BRAUN (Biochem. Z., 1931, **233**, 296—304).—The reactions of Deniges (A., 1909, ii, 272) and those with aliphatic

and heterocyclic amines, Na nitroprusside, or Ni and NH_2OH are not specific for methylglyoxal and cannot be used for its determination. The substance can be detected at a dilution of 1 : 250,000 by the colour which it produces with pure pyrrole and HCl. Of precipitation reactions the most sensitive is that with 2 : 4-dinitrophenylhydrazine, with which 0·001 mg. per c.c. of methylglyoxal can be detected.

W. McCartney.

Colorimetric micro-determination of methylglyoxal. H. K. Barrenscheen and M. Dreguss (Biochem. Z., 1931, **233**, 305—310; cf. preceding abstract).—A method by which 0·0005 mg. of the methylglyoxal in 2 c.c. of biological fluid can be colorimetrically determined as bis-2 : 4-dinitrophenylhydrazone is described. The accuracy is not affected by the presence of pyruvic acid, MeHCO, dextrose, lævulose, hexosediphosphate, or lactic acid even in concentrations several hundred times that of the methylglyoxal.

W. McCartney.

[Preparation of] heptaldoxime. E. W. Bousquet (Organic Syntheses, 1931, **11**, 54—56).

Action of iodine in alkaline solution on ketones, R·CO·CH_3. V. Cuculescu (Bul. Fac. Stiinte Cernauti, 1928, **2**, 137—142; Chem. Zentr., 1931, i, 604).—CHI_3 and the following products were obtained: from methyl ethyl ketone, propionic acid; methyl propyl, butyric acid; methyl butyl, valeric acid; methyl hexyl, heptoic acid; acetophenone, BzOH; *p*-methoxyacetophenone, anisic acid; trihydroxyacetophenone, 2 : 3 : 4-trihydroxybenzoic acid; pyruvic acid, oxalic acid. Acetoacetic acid gave no CHI_3.

A. A. Eldridge.

Dihydroxyacetone. H. G. Reeves and E. T. Renbom (Biochem. J., 1931, **25**, 412—413).—A pure and stable bimol. α-modification of dihydroxyacetone can be obtained by shaking "oxantin" in EtOH or $COMe_2$ and recrystallising it from hot EtOH.

S. S. Zilva.

Internal complex salts of bivalent iron. B. Emmert and R. Jarczynski (Ber., 1931, **64**, [*B*], 1072—1076).—Acetylacetone, benzoylacetone, and ethyl acetoacetate are converted by $FeSO_4$ in presence of an excess of pyridine into the *compounds* $C_{10}H_{14}O_4Fe,2C_5H_5N$, $C_{20}H_{18}O_4Fe,2C_5H_5N$, and $C_{12}H_{18}O_6Fe,2C_5H_5N$, respectively, whilst salicylaldehyde affords the *substance*, $C_{14}H_{10}O_4Fe,2C_5H_5N$. If pyridine is replaced by trialkylamines or piperidine, acetylacetone is converted into the *compound* $C_{10}H_{14}O_4Fe,1{\cdot}5H_2O$, which, after dehydration, can be sublimed, thus yielding *ferrous acetylacetone*, m. p. 201° after darkening at 150° and softening at 170°. The sesquihydrate is also formed in the presence of a little dil. NH_3, whereas much NH_3 yields the *substance* $C_{10}H_{14}O_4Fe,2NH_3$. The compounds are relatively stable when dry, moderately rapidly oxidised when moist. Under solvents they absorb more O_2 than is required for the conversion of Fe^{II} into Fe^{III}.

H. Wren.

Calculation of optical rotatory power of sugars. XII. Steric series. K. Freundenberg (Sitzungsber. Heidelberg, Akad. Wiss., 1931, No. 2, 3—8; Chem. Zentr., 1931, i, 1274).—Hudson's furoid structure for α-mannose, lyxose, rhamnose, α- and β-galactose, and β-fructose is unacceptable; agreement of the calc. and observed rotatory powers arises from the calculation, which is criticised.

A. A. Eldridge.

Oxidation of carbohydrates and fats by air in presence of yellow phosphorus. S. N. Chakravarti and N. R. Dhar.—See this vol., 691.

Monomethylglucose of Pacsu. P. A. Levene, G. M. Meyer, and A. L. Raymond (J. Biol. Chem., 1931, **91**, 497—504).—The substance described by Pacsu (A., 1925, i, 1242) as 4-methylglucose is 2-methylglucose (this vol., 71), a conclusion verified by prep. from it of its phenylhydrazone and of glucosazone (and not a methylglucosazone). Lehmann and Maquenne's method gives a reducing value 0·87 equiv. of O per mol. 2-Methylglucose diethylmercaptal (A., 1930, 1274; this vol., 71) was prepared from glucosediethylmercaptal by Pacsu's method and from Pacsu's methylglucose and ethyl mercaptan. The Me group must be in position 2 because the compound differs from 3-methylglucose, positions 4 and 5 are excluded by changes in rotation during glucoside formation, and the sugar is oxidised by NHO_3 to a methylsaccharic acid.

R. S. Cahn.

Structure of carbohydrates. I. Synthesis of a 5-methoxyketose. E. F. Hersant and W. H. Linnell (Quart. J. Pharm., 1931, 4, 52—100).—dl-5-*Methoxyfructose*, synthesised by a modification of Fischer's synthesis of acrose, has been converted into dl-*tetramethylfructopyranose*, which is the racemic form of normal tetramethylfructose. The latter, therefore, contains an amylene-oxide ring, in agreement with the conclusions of Haworth, but contrary to those of Hudson.

Improvements of known methods are employed in the first stages of the synthesis, which are as follows: (*a*) Nitromethane ⟶ β-nitro-αγ-dihydroxy-β-hydroxymethylpropane ⟶ β-hydroxylamino-αγ-dihydroxy-β-hydroxymethylpropane ⟶ dihydroxyacetoneoxime ⟶ dihydroxyacetone, and (*b*) glycerol ⟶ acraldehyde ⟶ β-chloropropionacetal ⟶ acraldehydeacetal ⟶ α-chloro-β-hydroxypropaldehydeacetal. The last-named compound is converted by refluxing with NaOMe in MeOH into β-*hydroxy-α-methoxypropaldehydeacetal*, b. p. 100—102°/4 mm., which is hydrolysed to β-*hydroxy-α-methoxypropaldehyde*, an oil, decomp. when heated (*oxime*, an oil; *diphloroglucinol compound*; p-*bromophenylhydrazone*, m. p. 160°).

Condensation of dihydroxyacetone with β-hydroxy-α-methoxypropaldehyde occurs in 0·1% $Ba(OH)_2$ solution during 3 weeks. The isolated product is a syrup, but by heating the mixture with phenylhydrazine a tarry mixture of osazones is obtained, from which dl-5-*methoxyfructosazone*, m. p. 182—185°, is isolated. Hydrolysis with conc. HCl and direct reduction of the osone by Zn and AcOH yields dl-5-*methoxyfructose*, m. p. 80—85°. By fermentation with yeast extract the *l*-isomeride is preferentially destroyed, and a min. value of $[\alpha]_D$ +30·6° in H_2O is deduced for the (—)*d*-form. The position of the OMe group is confirmed by the non-formation of a fructoside with MeOH containing 1% HCl. Treatment of *dl*-5-methoxyfructose with Me_2SO_4 and

NaOH, followed by MeI and Ag_2O, yields cryst. *tetramethylmethylfructoside*, m. p. about room temp. This resembles normal tetramethylmethylfructoside in its stability to $KMnO_4$ and its low rate of hydrolysis by HCl. Hydrolysis yields dl-*tetramethylfructose*, m. p. 95—96°, not depressed by admixture with an equal wt. of normal tetramethylfructose.

By oxidation of *dl*-tetramethylfructose with HNO_3 a syrupy *methylfructuronic acid* is obtained, further oxidised by $Ba(MnO_4)_2$ to dl-*trimethyl*-r-*arabonolactone*. Measurements of the change of sp. conductivity of the aq. solution showed that the rate of hydrolysis was approx. equal to that of normal trimethyl-δ-arabonolactone and much greater than that of trimethyl-γ-arabonolactone. R. K. Callow.

Optical rotation and atomic dimensions. IX. [α-]Halogenotetra-acetyl derivatives of mannose. Configurational pecularities. D. H. Brauns (J. Amer. Chem. Soc., 1931, 53, 2004—2005; cf. A., 1929, 913).—The four derivatives exhibit deviations from the regular relationship observed with the corresponding derivatives of other monose sugars, which are explained by models indicating that in the mannose derivatives the Ac group attached to the second C atom influences the halogens through the Me group. The consequences of the explanation are considered. J. G. A. Griffiths.

Syntheses in the carbohydrate group with the aid of sublimed ferric chloride. II. Preparation of cellobiosides of the α-series. G. Zemplén and Z. Csuros (Ber., 1931, 64, [*B*], 993—1000; cf. A., 1929, 683).—Cellibiose octa-acetate is boiled with measured amounts of EtOH and $FeCl_3$ in $CHCl_3$. With less than 1 mol. $FeCl_3$ per mol. of octa-acetate bioside formation occurs poorly in presence of a 50% excess of EtOH, since much material remains unattacked. With 1 mol. $FeCl_3$ the max. yield (about 20%) of α-ethylcellobioside is attained with a 20—50% excess of EtOH. Better results are inhibited by the deacetylating action of the $FeCl_3$, which cannot be avoided by abbreviating the duration of the change. Greater excess of EtOH hampers the reaction without displacing bioside formation in favour of the β-form. Reaction occurs in C_6H_6, but the yields are poor because the octa-acetate is sparingly sol. Negative results are obtained in anhyd. $COMe_2$ and when $FeCl_3$ is replaced by $HgCl_2$, $ZnCl_2$, or $CrCl_3$. With $Pr^{\beta}OH$ 24% yields are obtained, but no change is observed with MeOH or *tert*.-BuOH. α-*iso*Propylcellobioside hepta-acetate has m. p. 209°, +60·8° in $CHCl_3$. H. Wren.

Reactions relating to carbohydrates and polysaccharides. XXXV. Polysaccharide synthesis by the action of *Acetobacter xylinus* on carbohydrates and related compounds. H. L. A. Tarr and H. Hibbert (Canad. J. Res., 1931, 4, 373—388; cf. this vol., 827).—The most suitable medium for the prep. of polysaccharide films with the aid of *A. xylinus* is asparagine 0·1%, KH_2PO_4 0·5%, NaCl 0·1%, EtOH 0·5%, C source 5%. Replacement of asparagine by peptone or yeast water gives carbohydrate formation without other C source. Other N sources are less satisfactory. With this solution a max. yield (4·1%) is obtained from lævulose. Of the other C sources tried, only hexoses, or substances which might give rise to hexoses under the experimental conditions, were found to be effective. The polysaccharide formed is possibly identical with cellulose. A. A. Levi.

Asymmetric, catalytic racemisation of amygdalin. I. A. Smith (Ber., 1931, 64, [*B*], 1115—1123).—Racemisation of amygdalin by aq. KOH leads to a mandelic acid, $[\alpha]_D$ about +16° in H_2O, whereas with alkali in MeOH the sp. rotation of the resultant acid varies from feebly lævorotatory to +57·8°. Polarimetric observation of the aq. alkaline solutions shows a continuous increase in optical activity, whereas in MeOH an initial rapid rise is followed by a slow decline and finally by a gradual rise, which terminates with a much greater activity than at the end of the first phase. At the end of the initial rise the CN group is at any rate partly intact, since the product gives the characteristic magenta coloration with conc. H_2SO_4. At the end of the second phase the CN group appears to have entered into reaction and the presence of an OMe group in the mol. is established. This OMe group is present at the end of the third phase. *iso*Amygdalin is changed in the same manner as amygdalin by KOH in MeOH, but the first phase of this change is absent. H. Wren.

Reception of glucosyl by the hydroxyls in the anthraquinone nucleus. A. Müller (Ber., 1931, 64, [*B*], 1057—1067; cf. A., 1930, 71).—Quinalizarin is converted by acetocellobiosyl bromide and Ag_2O in presence of quinoline into 2-*acetocellobiosylquinalizarin*, m. p. 256—258°, $[\alpha]_D^{21}$ −48·94°. 1 : 8-*Dihydroxy*-2-*acetogalactoxyanthraquinone*, m. p. 264°, is obtained similarly. From 1 : 4 : 8-trihydroxyanthraquinone and acetobromoglucose followed by acetylation is derived 1 : 4(5)-*diacetoxy*-8-*acetoglucoxyanthraquinone*, m. p. 203°, $[\alpha]^{20}$ −17·65°. 2 : 3-*Diacetoglucoxyanthraquinone*, m. p. 236—237°, $[\alpha]^{20}$ −69·06°, 1 : 3-*diacetoglucoxyanthraquinone*, m. p. 228°, $[\alpha]^{20}$ −61·58°, and 1 : 7-*diacetoglucoxyanthraquinone*, m. p. 216°, $[\alpha]^{20}$ −89·00°, are obtained similarly from hystazarin, xanthopurpurin, and *m*-benzdioxyanthraquinone, respectively. Treatment of the requisite glucoside with MeI and Ag_2O affords 1-*methoxy*-8-*acetoglucoxyanthraquinone*, m. p. 227°, $[\alpha]^{20}$ −99·20°, 1-*methoxy*-2 : 7-*diacetoglucoxyanthraquinone*, m. p. 227—228°, $[\alpha]_D^{20}$ −48·93°, and 1 : 4(8)-*dimethoxy*-2-*acetoglucoxyanthraquinone*, m. p. 140—143°, $[\alpha]^{20}$ −13·03°. The *Na* salt of glucosylalizarin (monohydrate), glucosylchrysazin, Na_2 salts of 2 : 6-diglucosylrufiopin and 2-glucosyloxyanthrarufin, *NaH* and Na_2 salts of 2-glucosylquinalizarin and the *Na* salt of 2-glucosylpurpurin are described. All rotations are in $CHCl_3$. H. Wren.

Strophanthin. XX. Conversion of *iso*strophanthidic acid into the deoxo-derivative. W. A. Jacobs, R. C. Elderfield, T. B. Grave, and E. W. Wignall (J. Biol. Chem., 1931, 91, 617—623; cf. this vol., 606).—Heating the *semicarbazone* of *iso*strophanthidic acid, m. p. 305° (after darkening), with NaOEt at 180° gave *deoxo*-α-iso*strophanthidic acid*, $C_{23}H_{34}O_6$ (+approx. $1H_2O$), m. p. 215—217° (decomp.), which does not decolorise $KMnO_4$ in NH_3 solution and with H_2SO_4 gives a deep amber solution changing to

red with olive reflex on keeping. Reduction of *α-iso*-strophanthidic acid by Clemmensen's method in boiling MeOH (but not in AcOH) gave *methyl γ*-iso-*strophanthidolate*, $C_{24}H_{36}O_7$, m. p. 229—231°, $[\alpha]_D$ +98° in pyridine, but in MeOH below 30° *methyl* α-iso*strophanthidolate*, m. p. 223°, $[\alpha]_D^{24}$ —18·5° in pyridine. Attempts to replace the primary OH group of the latter by halogens failed. *iso*Strophanthidic acid and its Me ester in pyridine have $[\alpha]^{20}$ —14° and —15°, respectively. AcCl replaced only the secondary OH group of methyl *α-iso*strophanthidate, giving the *Ac* derivative, m. p. 156—157° (decomp., variable), which on hydrogenation in EtOH in the presence of PtO_2 gave *methyl acetyl*-α-iso*strophanthidolate*, m. p. 145° (decomp.), $[\alpha]_D^{23}$ —25° in pyridine. This with SO_2Cl_2 gave a neutral *sulphite*, $C_{24}H_{31}O_8S$, m. p. 220°, in which the primary and secondary OH groups are bridged by SO. Methyl *iso*strophanthidate gave similarly a neutral *sulphite*, $C_{24}H_{32}O_8S$, m. p. 228°, in which the tertiary OH and secondary OH groups are bridged by SO. R. S. CAHN.

Strophanthin. XXI. Correlation of strophanthidin and periplogenin. W. A. JACOBS and R. C. ELDERFIELD (J. Biol. Chem., 1931, **91**, 625—628; cf. preceding abstract).—*α-iso*Periplogenic acid (A., 1928, 1359), m. p. 215—217° (const. when dried at 100°/20 mm.), is identical with deoxo-*α-iso*strophanthidic acid (*loc. cit.*). The *Me* esters of both acids, prepared by diazomethane in $COMe_2$, had m. p. 242° (not 252° as previously stated), alone or mixed, $[\alpha]_D$ —30·2° and —33·2° in pyridine, and on oxidation with Kiliani's CrO_3 solution gave *methyl* α-iso*periplogonate* (*deoxy*-α-iso*strophanidonate*), $C_{24}H_{36}O_6$, m. p. 228° and 230°, with no depression on mixing, $[\alpha]_D$ —23° and —23·2° in pyridine, respectively. The sugar obtained from periplocymarin (*loc. cit.*) on hydrolysis with aq.-alcoholic HCl is identical with cymarose from cymarin (A., 1930, 1413), m. p. when dried, 100—102° (rapidly depressed by atm. H_2O to the previously recorded m. p. 93°) alone or mixed. Periplogenin is, therefore, deoxostrophanthidin, the CHO group of the latter being replaced by Me, and periplocymarin is deoxycymarin.

Methyl *iso*periplogonate on dehydration loses OH^{II}, yielding *methyl anhydro*iso*periplogonate*, which on hydrogenation gives a mixture of deoxy-derivatives, one of which is identical with methyl *iso*digitoxigonate. The acids obtained from the esters are also identical. Digitoxigenin is, therefore, deoxyperiplogenin and deoxodeoxystrophanthidin. R. S. CAHN.

Polarimetric reducing sugar relationships of starch hydrolytic products resulting from diastatic action. D. T. ENGLIS, G. T. PFEIFER, and J. L. GABBY (J. Amer. Chem. Soc., 1931, **53**, 1883—1889).—The polarisation–reduction ratios (expressed as Ventzke° 4-dm. tube/apparent maltose hydrate) of the hydrolysate of sol. starch by taka-diastase differ from the anticipated values. During the initial stages of hydrolysis the ratios are lower than the corresponding values using malt diastase, indicating differences in the initial course of hydrolysis by these amylases. Consistent results were not obtained. H. BURTON.

Carbohydrates and polysaccharides. XXXIV. Constitution of lævan and its relation to inulin. H. HIBBERT, R. S. TIPSON, and F. BRAUNS (Canad. J. Res., 1931, **4**, 221—239).—Lævan, m. p. 200° (softening at 182°), prepared by the action of *B. mesentericus* and of its enzyme prep. on sucrose, has $[\alpha]_D$ —45·3° in H_2O and gives, on hydrolysis with oxalic acid, lævulose in 97% yield. With Ac_2O and pyridine it affords *lævan triacetate*, m. p. 196° (softening at 106°), $[\alpha]_D$ +21·0° in $CHCl_3$, which regenerates lævan on treatment with KOH in EtOH. With Me_2SO_4 it affords *trimethyl-lævan*, m. p. 145—147°, $[\alpha]$ —89·0° in $CHCl_3$, which on hydrolysis yields 1 : 3 : 4-*trimethyl-γ-fructose*, m. p. 73°, $[\alpha]_D$ 16·5° in $CHCl_3$, +21·9° in CCl_4, and this combines with MeOH in presence of HCl to 1 : 3 : 4-*trimethylmethylfructoside*, b. p. 108—109°/0·024 mm., $[\alpha]_D$ +41·59° in $CHCl_3$, +57·35° in H_2O, which is also obtained when trimethyl-lævan is hydrolysed with MeOH containing HCl, and on methylation yields *tetramethyl-γ-fructose*, b. p. 87°/0·013 mm., $[\alpha]_D$ +29·53° in EtOH. The last on hydrolysis affords a *tetramethyl-γ-fructose*, b. p. 101°/0·030 mm., $[\alpha]_D$ +30·61° in H_2O. The constitution of 1 : 3 : 4-trimethylfructose was proved by oxidation to a dibasic *dimethyl-lactol acid*,

$$\begin{array}{l} CH(OMe)\cdot CH(CO_2H)\text{—} \\ CH(OMe)\cdot C(OH)(CO_2H) \end{array}\!\!>O$$

(*Ca* salt $+4H_2O$), which on esterification and methylation yields a *trimethyl-lactol acid dimethyl* ester, b. p. 112°/0·04 mm., $[\alpha]_D$ —19·4° in EtOH, from which the *diamide*, m. p. 192°, $[\alpha]_D$ —73·5° in H_2O, is obtained by the action of NH_3. The results indicate that lævan is a polymerised anhydro-fructofuranose with linkings at positions 2 and 6 of the fructose chain. B. LEVIN.

Two new crystalline dilævulose anhydrides from hydrolysed inulin. R. F. JACKSON and E. McDONALD (Bur. Stand. J. Res., 1931, **6**, 709—715).—Deacetylation of the mother-liquor from the crystallisation of dilævulose anhydride-I from hydrolysed inulin (A., 1929, 1280; cf. this vol., 72) and concentration affords successive crops of cryst. *dilævulose anhydride*-II, m. p. 198°, $[\alpha]_D^{20}$ +13·85° in H_2O, and III, m. p. 162°, $[\alpha]_D^{20}$ +135·64° in H_2O. Since the mean value $[\alpha]_D$ (+58·8°) of these three anhydrides agrees with that (55°) of the original mixture, the latter contains the three sugars in approx. equal proportions, and on this basis the mean mol. wt. of inulin is approx. 18,000. J. W. BAKER.

Least equivalent weight of cellulose. E. SCHMIDT, K. MEINEL, and W. JANDEBEUER (Naturwiss., 1931, **18**, 376).—From an examination of the cellulose obtained from different varieties of wood it is concluded that the least equiv. wt. corresponds with $(C_6H_{10}O_5)_{96}$. W. R. ANGUS.

Cellulose. XLII. Formation from cellulose fibres of a crystalline carbohydrate soluble in water and giving the Röntgen diagram of hydrocellulose. F. KLAGES (Ber., 1931, **64**, [*B*], 1193—1200; cf. this vol., 716).—Cellulose is converted by Ac_2O and H_2SO_4 into a mixture of acetates from which the glucose and cellobiose derivatives are greatly removed by crystallisation. The residual acetates are hydrolysed by Zemplén's method and the carbohydrates sol. in H_2O are fermented with yeast to remove dextrose. The unfermentable residue consists of cellobiose and a mixture of carbohydrates crystallis-

able from MeOH and H_2O. Fractional crystallisation results in the separation of products of I val. 17—20, $[\alpha]_D$ $+12\cdot5°$ to $+13\cdot7°$, and I val. 28—31, $[\alpha]_D$ $+18°$ to $+19°$, the properties of which agree closely with those of cellohexaose and cellotetraose (*loc. cit.*). All the preps. give sharply defined Röntgen diagrams, the interferences of which in position and intensity agree with those of hydrocellulose. It is assumed that a component closely related to hydrocellulose is invariably present. The possibility that this component is held in colloidal solution by carbohydrates which do not appear in the Röntgen diagram seems to be negatived by the readiness with which the preps. diffuse through a cellophane membrane; the various fractions obtained during dialysis all yield the hydrocellulose diagram. Although further purification cannot be effected by crystallisation from aq. MeOH, dialysis shows the products to be heterogeneous; the various fractions have approx. const. I val., whereas $[\alpha]^{20}$ varies between $+5\cdot0°$ and $-3\cdot9°$. The Röntgen diagrams of materials obtained from the mother-liquors of the crude preps. indicate the presence of cellobiose. They appear to consist invariably of mixtures of hydrocellulose and cellobiose, becoming poorer in the latter as I val. and optical activity decrease during crystallisation. Complete removal of cellobiose without affecting the hydrocellulose is impossible by means of emulsin. The products derived by restricted acetolysis have I val. similar to those described above, but considerably smaller optical activity. H. WREN.

Cellulose. XL. Dependence of viscosity of cellulose acetate solutions on purification of the fibre and conditions of acetylation. III. I. SAKURADA and K. HESS (Ber., 1931, 64, [*B*], 1174—1183).—With increasing purification of the fibre before acetylation, the apparent viscosity of the cellulose acetate solutions diminishes together with the strongly-marked anomaly with regard to the law of outflow. As with cellulose nitrate and NH_3–Cu–cellulose solutions (A., 1930, 1416; this vol., 469), the viscosimetric properties appear to be the result of fibre purification and de-organisation during which foreign matter with a great influence on the viscosity is removed, rather than of the existence of a large no. of chemical individuals with differing mol. wt. The samples used previously (*loc. cit.*) are moistened with 30% of H_2O and treated with Ac_2O and a little conc. H_2SO_4 in C_6H_6 at 55° for 16 hrs. With increase in the concentration of H_2SO_4 the viscosity of the acetates diminishes greatly. Determination of I vals. of the product indicates that the effect is due to the decomposing action of the acid on a substance accompanying cellulose in the fibres rather than to acetolytic degradation of cellulose. The Röntgen diagrams of certain of the acetates resemble those of cellulose acetate I. They represent non-homogeneous materials. After hydrolysis the products show the superposition of the interferences of natural cellulose and hydrocellulose. H. WREN.

Staudinger's relationship between viscosity and mol. wt. of preparations of cellulose. K. HESS and I. SAKURADA (Ber., 1931, 64, [*B*], 1183—1192).—The relationships $K_m = \eta_{sp.}/cM$ and $K_{cm} = M/Kc$ employed by Staudinger (A., 1930, 1415) are not independent; the uniformity of the results based on the two expressions does not necessarily substantiate Staudinger's reasoning. The applicability of the first equation depends on the certain determination of the val. $\eta_{sp.}$ as expression for the internal friction of the mols. This does not appear to be the case, since cellulose preps. have not been found which behave normally towards the law of outflow when investigated over a sufficiently wide range of concentration, dimension of capillary, and pressure. New measurements of the viscosity of cellulose acetate solutions of varied origin fail to confirm Staudinger's data, particularly with respect to the transition from the sol to gel condition. The constancy of the relationship $\eta_{sp.} \times$ I val. observed by Staudinger is considered to depend on the progressive removal during acetylation of integumental matter resulting in a diminution of viscosity and increased ease of attack by I with resulting higher I val. Such constancy is observed with products derived from the same fibre material in the course of a single reaction dependent on conditions of change, but not with preps. derived independently from different sources by various modes of chemical action. The propriety of applying Staudinger's method of the determination of the mol. wt. of highly-polymerised substances to cellulose preps. is denied. The relationship between Cu no. and viscosity is similar to that between I val. and viscosity. H. WREN.

Oxycellulose formation and histological structure of the cotton fibre. R. HALLER (Helv. Chim. Acta, 1931, 14, 578—593).—The different ways in which rupture of the cotton fibre can occur have been investigated by chemical modification of the material with different oxidising agents and acids, selectively staining the places at which attack is greatest by $SnCl_2$ and $AuCl_3$ solutions, and then causing disintegration to take place by swelling the fibres in NaOH or cuprammonium solutions. Oxycelluloses show transverse splitting and the formation of spirals, but the effects differ according to the oxidising agents used. Subsequent swelling with cuprammonium causes the hairs to split up into fine fibrils. Attack by acids appears to be more destructive, since the hairs are then broken into small fragments. Oxidation of hydrolysed acetate rayon produces no fibrils or spirals, so that this material has no such spiral structure. It is concluded that by the action of the oxidising agents the "binding substance" is first attacked and then dissolved in the alkali and that the more sparingly sol. lamella is then torn apart in the swelling process, thus liberating the fibrils which are the histological elements of the fibre. B. P. RIDGE.

Lignin and related compounds. VII. Kinetic study of the action of hypochlorous acid on spruce lignin and its bearing on the constitution of the spruce lignin molecule. H. HIBBERT and K. A. TAYLOR (Canad. J. Res., 1931, 4, 240—253).—The absorption of HOCl by lignin and methylated lignin at 0° is autocatalytic, due to the formation of HCl which strongly catalyses the reaction. The formation of HCl is independent of the absorption of HOCl. A comparison of the rates of absorption by lignin and

methylated lignin shows that the ketomethylene group if present plays no part in the reaction. The rapid absorption of Br from aq. Br at low concentrations by lignin dissolved in alkali indicates about 15% of a phenol nucleus, a value confirmed by the amount of HOCl absorbed. B. LEVIN.

[Preparation of] *n*-heptylamine. W. H. LYCAN, S. V. PUNTAMBEKER, and C. S. MARVEL (Organic Syntheses, 1931, **11**, 58—60).

α- and β-Forms of βδ-diaminopentane. C. J. DIPPELL (Rec. trav. chim., 1931, **50**, 525—546).—"α and "β"-βδ-Diaminopentanes are obtained in the approx. ratio of 3 : 7 by reduction of acetylacetone-dioxime with Na–Hg and AcOH or Na and EtOH (cf. A., 1898, i, 293; 1899, i, 562); Sn and HCl or H_2 and Pt-black failed as reducing agents. Complete conversion of the α- into the β-form could not be effected. By partial resolution of the (di)hydroxymethylenecamphor derivative the *dl*-configuration of the β-form is confirmed, a specimen of the l-*hydrobromide*, $[\alpha]_D$ −6·5°, being isolated. The following derivatives are described: *meso*- (α)-, b. p. 60—61°/22 mm. [*dihydrochloride*; *dihydrobromide*; *dichloroplatinate* ($+3H_2O$); *dichloroaurate*; *dipicrate*; *dipicrolonate*; *dibenzoyl*, m. p. 193—194°, and *hydroxymethylenecamphor* derivative, m. p. 174—175°]; *dl*-, b. p. 56—59°/22 mm. [*dihydrochloride*; *dihydrobromide*, *dinitrate*, m. p. 195; *dichloroplatinate* ($+1\frac{1}{2}H_2O$); *dichloroaurate*; *dipicrate*; *dipicrolonate*; *dibenzoyl*, m. p. 189°, and *dihydroxymethylenecamphor* derivative (various mixtures of *d*- and *l*-forms, partly separated by crystallisation)]. H. A. PIGGOTT.

Complex salts of cobalt and rhodium containing α- and β-βδ-diaminopentane. C. J. DIPPELL and F. M. JAEGER (Rec. trav. chim., 1931, **50**, 547—589).—The complex *salt* $[Co(\alpha\text{-}Ptn)_3]Cl_3,2H_2O$ (Ptn. denotes 1 mol. of βδ-diaminopentane; cf. preceding abstract) is obtained by interaction of α-βδ-diaminopentane with (1) $[Co(NH_3)_5Cl]Cl_2$ or (2) $[Co(\alpha\text{-}Ptn)_2Cl_2]Cl$ (see below) in water; the corresponding *bromide* ($+2H_2O$), *iodide* ($+1\frac{1}{2}$ or $2H_2O$), *nitrate* ($+3H_2O$), *perchlorate* ($+5H_2O$, $+1H_2O$), and *dithionate* (not analysed) are prepared from it by double decomp. The normal d-*tartrate* ($+1H_2O$) was partly resolved by crystallisation, and an optically impure l-*iodide*, $M[\alpha]_{5463}$ −1090°, was isolated. Corresponding salts of the β-base, which are generally more sol., are best prepared by method (2). The *chloride* ($+4H_2O$), *iodide* ($+3\frac{1}{2}H_2O$), *nitrate* ($+3H_2O$), *perchlorate* ($+3H_2O$), *dithionate*, and an optically impure l-*bromo-α-tartrate*, $[\alpha]_{5590}$ −67°, are described. The *salt* $[Co(en)_2\,\alpha\text{-}Ptn]Br_3,1\frac{1}{2}H_2O$ is prepared from the corresponding *praseo*-chloride of ethylenediamine and the α-base.

The corresponding Rh salts are prepared by a modification of Jaeger and Blumendal's method (A., 1928, 1172) or by that of Lebedinski (A., 1928, 35). The *chloride* $[Rh(\alpha\text{-}Ptn)_3]Cl_3,2H_2O$ (also $+3H_2O$), *bromide* ($+2H_2O$, isomorphous with chloride trihydrate), *iodide* ($+1\frac{1}{2}H_2O$), *nitrate* ($+1\frac{1}{2}H_2O$), and *perchlorate* ($+4H_2O$) are described; the mother-liquors from recrystallisation of the last are lævorotatory, and after growth of a *Penicillium glaucum* an inactive double *salt*, $[Rh(\alpha\text{-}Ptn)_3](ClO_4)_3,[Rh(\alpha\text{-}Ptn)_3]Cl_3$, was separated. Resolution was effected by *d*-α-nitrocamphor; the d-*salt* ($+4H_2O$), $[\alpha]_D$ +179°, gave an *iodide* ($+2H_2O$), $[\alpha]_{5463}$ +78·5°. Corresponding salts of the β-base are similarly prepared. The *chloride* ($+4H_2O$), *iodide* ($+3\frac{1}{2}H_2O$), *bromide* ($+4H_2O$), *nitrate* ($+2H_2O$), *perchlorate* ($+2\frac{1}{2}H_2O$), d-α-*tartrate* ($+6H_2O$), $[\alpha]_{5463}$ +62° [α-*iodide* ($+1H_2O$), $[\alpha]_{5463}$ +46°], and l-l-*tartrate* ($+6H_2O$), $[\alpha]_{5463}$ −61° (prepared from mother-liquors of preceding compound by double decomp.) [l-*iodide* ($+1H_2O$), $[\alpha]_{5463}$ −46°]. A partial asymmetric synthesis of d-β*δ-diaminopentane*, $[\alpha]_D$ +14·5° (as dihydriodide), was achieved by decomp. of the *d*-iodide with N_2H_4 and KOH at 100°.

The *salt* $[Co(\alpha\text{-}Ptn)_2(NO_2)_2]NO_3,H_2O$ (or nitrite ?) is obtained by interaction of the base with aq. $K_3Co(NO_2)_6$; it is converted into the *bromide* ($+1H_2O$) by double decomp., into the *salt* $[Co(\alpha\text{-}Ptn)_2Cl_2]Cl$ by boiling with aq. HCl and precipitating with EtOH and Et_2O, into the *salt* $[Co(\alpha\text{-}Ptn)_2CO_3]Cl,H_2O$ by aq. Na_2CO_3 at 100°, and into the *oxalate* $[Co(\alpha\text{-}Ptn)_2C_2O_4]_2C_2O_4,4H_2O$ by $K_2C_2O_4$; this with conc. HCl gives the *salt* $[Co(\alpha\text{-}Ptn)_2C_2O_4]Cl$.

The *salt* $[Co(\beta\text{-}Ptn)_2Cl_2]Cl$ is obtained by passing air free from CO_2 through a solution of $CoCl_2,6H_2O$ and the base; in water the yield is 50%, and in EtOH 86—90%. It is converted as before into the *carbonato*-salt $[Co(\beta\text{-}Ptn)_2CO_3]Cl,1\frac{1}{2}H_2O$, but $K_2C_2O_4$ gives $[Co(\beta\text{-}Ptn)_2C_2O_4]Cl,5H_2O$. The *nitrate* $[Co(\beta\text{-}Ptn)_2(NO_2)_2]NO_3$ is prepared similarly to the α-salt. Crystallographic data for the majority of these complex salts are given. H. A. PIGGOTT.

Determination of choline in dilute solutions. L. PINCUSSEN and E. VON HEYDEN (Biochem. Z., 1931, **234**, 484—488; cf. A., 1930, 752).—The ppt. formed when excess of $AuCl_3$ solution is added to a choline solution does not decompose when the solution is conc. and can be freed from $AuCl_3$ by washing with H_2O. The choline–Au compound can be converted into choline iodide, of which the choline content can be determined as previously described. After the addition of the $AuCl_3$ the whole operation should be carried out in the same vessel, a suitable type of which is described. W. MCCARTNEY.

Sphingosine. E. KLENK and W. DIEBOLD (Z. physiol. Chem., 1931, **198**, 25—32).—The *N*-containing product of the action of O_3 on triacetylsphingosine is shown to be the triacetyl derivative of α-amino-βγ-dihydroxy-η-butyric acid. Sphingosine, m. p. 82·5° (cf. A., 1900, i, 319, 75—80°), is therefore $CH_3\cdot[CH_2]_{12}\cdot CH\!:\!CH\cdot CH(NH_2)\cdot CH(OH)\cdot CH_2\cdot OH$ (cf. A., 1930, 73).

The sphingosines prepared by splitting cerebroside mixtures with aq. H_2SO_4 and H_2SO_4 in MeOH respectively and subsequent hydrolysis with KOH in MeOH give *Ac* derivatives, m. p. 102·5—103° (97% yield, $[\alpha]_D$ −24·09° in AcOH) and 97—98° (40—50% yield) (cf. A., 1912, i, 373). Acetylation of uncryst. sphingosine gives a very poor yield. O_3 splits the high-melting Ac derivative to an aldehyde, which on acid hydrolysis and subsequent Br oxidation gives monohydrated *α-amino-βγ-dihydroxy-η-butyric acid* (m. p. about 135°, converted into a *lactone*, $[\alpha]_D^{13}$ −33·45° in H_2O), which is reduced by HI to a sweet,

water-sol. aminobutyric acid, m. p. 280—285° (decomp.). A. RENFREW.

Syntheses with glucosamine. M. BERGMANN and L. ZERVAS (Ber., 1931, 64, [*B*], 975—980).—*d*-Glucosamine hydrochloride is transformed by anisaldehyde and NaOH into p-*methoxybenzylidene*-d-*glucosamine*, m. p. 166° (corr., decomp.), transformed by Ac_2O in pyridine into the corresponding *tetra-acetate*, m. p. 188° (corr.), $[\alpha]_D^{17}$ +98·6° in $CHCl_3$. Treatment of the last-named with HCl in boiling $COMe_2$ yields anisaldehyde and *tetra-acetyl*-d-*glucosamine hydrochloride*, darkening above 230°, $[\alpha]_D^{17}$ +29·7° in H_2O, from which β-penta-acetylglucosamine, m. p. 187° (corr.), is obtained by means of boiling Ac_2O and AcONa and *tetra-acetyl*-d-*glucosamine*, m. p. 143° (corr.), $[\alpha]_D$ +25·9° in $CHCl_3$, by means of AcONa. With chloroacetyl chloride in $CHCl_3$ the free base yields *tetra-acetyl*-α-*chloroacetyl*-d-*glucosamine*, m. p. 165—166° (corr.). *Tetra-acetyl*-α-*bromopropionyl*-d-*glucosamine*, m. p. 151° (corr.), is converted by NH_3 in MeOH at 0° into the anhydride $OH\cdot CH_2\cdot[CH\cdot OH]_3\cdot C{<}\genfrac{}{}{0pt}{}{CH{=}N}{N{-}CO}{>}CHMe$ of Weizmann and Hopwood (A., 1913, i, 958). *Benzoyltetra-acetyl*-d-*glucosamine*, m. p. 240° (corr.), $[\alpha]_D^{17}$ +41·9° in $CHCl_3$, is hydrolysed by aq.-alcoholic NaOH to *benzoyl*-d-*glucosamine*, m. p. 196—200° (corr.). H. WREN.

Urethanes. V. New acyl diurethanes and their reactions with ammonia and amines. S. BASTERFIELD, C. V. WILSON, and (MISS) M. E. GRIEG (Canad. J. Res., 1931, 4, 361—371; cf. A., 1928, 53).—Acyl diurethanes from dibasic acids are the more readily attacked by amines the stronger is the acid for a given amine, or the stronger is the amine for a given acid. Acyldicarbamides are stable to amines when the ionisation const. of the acid is approx. 10^{-5} or less. The reaction mixtures for the prep. of the following urethanes must be kept some days before being heated. Succinyl chloride and urethane give *succinyl diurethane*, m. p. 155° (yield 25%), also obtained from succinic acid, $POCl_3$, and urethane (yield 38%). With NH_3 it gives succinamide; with NH_2Et succindiethylamide and urethane; and with NH_2Ph at 150° for 1 hr. *succinyldiphenylcarbamide*, m. p. 236° (yield 16%) (converted by NH_2Ph into succinanilide and diphenylcarbamide), and *phenylcarbamidosuccinyl urethane*, m. p. 163° (converted by NH_2Ph into succinyldiphenylcarbamide). More prolonged heating of succinyl diurethane with NH_2Ph, or a higher temp., gives succinanilide and diphenylcarbamide. Glutaric acid, $POCl_3$, and urethane give *glutaryl diurethane*, m. p. 192° (yield 75%), converted by NH_3 into glutaramide and a *substance*, m. p. 265°; by NH_2Et into glutardiethylamide; and by NH_2Ph into *glutaryldiphenylcarbamide*, m. p. 219—220°, or at a higher temp. into diphenylcarbamide and probably glutaranilide. *Adipyl diurethane*, m. p. 174° (prepared as above), gives with aq. NH_3 adipamide, m. p. 217°, and a *substance*, m. p. 300° (no action with NH_3 in EtOH); with NH_2Et *adipdiethylamide*, m. p. 164°; and with NH_2Ph *adipyldiphenylcarbamide*, m. p. 225°, and (at higher temp.) *phenylcarbamidoadipyl urethane*, m. p. 172°, diphenylcarbamide, and adipanilide. Bromomalonyl diurethane (from the bromination of malonyl diurethane) gives with NH_2Et bromomalondiethylamide and ethyl allophanate, and with NH_2Ph diphenylcarbamide and a halogen-free *substance*, m. p. 300°. Phenylmalonic acid (A., 1918, i, 271; 1894, i, 376), $POCl_3$, and urethane give allophanic ester and 3-*nitrophthalyl diurethane*, m. p. 115—122° (decomp.), also obtained from the acid chloride, urethane, and pyridine in The above diurethane heated in EtOH gives 3-nitrophthalimide, and in C_6H_6 3-*nitrocarbethoxyphthalimide*, m. p. 95°.
A. A. LEVI.

Reciprocal reaction between α-oxides and esters of amino-acids. V. Alkylaminopropionic acids, α- and β-series. A. I. KIPRIANOV and D. M. KRASINSKAYA (Ukrain. Chem. J., 1930, 5, [Sci.], 353—363).—The reaction between ethylene oxide and ethyl α-ethylaminopropionate gives a mixture of α-*ethyl hydroxyethylaminopropionic acid*, m. p. 126·5—127·5° (*Cu* salt), and its *lactone*, b. p. 100—110°/6 mm. (*picrate*, m. p. 156—157°). *iso*Butylene oxide gives the *lactone* of α-*ethylhydroxyisobutylaminopropionic acid*, b. p. 121·5—123°/16—17 mm. (*picrate*, m. p. 154·5—155°). Ethylene oxide and ethyl β-methylaminopropionate gave a distillate, b. p. 40—200°/4—5 mm., the nature of which was not determined.
E. B. UVAROV.

[Preparation of] α-amino*iso*butyric acid. H. T. CLARKE and H. J. BEAN (Organic Syntheses, 1931, 11, 4—6).

Cuprous derivatives of some thiol compounds. N. W. PIRIE (Biochem. J., 1931, 25, 614—628).—Acetylcysteine, chloroacetylcysteine, glycylcysteine, the Me ester of acetylcysteine, and Me_2 ester of cinnamylcysteine have been prepared in a pure state and cinnamylcysteine Me ester, acetylcysteine Pr ester, and benzoylcysteine in an impure state as well as their Cu^{II} derivatives. Complexes with $CuSO_4$ of glycylcysteine, $C_5H_9O_3N_2SCu,CuSO_4$, and glutathione, $[(CuSG)_2Cu_2SO_4]_2SO_4$, have been obtained.
S. S. ZILVA.

Oxidation of cobaltous cysteine. E. C. KENDALL and J. E. HOLST (J. Biol. Chem., 1931, 91, 435—474).—From an electrometric study of the oxidation of cobaltous cysteine by 13 oxidising agents it is concluded that four reactions take place, viz., (i) $3Co^{\cdot\cdot}(SR)_2$+oxidising agent $\longrightarrow$ $Co^{\cdot\cdot\cdot}(SR)_3+Co^{\cdot\cdot}$, (ii) $Co^{\cdot\cdot\cdot}(SR)_3 \longrightarrow Co^{\cdot\cdot}(SR)_2+RS'$, (iii) $2RS'$+oxidising agent $\longrightarrow (SR)_2$, and (iv) $Co^{\cdot\cdot}+2RS' \longrightarrow Co(SR)_2$ (contrast A., 1929, 1284). The velocities of (i) and (iii) depend on the oxidising agent used, those of (ii) and (iv) are fixed for given temp. and $[H^{\cdot}]$, but that of (iv) is influenced by the presence of certain anions. It is probable that the six co-ordination valencies of the brown $Co^{\cdot\cdot\cdot}$ complex, which consists of 1 Co atom and 2 cysteine mols., are satisfied by the SH, NH_2, and CO_2H groups, which are all necessary for its formation. One equivalent of sodium indigotindisulphonate was required to oxidise 2 mols. of cysteine plus 1 mol. of Co, neither Co nor cysteine remaining in solution; other proportions of cysteine to Co required an amount of dye equiv. to half the no. of mols. of cysteine or the no. of mols. of Co, whichever was the less, and Co or cysteine remained in solution; in the latter case only, some cystine was formed.

H_2O_2 and O_2 converted 77% into the $Co^{\cdots}$ complex and 23% into cystine. Dibromophenol-indophenol converted 89% into the $Co^{\cdots}$ complex and 11% of the SH group combined with the quinone form of the dye. However, addition of cysteine and $CoSO_4$ to dibromophenol-indophenol caused oxidation of two thirds of the SH group to the cobaltic cysteine complex. With $K_3Fe(CN)_6$ the ferrocyanide formed decomposed the cobaltous cysteine into Co ferrocyanide and cysteine, which was then oxidised to cystine, one third of the SH being so oxidised, even in the presence of excess of Co. Agreement observed using the last three oxidising agents (A., 1929, 1011) is fortuitous. Cobaltous cysteine is oxidised by cystine completely but slowly (contrast *loc. cit.*), by $Na_2S_2O_4$ and Na_2SO_3 (90% in 24 hrs.), but not by $Na_2S_2O_3$. H_2S precipitates CoS from cobaltous cysteine, and from the $Co^{\cdots}$ complex in the presence of HCl, but not from the latter at p_H 7·4. NaCN, CH_2O, and MeCHO decompose cobaltous cysteine, thus preventing its oxidation to the $Co^{\cdots}$ complex. Measurement of the intensities of colour of the $Co^{\cdots}$ complex formed by air, H_2O_2, and dibromophenol-indophenol confirmed the above conclusions, but was not possible with other oxidising agents. R. S. CAHN.

Biochemistry of sulphur. IX. Determination of cysteine in presence of glutathione. M. X. SULLIVAN and W. C. HESS (U.S. Public Health Service, Reprint No. 1450; cf. A., 1930, 803).—The presence of NaCN as antioxidant and the use of a larger quantity of Na 1 : 2-naphthoquinone-4-sulphonate prevent the inhibition of the cysteine reaction (A., 1926, 1266) by glutathione even in the ratio 100 : 1. Practical details are given.

H. A. PIGGOTT.

Preparation of aliphatic amides. J. A. MITCHELL and E. E. REID (J. Amer. Chem. Soc., 1931, **53**, 1879—1883).—Fatty acid amides are obtained in good yield when NH_3 is passed through the acid (acetic—octoic) at 160—190°; the water formed during the reaction is continually removed and the amides are purified by distillation and subsequent crystallisation. The reaction velocity is appreciably slower with the higher acids, and amides could not be prepared from palmitic or stearic acid. The corresponding dimethylamides are prepared similarly, using $NHMe_2$. The following m. p. (all corr.) are recorded : acetamide, 81·5°; propionamide, 81·3°; butyramide, 115°; valeramide, 105·8°; hexoamide, 101·5°; heptoamide, 96·5°; octoamide, 106°. H. BURTON.

[Amide and imide chlorides.] A. HANTZSCH (Ber., 1931, **64**, [*B*], 1219; cf. this vol., 608).—A correction with regard to the work of von Braun and Heymons (this vol., 236). H. WREN.

Action of organomagnesium compounds on acetdiethylamide. (MLLE.) M. MONTAGNE (Compt. rend., 1931, **192**, 1111—1113).—MgEtBr reacts with acetdiethylamide to give, mainly, (65%) *acetoacetdiethylamide*, b. p. 126—127°/15 mm. (also obtained by prolonged action of $NHEt_2$ on ethyl acetoacetate), and methyl ethyl ketone. With MgPhBr the main product is acetophenone (40—50% yield), only 30% of the β-ketonic amide being obtained.

J. W. BAKER.

Production of acetoacetarylides from acetoacetic ester and primary aromatic amines. L. LIMPACH (Ber., 1931, **64**, [*B*], 970—971).—The compounds are obtained in more than 90% yield by adding the base (aniline, *p*-toluidine, *p*-xylidine, *o*- and *p*-anisidine, *p*-phenetidine, *m*-amino-*p*-tolyl methyl ether) to a large excess of Et acetoacetate heated at about 160° and keeping the mixture for a short period at this temp. H. WREN.

[Preparation of] *iso*propyl thiocyanate. R. L. SHRINER (Organic Syntheses, 1931, **11**, 92—93).

Complex metal–thiocarbamide salts and a non-complex arsenic–thiocarbamide compound. G. WALTER [with E. HAMMERLE and K. OESTERREICH] (Ber., 1931, **64**, [*B*], 1087—1095).—The compound $[CuThi_3]Cl$ $[Thi{=}CS(NH_2)_2]$ can be prepared from CuCl or $CuCl_2$ in boiling EtOH or cold H_2O. It is oxidised by dil. H_2O_2 or $KMnO_4$ to the *substance* $[CuThiCl]_2H_2O$, thus indicating the existence of the equilibria $[CuThi_3]'+H_2O \rightleftharpoons [CuThi_2H_2O]'+Thi$ and $[CuThi_2(H_2O)]'+H_2O \rightleftharpoons [CuThi(H_2O)_2]'-Thi$. The compound $2CoCl_2,7Thi$ is converted by pyridine according to experimental conditions into the substances $CoCl_2,2C_5H_5N$ and $CoCl_2,4C_5H_5N$. From the three cuprous thiocarbamide chlorides $CuCl,2C_5H_5N$ is obtained; the reaction is reversible. Analogously, $2NiCl_2,7Thi$ is converted into $NiCl_2,4C_5H_5N$, but definite results were not obtained with $[AgThi_2]NO_3$, $[AgThi]NO_3$,$CaCl_2$,5Thi,$6H_2O$, and $BiCl_3$,3Thi.

The action of As_2O_3 on thiocarbamide consists essentially in desulphurisation, but a solution of $AsCl_3$ and thiocarbamide containing HCl deposits As_2O_3 and As_2S_3 and the filtrate slowly yields the *substance* $C_2H_8ON_4S_2AsCl$, which decomposes in contact with most solvents with production of cryst. As_2S_3. Boiling water transforms it into As_2S_3, As_2O_3, carbamide, thiocarbamide, and HCl. Thiocarbamide and PCl_3 afford thiocarbamide hydrochloride, converted by CuCl in boiling water into $[CuThi_3]Cl$. Three mols. of thiocarbamide absorb, as max., 1 mol. of CuCl. Ag_3AsO_4 and thiocarbamide give the *compound* $[AgThi_3]_2HAsO_4$, m. p. 140°.

H. WREN.

Demonstration of the formation of hydrogen cyanide from methylamine. H. EMDE and T. HORNEMANN (Z. angew. Chem., 1931, **44**, 278).—NH_2Me solution is sprayed on to a piece of ice held close to a Bunsen flame; the resulting solution gives the reactions of HCN. H. F. GILLBE.

Constitution of the cyanogen halides. III. Reactions of cyanogen bromide. E. V. ZAPPI and S. ELORZA.—See this vol., 696.

[Preparation of] cyanogen bromide. W. W. HARTMAN and E. E. DREGER (Organic Syntheses, 1931, **11**, 30—31).

ψ-Halogens. XIII. Addition of iodo-oxy-cyanogen to olefines. L. BIRCKENBACH and M. LINNARD [with M. STEPHAN] (Ber., 1931, **64**, [*B*], 961—968; cf. A., 1930, 1564).—*cyclo*Hexene is converted by CN·OI in Et_2O at −80° in absence of light into 2-*iodo*cyclo*hexylcarbimide*, b. p. 94°/2 mm., transformed by NH_3 into 2-*iodo*cyclo*hexylcarbamide*, m. p. 155°. Since under the experimental conditions the

carbimide does not react appreciably with AgCNO and *cyclo*hexene does not add I, the CN·OI can be prepared *in situ* by the action of I on a slight excess of AgCNO. Trimethylethylene adds the ψ-halogen rather more slowly, yielding exclusively *iodo-β-methylbutylcarbimide*, b. p. 80°/10 mm., m. p. −64° to −62°, whence *iodo-β-methylbutylcarbamide*, m. p. (indef.) 120—130° after darkening at 70—80°. Technical amylene behaves similarly. With CN·OI in Et_2O at −80°, ethylene yields an unstable oil which decomposes rapidly at room temp. and appears to be a mol. compound of the reactants. At −15°, the separation of the oil is avoided; β-iodoethylcarbimide is formed, converted by NH_3 into *β-iodoethylcarbamide*, m. p. 103°. Δ^{α}-Phenylpropene gives the corresponding iodocarbimide in 90—95% yield. CN·OI resembles CNS in its behaviour towards isoprene, addition occurring in the mol. ratio 1 : 1 even in the presence of excess of ψ-halogen. H. WREN.

ψ-Halogens. XIV. Reaction products of αβ-iodocarbimides. L. BIRCKENBACH and M. LINHARD [with M. STEPHAN] (Ber., 1931, **64**, [*B*], 1076—1087; cf. preceding abstract).—β-Iodoethylcarbamide is converted by aq. KOH into 2-amino-oxazoline, isolated as the picrate, m. p. 187—188°. With NH_2Ph, β-iodoethylcarbimide in Et_2O affords *N′-phenyl-N-β-iodoethylcarbamide*, m. p. 156°. 2-Iodo*cyclo*hexylcarbimide is converted by the requisite base or alcohol into *N′-phenyl-N-2-iodo*cyclo*hexylcarbamide*, m. p. 127°, *β-phenyl-2-iodo*cyclo*hexylsemicarbazide*, m. p. 133°, *Me*, m. p. 135°, *Et*, m. p. 120°, and *Bu*, m. p. 84°, *2-iodo*cyclo*hexylcarbamate*. 2-Iodo*cyclo*hexylcarbamide with aq. KOH gives *2-amino-4 : 5-*cyclo*hexano-oxazoline*, $\begin{matrix}CH_2\cdot CH_2\cdot CH\cdot N{:}C\cdot NH_2\\ CH_2\cdot CH_2\cdot CH\text{——}O\end{matrix}$ (hygroscopic *hydrochloride*, m. p. about 120°; *picrate*, m. p. 202°). With aq. KOBr the oxazoline hydrochloride gives *2-dibromoamino-4 : 5-*cyclo*hexano-oxazoline*, m. p. 97° (decomp.) after darkening at 90°. Boiling H_2O transforms *N′*-phenyl-*N*-2-iodo*cyclo*hexylcarbamide into *2-anilino-4 : 5-*cyclo*hexano-oxazoline*, m. p. 123°, and β-phenyl-2-iodo*cyclo*hexylsemicarbazide into *2-β-phenylhydrazino-4 : 5-*cyclo*hexano-oxazoline*, m. p. 127° (*picrate*, m. p. 175°; *hydrochloride*, m. p. 170°). With conc. HCl 2-iodo*cyclo*hexylcarbimide yields *2-iodo*cyclo*hexylamine hydrochloride*, m. p. 157—159°, transformed by aq. $AgNO_3$ into 2-hydroxy*cyclo*hexylamine hydrochloride, m. p. 174—175°. Iodocarbimidopropylbenzene and 30% HCl afford a mixture of iodoaminopropylbenzene hydrochlorides converted by hot H_2O into aminohydroxypropylbenzene hydrochlorides, from which a *hydrochloride*, m. p. 169°, is isolated, giving *β-amino-α-hydroxy-*n*-propylbenzene*, m. p. 76—78°. This is resolved by *d*-tartaric acid, yielding l-*β-amino-α-hydroxy-*n*-propylbenzene*, m. p. 76—78°, $[\alpha]_D^{18}$ −33·57° in EtOH (*hydrochloride*, m. p. 179—180°, $[\alpha]^{20}$ −43·23° in H_2O). Iodocarbimidopropylbenzene and NH_3 in Et_2O give a mixed product from which *iodocarbamidopropylbenzene*, m. p. 105°, is isolated. It is converted by hot H_2O into *α-amino-phenylmethyloxazoline*, m. p. 159°, whereas the mixed product (*v.s.*) gives also an isomeric *oxazoline*, m. p. 197°. Treatment of the base, m. p. 159°, with *d*-tartaric acid affords a d-*2-aminophenylmethyloxazoline*, m. p. 188°, $[\alpha]^{20}$ +25·3° in EtOH (*hydrogen* d-*tartrate*, m. p. 158—159°). H. WREN.

Butenonitriles. G. HEIM (Bull. Soc. chim. Belg., 1931, **40**, 201—219).—Dehydration of β-hydroxybutyronitrile with conc. H_2SO_4 gives a mixture (40% yield) of 36% of *cis*- and 64% of *trans*-crotononitriles. Dehydration with P_2O_5 in presence or absence of $CHCl_3$ affords mixtures (40 and 57% yields, respectively) containing little of the *cis*-form, much *trans*-form, and much vinylacetonitrile. α-Hydroxybutyronitrile and P_2O_5 give a product (45% yield) consisting of *cis*- (56%) and *trans*- (33%) -crotononitriles, and vinylacetonitrile. α- and β-Chlorobutyronitriles give with quinoline good yields of the mixed crotononitriles; the *cis*-form predominates. Cyanoacetic acid and MeCHO in pyridine afford a small amount of mainly *cis*-crotononitrile. H. BURTON.

Decomposition of the optically active diazo-ester from aminolauric acid. F. E. RAY and W. R. BUNTING (Proc. Iowa Acad. Sci., 1929, **36**, 271—274).—The diazo-compound obtained from the *cis*-acid gives on distillation an unsaturated fraction corresponding with 60·5% of the distillate. Skinner's ether acid (A., 1923, i, 791) found in the decomp. of the *trans*-amino ester was not detected.

CHEMICAL ABSTRACTS.

Action of arsenic chloride on ethyl sodiomalonate. L. GUGLIALMELLI and C. RUÍZ (Anal. Asoc. Quím. Argentina, 1930, **18**, 173—180).—The existence of the so-called ethyl arsinotrimalonate of Zappi (A., 1930, 899) is theoretically improbable and cannot be confirmed in practice. R. K. CALLOW.

Preparation and assay of Zerevitinov's and Sudborough's reagents. E. V. ZAPPI and H. DEGIORGI (Anal. Asoc. Quím. Argentina, 1930, **18**, 214—218).—Solutions of MgMeI in *iso*amyl ether prepared by the methods of Zerevitinov or of Sudborough and James are, respectively, 0·90*N* and 1·16*N*. The same results are obtained with either in the determination of OH groups. The turbidity of the solutions is of no consequence. R. K. CALLOW.

Pyrogenetic decomposition of benzene, toluene, and xylene at high pressure. R. ODA (J. Soc. Chem. Ind. Japan, 1931, **34**, 142—144B).—The decomp. of C_6H_6 by heating for 8 hrs. at 500° up to 270 atm., in presence of H_2 and with or without a catalyst (Al_2O_3) proceeds to only a slight extent, yielding CH_4 and 1—1·8% of Ph·Ph. Toluene is decomposed more readily, yielding C_6H_6 and complex hydrocarbons which are probably derivatives of Ph·Ph. Xylene yields C_6H_6, toluene, and complex liquid and solid hydrocarbons; the solid products appear to be anthracene derivatives. H. F. GILLBE.

Aromatic substitution with fluorine. W. D. BANCROFT and S. F. WHEARTY, jun. (Proc. Nat. Acad. Sci., 1931, **17**, 183—186).—Action of F_2 on C_6H_6 gives C, HF, and CF_4. If the F_2 is diluted with N_2 a tar containing F is formed, a similar result being obtained with toluene. Regulated action of F_2 on hexachlorobenzene gives *tetrachlorodifluorobenzene*, b. p. 230—240°, and *trichlorotrifluorobenzene*, b. p. 140—150°. Similar treatment of *s*-trichlorobenzene

gives *dichlorotrifluorobenzene*, b. p. 75°/25 mm., 150°/760 mm. (decomp.). A. A. LEVI.

Action of phosphorus pentachloride on ω-chloroallylbenzene derivatives. L. BERT and R. ANNEQUIN (Compt. rend., 1931, **192**, 1107—1108).—ω-Chloroallyl derivatives of C_6H_6 (A., 1925, i, 803) are converted by heating with PCl_5 into the corresponding βγγ-trichloro-*n*-propylbenzenes and thus are obtained *βγγ-trichloro-*n*-propylbenzene*, b. p. 135—136°/13 mm., m-*βγγ-trichloro-*n*-propyltoluene*, b. p. 158—160°/19 mm., and 4-*βγγ-trichloro-*n*-propyl-*m*-xylene*, b. p. 167—168°/17 mm. All b. p. are corr. J. W. BAKER.

ωω′-Dichloro-*p*-xylene, *p*-di-(β-hydroxyethyl)-benzene, and *p*-divinylbenzene. S. SABETAY (Compt. rend., 1931, **192**, 1109—1110).—*p*-Xylylene chloride is obtained in 30—50% yield by passing HCl into a suspension of trioxymethylene and $ZnCl_2$ in BzCl at 80—100° (cf. Blanc, A., 1923, i, 549). It is converted through the dinitrile into Et *p*-phenylene-diacetate, which is reduced in BuOH solution by Na and boiling toluene to p-*di-*(β-*hydroxyethyl*)*benzene*, m. p. 86°, converted by distillation with KOH under reduced pressure into *p*-divinylbenzene, m. p. 28—29°, which, contrary to Lespieau and Deluchat (A., 1930, 588), is stable when freed from traces of halogen acids. J. W. BAKER.

[Preparation of] **bromomesitylene.** L. I. SMITH (Organic Syntheses, 1931, **11**, 24—25).

Dihalogenocyanoacetyl derivatives of mesitylene. R. C. FUSON and R. G. BEVERIDGE (J. Amer. Chem. Soc., 1931, **53**, 1985—1988).—Chloroacetyl-mesitylene and alcoholic KCN give *cyanoacetyl-mesitylene*, m. p. 108—109° [*dinitro*-derivative, m. p. 170·3—171·3° (corr.)], converted by sodium hypohalite into *dibromocyanoacetylmesitylene*, m. p. 81—82° (*dinitro*-derivative, m. p. 97—98°), and *dichloro-cyanoacetylmesitylene*, m. p. 38—39°. *Di*(*cyanoacetyl*)-*mesitylene*, m. p. 52—53°, is similarly converted into *di*(*dichlorocyanoacetyl*)-, m. p. 52—53°, and *di*(*di-bromocyanoacetyl*)-*mesitylene*, m. p. 121·2—122·2° (corr.). All the dihalogenoacetyl derivatives are stable to cold alkali. H. BURTON.

[Preparation of] **1 : 2 : 3 : 5-tetramethylbenzene (*iso*durene).** L. I. SMITH (Organic Syntheses, 1931, **11**, 66—69).

Reduction of nitro-derivatives of diphenyl. II. L. GUGLIALMELLI and M. R. FRANCO (Anal. Asoc. Quím. Argentina, 1930, **18**, 190—209).—2 : 4′-Dinitrodiphenyl, prepared by nitrating 4-nitrodiphenyl, is readily purified by distillation at 242—246°/2 mm. 2-Nitro-4′-aminodiphenyl is best prepared from it by reduction with sodium polysulphide in H_2O or aq. $COMe_2$ (A., 1930, 762). An (?)*azoxy*-compound, m. p. 85°, is formed as a by-product. R. K. CALLOW.

Polymerides and polymerisation. II. Pyrolysis of polyindene and polymerisation of di-indene. G. S. WHITBY and M. KATZ (Canad. J. Res., 1931, **4**, 344—360; cf. A., 1928, 627).—Di-indene (improved prep.) polymerises under the same conditions as indene, but more slowly. Di-indene and indene heated together at 177° for 15 days give 33%, and at 197° for 5·5 days 46·6%, of tri-indene. High polymerides of indene (made approx. homogeneous by fractionation) heated at temp. below that necessary for pyrolysis give compounds corresponding approx. with $(C_8H_9)_6$. Lower polymerides undergo less change under these conditions. Pyrolytic distillation of di-indene at 2 mm. gives 74% of indene. Similar treatment of polyindenes gives indene, di- and tri-indene, polymerides up to approx. $(C_8H_9)_6$, and truxene. Br absorption shows the presence of one double linking in all polyindenes examined. It is considered that polyindenes are straight-chain compounds (cf. A., 1929, 1435), their formation involving the wandering of a H atom, and addition to a double linking, viz., CH_2·CH:CH+CH:CH= CH_2·CH_2·CH·C:CH. Pyrolysis follows a reverse change and may take place in any part of the chain, or in more than one place at a time. A. A. LEVI.

[**Reactivity of halogen in halogenonitro-derivatives of naphthalene.**] H. W. TALEN (Ber., 1931, **64**, [*B*], 1218).—Previous to Salkind's work (this vol., 474) the problem has been investigated (cf. A., 1926, 1029; 1928, 405). H. WREN.

Thiele's theory of partial valencies. Law of periodicity. VI. P. PETRENKO-KRITSCHENKO (J. pr. Chem., 1931, [ii], **130**, 45—48).—The inactivity of the double linking in benzhydrylidenefluorene and its activity in bisdiphenylene-ethylene and dixanthylene (cf. A., 1930, 1569), for which Thiele's hypothesis offers no satisfactory explanation, is in accordance with the law of periodicity (cf. A., 1925, ii, 1122). H. A. PIGGOTT.

Polynuclear, aromatic hydrocarbons and their derivatives. VIII. 2′ : 3′-Naphtho-1 : 2-anthracene [2 : 3 : 6 : 7-dibenzanthracene-9 : 10-diyl] and its oxidation products. E. CLAR and F. JOHN (Ber., 1931, **64**, [*B*], 981—998; cf. A., 1929, 689).—*m*-Xylene, CH_2PhCl, and Al–Hg afford 4-benzyl-*m*-xylene, b. p. 280—290°, converted by BzCl and $AlCl_3$ in presence of CS_2 into 6-*benzoyl-4-benzyl-*m*-xylene*, m. p. 68°, condensed in presence of Cu powder to a mixture of the corresponding *lin*- and *ang*-hydrocarbons. The latter substances are separated by treatment with chloranil in boiling xylene, which precipitates bluish-violet 2 : 3 : 6 : 7-dibenzanthracene-9 : 10-diyl, leaving the isomeric hydrocarbon unattacked. Extension of this treatment to 2′ : 3′-naphtho-1 : 2-anthracene (*loc. cit.*) shows the material to be a mixture of 2 : 3 : 6 : 7-dibenz-9 : 10-dihydroanthracene and true 2′ : 3′-*naphtho*-1 : 2-*anthracene*, m. p. 257° (*picrate*, m. p. 184°), almost quantitatively oxidised to the corresponding diquinone. 7 : 7′-*Dimethyl*-2′ : 3′-*naphtho*-1 : 2-*anthracene*, m. p. 225° after softening at 220°, is described. *Di*-1 : 2′-p′-*tolyl*-2 : 3 : 6 : 7-*anthracene*-9 - 10-*diyl* is oxidised to di-1′ : 2′-*p*′-tolyl-2 : 3 : 6 : 7-anthraquinone, converted by aq. KOH into a mixture of 2 : 6- and 2 : 7-methylnaphthalenecarboxylic acids. H. WREN.

[Preparation of] ***p*-iodoaniline.** R. Q. BREWSTER (Organic Syntheses, 1931, **11**, 62—64).

Rearrangement of alkylanilines. IV. Formation of olefines from alkylaniline hydrobromides. W. J. HICKINBOTTOM and S. E. A. RYDER (J.C.S., 1931, 1281—1288).—The hydro-

bromides of ethyl-, *n*-propyl, *n*- and *iso*-butyl, and *iso*amyl-anilines decompose when heated at 238—302°, forming olefine and alkyl bromide. The proportion of olefine increases with rise in temp. and ascent of the series. The corresponding *p*-aminoalkylbenzenes (A., 1927, 236) are also produced. Bennett and Chapman's explanation (Ann. Reports, 1930, 124) of the formation of *p*-amino-*tert*.-butylbenzene from *iso*butylaniline hydrobromide is held to be invalid. iso*Amylaniline hydrobromide* has m. p. 148—151°.

H. BURTON.

Symmetrical triad prototropic systems. VII. Analogy between symmetrical triad systems and aromatic side-chain reactivity, and effect of *p*-substitution on mobility and equilibrium in the αγ-diphenylmethyleneazomethine system. C. W. SHOPPEE (J.C.S., 1931, 1225—1240).—The effects of *p*-substituents (R=NMe$_2$, Me, OMe, halogen) on mobility and equilibrium in the system $C_6H_4R\cdot CH{:}N\cdot CH_2Ph \rightleftharpoons C_6H_4R\cdot CH_2\cdot N{:}CHPh$ are the same as those recorded (A., 1930, 912) for the αγ-diphenylpropene system. The results are discussed in conjunction with those of Kindler (A., 1927, 55) on the alkaline hydrolysis of *p*-substituted Et benzoates, and of Lapworth and Manske (A., 1928, 1245) on cyanohydrin formation.

The following azomethines, which when treated with an excess of *p*-nitrophenylhydrazine acetate undergo quant. fission to the appropriate aldehyde-*p*-nitrophenylhydrazone and the complementary benzylamine, are new: p-*chloro*-, m. p. 34°, p-*bromo*-, m. p. 43°, p-*iodo*-, m. p. 56°, p-*dimethylamino*- (I), b. p. 248°/18 mm., m. p. 75°, p-*methyl*-, b. p. 210°/25 mm., m. p. 27°, and p-*acetamido*-, m. p. 158°, -*benzylidenebenzylamines*; *benzylidene*-p-*chloro*-, m. p. 36—37°, -p-*bromo*-, m. p. 54·5°, -p-*iodo*-, m. p. 58·5°, -p-*dimethylamino*- (II), m. p. 57°, and -p-*methyl*-, b. p. 190—196°/20 mm., -*benzylamines*. The *methiodides* of I and II have m. p. 159—160° and 181°, respectively. p-*Chloro*-, m. p. 216·5°, p-*bromo*-, m. p. 205·5°, p-*iodo*-, m. p. 201°, p-*methoxy*-, m. p. 161°, p-*acetamido*-, m. p. 262°, and p-*dimethylamino*-, m. p. 182°, -*benzaldehyde*-p-*nitrophenylhydrazones* are prepared. p-*Dimethylaminobenzaldehyde*-p-*bromophenylhydrazone* has m. p. 181° (decomp.). p-*Chlorobenzylphthalimide*, m. p. 124°, is converted by alkaline hydrolysis into p-*chlorobenzylphthalamic acid*, m. p. 185°, and thence by 20% HCl into *p*-chlorobenzylamine, b. p. 108—109°/14 mm. [carbonate, m. p. 118—119°; *picrate*, m. p. 210—211° (decomp.); *benzoate*, m. p. 155—156°; Ac derivative, m. p. 106—107°]. *p*-Bromobenzylamine, b. p. 118—119°/10 mm., m. p. 25—25·5° (*picrate*, m. p. 221°; *benzoate*, m. p. 162°; *Ac* derivative, m. p. 113°), is obtained similarly from p-*bromobenzylphthalimide*, m. p. 133°, and p-*bromobenzylphthalamic acid*, m. p. 185°. *p*-Iodobenzylamine, m. p. 45° [*picrate*, m. p. 231° (decomp.)], the *Ac* derivative, m. p. 132°; of which is prepared from acetbenzylamide, m. p. 60—61° (lit. 133°), and ICl in AcOH, could not be obtained from p-*iodobenzylphthalimide*, m. p. 137°, by way of p-*iodobenzylphthalamic acid*, m. p. 185°. Reduction of *p*-dimethylaminobenzaldoxime with 3% Na–Hg and AcOH gives p-*dimethylaminobenzylamine*, b. p. 158—159°/25 mm. [*mono*-. m. p. 187—189° (decomp.), and *di*-, m. p. 179—180° (decomp.), -*picrates*; *Ac* derivative, m. p. 79°; *benzoate*, m. p. 156·5°]. The *mono*- and *di*-*picrates* of *p*-aminobenzylamine have m. p. 163° and decomp. above 250°, respectively.

H. BURTON.

Reactions of substituted ammonium aryloxides and related compounds. I. Preparation and thermal decomposition of tetrasubstituted ammonium aryloxides. (MISS) R. V. HENLEY and E. E. TURNER (J.C.S., 1931, 1172—1181).—Thermal decomp. of *phenyltrimethylammonium phenoxide*, m. p. 58—59°; o-, m. p. 117—117·5°, m-, and p-, m. p. 118—119°, -*nitrophenoxides*; 2 : 4-*dinitrophenoxide*, m. p. 121—123° after softening at 90°; m-4-*xylyloxide*, and α-*naphthoxide*, m. p. 107—108°, gives in each case $NPhMe_2$ and the corresponding phenol methyl ether. *Phenylbenzyldimethylammonium* o-*nitro*-, m. p. 91—92°, and 2 : 4-*dinitro*-, m. p. 138—138·5°, -*phenoxides* afford $NPhMe_2$ and the appropriate phenol benzyl ether, whilst *phenyldimethylethylammonium* 2 : 4-*dinitrophenoxide*, m. p. 55—57°, gives $NPhMe_2$, NPhMeEt, 2 : 4-dinitroanisole, and 2 : 4-dinitrophenetole. *Phenyltrimethylammonium thiophenoxide*, m. p. 83—83·5°, yields $NPhMe_2$ and thioanisole, whilst *phenyltrimethylarsonium thiophenoxide*, m. p. 144—145°, gives $AsPhMe_2$ and thioanisole. The above aryloxides, prepared from the hydroxides and appropriate phenol, react with MeI thus: $NR_4\}OAr + MeI = NR_4\}I + MeOAr$.

H. BURTON.

Amino-alcohols. VI. Preparation and pharmacodynamic activity of four isomeric phenylpropylamines. W. H. HARTUNG and J. C. MUNCH (J. Amer. Chem. Soc., 1931, 53, 1875—1879). —α-Phenylpropylamine, b. p. 100—105°/35 mm. [hydrochloride, m. p. 189·5° (corr.) (lit. 194°)], γ-phenylpropylamine, and β-phenylpropylamine are prepared by catalytic reduction (A., 1929, 184) of propiophenoneoxime, cinnamaldoxime, and α-phenylpropionitrile, respectively. β-Amino-α-phenylpropyl alcohol and conc. HCl at 110—115° give the corresponding chloride [*hydrochloride*, m. p. 201° (corr.)], reduced catalytically (Pd) to β-phenyl*iso*propylamine. The phenylpropylamines containing the β-phenylethylamine skeleton cause a pronounced rise in blood pressure; substitution of Me on either of the C atoms in this grouping confers oral activity.

H. BURTON.

Use of arylcarbimides in identifying hydroxylic compounds. G. T. MORGAN and A. E. J. PETTET (J.C.S., 1931, 1124—1126).—The p-*xenylcarbamates*, $C_6H_5\cdot C_6H_4\cdot NH\cdot CO_2R$, of the following compounds, prepared from p-*xenylcarbimide*, m. p. 56°, b. p. 283° (decomp.) (obtained together with s-*di*-p-*xenylcarbamide*, m. p. 312°, from the action of $COCl_2$ on a toluene solution of *p*-xenylamine), are less readily fusible than the corresponding phenylcarbamates: MeOH, m. p. 127°; EtOH, m. p. 119°; PrOH, m. p. 129°; Pr$^{\beta}$OH, m. p. 138°; BuOH, m. p. 109°; *n*-amyl alcohol, m. p. 99°; *cyclo*hexanol, m. p. 166°; phenol, m. p. 173°; *o*-cresol, m. p. 151°; *m*-cresol, m. p. 164°; *p*-cresol, m. p. 198°; benzyl alcohol, m. p. 156°; *o*-4-xylenol, m. p. 183°; *m*-2-xylenol, m. p. 198°; *m*-4-xylenol, m. p. 184°; *m*-5-xylenol, m. p. 150°; *p*-xylenol, m. p. 162°; ψ-cumenol, m. p. 196°; thymol, m. p. 194°; carvacrol, m. p. 166°; α-naphthol, m. p. 190°;

homocatechol, m. p. 193°; orcinol, m. p. 196°. The use of *p*-xenylcarbimide is recommended in the separation and characterisation of phenols.

F. R. SHAW.

[Preparation of] 2 : 4-tolylenediamine. S. A. MAHOOD and P. V. L. SCHAFFNER (Organic Syntheses, 1931, **11**, 32—35).

Supposed *meri*quinonoid compounds from diphenyl-*p*-phenylenediamine and triarylcarbonium salts. H. W. SCHWECHTEN (Ber., 1931, **64**, [*B*], 971—975).—Contrary to Lifschitz (this vol., 349), the ability of diphenyl-*p*-phenylenediamine in $CHCl_3$ to yield intensely-coloured solutions with quinones and dil. HCl or quinonoid salts is not a " sp. test for quinonoid structure, particularly in salts." The coloration is produced by all sufficiently powerful oxidising agents (benzoyl peroxide), but not by all quinones (2 : 5-dimethoxy- and 2 : 5-diethoxy-*p*-benzoquinone; α- and β-naphthaquinone) and is due to the *meri*quinonoid cation, $[NHPh\cdot C_6H_4\cdot NHPh]^+$. Since the *meri*quinonoid *diphenyl*-p-*phenylenediamine perchlorate* crystallises almost quantitatively from the solutions, the additive compounds of *meri*quinonoid salts with quinones or triarylcarbonium salts (as assumed by Lifschitz) do not exist in the solid state and the spectroscopic identity of the different solutions renders their existence in solution improbable. In glacial AcOH or $CHCl_3$ tetramethyl-*p*-phenylenediamine or diphenyldimethyl-*p*-phenylenediamine is oxidised as smoothly as diphenyl-*p*-phenylenediamine to the corresponding *meri*quinonoid salts, thus confirming the author's theory.

H. WREN.

[Preparation of] azoxybenzene. H. E. BIGELOW and A. PALMER (Organic Syntheses, 1931, **11**, 16—18).

Fastness to light of azo-colours. J. S. P. BLUMBERGER.—See this vol., 806.

Colour and constitution from the viewpoint of recent electronic theory. IV. H. H. HODGSON (J. Soc. Dyers and Col., 1931, **47**, 93—96).—By means of the electronic theory it is possible to explain (cf. A., 1930, 1175) the relations between the colour and constitution of dyes better than by the old valency-linking conception, and this is shown by reference to various dyes, including chrysophenine, and the Witt chromophore theory. The electronic theory is also used to explain various anomalous reactions of certain compounds, *e.g.*, the separation of the xylidines by the CH_2O and H_2SO_4 methods, the decomp. of diazonium salts by aliphatic alcohols, and the production of 3 : 5-dinitro-*p*-cresol by heating 3 : 5-dinitrotoluene with NaOH and precipitated HgO.

A. J. HALL.

Metallic aminoazo- and hydroxyazo-complexes. G. B. CRIPPA and M. LONG (Gazzetta, 1931, **61**, 99—107; cf. A., 1927, 352, 1180).—3-Amino-2-benzeneazoacenaphthene forms a *Ni* compound, $(C_{18}H_{15}N_3)_2Ni$, m. p. 320°, and analogous *Co*, m. p. 308°, and *Cu*, m. p. 312°, compounds. 1-Phenyl-3-methyl-4-benzeneazo-5-pyrazolone forms similar *Co*, m. p. 279—280°, *Ni*, m. p. 241°, and *Cu* compounds, m. p. 228°. *p*-2-Naphtha-1′ : 2′-triazolylbenzeneazo-β-naphthylamine also forms cryst. *Ni*, *Co*, and *Cu* compounds. The analogy between these compounds and the azo-metallic complexes of the naphthalene and phenanthrene series indicates that the azo-derivative reacts with the metallic salt in the hydroxylic and not in the ketonic form. Structural formulæ in accord with this conclusion are suggested.

T. H. POPE.

New mordant azo-dye from the condensation of aminothiosalicylic acid with chlorodinitrobenzene. V. G. GULINOV (Ukrain. Chem. J., 1930, **5**, [Tech.], 249—253).—The condensation of aminothiosalicylic acid with chlorodinitrobenzene gives a nitro-dye, reduction of which gives a diamino-derivative. The diazotised product couples with β-naphthol to give a mordant dye.

E. B. UVAROV.

Interaction of halogen-substituted *p*-tolylhydrazines with chloral. F. D. CHATTAWAY and T. E. W. BROWNE (J.C.S., 1931, 1088—1092; cf. A., 1928, 55, 1368).—Chloral and 3-bromo-*p*-tolylhydrazine hydrochloride in H_2O give a hydrazone which passes at 65—70° into ββ-*dichloro*-α-3-*bromo*-p-*tolueneazoethylene* (I), m. p. 67°, by reversible loss of HCl, since treatment of this with HCl in Ac_2O affords *chloral*-N-*acetyl*-3-*bromo*-p-*tolylhydrazone*, m. p. 187° (decomp.). Chlorination of I in AcOH below 30° yields *pentachloro*-5-*chloro*-3-*bromo*-p-*tolueneazoethane*, m. p. 113°, whilst bromination gives β-*chloro*-αβ-*dibromo*-α-3-*bromo*-p-*tolueneazoethylene*, m. p. 91°. Chloral and the hydrazine in EtOH afford *ethyl glyoxylate* 3-*bromo*-p-*tolylhydrazone*, m. p. 60°, brominated to *ethyl bromoglyoxylate* 3-*bromo*-p-*tolylhydrazone*, m. p. 98°, also formed from Br_2 and ethyl 3-bromo-*p*-tolueneazoacetoacetate. The following are prepared similarly from 3 : 5-dibromo-*p*-tolylhydrazine: ββ-*dichloro*-α-3 : 5-*dibromo*-p-*tolueneazoethylene*, m. p. 50°; *pentachloro*-3 : 5-*dibromo*-p-*tolueneazoethane*, m. p. 128°; β-*chloro*-αβ-*dibromo*-α-3 : 5-*dibromo*-p-*tolueneazoethylene*, m. p. 87°; *ethyl glyoxylate, ethyl bromoglyoxylate*, and *glyoxylic acid* 3 : 5-*dibromo*-p-*tolylhydrazones*, m. p. 83°, 64°, and 163° (decomp.), respectively.

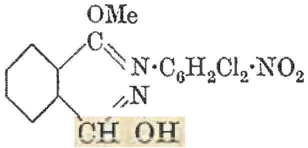
H. BURTON.

Reaction of certain diazosulphonates derived from β-naphthol-1-sulphonic acid. IV. Constitution of condensation products of diazo-compounds with β-naphthol derivatives substituted in the 1-position. F. M. ROWE and A. T. PETERS. **V. 4′-Nitro- and 4′-amino-derivatives of 3-phenyl-4-methylphthalaz-1-one.** F. M. ROWE, E. LEVIN, and A. T. PETERS. **VI. Preparation of phthalazine, phthalazone, and phthalimidine derivatives from 2 : 6-dichloro- and 2 : 6-dibromo-4-nitroaniline.** F. M. ROWE, C. DUNBAR, and N. H. WILLIAMS (J.C.S., 1931, 1065—1067, 1067—1073, 1073—1088).—IV. The condensation products from diazotised *p*-nitroaniline and 1-halogeno- or 1-methyl-β-naphthol (Pollak and Gebauer-Fulnegg, A., 1929, 58) are diazo-oxides, since treatment with alkali causes decomp., or, in the case of the halogeno-derivatives, conversion into Para-red. Coupling with β-naphthol-1-sulphonic acid leads to the formation of sodium 1-*p*-nitrobenzeneazo-β-naphthaquinone-1-sulphonate (and not a diazo-oxide as stated by Bucherer and Tama, A., 1930, 1280), convertible as previously described (A., 1926, 625) into sodium hydrogen 3-*p*-nitrophenyl-1 : 3-dihydrophthalazine-4-acetate-1-

sulphonate and 1-hydroxy-3-*p*-nitrophenyl-1 : 3-dihydrophthalazine-4-acetic acid, m. p. 241°, which are the compounds $C_{16}H_{10}O_6N_3SNa,H_2O$ and $C_{16}H_{11}O_3N_3,2H_2O$ (the m. p. 310—315° is an error for 239°), of Bucherer and Tama (*loc. cit.*).

V. The substance, m. p. 247°, previously obtained (A., 1926, 625) by the action of $Na_2Cr_2O_7$ and dil. H_2SO_4 on 1-hydroxy-3-*p*-nitrophenyl-1 : 3-dihydrophthalazine-4-acetic acid is 3-p-*nitrophenyl*-4-*methylphthalaz*-1-*one* (I), m. p. 251° (*sulphate*, m. p. 246°; *picrate*, m. p. 208°); the acetic acid grouping is decarboxylated. Reduction of I with aq. Na_2S gives 3-p-*aminophenyl*-4-*methylphthalaz*-1-*one* (II), m. p. 277° (*Ac* derivative, m. p. 316—317°), also formed when 1-hydroxy-3-*p*-aminophenyltetrahydrophthalazine-4-acetic acid is heated with alcoholic KOH or aq. Na_2CO_3. Treatment of I with Me_2SO_4 in $PhNO_2$, removal of volatile products with steam, and basifying (Na_2CO_3) the residue gives an orange-red substance, which when crystallised (from AcOEt or EtOH) loses H_2O forming 1-*methoxy*-3-p-*nitrophenyl*-4-*methylene*-3 : 4-*dihydrophthalazine*, m. p. 134°, demethylated to I. Reduction of II with Zn dust and dil. HCl affords N-p-*aminophenyl*-3-*methylphthalimidine*, m. p. 166° (*Ac* derivative, m. p. 250°), convertible into N-p-*hydroxyphenyl*-3-*methylphthalimidine*, m. p. 192° (*Et ether*, m. p. 136°).

VI. The conversion of 2′ : 6′-dichloro- and 2′ : 6′-dibromo-4′-nitrobenzeneazo-β-naphthol-1-diazosulphonates through the sodium 1-2′ : 6′-dihalogeno-4′-nitrobenzeneazo-β-naphthaquinone-1-sulphonates into *sodium hydrogen* 3-2′ : 6′-*dichloro*- and 3-2′ : 6′-*dibromo*-4′-*nitrophenyl*-1 : 3-*dihydrophthalazine*-4-*acetate*-1-*sulphonates* proceeds less readily than with the unhalogenated analogue (A., 1926, 625), owing to the increased tendency to formation of 2′ : 6′-dihalogeno-4′-nitrobenzeneazo-β-naphthol. Acid hydrolysis of the new salts gives 1-*hydroxy*-3-2′ : 6′-*dichloro*-4′-*nitrophenyl*-, m. p. 245° [*Me* ester (+MeOH or C_6H_6), m. p. (solvent-free) 169°; *Et* ester (+C_6H_6), m. p. 162°; *Ac* derivative (+EtOH), m. p. 110—112°, resolidifying with m. p. 202—204°; *anilide*, m. p. 289°], and 1-*hydroxy*-3-2′ : 6′-*dibromo*-4′-*nitrophenyl*-1 : 3-*dihydrophthalazine*-4-*acetic acid*, m. p. 245° [*Me* ester, m. p. 176°; *Et* ester (+EtOH), m. p. (EtOH-free) 182°; *anilide*, m. p. 280°], reduced by $SnCl_2$ and conc. HCl to 1-*hydroxy*-3-2′ : 6′-*dichloro*-4′-*aminophenyl*-, m. p. 242° [*Ac* derivative, m. p. 282° (decomp.)], and 1-*hydroxy*-3-2′ : 6′-*dibromo*-4′-*aminophenyl*-*tetrahydrophthalazine*-4-*acetic acid*, m. p. 261° (*Ac* derivative, m. p. 270°). These are converted by dil. H_2SO_4 at 140° into 2′ : 6′-*dichloro*-4′-*amino*- (III), m. p. 302° (*Ac* derivative, m. p. 334°), and 2′ : 6′-*dibromo*-4′-*amino*-3-*phenylphthalaz*-1-*one* (+AcOH) (IV), m. p. 304° (*Ac* derivative, m. p. 338°). Reduction of III with Zn dust and dil. HCl gives 2′ : 6′-*dichloro*-4′-*amino*-N-*phenylphthalimidine* (V), m. p. 253° (*Ac* derivative, m. p. 239°), convertible into 2′ : 6′-*dichloro*-N-*phenylphthalimidine*, m. p. 146°, whilst IV furnishes similarly 2′-*bromo*-4′-*amino*-, m. p. 178° (*Ac* derivative, m. p. 272°), or 4′-amino-*N*-phenylphthalimidine (VI) [the Ac derivative has m. p. 272° (cf. A., 1926, 625, 196°), according to the conditions used]. 2′ : 6′-*Dichloro*- (VII), m. p. 315° (decomp.) (*picrate*, m. p. 233°), and 2′ : 6′-*dibromo*-4′-*nitro*-3-*phenylphthalaz*-1-*one* (+AcOH) (VIII), m. p. 306° (*picrate*, m. p. 252°), are reduced by aq. Na_2S to III and IV and by Zn dust and dil. HCl to V and VI, respectively. Methylation of VII (as in Part II) gives a *substance* (probably of annexed formula), m. p. 235°



(from AcOEt), which forms compounds with MeOH (m. p. 157°) and EtOH (m. p. 111°); when these compounds are heated they give the substance, m. p. 235°. Similar methylation of VIII affords analogous substances, m. p. 228°, 138°, and 110—112°, respectively. 2′ : 6′-*Dichloro*-, m. p. 240° (decomp.) (*picrate*, m. p. 225°), and 2′ : 6′-*dibromo*-4′-*nitro*-3-*phenyl*-4-*methylphthalaz*-1-*one*, m. p. 254° (*picrate*, m. p. 215°), are methylated similarly to 2′ : 6′-*dichloro*-, m. p. 136°, and 2′ : 6′-*dibromo*-4′-*nitro*-1-*methoxy*-3-*phenyl*-4-*methylene*-3 : 4-*dihydrophthalazine*, m. p. 129°, reduced by aq. Na_2S to 2′ : 6′-*dichloro*- (IX), m. p. 325° (*Ac* derivative, m. p. 311°), and 2′ : 6′-*dibromo*-4′-*amino*-3-*phenyl*-4-*methylphthalaz*-1-*one* (X), m. p. 315° (*Ac* derivative, m. p. 315°), also obtainable from the 1-hydroxy-3-dihalogenoaminophenyltetrahydrophthalazine-4-acetic acids. Reduction of IX with Zn dust and dil. HCl affords 2 : 6-dichloro-*p*-phenylenediamine, whilst X gives some 2′-*bromo*-4′-*amino*-N-*phenyl*-3-*methylphthalimidine*, m. p. 216° (*Ac* derivative, m. p. 266°), in addition to 2 : 6-dibromo-*p*-phenylenediamine. H. BURTON.

Bromophenols. XXXVI. Dichloro- and trichloro-phenols and their bromination products. M. KOHN and S. FINK (Monatsh., 1931, 58, 73—91).—2 : 5-Dichloroanisole (improved prep. from 2 : 5-dichloroaniline given) with mixed acids affords its 4 : 6-*dinitro*-derivative, m. p. 61—62°. 2 : 5-Dichlorophenol with Br_2 and AcOH gives 2 : 5-*dichloro*-4 : 6-*dibromophenol*, m. p. 100·5° (corresponding *anisole*, b. p. 303—307°/749 mm., m. p. 86—87°), oxidised by fuming HNO_3 to 2 : 5-*dichloro*-6-*bromo*-p-*benzoquinone*, m. p. 161°, reduced by H_2SO_3 to 2 : 5-*dichloro*-6-*bromoquinol*, m. p. 166° (*Bz* derivative, m. p. 141°), whilst Br and Fe powder give 2 : 5-*dichloro*-3 : 4 : 5-*tribromophenol*, m. p. 206° (crystallographic data by HLAWATSCH) (corresponding *anisole*, b. p. 352—355°/751 mm., m. p. 143—144°). Cl in AcOH converts 2 : 5-dichlorophenol into 2 : 4 : 5-trichlorophenol (Holleman, A., 1921, i, 102), converted by Br in AcOH into its 6-*bromo*-, m. p. 81° (*Bz* derivative, m. p. 116—117°), and by excess of Br into its 3 : 6-*dibromo*-, m. p. 195° (*Bz* derivative, m. p. 176°), derivative, and by HNO_3–AcOH to the 6-*nitro*-derivative, m. p. 81°. Debromination of either 2 : 4 : 6-trichloro-4 : 5-dibromo- (A., 1927, 51) or -3-bromo- (*ibid.*, 967) -phenol with Zn and AcOH affords 2 : 4 : 6-trichlorophenol (*anisole*, m. p. 61—62°; *Bz* derivative, m. p. 75°), thus proving the constitution of the parent compounds. Crystallographic data for 3-chloro-2 : 4 : 5 : 6-tetrabromophenol (A., 1926, 52) are given. J. W. BAKER.

Bromophenols. XXXVII. Brominated quinol and methylquinol ethers. M. KOHN and L. STEINER (Monatsh., 1931, 58, 92—107).—The product, m. p. 70°, of bromination of *p*-hydroxy-

anisole in CCl_4 or AcOH (Benedikt, *ibid.*, 1880, **1**, 368) is probably a mixture of the 2 : 5- and 3 : 5-dibromo-derivatives (giving an *Ac* derivative, m. p. 86°), since debromination of 2 : 3 : 5-tribromo-4-hydroxyanisole (A., 1925, i, 1265) (*Ac* derivative, m. p. 91°) affords pure 2 : 5-*dibromo-4-hydroxyanisole*, m. p. 113° (*dimethyl ether*, m. p. 149°), whilst Ac_2O, AcOH, and Zn convert it into an Ac derivative, m. p. 89°, of dibromo-4-hydroxyanisole. The dibromonitro-4-hydroxyanisole obtained by Kohn and Grün (*loc. cit.*) gives a *dimethyl ether*, m. p. 159°. Quinol dimethyl ether with PBr_5 affords the 2 : 5-dibromo-, m. p. 147°, and the liquid monobromo-derivative. Bromoanil is converted by p-MeC_6H_4·OK into 2 : 5-*dibromo*-3 : 6-*di*-p-*tolyloxy*-p-*benzoquinone*, decomp. 230°, converted by Zn and AcOH successively into the corresponding quinol, and 2 : 5-*di*-p-*tolyloxyquinol*, m. p. 186° (*Ac*, m. p. 139°, and *Bz*, m. p. 174°, derivatives; *dimethyl ether*, m. p. 120°), which is obtained pure by again reducing the 2 : 5-*di*-p-*tolyloxy*-p-*benzoquinone*, m. p. 212°, obtained by oxidation. Tetrabromo-o-cresol (A., 1927, 967) is oxidised by fuming HNO_3 to the tribromotoluquinone, converted by HBr in AcOH and subsequent methylation into 3 : 4 : 6-*tribromo*-2 : 5-*dimethoxytoluene*, m. p. 163°, also obtained by bromination of 3-bromo-2 : 5-dimethoxytoluene (A., 1924, i, 1264). 2 : 6-Dibromo-5-methyl-p-benzoquinone (by oxidation of tribromo-m-cresol; Claus and Hirsch, A., 1889, 389) is reduced by H_2SO_3 and methylated to 4 : 6-*dibromo*-2 : 5-*dimethoxytoluene*, b. p. 289—303°/748 mm., m. p. 73°, further brominated to the 3 : 4 : 6-*tribromo*-derivative, m. p. 159°.

J. W. BAKER.

Symmetrical halogenophenols. P. BRENANS and K. YEN (Compt. rend., 1931, **192**, 1037—1039).—4-*Bromo-2-iodophenol*, m. p. 71° (*acetate*, m. p. 60°; *benzoate*, m. p. 90°; *Et ether*, m. p. 34°), gives with I 4-bromo-2 : 6-di-iodophenol, and 4 : 6-dibromo-2-iodophenol (cf. A., 1928, 631), also formed by the action of 1 and 2 mols. respectively of Br in AcOH on iodophenol. 6-Chloro-2 : 4-di-iodophenol, m. p. 96° (*acetate*, m. p. 90°; *benzoate*, m. p. 97°; *Et ether*, m. p. 68°), is formed by the action of 1 mol. of Cl_2 in AcOH on 2 : 4-di-iodophenol (cf. J.C.S., 1913, **103**, i, 220).

A. RENFREW.

Chlorination of iodophenols. IV. Action of chlorine on derivatives of p-iodophenol. D. MATHESON and H. MCCOMBIE (J.C.S., 1931, 1103—1110).—*Iododichlorides* [the m. p. (decomp.) are given in parentheses] of the following compounds are described : (*a*) p-iodophenyl alkyl ethers : n- and *iso*-propyl; β-*bromoethyl*, m. p. 68° (101°); βγ-*dichloro*- (81°) and βγ-*dibromo-propyl*, m. p. 50·5° (87°); *benzyl*, m. p. 62° [the *iododichloride* decomposes to 2-*chloro-4-iodophenyl benzyl ether*, m. p. 64° (92°)]; (b) p-iodophenyl esters : p-*toluenesulphonate*, m. p. 99° (115°); *cinnamate*, m. p. 122° (121°); αβ-*dichloro*-, m. p. 127° (170°), and αβ-*dibromo*-, m. p. 153° (130°), -β-*phenylpropionates*; (c) 2-*chloro-4-iodophenyl* βγ-*dichloro*- (101°) and βγ-*dibromo*-, m. p. 48° (130°), -*propyl ethers*; ω-p-iodophenoxyacetophenone, m. p. 103° (75°); p-*iodophenyl ethyl carbonate*, m. p. 38° (132°); *di*-p-*iodophenyl carbonate*, m. p. 193° (*bisiododichloride*). The iododichlorides from the esters and halogenated ethers, *i.e.*, compounds containing negative groups in the side-chain, tend to be more stable than those from the unsubstituted ethers. The iododichloride from p-iodoanisole decomposes when warmed, forming 2-*chloro-4-iodoanisole*, m. p. 83°; the *iododichloride*, m. p. 73° (decomp.), of this gives similarly 2 : 6-*dichloro-4-iodoanisole*, m. p. 75—76° [*iododichloride*, m. p. 97° (decomp.)]. 2-*Chloro-4-iodophenetole*, m. p. 47°, is obtained from the *iododichloride*, m. p. 73·5° (decomp.), of p-iodophenetole. p-*Iodophenyl phenylcarbamate*, m. p. 148°, and Cl_2 in $CHCl_3$ give the *iododichloride*, m. p. 142° (decomp.), of p-*iodophenyl* 2 : 4-*dichlorophenylcarbamate*, m. p. 151·5°. Chlorination of p-iodoanisole in CCl_4 at 70—80° for 4 days affords *pentachloroanisole*, m. p. 108°. p-*Iodophenyl allyl ether* has b. p. 145°/15 mm.

H. BURTON.

Catalytic reduction of mixtures of p-nitro- and -nitroso-phenols with aldehydes and ketones. R. T. MAJOR (J. Amer. Chem. Soc., 1931, **53**, 1901—1908).—Catalytic reduction (Adams) of a mixture of p-nitro- or p-nitroso-phenol and $COMe_2$ gives p-aminophenol and 45% of p-*iso*propylaminophenol [*hydrochloride*, m. p. 189°; *nitroso*-derivative, m. p. 112—113°; *phenylcarbimide* derivative, m. p. 214—215° (decomp.); ON-*dibenzoyl* derivative, m. p. 174—175°], also obtained by reduction of p-*iso*propylideneaminophenol. The *sec.*-base is not formed when a mixture of $COMe_2$ and p-aminophenol is treated similarly. The following changes probably occur :

$$OH\cdot C_6H_4\cdot NO_2 \longrightarrow OH\cdot C_6H_4\cdot NH\cdot OH \xrightarrow{Me_2CO} OH\cdot C_6H_4\cdot N(:O):CMe_2 \longrightarrow OH\cdot C_6H_4\cdot NH\cdot CHMe_2.$$

Similarly, p-nitrophenol and methyl ethyl ketone afford some p-sec.-*butylaminophenol*, m. p. 118—119° (*hydrochloride*); with $COEt_2$, p-α-ethylpropylaminophenol [*nitroso*-derivative, m. p. 89—90° (*hydrochloride*)] is formed. Benzoylation of the reduction product from 2 : 4-dinitrophenol and $COMe_2$ gives 2-*benzamido-4-benzoyl*iso*propylaminophenyl benzoate*, m. p. 171°; under similar conditions 2 : 4-dinitrophenetole affords 2 : 4-*dibenzamidophenetole*, m. p. 189°. Reduction of a mixture of PhCHO and p-nitro- or p-amino-phenol yields p-dibenzylaminophenol (*benzoate*, m. p. 143—144°); p-benzylaminophenol is formulated as an intermediate which subsequently reacts thus : $OH\cdot C_6H_4\cdot NH\cdot CH_2Ph + PhCHO \longrightarrow OH\cdot C_6H_4\cdot N(CH_2Ph)\cdot CHPh\cdot OH \xrightarrow{I_2} OH\cdot C_6H_4\cdot N(CH_2Ph)_2$. No *sec.*-alkylaminophenol is obtained from p-nitrophenol and acetophenone or menthone, or from $COMe_2$ and o- or m-nitrophenol, $PhNO_2$, or p-nitrophenetole.

H. BURTON.

Identification of phenols as esters of 3 : 5-dinitrobenzoic acid. M. PHILLIPS and G. L. KEENAN (J. Amer. Chem. Soc., 1931, **53**, 1924—1928).—3 : 5-Dinitrobenzoyl *derivatives* of the following phenols are described [the m. p (all corr.) are given in parentheses]: phenol (145·8°); o- (138·4°), m- (165·4°), and p-cresol (188·6°); o-4-xylenol (181·6°); m-2- (158·8°), m-4- (164·6°), and m-5-xylenol (195·4°); p-xylenol (137·2°); thymol (103·2°); p-*cyclo*hexylphenol (168°); guaiacol (141·2°); eugenol (130·8°); *iso*eugenol (158·4°); α- (217·4°) and β-naphthol (210·2°); creosol (3-methoxy-p-cresol), b.p. 219—221° (170·6°), prepared by the Clemmensen reduction of vanillin; 2-*methoxy-4-propylphenol*, b. p. 251—253° (corr.)/765·8 mm.

(116·2°), obtained by the catalytic reduction of eugenol. Optical properties of the 3 : 5-dinitrobenzoates are recorded. H. BURTON.

Dealkylation of phenolic ethers by pyridine and piperidine. R. S. CAHN (J.C.S., 1931, 1121—1123; cf. this vol., 625).—The numbers quoted after the following phenol ethers are the % hydrolysis taking place when they are heated with an excess of pyridine and piperidine respectively (in some cases 0 represents slight hydrolysis): codeine, 0, —; *o*-nitroanisole, 0, about 40; *m*-nitroanisole, 0, 0; *p*-nitroanisole, 0, 0; 2 : 4-dinitroanisole, about 70, 100; 3 : 5-dinitroanisole, 0, 0; 2 : 4-dinitrodiphenyl ether, 0, 100; 2 : 4 : 6-trinitroanisole, 100, 100; 3-nitro-*p*-tolyl methyl ether, 0, about 20; 5-nitro-*o*-tolyl methyl ether, 100, almost 100; 6-methoxy-*m*-toluic acid, 0, —; 5-nitro-6-methoxy-*m*-toluic acid, 0, —; 2 : 4 : 6-trichloroanisole, 0, —. 2 : 4-Dinitroanisole is the only ether which resembles the diphenyl ethers in yielding a phenylpiperidine derivative. H. BURTON.

3-Ethoxy-*p*-cresol. W. STEINKOPF and O. KLOPFER (Ber., 1931, 64, [*B*], 990—993).—3-Ethoxy-*p*-cresol, m. p. 34° (m-*nitrobenzoate*, m. p. 132°), is prepared by treating Na homocatechol-5-sulphonate with Et *p*-toluenesulphonate and subsequent removal of the SO_3H group by superheated steam or directly from homocatechol; addition of EtOH greatly improves the yield. The constitution of the compound is confirmed by its formation from 4-nitro-3-ethoxytoluene. The *acetate*, b. p. 256—258°, is converted by $KMnO_4$ and subsequent hydrolysis into 4-*hydroxy*-3-*ethoxybenzoic acid*, m. p. 225°. Creosol is prepared in 94% yield from Na homocatechol-5-sulphonate and Me *p*-toluenesulphonate in presence of MeOH. H. WREN.

Rearrangement of saturated phenyl alkyl ethers. Synthesis of *iso*propyl-phenol and -cresols. J. B. NIEDERL and S. NATELSON (J. Amer. Chem. Soc., 1931, 53, 1928—1934).—When phenyl *iso*propyl ether is heated with conc. H_2SO_4 in AcOH, *o*-*iso*propylphenol is obtained. Similarly, o-*tolyl* iso*propyl ether*, b. p. 192°, gives 5-*iso*propyl-*o*-cresol, convertible into 5-iso*propyl*-o-*tolyloxyacetic acid*, m. p. 87—88°; m-*tolyl* iso*propyl ether*, b. p. 195°, affords an iso*propyl*-m-*cresol*, b. p. 230—235°, converted into an iso*propyl*-m-*tolyloxyacetic acid*, m. p. 141°; p-*tolyl* iso*propyl ether*, b. p. 195°, 84°/12 mm., yields 3-iso*propyl*-p-*cresol*, b. p. 234—237°, convertible into 3-iso*propyl*-p-*tolyloxyacetic acid*, m. p. 126.° H. BURTON.

Crotyl ethers of phenol. C. D. HURD and F. L. COHEN (J. Amer. Chem. Soc., 1931, 53, 1917—1922).—Phenyl α-methylcrotyl (α-methyl-Δ^β-butenyl), *phenyl α-ethylcrotyl*, b. p. 116—118°/15 mm., and *phenyl α-propylcrotyl ethers*, b. p. 153—154°/23 mm., prepared from phenol and the appropriate crotyl chloride in presence of K_2CO_3, Et_2O, and $COMe_2$, rearrange when heated at 200°, 200—205°, and 228—230°, respectively, into *o*-α-methylcrotyl-, o-α-*methyl*-Δ^β-*pentenyl*-, b. p. 143—145°/15 mm., and o-α-*methyl*-Δ^β-*hexenyl-phenol*, b. p. 154—155°/14 mm., respectively. *Phenyl ααγ-trimethylcrotyl ether* decomposes at 160—170° to phenol, ββ-dimethyl-$\Delta^{\alpha\gamma}$-pentadiene, and tar. The rearrangement of aryl crotyl ethers is considered to be a special case of three-C tautomerism involving the formation of free radicals. H. BURTON

[Preparation of] 1-amino-β-naphthol hydrochloride. J. B. CONANT and B. B. CORSON (Organic Syntheses, 1931, 11, 8—11).

[Preparation of] 1-amino-β-naphthol-4-sulphonic acid. L. F. FIESER (Organic Syntheses, 1931, 11, 12—14).

Debromination with benzene and aluminium chloride. M. KOHN (Monatsh., 1931, 58, 108—111).—The 3 : 5 : 3′ : 5′-tetrabromo-derivative of ββ-4 : 4′-dihydroxydiphenyl-*n*-propane (crystallographic data by HLAWATSCH) is converted by anhyd. $AlCl_3$ in C_6H_6 into PhOH and PhBr. J. W. BAKER.

Quinol pyridinium salts. E. KOENIGS and H. GREINER (Ber., 1931, 64, [*B*], 1045—1048).—BzCl, pyridine, and *p*-benzoquinone in presence of Cu powder afford quinol dibenzoate, m. p. 203—205°, and quinolpyridinium chloride. The last-named substance does not react with NH_2Ph, but is transformed by $SOCl_2$ into chloranil. 1 : 4-Dihydroxynaphthalene-pyridinium chloride, m. p. 210—220° (decomp.), is converted by $SOCl_2$ into 2 : 3-*dichloro*-1 : 4-*naphthaquinone*, m. p. 189—192°, and by NH_2Ph in MeOH into a *compound*, $C_{27}H_{20}O_3N_2$, m. p. 194°. Quinol-quinolinium chloride and $SOCl_2$ afford the *substance* $C_{15}H_9O_2NCl_4$, m. p. 274°. H. WREN.

Thioquinols. L. A. WARREN and S. SMILES (J.C.S., 1931, 1192—1196).—1-Arylthiol-β-naphthols (1 mol.) are converted by a 10% solution of HNO_3 (1 mol.) in AcOH into *quinonitroles* (*aryl* 1-*nitro*-2-*keto*-1 : 2-*dihydro*-α-*naphthyl sulphides*). The following are described: β-*naphthyl*, m. p. 116° (decomp.); p-*tolyl*, m. p. 112° (decomp.); o-*nitrophenyl*, m. p. 105° (decomp.), and p-*nitrophenyl*, m. p. 116° (decomp.). When these quinonitroles are warmed in AcOH, hydrolysis (replacement of NO_2 by OH) is the main process; the resultant thioquinols decompose to aryl mercaptans, which are isolated as disulphides. Migration of the NO_2 group may occur concurrently; o-, m. p. 192°, and p-, m. p. 187°, -*nitrophenyl* ?-*nitro*-2-*hydroxy*-α-*naphthyl sulphides* are thus obtained from the above *o*- and *p*-nitrophenyl derivatives. 1-*Nitro*-2′-*hydroxy*-2-*keto*-1 : 2-*dihydrodi*-α-*naphthyl sulphide*, m. p. 116° (decomp.) [2′-*Me ether*, m. p. 105° (decomp.)], obtained from β-naphthol 1-sulphide (monomethyl ether) and HNO_3 in AcOH, decomposes in warm AcOH to dehydro-β-naphthol 1-disulphide. 1-*Nitro*-2-*keto*-2′-*acetoxy*-1 : 2-*dihydrodi*-α-*naphthyl sulphide*, m. p. 102° (decomp.), prepared from the *monoacetyl* derivative, m. p. 164°, of β-naphthol 1-sulphide, gives similarly β-naphthol 1-disulphide diacetate. 1-*Nitro*-2′-*hydroxy*-2-*keto*-1 : 2-*dihydrodi*-α-*naphthyl disulphide* has m. p. 109° (decomp.). β-Naphthol 1-sulphide (1-disulphide) and 2 mols. of HNO_3 in AcOH give *di*-1-*nitro*-2-*keto*-1 : 2-*dihydro*-α-*naphthyl sulphide*, m. p. 121° (decomp.) [*disulphide*, m. p. 124—127° (decomp.)]. β-Naphthol *iso*sulphide yields nitrodehydro-β-naphthol 1-sulphide (J.C.S., 1914, 105, 1746) with 1 mol. of HNO_3. H. BURTON.

Organic gold compounds. Z. LEDÓCHOWSKI (Rocz. Chem., 1931, 11, 203—220).—*Thioguaiacyl*

auric chloride, prepared by the interaction of thioguaiacol and $AuCl_3$ in Et_2O, decomposes at 100° to yield *auric* o-*anisyl sulphide*, $(OMe{\cdot}C_6H_4{\cdot}S)_3Au$. Using AuCl, aurous *o*-anisyl sulphide, $OMe{\cdot}C_6H_4{\cdot}SAu$, is obtained. 3-*Ethylxantho*-4-*methoxybenzoic acid*, m. p. 185—186°, prepared by the action of potassium ethyl xanthate on 2-methoxydiazobenzene-5-carboxylic acid, yields on alkaline hydrolysis 4-*methoxy*-3-*mercaptobenzoic acid*, decomp. 220°, which combines with $AuCl_3$ to produce the compound $OMe{\cdot}C_6H_3(CO_2H){\cdot}SAuCl_2$; this when heated at 100° yields the substance $[OMe{\cdot}C_6H_3(CO_2H){\cdot}S]_3Au$, whilst on keeping it is converted into the compound $OMe{\cdot}C_6H_3(CO_2H){\cdot}SAu$, which can also be prepared from AuCl and thioguaiacolcarboxylic acid. 2-*Ethylxantho*-5-*nitroanisole*, m. p. 77—78°, yields on hydrolysis the corresponding *mercapto*-compound (not isolated), which is converted into 5-*amino*-2-*mercapto-anisole* (an oil), and this yields the compound $OMe{\cdot}C_6H_3(NH_2){\cdot}SAuCl_2$, with $AuCl_3$, and $OMe{\cdot}C_6H_3(NH_2){\cdot}SAu$ with AuCl. The latter substance is converted by heating at 100° into $[OMe{\cdot}C_6H_3(NH_2){\cdot}SAu_4]_2$. R. TRUSZKOWSKI.

Derivatives of nuclear methoxylated β-phenylethylamines. M. P. J. M. JANSEN (Rec. trav. chim., 1931, **50**, 617—637).—The following are described: β-2 : 4 : 5-trimethoxyphenylethylamine [*hydrochloride*, m. p. 190°; *sulphate*, m. p. 203—205° (decomp.); *carbamido*-, m. p. 148°, *phenylcarbamido*-, m. p. 148°; 2 : 4-*dinitrophenyl*-, m. p. 158°, and 2 : 4-*dinitro*-1-*naphthyl*-, m. p. 150°, derivatives; *oxaldi*-β-2 : 4 : 5-*trimethoxyphenylethylamide*, m. p. 182°]: β-phenylethylamine [phenylcarbamido-, m. p. 153—154° (cf. J.C.S., 1911, **99**, 1338); 2 : 4-*dinitrophenyl*-, m. p. 155°, and 2 : 4-*dinitro*-1-*naphthyl*-, m. p. 135°, derivatives]: β-4-methoxyphenylethylamine [*carbamido*-, m. p. 132·5°; *phenylcarbamido*-, m. p. 162°, 2 : 4-*dinitrophenyl*-, m. p. 142°, and 2 : 4-*dinitro*-1-*naphthyl*-, m. p. 105·5°, derivatives; *oxaldi*-β-4-*methoxyphenylethylamide*, m. p. 191°]: β-3 : 4 : 5-trimethoxyphenylethylamine [*carbamido*-, m. p. 143°, *phenylcarbamido*-, m. p. 125°, 2 : 4-*dinitrophenyl*-, m. p. 168·5°, and 2 : 4-*dinitro*-1-*naphthyl*-, m. p. 148·5°, derivatives; *oxaldi*-β-3 : 4 : 5-*trimethoxyphenylethylamide*, m. p. 194°]: β-3 : 4-dimethoxyphenylethylamine (*carbamido*-, m. p. 162°; *phenylcarbamido*-, m. p. 151°; 2 : 4-*dinitrophenyl*-, m. p. 109°, and 2 : 4-*dinitro*-1-*naphthyl*-, m. p. 148°, derivatives). No simple relation appears to exist between m. p. and constitution of these derivatives. The *chloroplatinates* and *mercurichlorides* of all these bases are prepared microchemically, and photomicrographs are given. H. A. PIGGOTT.

Methylurethanes of α-3-hydroxy-4-methoxy- and α-4-hydroxy-3-methoxy-phenylethyldimethylamines and their miotic activities. EDGAR STEDMAN and ELLEN STEDMAN (J.C.S., 1931, 1126—1131).—Benzoyl*iso*vanillin and MgMeI give small amounts of 3-*hydroxy*-4-*methoxyphenylmethylcarbinol*, m. p. 94°, or its 3-*Bz* derivative, m. p. 138°. α-3-*Hydroxy*-4-*methoxyphenylethyldimethylamine*, m. p. 99—100° [*methylurethane methiodide*, m. p. 177° (decomp.)], is obtained from the benzoylated carbinyl chloride and $NHMe_2$ in C_6H_6. α-4-*Hydroxy*-3-*methoxyphenylethyldimethylamine*, m. p. 90—91° [*methylurethane hydrochloride*, m. p. about 145° (decomp.)], is obtained similarly from α-4-*benzoyloxy*-3-*methoxyphenylethyl chloride*, m. p. 98—99°. The urethane derivatives possess miotic activities which are considerably smaller than that of α-*m*-hydroxyphenylethyldimethylamine methylurethane (miotine) (A., 1929, 692). H. BURTON.

Preparation of optically active and inactive β-chloro-α-aminodibenzyl, diphenylethyleneimine, and the optically active stilbene dichlorides. A. WEISSBERGER and H. BACH (Ber., 1931, **64**, [*B*], 1095—1108).—Treatment of *l*-*iso*-hydrobenzoin, $[\alpha]_D^{20}$ −91·2° in EtOH, with PCl_5 in $CHCl_3$ affords inactive α-stilbene dichloride with some dextrorotatory stilbene chlorohydrin. α-Amino-β-hydroxydibenzyl is transformed by PCl_5 in $CHCl_3$ or AcCl mainly into iso-β-*chloro*-α-*aminodibenzyl*, m. p. 59—59·5°, with small amounts of β-*chloro*-α-*amino-dibenzyl*, m. p. 122—123° (decomp.). The last-named compound is prepared in more favourable proportion by treatment of *dl*-*iso*-α-amino-β-hydroxydibenzyl with PCl_5 in $CHCl_3$. *d*-*iso*-α-Amino-β-hydroxydibenzyl hydrochloride suspended in $CHCl_3$ is chlorinated with PCl_5 and the mixture of bases is separated by treatment with bromocamphorsulphonic acid in dioxan. The sparingly sol. camphorsulphonate yields d-iso-β-*chloro*-α-*aminodibenzyl*, m. p. 73—74°, $[\alpha]^{20}$ +26·7° in EtOH (*hydrochloride*, $[\alpha]_D^{20}$ +51·8° in EtOH), whereas the filtrate affords d-β-*chloro*-α-*aminodibenzyl*, m. p. 127—129° (decomp.) [*hydrochloride*, $[\alpha]_D$ +133·6° in EtOH]. Similarly, *l*-*iso*-α-amino-β-hydroxydibenzyl affords l-iso-β-*chloro*-α-*aminodibenzyl*, m. p. 73—74°, $[\alpha]_D^{20}$ −26° in EtOH (*hydrochloride*, $[\alpha]^{20}$ −51·1° in EtOH), and l-β-*chloro*-α-*aminodibenzyl*, m. p. 127—129° (decomp.) [*hydrochloride*, $[\alpha]_D$ −133·3° in EtOH]. *cis*-αβ-Diphenylethyleneimine, m. p. 82—83°, is obtained from *l*- or *d*-*iso*-β-chloro-α-aminodibenzyl hydrochloride by the action of KOH in EtOH and is transformed by $2N$-H_2SO_4 into *iso*-α-amino-β-hydroxydibenzyl, m. p. 128—129°. *dl*-β-Chloro-α-aminodibenzyl hydrochloride gives dl-trans-αβ-*diphenylethyleneimine*, m. p. 46—47°, converted by HCl in C_6H_6 and Et_2O into dl-β-chloro-α-aminodibenzyl. *l*-β-Chloro-α-aminodibenzyl with KOH in EtOH affords l-trans-αβ-*diphenylethyleneimine*, m. p. 57—58° and 62—63°, $[\alpha]_D^{20}$ −340·5° in EtOH; d-trans-αβ-*diphenylethyleneimine* has m. p. 57—58° and 62—63°, $[\alpha]_D^{20}$ +347·4° in EtOH, whilst the mixture of equal proportions of the antipodes has m. p. 46—47°. *d*-*iso*-β-Chloro-α-aminodibenzyl hydrochloride in glacial AcOH saturated with HCl is converted by NOCl into α-stilbene dichloride, m. p. 190—191°, and l-β-*stilbene dichloride*, m. p. 79·5—80·5°, $[\alpha]^{20}$ −103·3° in EtOH, whereas from *l*-*iso*-β-chloro-α-aminodibenzyl there is obtained α-stilbene dichloride and d-β-*stilbene dichloride*, m. p. 79—80°, $[\alpha]^{20}$ +102·6° in EtOH. The mixture of equal proportions of the antipodes gives β-stilbene dichloride, m. p. 91·5—92·5°, the racemic nature of which is thereby established. When similarly treated, *d*-β-chloro-α-aminodibenzyl gives α-stilbene dichloride. H. WREN.

Triphenylmethyl hydrogen peroxide. H. WIELAND and J. MAIER (Ber., 1931, **64**, [*B*], 1205—1210).

—The interaction of CPh_3Cl and 30% H_2O_2 in presence of $COMe_2$ gives *triphenylmethyl hydrogen peroxide*, m. p. 81—82° (slight decomp.), best isolated as the pyridinium chloride additive *product* obtained by treating the ethereal solution with pyridine and HCl in Et_2O. It liberates I from NaI in $COMe_2$, but forms also triphenylcarbinol and phenol. It is stable when pure at room temp., but when impure or when heated it decomposes into phenol, benzophenone, and a little triphenylmethyl peroxide. Bivalent Fe in alkaline solutions and palladised $BaSO_4$ in C_6H_6 are without action. BzCl in pyridine, $NPhMe_2$, or with K_2CO_3 in C_6H_6 accelerates the fission without taking part in the change. In presence of an excess of KOH benzoylation takes place with production of *phenoxydiphenylmethyl benzoate*, $Ph\cdot CO_2\cdot CPh_2\cdot OPh$, m. p. 148°, hydrolysed by KOH in MeOH to BzOH, phenol, and benzophenone. Triphenylmethyl peroxide is formed from H_2O_2, CPh_3Cl, and conc. alkali in presence of C_6H_6. Triphenylmethyl perbenzoate could not be obtained from perbenzoic acid and CPh_3Cl. H. WREN.

[Constitution of colourless and coloured triphenylmethyl derivatives.] I. LIFSCHITZ (Ber., 1931, **64**, [*B*], 1218; cf. this vol., 349).—The presence of a mol. of pyridine in the salt originally formulated CPh_3Cl,H_2O has been recognised by Helferich (A., 1926, 517). H. WREN.

Tetraphenylmethane derivatives: non-quinonoid dyes. I. R. N. SEN and S. K. BANERJEE (J. Indian Chem. Soc., 1931, **8**, 77—86).—Tri-*p*-aminotriphenylcarbinol is condensed in presence of NaOAc with NH_2- and OH-derivatives of C_6H_6 to give CPh_4 derivatives substituted in all four nuclei. From these are prepared other derivatives by substitution of OH for NH_2. An account of their dyeing properties on wool and silk is given. These compounds contain no chromophores or quinonoid structure. The following are described: *tetra*-p-*aminotetraphenylmethane* [*monoacetyl*, s-*tetrabenzoyl*, *tetramethyl*, and s-*tetra-acetyl*, m. p. 218° (decomp.), derivatives]; *tri*-p-*amino*-p-*dimethylamino*-; p-*dimethylaminotri*-p-*hydroxy*-; *tri*-p-*amino*-p-*hydroxy-tetraphenylmethane*; *tri*-p-*amino*-p-*methoxy*-; *tri*-p-*hydroxy*-p-*methoxy*-; *tetra*-p-*hydroxy*- (Ag_4 salt); p-*acetamidotri*-p-*hydroxy*-; *tri*-p-*amino*-2 : 4-*dihydroxy*-, m. p. 160° (decomp.); 2 : 4 : 4′ : 4″ : 4‴-*pentahydroxy*- (Ag_5 salt); *tri*-p-*amino*-2 : 3 : 4-*trihydroxy*-; and 2 : 3 : 4 : 4′ : 4″ : 4‴-*hexahydroxy-tetraphenylmethane* (Ag_6 salt); *tri*-p-*amino*-4-*hydroxytetraphenylmethane*-3-; *tetra*-p-*hydroxytetraphenylmethane*-3-; *tri*-p-*amino*-4-*hydroxytetraphenylmethane*-2-; *tetra*-p-*hydroxytetraphenylmethane*-2-; *tri*-p-*amino*-2-*hydroxytetraphenylmethane*-5-; 2 : 4′ : 4″ : 4‴-*tetrahydroxytetraphenylmethane*-5-; *tri*-p-*aminotriphenyl*-4-*hydroxy*-3-*methylmethane*-5-, m. p. 87—90°; *tetra*-p-*hydroxytriphenyl*-3-*methylmethane*-5-; *tri*-p-*amino*-2 : 3 : 4-*trihydroxytetraphenylmethane*-6-; and 2 : 3 : 4 : 4′ : 4″ : 4‴-*hexahydroxytetraphenylmethane*-6-*carboxylic acid*. D. A. FAIRWEATHER.

Behaviour of ergosterol and its derivatives towards maleic anhydride. A. WINDAUS and A. LUTTRINGHAUS (Ber., 1931, **64**, [*B*], 850—854).—In their behaviour towards maleic anhydride, ergosterol derivatives can be divided into three classes. The first of these, including dehydroergosterol, one of the three *iso*ergosterols obtained by the action of mineral acid on ergosterol and certain irradiation products of the last-named substance, undergoes extensive condensation within a few days at room temp. or a few hr. at 80°. The second group comprises compounds which do not act considerably under these conditions, but condense extensively at 135° and contain ergosterol. Two *iso*ergosterols, ergosterol *D* and *F*, dihydroergosterol, suprasterol I and II fall into the third group, with which considerable reaction is not observed at 135°. In the compounds of the first two groups the presence of a system of conjugated linkings is indicated. Such a system is probably not present in the compounds of the third group, the slight activity of which is attributed to decomp. products resulting from the temp. employed. "*Ergosterol maleic acid*," $C_{31}H_{46}O_5$, m. p. 202—206° (decomp.), $[\alpha]^{19}$ − 178·5° in $COMe_2$, the *Ac* derivative of *ergosterol maleic anhydride*, $C_{33}H_{46}O_5$, m. p. 200—201°, $[\alpha]_D^{18}$ −147·4° in $CHCl_3$, and *dehydroergosteryl acetate maleic anhydride*, m. p. 205°, $[\alpha]_D^{17}$ +69·35° in $CHCl_3$, are described. H. WREN.

[Preparation of] o-toluic acid. H. T. CLARKE and E. R. TAYLOR (Organic Syntheses, 1931, **11**, 96—97).

[Preparation of] α-naphthoic acid. H. GILMAN, N. B. ST. JOHN, and F. SCHULZE (Organic Syntheses, 1931, **11**, 80—83).

Optical resolution of 3 : 5-dinitro-6-α-naphthylbenzoic acid. (MISS) M. S. LESSLIE and E. E. TURNER (J.C.S., 1931, 1188—1192).—Ethyl 2-chloro-3 : 5-dinitrobenzoate and 1-iodonaphthalene with Cu-bronze at 210° give the *Et* ester, m. p. 109—110°, of dl-3 : 5-*dinitro*-6-α-*naphthylbenzoic acid*, m. p. 184—185° (*amide*, m. p. 96—97°). The acid is resolved by brucine into the d-, m. p. 179—180° $[\alpha]_{5791}^{20}$ +63·4° in $COMe_2$ (*acid chloride*, m. p. 132—133°; *amide*, m. p. 168—169°), and l-*isomerides*. The *l*-acid is not racemised by boiling *N*-NaOH, and hydrolysis of the *d*-acid chloride with *N*-NaOH gives the acid, $[\alpha]_{5791}^{20}$ +61·3° in $COMe_2$. H. BURTON.

[Preparation of] ethyl phenylcyanopyruvate. R. ADAMS and H. O. CALVERY (Organic Syntheses, 1931, **11**, 40—41).

Anacardic acid. A. J. H. SMIT (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 165—168).—Anacardic acid, extracted from the husk of the fruit of *Anacardium occidentale*, on hydrogenation in EtOAc (Pt-black catalyst) yields a *tetrahydroanacardic acid*, m. p. 92°, not identical with tetrahydropelandjauic acid. It gives a violet coloration with $FeCl_3$ in alcoholic solution, indicating CO_2H and OH groups in the *o*-position. Anacardic acid loses CO_2 at 220°, yielding a phenol $C_{21}H_{31}\cdot OH$, b. p. 205°/0·4 mm., the Me ether of which (b. p. 202°/0·5 mm.) on hydrogenation as before yields a *compound*, $C_{22}H_{38}O$, m. p. 30°. Anacardic acid with Me_2SO_4 and NaOH solution gives *methyl methylanacardate*, b. p. 220—222°/0·5 mm., the *tetrahydro*-derivative, m. p. 38°, of which on oxidation with CrO_3 in AcOH gives palmitic acid. The phenol $C_{21}H_{31}\cdot OH$ on hydrogenation (PtO_2 in AcOH) gives the *compound* $C_{21}H_{41}\cdot OH$, m. p. 31°. This with $ZnCl_2$ at 220° gives the *hydrocarbon* $C_{21}H_{42}$, which on

further hydrogenation gives *pentadecyl*cyclo*hexane*, m. p. 25°, b. p. 178°/0·7 mm., confirmed by synthesis. It is concluded that anacardic acid is a lower homologue of pelandjauic acid, with a difference of two CH_2 groups, and the formula is $C_{15}H_{27}\cdot C_6H_3(OH)\cdot CO_2H$.
J. W. SMITH.

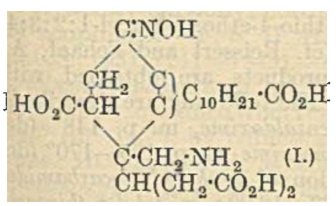
[Preparation of] *s*- and *as*-*o*-phthaloyl chloride. E. OTT (Organic Syntheses, 1931, **11**, 88—91).

3-Nitrophthalic acid series. H. W. UNDERWOOD, jun., and R. L. WAKEMAN (J. Amer. Chem. Soc., 1931, **53**, 1839—1842).—*Phenol*-3-*nitrophthalein*, m. p. 204—205°, obtained in 2% yield from phenol and 3-nitrophthalic anhydride in presence of conc. H_2SO_4 at 170—220°, dissolves in NaOH solution with a violet colour. A dil. alkaline solution of *resorcinol*-3-*nitrophthalein*, m. p. 260°, exhibits a green fluorescence which is not so marked as that of fluorescein. Methyl and methyl (1) hydrogen 3-nitrophthalates are unaffected by boiling Ac_2O in AcOH; methyl (2) hydrogen 3-nitrophthalate is similarly converted into 3-nitrophthalic anhydride. 3-Nitrophthalamide and the isomeric 3-nitrophthalamic acids are all converted by boiling with AcOH and Ac_2O into 3-nitrophthalimide.
H. BURTON.

2 : 4 : 5-Trimethoxybenzoic acid, a derivative of dehydrodeguelin. E. P. CLARK (J. Amer. Chem. Soc., 1931, **53**, 2007—2008).—Oxidation of dehydrodeguelin with $KMnO_4$ in $COMe_2$ gives probably 2-hydroxy-4 : 5-dimethoxybenzoic acid, m. p. 210° (decomp.), methylated to 2 : 4 : 5-trimethoxybenzoic acid.
H. BURTON.

Action of sodium ethoxide on ethyl *cyclo*hexane-2 : 3-dione-1 : 4-dicarboxylate. L. S. DEDUSSENKO (Acta Univ. Asiæ Med., 1928, **1**, 3—16; Chem. Zentr., 1931, i, 1443—1444).—In abs. EtOH solution ethyl *cyclo*pentan-2-ol-1 : 2 : 3-tricarboxylate is obtained; with Na and NaOEt in Et_2O solution the dionedicarboxylate is regenerated. Condensation of ethyl adipate and oxalate by Naumow's method forms ethyl *cyclo*pentan-1-one-2-carboxylate, *cyclo*hexane-2 : 3-dione-1 : 4-dicarboxylate, Δ^1-*cyclo*pentene-1 : 2 : 3-tricarboxylate, and oxaladipate.
A. A. ELDRIDGE.

Bile acids. XXX. M. SCHENCK (Z. physiol. Chem., 1931, **196**, 276—282).—The acid I (A., 1919, i, 331) is obtained from the corresponding lactam by hydrolysis with 20% HCl, or by similar hydrolysis of the keto-lactam (*i.e.*, O in place of C:NOH) and oximation of the product. It is not ob-



tained by reduction of the nitro-compound [I, $-CH:C(NO_2)-$ in the place of $-CH_2\cdot C(:NOH)-$, cf. A., 1930, 915] with Zn and NH_3 or with Na–Hg, nor could any definite product be obtained by boiling with NaOH, or oxidation with alkaline $KMnO_4$, sparingly sol. Cu salts being isolated in every case. Oxidation of I with warm alkaline $KMnO_4$ gives an *acid* $C_{24}H_{38}O_9N_2$ or $C_{24}H_{36}O_9N_2$, decomp. 276° (isolated as *Cu* salt), which no longer has the reactions of an oxime.
H. A. PIGGOTT.

Bile acids. XXXIV. Bromination and degradation of some keto-acids. H. WIELAND and T. POSTERNAK. **XXXV. Deoxybilianic acid and pyrocholoidanic acid.** H. WIELAND, L. ERTEL, and W. SCHONBERGER (Z. physiol. Chem., 1931, **197**, 17—30, 31—41; cf. this vol., 352).—XXXIV. Bromination of 7-ketocholanic acid yields 6-*bromo*-7-*ketocholanic acid*, m. p. 187—188° (decomp.), which with KOH in MeOH furnishes 6-*hydroxy*-7-*ketocholanic acid*, m. p. 132—134°; when oxidised with CrO_3 in AcOH it gives the tricarboxylic acid, m. p. 262°. The 6-hydroxy-7-keto-acid on oxidation forms 6 : 7-*diketocholanic acid*, m. p.166—168° [*bromo*-derivative, m. p. 238° (decomp.)]. The Br compound with KOH in MeOH furnishes a *dimethyl ether*, $C_{26}H_{42}O_6$, m. p. 152°, with aq. NaOH, *hydroxydiketocholanic acid*, m. p. 166—168° (decomp.). Heating the latter with KOH in MeOH or the Br derivative with Zn dust in AcOH gives the *enol* form, m. p. 146—148° (*Ac* derivative, m. p. 158°). Both keto- and enol forms yield the *oxime*, m. p. 220—222°. The enol furnishes a *nitrate*, m. p. 176—178° (decomp.), and on oxidation with $KMnO_4$ or CrO_3 in AcOH a *ketodicarboxylic acid*, m. p. 203—205° (decomp.). Dehydroanthropodeoxycholic acid with Br furnishes a *bromo*-derivative, m. p. 186—188° (decomp.). 7 : 12-Diketocholanic acid yields a *dibromo*-derivative, m. p. 183—185° (decomp.).

XXXV. β-Deoxybilianic acid, $[\alpha]^{20}$ +45·8°, with HNO_3 yields β-*choloidanic acid*, m. p. 300—302° (decomp.), $[\alpha]_D^{?}$ −5·75° (*Me_5* ester, b. p. 250—260°/0·27 mm.), which when heated forms pyrocholoidanic acid (*Me_2* ester, m. p. 95°). Bromination of the β-deoxy-acid yields *bromo*-β-*deoxybilianic acid*, m. p. 208—210° (decomp.), which with aq. NaOH furnishes 6-*hydroxy*-β-*deoxybilianic acid*, m. p. 183° (*lactone*, m. p. 263°; *Me_3* ester, m. p. 140·5°; *Me_2* ester of lactone, m. p. 200°). Oxidation of the bromo- and hydroxy-acids with HNO_3 furnishes β-choloidanic acid, and oxidation of the hydroxy-acid with CrO_3 in AcOH yields 6-*keto*-β-*deoxybilianic acid*, m. p. 193° (decomp.), $[\alpha]_D$ +53·82° [*enol* form, m. p. 198° (decomp.), $[\alpha]_D$ +83·40°].
J. H. BIRKINSHAW.

Bile acids. XV. *apo*Cholic acid and "dihydroxycholenic of m. p. 259—260°." W. BORSCHE and A. R. TODD (Z. physiol. Chem., 1931, **197**, 173—190; cf. A., 1928, 1244).—Distillation of *apo*cholic acid yields apo*choladienic acid*, m. p. 132—133°, $[\alpha]_D^{18\cdot5}$ +27·4 (*Me* ester, m. p. 43·5°), which on catalytic hydrogenation furnishes apo*cholanic acid*, m. p. 143—144°, $[\alpha]_D^{11}$ +37° (*Me* ester, m. p. 55—56°). Oxidation of *apo*cholic acid with CrO_3 gives dehydro-*apo*cholic acid (*dioxime*, m. p. 120—123°), with $KMnO_4$ dihydroxycholadienic acid, with perbenzoic acid *apocholic acid oxide*, m. p. 205° (+EtOH) (*Me* ester, m. p. 182—185°), and dihydroxycholadienic acid (*Me* ester, m. p. 136—138°). Dil. H_2SO_4 converts *apo*cholic acid oxide into dihydroxycholadienic acid; reduction of either compound yields *apo*cholic acid. 3 : 7-Dihydroxycholenic acid of m. p. 259—260° with CrO_3 yields 3 : 7-*diketocholenic acid*, m. p. 158° [*dioxime*, m. p. 208° (decomp.)], with $KMnO_4$ 3 : 7 : 13 : 14-*tetrahydroxycholanic acid*, m. p. 219—220° (*Me* ester, m. p. 205—206°), and the Me ester with perbenzoic acid, *methyl dihydroxycholenate oxide*,

m. p. 235—236°, and methyl dihydroxycholadienate. J. H. BIRKINSHAW.

Mechanism of oxidation processes. XXVIII. Autoxidation of aldehydes. H. WIELAND and D. RICHTER (Annalen, 1931, **486**, 226—242).—The observations of Kuhn and Meyer (A., 1929, 152) that purified PhCHO is not autoxidised have been confirmed for solutions in C_6H_6 and in conductivity water. With $FeCl_3$ as catalyst, there is an induction period which depends on the reduction to the Fe^{II} state, since the latter is more effective. Aliphatic aldehydes are catalysed only by Fe^{II} salts; at the same time, there is a limiting concentration of the latter, 1 at. of Fe activating 5 mols. of O_2, and there is a definite relationship to the amount of aldehyde oxidised. After the induction period is complete, the reaction is independent of the Fe concentration, but is roughly proportional to that of the aldehyde.

Whilst there is no measurable autoxidation of aliphatic aldehydes with $FeCl_3$, in aq. solution, that of PhCHO is readily catalysed, the velocity depending on the concentration of Fe and being proportional to that of the aldehyde. The autoxidation of PhCHO by $FeCl_3$ is not influenced by light in aq. solution, but is considerably accelerated in C_6H_6 solution; hence the active rays must be absorbed by H_2O. Surface reaction appears to play no part in the mechanism. Minimal quantities of "anti-oxygens," such as I and $NHPh_2$, completely inhibit oxidation. (This also applies to MeCHO catalysed by $FeCl_2$.) No reaction takes place in the absence of $FeCl_3$ with PhCHO alone or in C_6H_6 solution (with or without addition of H_2O).

The brown coloration described by Kuhn and Meyer is due to a complex Fe^{III} salt of perbenzoic acid and takes no part in the reaction. The iron-catalysed reaction takes place through the true aldehyde and not the hydrated form, the CO group being activated by the Fe salt. Perbenzoic acid is probably formed by direct addition of O to PhCHO; H_2O_2, if formed, could not be detected in presence of Fe salts. The autoxidation of phenylglyoxal hydrate is not catalysed by Fe salts, although it is affected by Pd-black. This indicates that the catalytic action of Fe salts is different from that of other types of compounds and of enzymes. F. R. SHAW.

Reactivity of positive hydrogen atoms. VI. Condensations of active methylene compounds with aromatic aldehydes. W. DILTHEY and W. NAGEL (J. pr. Chem., 1931, [ii], **130**, 147—162).—Condensation of dibenzyl ketone with either Schiff's bases CHR:NR′ or their components affords products of the type CHR(NHR′)·CHPh·CO·CH_2Ph, and thus are obtained β-*anilino*-αβ-*diphenylethyl*, m. p. 177°, β-*anilino*-α-*phenyl*-β-p-*anisylethyl*, m. p. 147°, and β-*anilino*-α-*phenyl*-β-3:4-*methylenedioxyphenylethyl*, m. p. 164—166°, *benzyl ketone*. All these require long heating with HCl–AcOH to convert them into the corresponding unsaturated ketones, CHR:CHPh·CO·CH_2Ph, which, however, are readily formed from the corresponding β-*diethylamino*-compounds, m. p. 117—118°, 137°, and 134—135°, respectively. Thus whilst $NHEt_2$ reacts in a similar manner to piperidine (A., 1929, 928), NH_2Ph reacts thus: PhCHO+NH_2Ph⟶CHPh:NPh $\xrightarrow{CO(CH_2Ph)_2}$ NHPh·CHPh·CHPh·CO·CH_2Ph⟶ CHPh:CPh·CO·CH_2Ph+NH_2Ph. The NH_2Ph adduct of phenyl styryl ketone is formed by condensation of NH_2Ph with the Schiff's base or its components and, on account of its stability and insolubility, will not react with a second mol. of acetophenone to form the 1:5-diketone. $COMe_2$ condenses with benzylideneaniline (or its components) to give two forms of the monoaniline adduct NHPh·CHPh·CH_2·CO·CH:CHPh, m. p. 129—130° and m. p. 140° (A., 1899, 896), converted into a cyclic form, NPh$<\begin{matrix}CHPh\cdot CH_2\\CHPh\cdot CH_2\end{matrix}>$CO, m. p. 205°, of dibenzylideneacetophenone, and with anisylideneaniline to give the corresponding *monoaniline* adduct, m. p. 141—142°. On the other hand, αε-diketo-αβγε-tetraphenyl-*n*-pentane is formed in varying yields when phenyl β-piperidino-β-phenylethyl ketone and deoxybenzoin are heated together in various solvents, or when chalkone and deoxybenzoin are heated together in solvents, b. p. above 100° (methyl*cyclo*hexane, *iso*butyl alcohol, toluene, or AcOH), or even without solvent at 123° and higher. The formation of 1:5-diketones is therefore formulated: R·CHO+$2NHC_5H_{10}$⟶H_2O+R·CH$(NC_5H_{10})_2$ $\xrightarrow{CH_2R'\cdot CO\cdot R''}$ $C_5H_{10}NH$+CHR(NC_5H_{10})·CHR′·COR″⟶ $C_5H_{10}NH$+CHR:CR′·COR″ $\xrightarrow{CH_2R'\cdot COR''}$ CHR(CHR′·COR″)$_2$, and not as suggested by Ruhemann and Watson (J.C.S., 1904, **85**, 460, 1170). J. W. BAKER.

Action of thiocarbimides on oximes. II. C. V. GHEORGHIU (J. pr. Chem., 1931, [ii], **130**, 49—70; cf. this vol., 210).—Nuclear substituted aromatic oximes, *e.g.*, the chloro-, nitro-, and acylamino-benzaldoximes, and *m*-nitroacetophenoneoxime, do not interact with phenyl-, *o*- or *p*-tolyl-thiocarbimides, except, in the case of the nitrobenzaldoximes alone, in alkaline solution, when decomp. products of the primary additive compound are formed (*e.g.*, the nitrile, carbanilide, anilide, and a thiosulphate). *p*-Dimethylaminobenzaldoxime interacts readily but decomp. products alone are isolated. Oximes of the corresponding NH_2-compounds give arylthiocarbamido-oximes only, except in the case of *o*-aminobenzaldoxime, which in EtOH solution gives a 4-hydroxy-2-thio- and 2-thio-4-ethoxy-3-aryl-1:2:3:4-tetrahydroquinazoline (cf. Reissert and Schaaf, A., 1927, 62). Identical products are obtained with *o*-aminobenzaldehyde. The following are described: p-*phenylthiocarbamido-benzaldoxime*, m. p. 148° (decomp.), and -*acetophenoneoxime*, m. p. 165—170° (decomp.) (also by oximation of p-*phenylthiocarbamidoacetophenone*, m. p. 163—164°); p′-*tolyl*-p-*thiocarbamidobenzaldoxime*, m. p. 172—173° (decomp.); m-*aminoanisaldoxime*, m. p. 132—133° [*phenylthiocarbamido*-derivative, m. p. 152° (decomp.)]; 2-*thio*-4-*ethoxy*-3-o-*tolyl*-, m. p. 228—230°, and 2-*thio*-4-*ethoxy*-3-p-*tolyl*-1:2:3:4-*tetrahydroquinazoline*, m. p. 169—171°. The last two were also formed by interaction of isatin with *o*- or *p*-tolylthiocarbimide and decomp. of the resulting 4-*hydroxy*-2-*thio*-3-o-*tolyl*-, m. p. 138—145° (decomp.), and -3-p-*tolyl*-1:2:3:4-*tetrahydro*-

quinazoline-4-*carboxylic acid*, m. p. 153—155° (decomp.), by boiling with EtOH (Reissert and Schaaf, *loc. cit.*). H. A. PIGGOTT.

Nitration of 2 : 4 : 6-trimethylbenzaldehyde. L. E. HINKEL, E. E. AYLING, and W. H. MORGAN (J.C.S., 1931, 1170—1172).—2 : 4 : 6-Trimethylbenzaldehyde with HNO_3 (*d* 1·5) and AcOH gives the *mononitro*-derivative (I), m. p. 61° (*phenylhydrazone*, m. p. 102°); with HNO_3 (*d* 1·42) and conc. H_2SO_4, the *dinitro*-derivative (II), m. p. 166° (*phenylhydrazone*, m. p. 209°), results. More vigorous nitration affords II and trinitromesitylene. I with HNO_3 (*d* 1·42) and conc. H_2SO_4 yields II, which with HNO_3 (*d* 1·5) and conc. H_2SO_4 gives trinitromesitylene. H. BURTON.

Phenylacetaldehyde and its polymerisation. J. R. POUND (J. Physical Chem., 1931, **35**, 1174—1179).—The *d* and *n* of phenylacetaldehyde increase linearly with time. Viscosity increases more rapidly than corresponds with linearity. Abnormal changes occur during the first few hrs. The rate of polymerisation is const. at a given temp. and finally crystals of the polymeride are formed. Cryoscopic measurements in ethylene dibromide, $COMe_2$, and *cyclo*hexanol indicate a mol. wt. corresponding with $(C_8H_8O)_3$, and in $CHBr_3$, with $(C_8H_8O)_6$. L. S. THEOBALD.

Synthesis of cinnamaldehyde and nuclear-substituted homologues. L. BERT and R. ANNEQUIN (Compt. rend., 1931, **192**, 1315—1317).—ω-Chloroallylbenzene is converted into its dichloride by warming with PCl_5 or into its dibromide by Br in $CHCl_3$ in the cold. Either of these interacts vigorously with solutions of NaOMe or NaOEt at their b. p. with formation of the corresponding acetals of cinnamaldehyde, which are readily hydrolysed to cinnamaldehyde by boiling dil. HCl. The method is equally applicable to homologues of ω-chloroallylbenzene. H. A. PIGGOTT.

Preparation of phenylglyoxal. M. HENZE (Z. physiol. Chem., 1931, **198**, 82—84).—Oxidation of benzoylcarbinol in aq. EtOH by $Cu(OAc)_2$ gives, after several days, phenylglyoxal in 60% yield. A *by-product*, m. p. 51°, which reduces Fehling's solution, is formed. With acetoacetic acid, phenylglyoxal gives the *ketol*, $OH\cdot CHBz\cdot CH_2Ac$, m. p. 61° (cf. A., 1930, 1022). A. RENFREW.

Hydroxy-carbonyl compounds. I. Synthesis of scopoletin. F. S. H. HEAD and A. ROBERTSON (J.C.S., 1931, 1241—1245).—5-*Amino*-2-*methoxyphenyl* p-*toluenesulphonate*, m. p. 151° (*Ac* derivative, m. p. 138—139°), obtained from the 5-nitro-derivative, m. p. 149° (lit. 145°), by reduction with anhyd. $SnCl_2$ and conc. HCl in AcOH, is converted into 5-*hydroxy*-2-*methoxyphenyl* p-*toluenesulphonate*, m. p. 124°, and thence, by hydrolysis, into 2 : 4-dihydroxyanisole, m. p. 72° (lit. 66—68°). This is converted by the usual method into 2 : 4-*dihydroxy*-5-*methoxybenzaldehyde*, m. p. 152° (*diacetate*, m. p. 119°), which with Ac_2O and AcONa gives the *O*-Ac derivative of scopoletin (7-hydroxy-6-methoxycoumarin). 2-*Benzyloxy*-p-*anisidine* (*Ac* derivative, m. p. 135°) has m. p. 100—101°). H. BURTON.

Alkyl*cyclo*pentanones. I. Derivatives of 3-methyl*cyclo*pentanone. R. D. DESAI (J.C.S., 1931, 1216—1225).—3-Methyl*cyclo*pentanone (convenient prep. given), ethyl cyanoacetate, and NH_3 in EtOH give the *imide* (I), m. p. 194°, of 3-methyl*cyclo*pentane-1 : 1-dicyanoacetic acid, hydrolysed by conc. H_2SO_4 to the *imide*, m. p. 235—236° (decomp.), of αα'-dicarbamyl-3-methyl*cyclo*pentane-1 : 1-diacetic acid, and by 60% H_2SO_4 to 3-*methyl*cyclo*pentane*-1 : 1-*diacetic acid*, m. p. 135° (*Ag* salt; *imide*, m. p. 133—134°; *Et* ester, b. p. 156°/15 mm.; *dianilide*, m. p. 174°; *di*-p-*toluidide*, m. p. 192°; *anhydride*, b. p. 177°/10 mm.; *anilic acid*, m. p. 115—116°; *anil*, m. p. 125°). Saturation of the mother-liquors from the prep. of I with NH_3 gives (after 2 weeks) the *di-iminodi-imide* (II), m. p. 285° (decomp.), and *di-imide*, not melted at 300°, of 3-methyl*cyclo*pentane-1 : 1-dimalonic acid, and a little 3-*methyl*cyclo*pentylidenecyanoacetamide*, m. p. 151—152°; II is also formed from the pentanone (1 mol.) and cyanoacetamide (2 mols.) in dil. EtOH containing piperidine. 3-Methyl*cyclo*pentanone, ethyl cyanoacetate, and piperidine give *ethyl* 3-*methyl*cyclo*pentylidenecyanoacetate* (III), b. p. 160—161°/120 mm., m. p. 66° [free *acid*, m. p. 145—146°, obtained by Harding, Haworth, and Perkin's method (J.C.S., 1908, **93**, 1947)], which contains αβ- and βγ-forms. Reduction of III with Al–Hg in moist Et_2O affords *ethyl* 3-*methyl*cyclo*pentylcyanoacetate*, b. p. 148°/20 mm., hydrolysed to 3-*methyl*cyclo*pentylmalonic acid*, m. p. 155° (decomp.) (*Et* ester, b. p. 146°/20 mm.; *dianilide*, m. p. 238°). 3-*Methyl*cyclo*pentylacetic acid* (*Et* ester, b. p. 94°/15 mm.) has b. p. 141°/25 mm. 3-*Methyl*-$\Delta^{1:2\ (\text{or}\ 5)}$-cyclo*pentenylacetonitrile*, b. p. 82°/10 mm. (*piperonylidene* derivative, m. p. 95°), obtained when 3-methyl*cyclo*pentylidenecyanoacetic acid is heated (vac.), reacts in the αβ-form with sodiocyanoacetamide, forming an imino-imide, hydrolysed by dil. HCl to the *imide*, m. p. 167—168°, of α-cyano-3-methyl*cyclo*pentane-1 : 1-diacetic acid. *Ethyl* α-*cyano*-α-3-*methyl*-$\Delta^{1:2\ (\text{or}\ 5)}$-cyclo*pentenylpropionate*, b. p. 140°/30 mm., from III, MeI, and NaOEt, is hydrolysed by NaOMe to α-3-*methyl*cyclo*pentylidene*-1-*propionitrile*, b. p. 132°/50 mm. KCN and III in EtOH give *ethyl* 1-*cyano*-3-*methyl*cyclo*pentylcyanoacetate*, b. p. 180°/11 mm., and 1-*cyano*-3-*methyl*cyclo*pentylacetonitrile*, b. p. 146°/10 mm., both hydrolysed by 50% HCl to 1-*carboxy*-3-*methyl*cyclo*pentane*-1-*acetic acid*, m. p. 125° (*Ag* salt; *Et* ester, b. p. 142°/15 mm.; *anhydride*, b. p. 151°/15 mm.; *anilic acid*, m. p. 159°; *anil*, m. p. 90—91°; *imide*, m. p. 98°), and a small amount of another acid, m. p. 105—110°. H. BURTON.

Synthesis of 4 : 5-benz*cyclo*heptanone. B. KUBOTA and T. ISEMURA (Bull. Chem. Soc. Japan, 1931, 6, 103—106).—*o*-Phenylenedipropionic acid (improved prep.; cf. this vol., 351) converted into the *Th* salt and heated at 200°/0·1 mm., gives 4 : 5-*benz*cyclo*heptanone*, m. p. 41—42°, b. p. 155—175°/0·1 mm. (*phenylhydrazone*, m. p. 85°). A. A. LEVI.

Beckmann transformation. I. Production of amidines and mechanism of their formation. H. STEPHEN and W. BLELOCH (J.C.S., 1931, 886—895).—SO_2Cl_2 in Et_2O is recommended for the Beckmann transformation. The oxime hydrochloride is first precipitated, and this changes to a yellow oil (also

obtained from the oxime hydrochloride and SO_2Cl_2), which evolves HCl, giving a darker oil. Both oils with water give amide and amidine, the latter being detected in all cases of the transformation examined irrespective of the reagent employed. It is suggested that the yellow oil is an amidodichloride or its hydrochloride. The effect of heat on oximes in presence of HCl in causing Beckmann transformation is confirmed (cf. Lachman, A., 1924, i, 861), amidines being also produced. By a similar method, besides the usual anilides, the oximes of acetophenone, *p*-methylacetophenone, propiophenone, *n*-butyrophenone, phenyl benzyl ketone, and benzophenone give diphenylacetamidine, di-*p*-tolylacetamidine, diphenylpropionamidine, diphenyl-*n*-butyramidine (trace), diphenylphenacetamidine (m. p. 91°, also from phenylacetanilide and PCl_5, followed by NH_2Ph; cf. Luckenbach, A., 1884, 1134), and diphenylbenzamidine respectively (yields 15—20%). *p*-Ethoxybenzophenone gives an *oxime*, m. p. 135—136°, unchanged by crystallisation. This by the Beckmann transformation gives *p*-ethoxybenzanilide, benz-*p*-phenetidide, and a mixture of amidines (in small amount). Fractionation of the hydrochloride of the above oxime gives an isomeric *oxime*, m. p. 159—160°. The following mechanism is suggested for the formation of the amidines: the oxime gives the imidochloride, converted by HCl into amidodichloride. Imidochloride and amidodichloride then combine to give dichloroacylamidine, RC(:NR)·NR·CRCl₂, hydrolysed to amidine and acid, RC(:NR)·NHR+R·CO₂H+2HCl. Benzanilideimidochloride with HCl in Et_2O gives *benzanilideamidodichloride hydrochloride*, m. p. 69—72° (decomp.). When solidified and reheated it melts at 41° (imidochloride). The imidochloride is also obtained from the hydrochloride or its Et_2O solution under reduced pressure, evidence being found that loss of HCl occurs in two stages (through the amidodichloride). With water the hydrochloride gives benzanilide (and a little diphenylbenzamidine, probably arising from the presence of a little imidochloride in the amidodichloride hydrochloride). From the hydrochloride kept at 40° diphenylbenzamidine, benzanilide, and BzOH are obtained, the yield of amidine being increased by previous addition of imidochloride. Benzoyldiphenylbenzamidine (cf. J.C.S., 1902, **81**, 594), which should arise by hydrolysis of the hypothetical dichlorobenzoyldiphenylbenzamidine, was not detected. A. A. LEVI.

[Isomerism of oximes.] T. P. RAIKOVA (Ber., 1931, **64**, [*B*], 989—990).—The possible existence of structurally isomeric oximes of the type of those derived from phenacyl-*p*-toluidine by Busch and Kämmerer (A., 1930, 603) has been foreseen by the author (A., 1929, 911, 1276). H. WREN.

Ketoximes and their phenylcarbamido-derivatives. A. OBREGIA and C. V. GHEORGHIU (J. pr. Chem., 1931, [ii], **130**, 71—74).—The phenylcarbamido-derivatives obtained by interaction of ketoximes with phenylthiocarbimide (cf. this vol., 210) undergo fission by Br to give phenylcarbimide dibromide, which readily displaces I from KI. This series of reactions may be used as a test for ketoximes. H. A. PIGGOTT.

Modification of the Reformatsky reaction. J. A. NIEUWLAND and S. F. DALY (J. Amer. Chem. Soc., 1931, **53**, 1842—1846).—α-Chloro-esters react with aldehydes or ketones in presence of Zn and Cu powder (or CuO) preferably in C_6H_6; reaction does not occur with Zn alone. The catalytic action of the Cu is ascribed to the formation of a complex with the carbonyl compound which then reacts with the zinc-chloro-ester compound. Various examples are given including the preparation of β-*hydroxy*-α-*phenyl*-β-*anisylbutyric acid*, m. p. 75° (*Me* ester, b. p. 113—115°/20 mm.). H. BURTON.

Derivatives of benzanthrone. A. PIERONI (Annali Chim. Appl., 1931, **21**, 155—169).—*Nitrobenzanthrone*, m. p. 246—247°, formed, together with *tri*- (m. p. 282°) and *tetra-nitro*- [m. p. about 303° (decomp.)] derivatives, by nitration in glacial AcOH, is stable to CrO_3, but is readily reducible to the corresponding *aminobenzanthrone*, m. p. 239° (*Ac* derivative, m. p. 277—278°), which yields anthraquinone-1-carboxylic acid on oxidation. Reduction of the nitrobenzanthrone with $Na_2S_2O_4$ in alkaline solution gives, besides the NH_2 compound, an orange-yellow compound with the properties of an azo-indicator. Reduction of the NO_2 compound with $NaNH_2$ yields an isomeric *aminobenzanthrone*, m. p. 185°, and a violet-brown vat dye, which dyes cotton deep violet, the colour having the fastness and brilliancy obtained with violanthrone. *m*-4-Aminonaphthaleneazobenzoic acid, m. p. 214°, obtained from diazotised *m*-aminobenzoic acid and α-naphthylamine; *m*-naphthaleneazobenzoic acid, m. p 204°, and a reduction product of this, m. p. 190°; *m*-2-aminonaphthaleneazobenzoic acid, m. p. 225°; 4-*amino*-1 : 1′-*dinaphthylene* 2 : 2′-*oxide*, m. p. 260°; and *dibenzoyldinaphthylene oxide*, m. p. 196°, were prepared. Furoperylene (cf. Weitzenböck and Seer, A., 1913, i, 847) may be readily obtained by heating 1 : 1′-dinaphthylene 2 : 2′-oxide with $AlCl_3$ in CS_2. T. H. POPE.

[Preparation of] thiobenzophenone. H. STAUDINGER and H. FREUDENBERGER (Organic Syntheses, 1931, **11**, 94—95).

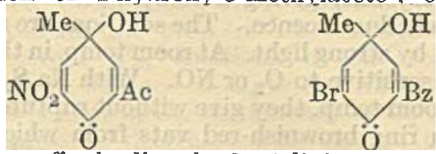
Oxidative processes. IV. Velocity of racemisation of *d*-benzoin in alkaline solutions. A. WEISSBERGER, A. DÖRKEN, and W. SCHWARZE (Ber., 1931, **64**, [*B*], 1200—1204; cf. A., 1930, 1185).—The velocity of racemisation of *d*-benzoin by MeONa in MeOH is proportional to the concentration of alkali, and is therefore (*loc. cit.*) proportional to the concentration of the ions R·CH(Ō)·CO·R, which undergo transformation into the diol or its ions. Since ionisations occur with very great rapidity, the slowest process governing the whole reaction is the isomerisation of the benzoin anion into that of the enediol. The autoxidation of benzoin, its reaction with Fehling's solution, and its racemisation are therefore controlled by the same slowest change. Provided that each enolised benzoin mol. enters into reaction with O, the autoxidation and racemisation of benzoin under like external conditions must proceed at equal rates; this is found to be the case. H. WREN.

Mixed benzoins. IV. Determination of the structure of mixed benzoins by the Beckmann

reaction. J. S. Buck and W. S. Ide (J. Amer. Chem. Soc., 1931, **53**, 1912—1917).—The mixed benzoins prepared from *o*-chlorobenzaldehyde and veratraldehyde, anisaldehyde, *p*-dimethylaminobenzaldehyde, and piperonal are 3 : 4-dimethoxybenzoyl- (*oxime*, m. p. 149°), anisoyl- (*oxime*, m. p. 144°), *p*-dimethylaminobenzoyl- (*oxime*, m. p. 156—158°), and 3 : 4-methylenedioxybenzoyl-*o*-chlorophenylcarbinols (*oxime*, m. p. 149°), respectively, since treatment of the oximes with benzenesulphonyl chloride and alkali gives *o*-chlorobenzaldehyde in each case; veratronitrile, anisonitrile, *p*-dimethylaminobenzonitrile, and piperonitrile, respectively, are also formed. The benzoins from PhCHO and anisaldehyde, piperonal, and *p*-dimethylaminobenzaldehyde are shown similarly to be anisoyl- (I) (*oxime*, m. p. 140°), 3 : 4-methylenedioxybenzoyl- (*oxime*, m. p. 158°), and *p*-dimethylaminobenzoyl-phenylcarbinols (*oxime*, m. p. 140°), respectively. The deoxybenzoins (this vol., 732) obtained from the above benzoins are all formed (except that from I) by the reduction of the >CH·OH grouping. H. Burton.

***cyclo*Hexanonebenzil.** C. F. H. Allen (Canad. J. Res., 1931, **4**, 264—273).—*cyclo*Hexanone reacts with benzil to give cyclo*hexanonebenzil*, $Ph·CO·CPh(OH)·C_6H_9O$ (I), m. p. 137°, the constitution of which is proved by the formation of a *monoacetate* and a *dioxime*, m. p. 198—199° (decomp.), and a determination of the number of active H atoms (Zerevitinov). The *monophenylhydrazone*, m. p. 193°, boiled in AcOH for 1 hr. gives a *substance* which, cryst. from pyridine ($+1C_5H_5N$), has m. p. 236°, mol. wt. 800, or cryst. from dioxan, m. p. 227°, mol. wt. 1600. With iodine 2 : 4-dinitrophenylhydrazine gives a *substance*, m. p. 215°; Br gives a gum and HBr. With acids under a variety of conditions, AcCl or $SOCl_2$, I gives a yellow gum, which on distillation under reduced pressure yields 1 : 2-*diphenyl*-3 : 4 : 5 : 6-*tetrahydrocoumarone*, m. p. 120°, also obtained from desyl chloride and the Na derivative of *cyclo*hexanone. The coumarone on oxidation with $KMnO_4$ gives benzil. Although halochromism is shown by I, no evidence for the existence of a free radical was obtained. J. D. A. Johnson.

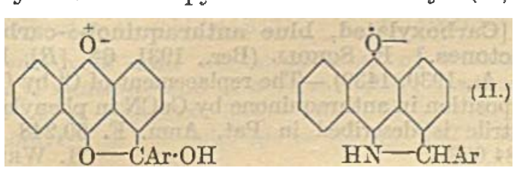
Quinonitroles. G. Wittig and W. Schulze (J. pr. Chem., 1931, [ii], **130**, 81—91).—6-Hydroxy-3-methylacetophenone is converted by nitric acid (*d* 1·5) into 5-*nitro*-3-*acetyl*-1 : 4-*methylquinonitrole* (I), m. p. 147—147·5° (cf. A., 1928, 888), converted by excess of NaOH, $NHPh·NH_2$ in AcOH, $NH_2·NH·CO·NH_2$, or by H_2SO_4 or HCl into 3 : 5-dinitro-*p*-cresol, and by excess of Bz_2O at 150° into 5-*nitro*-3-*benzoyl*-1 : 4-*methylquinonitrole*, m. p. 126—126·5° (similarly converted into 3 : 5-dinitro-*p*-cresol), identical with a specimen obtained by the action of warm HNO_3 (1 : 1) on 6-hydroxy-3-methylbenzophenone. 6-Hydroxy-3-methylacetophenone gives a 5-*bromo*-derivative, m. p. 88·5—89·5°, converted by N_2O_3 in AcOH solution into 5-*bromo*-3-*acetyl*-1 : 4-*methylquinonitrole*, m. p. 109—109·5°, converted by alkali into 5-bromo-2-nitro-*p*-cresol. Similarly, 5-*bromo*-6-*hydroxy*-3-*methylbenzophenone*, m. p. 77—78°, affords 5-*bromo*-3-*benzoyl*-1 : 4-*methylquinonitrole*, m. p. 88°, converted by warm, abs. Et_2O into 5-*bromo*-3-*benzoyl*-1 : 4-*methyl*-ψ-*quinol* (II), m. p. 151—153°. Nitration of 4-hydroxy-3-methylaceto-, or -benzo-

(I.)  (II.)

phenone affords directly 3 : 5-dinitro-*o*-cresol, whilst 2 : 4-*diacetylphenol*, m. p. 90—91° (obtained from $AlCl_3$ and *p*-hydroxyacetophenone acetate), affords indefinite products. Similar indefinite results are obtained with 3-*benzoyl*-5-*acetyl*-p-*cresol*, m. p. 102—103°, prepared by the action of $AlCl_3$ at 140° on the *acetate*, m. p. 64—65°, of 6-hydroxy-3-methylbenzophenone. J. W. Baker.

Nuclear hydrogenation of polynuclear quinones. IV. Amino- and hydroxy-anthraquinones hydrogenated in the nucleus. A. Skita and J. Müller (Ber., 1931, **64**, [*B*], 1152—1157).—Under suitable conditions of acidity and concentration of catalyst, 2-aminoanthraquinone is hydrogenated in presence of colloidal Pt to 2-*amino*-5 : 6 : 7 : 8-*tetrahydroanthraquinol hydrochloride*, m. p. 255—256° after softening at 210°; the free quinol is readily oxidised by air to 2-*amino*-5 : 6 : 7 : 8-*tetrahydroanthraquinone*, m. p. 198°, converted by reductive acetylation into the corresponding *quinol* O-*diacetate*, m. p. 243—245°. When diazotised and warmed with water the quinone affords 2-*hydroxy*-5 : 6 : 7 : 8-*tetrahydroanthraquinone*, decomp. 235°, transformed by AcOH, Ac_2O, and AcONa into 2-*acetoxy*-5 : 6 : 7 : 8-*tetrahydroanthraquinone*, m. p. 120°, whereas Zn and AcOH yield a *compound*, $C_{24}H_{26}O_7$, m. p. 234°. Catalytic hydrogenation of 1-aminoanthraquinone involves the loss of NH_3 and leads ultimately to 1-*hydroxy*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydroanthraquinone*, m. p. 224—225°, converted by Ac_2O and AcONa into the O-*diacetyl* derivative of 1-*hydroxyhexahydroanthraquinol*, m. p. 212°, hydrolysed to 1-hydroxyoctahydroanthraquinone. Reduction of the last-named compound with Zn and HCl in EtOH and admixture of the product with the initial material affords 1-*hydroxyoctahydroanthraquinhydrone*, softening between 208° and 223°. Partial reduction of 1-aminoanthraquinone gives 1-*hydroxy*-5 : 6 : 7 : 8-*tetrahydroanthraquinone*, converted by reductive acetylation into the O-*diacetate* of 1-*hydroxy*-5 : 6 : 7 : 8-*tetrahydroanthraquinol*, m. p. 208°. H. Wren.

Free organic radicals. VIII. Radicals with univalent oxygen in homogeneous, crystalline form. R. Scholl [with S. Hass and H. von Hoessle] (Ber., 1931, **64**, [*B*], 1158—1170).—The compounds regarded previously as aroyloxanthronyls are shown to be radicals with univalent O which are exclusively monomeric in solution and have no tendency towards dimerisation. They are termed hydroxyaryl*peri*hydrofuranoanthroxyls (cf. I) and are closely allied to the pyrrolinoanthranolazyls (II).

(I.)  (II.)

Cryst. from Ac_2O, they form dark bluish-violet or violet-red crystals, giving coloured solutions often showing vivid fluorescence. The solutions are rapidly decolorised by strong light. At room temp. in the dark they are insensitive to O_2 or NO. With $Na_2S_2O_4$ and NaOH at room temp. they give without rupture of the hydrofuran ring brownish-red vats from which they are immediately re-formed by exposure to air. The corresponding phenol acids are also autoxidisable. In hot NaOH the hydrofuran ring is ruptured with formation of vats of 1-aroylanthraquinones, sensitive to air. The univalent O atom removes K from ethereal potassium phenyl diphenylyl ketone with production of an autoxidisable K salt similar to that obtained in a cold alkaline $Na_2S_2O_4$ vat. Corresponding with the three centres of attraction (one at the univalent O and two at the *meso*-C atoms) they require 3Br or 3OH when titrated with Br or $KMnO_4$, giving products converted by steam, particularly in presence of KI, into 1-aroylanthraquinones. Towards $H_2S_2O_8$ or CrO_3 they behave as anthracene derivatives with a single centre of attraction at one *meso*-C atom (cf. oxanthronyls); when titrated until colourless they acquire OH or O respectively, probably yielding peroxides in the latter instance. Their action is similar towards quinones, with which they give colourless quinol ethers. With conc. H_2SO_4, $HClO_4$, and HCl they give green, radical oxylium salts. They are decolorised and decomposed by HCl or H_2SO_4 in AcOH or by NaOH in pyridine.

Hydroxyphenyl*peri*hydrofuranoanthroxyl and Br in CCl_4 yield a product from which 1-benzoylanthraquinone is obtained by removal of solvent with or without steam; with undiluted Br it affords *tribromo-1-benzoylanthraquinone*, m. p. 268·5—269·5°. *fur-Hydroxyphenyl-2-methyl-1 : 9-hydrofurano-10-anthroxyl*, m. p. 174—175°, is obtained from 1-benzoyl-2-methylanthraquinone. Directions are given for the prep. of *fur*-1-hydroxy-1-phenyl-1 : 9-hydrofurano-10-anthroxyl from conc. H_2SO_4 and 1-benzoylanthraquinone. H. WREN.

Free organic radicals. IX. Radical sulphonic acids with univalent oxygen from 1-aroylanthraquinones and concentrated or fuming sulphuric acid. R. SCHOLL and H. SEMP (Ber., 1931, **64**, [*B*], 1170—1174; cf. preceding abstract).—Aryl 1-anthraquinonyl ketones (Ar=Ph, *p*-chlorophenyl, *m*- and *p*-xylyl, α-naphthyl) are slowly converted by conc. H_2SO_4 at 100° or by 30% oleum at room temp. into green dyes sol. in H_2O to unstable, dark blue solutions. The green solutions are identical with those obtained similarly from hydroxyaryl*peri*hydrofuranoanthroxyls as shown spectroscopically and by titration with $K_2Cr_2O_7$. The action of the acid on the ketone consists therefore in the addition of H and formation of a radical sulphonic acid with univalent O atom. H. WREN.

[Carboxylated, blue anthraquinol-α-carboxylactones.] R. SCHOLL (Ber., 1931, **64**, [*B*], 1219; cf. A., 1930, 1439).—The replacement of Cl by CN in α-position in anthraquinone by CuCN in phenylacetonitrile is described in Pat. Anm. F. 60,248 (G.P. 484,663). H. WREN.

Quinizarin derivatives. H. WALDMANN [with H. HARTISCH] (J. pr. Chem., 1931, [ii], **130**, 92—102).—5 : 8-Dichloro-1 : 4-dimethoxyanthraquinone (A., 1930, 1043) is converted by heating with *p*-toluenesulphonamide, fused NaOAc, and a trace of $Cu(OAc)_2$ in $PhNO_2$ at 200—210°, into the corresponding 5 : 8-*di*-p-*toluenesulphonamido*-derivative, m. p. 275°, hydrolysed by cold conc. H_2SO_4 to the 5 : 8-*diamino*-compound, decomp. 250° (Ac_2 and Bz_2, both m. p. above 300°, derivatives), further hydrolysed by conc. H_2SO_4 at 120° to 5 : 8-*diaminoquinizarin*, not melting at 300° (Bz_2 derivative, m. p. 284—285°). Hydrolysis of 1 : 4-dimethoxyanthraquinone with conc. H_2SO_4 at 110° affords 1-*hydroxy-4-methoxyanthraquinone*, m. p. 167—168°, identical with a specimen synthesised by conversion of 4-*chloro*-1-*hydroxyanthraquinone*, m. p. 193—194° (from phthalic anhydride, *p*-chlorophenol, and NaCl–$AlCl_3$ at 200—220°), into the 4-*chloro*-1-*methoxy*-compound, m. p. 168°, by the action of methyl *p*-toluenesulphonate and anhyd. K_2CO_3 at 170°, and subsequent replacement of Cl by OH by NaOH in MeOH at 110°. From the appropriate halogenophthalic anhydride are prepared (*loc. cit.*): 5 : 6-, m. p. 239° (lit., m. p. 208°), and 5 : 7-, m. p. 231—232°, -*dichloroquinizarin*, and 5-*chloroquinizarin*, m. p. 243° (*diacetate*, m. p. 205°). The last-named is similarly converted successively into 5-*chloro*-, m. p. 208°, 5-p-*toluenesulphonamido*-, m. p. 197°, and 5-*amino*-, m. p. 242—243°, -1 : 4-*dimethoxyanthraquinone*, and, finally, into 5-*aminoquinizarin*, m. p. 212—213°. The Sandmeyer reaction converts the last-named into 5-*bromoquinizarin*, m. p. 212°, also obtained by condensing quinol with 3-bromophthalic anhydride. 5-Chloroquinizarin is converted by NH_2Ph and NaOAc at 170° into 5-*anilinoquinizarin*, m. p. 223°. J. W. BAKER.

Preparation and properties of aqueous carotene solutions. A. FODOR and R. SCHOENFELD (Biochem. Z., 1931, **233**, 243—244).—The prep. of colloidal (negatively-charged) solutions of carotene and the change of absorption spectrum on passing O_2 through the solution are described. P. W. CLUTTERBUCK.

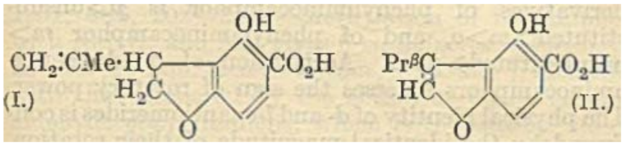
Isomeric carotenes and their derivatives. P KARRER, H. VON EULER, H. HELLSTROM, and M. RYDBOM (Svensk Kem. Tidskr., 1931, **43**, 105—109).—The colloidal solutions of α- and β-carotene in aq. $COMe_2$ are remarkably stable and little difference in the behaviour of the isomerides towards atm. O_2 is observed. Solutions of the β-compound are less stable towards irradiation than those of the α-compound. The growth-promoting power of β-carotene is greater than that of its isomeride; its initial action is considerably more rapid, but the difference tends to disappear in course of time. The isomeric carotenes are reduced by Al–Hg mainly to non-cryst. dihydrocarotenes less stable than the initial products and possessing marked growth-producing power, that of the β-dihydro-compound being somewhat greater than that of the α-isomeride. Carotene, regenerated from the tri-iodide, has growth-producing power. H. WREN.

Orange skin pigment. L. ZECHMEISTER and P. TUZSON (Naturwiss., 1931, **14**, 307).—Orange (and "mandarine") skin contains an alkali-sol. pigment, and a carotenoid, the latter consisting of a hydrocarbon

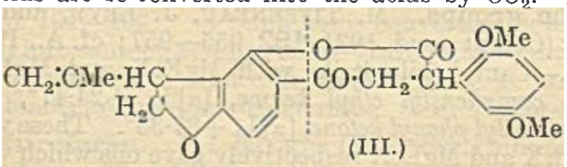
and a polyene ester. Alkaline hydrolysis of the ester gives a cryst. xanthophyll derivative probably identical with that obtained from *Viola tricolor* (Kuhn and Winterstein, this vol., 491). It gives a blue colour with dil. mineral acids. A. A. LEVI.

Composition and properties of certain red and yellow plant pigments. L. N. BILGER (Bull. Basic Sci. Res., 1931, **3**, 37—46).—The pigment (I) from Japan red pepper differs from that from paprika, and from lycopene. It has m. p. 167—169° (120—121° after slight fading; 50—60° after complete fading), and contains C 74·69, H 9·95, 10·26, O 15·36, 15·05%; it is optically inactive. The dry crystals of I, lycopene, carotene, and capsanthin are readily bleached by air and light. Alcoholic solutions of I and carotene, when enclosed with air in stoppered tubes, may be kept for weeks in daylight at room temp. and for months at 0° without fading. The bleaching of alcoholic and $CHCl_3$ solutions by exposure to ultra-violet light or *X*-rays is described. The absorption spectra also were studied. CHEMICAL ABSTRACTS.

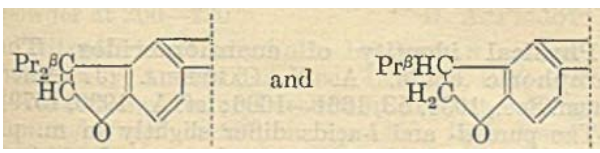
Rotenone, the active constituent of the *Derris* root. VII. Constitution of rotenone. S. TAKEI, S. MIYAJIMA, and M. ŌNO (Ber., 1931, **64**, [*B*], 1000—1007).—The modified constitutions, I and II (cf. A., 1930, 1044), are assigned to tubaic and rotenic acids,



since the hydroxyl group has different properties in the two acids, although its very slow methylation suggests that it is *ortho* to the carboxyl group. Decarboxylated rotenic acid affords resorcinol when fused with KOH. The phenols from the decarboxylated acids are re-converted into the acids by CO_2. The



constitution III is ascribed to rotenone. To *iso*-rotenone and dihydrorotenone the constitutions



are respectively assigned. The constitution of the transformation products of rotenone is described in detail. The following observations appear new. iso*Rotenone*isooxime, $C_{23}H_{22}O_5{:}N{\cdot}OH$, has m. p. 192°, whereas *iso*rotenoneoxime has m. p. 230°. Dehydrorotenone is oxidised by CrO_3 in AcOH to rotenonone, m. p. 298°. Derrisic acid with alkaline $KMnO_4$ affords derric, rissic, and tubaic acids. Rotenic acid is obtained from rotenononic acid and molten KOH. Derritol is oxidised by alkaline $KMnO_4$ to tubaic acid and an acid, m. p. 199°. H. WREN.

Resin. I. Preparation and autoxidation of precipitated lead rosinate. W. A. LA LANDE, jun. (J. Amer. Chem. Soc., 1931, **53**, 1858—1868).—An apparatus for the prep. of Pb rosinate (Pb 24·0—24·2%) from 2% solutions of Na rosinate and $Pb(OAc)_2$ in absence of O_2 is described. When Pb rosinate is kept in O_2, the amount of O_2 absorbed at const. pressure decreases with rise in temp., thus indicating a reversibility of the initial reaction. Max. dissociation is reached when the rosinate retains 1 at. equiv. O. Oxidised samples of Pb rosinate lose O_2 when they are heated in N_2; the resultant products re-absorb O_2 slowly. At 28°/60 atm. lead rosinate absorbs 2 mols. O_2 per mol. H. BURTON.

α-Elemic acid. K. H. BAUER and A. DIMOKOSTOULOS (Arch. Pharm., 1931, **269**, 218—224).—α-Elemolic acid, $C_{27}H_{42}O_3$, m. p. 215—216°, $[\alpha]^{20}$ +20·5°, extracted by alkali from an Et_2O solution of elemi resin, is oxidised by CrO_3 to α-elemonic acid, $C_{27}H_{40}O_3$, m. p. 274° (*dihydro*-compound, m. p. 264—265°), the oxime of which, m. p. 230—231°, is reduced by Na–Hg and EtOH to *aminohydroelemic acid*, m. p. 225°, converted by HNO_2 into *γ-dihydroelemolic acid*, $C_{27}H_{44}O_3$, m. p. 252°. Both α-elemolic and α-elemonic acids yield on ozonisation MeCHO, indicating the presence of the grouping CHMe:C<. C. HOLLINS.

Euphorbium resin. II. Euphorbol. K. H. BAUER and G. SCHRÖDER (Arch. Pharm., 1931, **269**, 209—218; cf. A., 1929, 137, 568; this vol., 625).—α-Euphorbol (Bauer and Schenkel's euphorbol, of which Müller's vitorbol is an impure form), $C_{26}H_{46}O$, m. p. 127—128° (*α-naphthylurethane*, m. p. 174°; *dibromide*, m. p. 169—170°), is best prepared from crude euphorbon by boiling with animal charcoal in MeOH. The mother-liquors deposit after some days *β-euphorbol*, $C_{31}H_{52}O$, m. p. 89—90° (*α-naphthylurethane*, m. p. 51 ; *dibromide*). Both are monohydric alcohols having one double linking probably in a terminal position. They give on hydrogenation *dihydro*-compounds, m. p. 133° and 122°, respectively, and by dehydration with PCl_5 in light petroleum *α-euphorbodiene*, m. p. 85°, and *euphorbodiene*, b. p. 232—235°/5 mm.; the latter takes up 4H to give *β-euphorbane*, b. p. 239—242°/vac. (decomp.). C. HOLLINS.

Colouring matter of moulds. A. BLOCHWITZ (Ber. deut. bot. Ges., 1931, **49**, 132—137).—A review of the pigments of the conidia of the moulds and their colour reactions with KOH and HCl is given. B. LEVIN.

Perfumes in fungi. D. AYE (Arch. Pharm., 1931, **269**, 246—251).—12 kg. of *Trametes suaveolens* gave on steam-distillation 0·7 g. of oil which deposited yellow crystals with an odour of anise. Hydrolysis of the oil or the crystals gave anisic acid. *Psalliota campestris*, *Boletus edulis*, *Pleurotus ostreatus*, and *Polyporus igniarius* yielded no anisic acid. The last-named gave an oil setting to crystals, m. p. 45°, hydrolysed to an acid, m. p. 25°. C. HOLLINS.

Hydrolysis and decomposition of menthyl methyl xanthate and of bornyl methyl xanthate. (MISS) I. M. MCALPINE (J.C.S., 1931, 1114—1121).—In contrast to the sulphonates (cf. A., 1927, 364;

1928, 1253) menthyl and bornyl methyl xanthates are not affected by aq. KOH, but are hydrolysed by alcoholic KOH to the terpene alcohol without racemisation, and partly hydrolysed by $Ba(OH)_2$ to give "stable" forms of the original ester, differing only from it in increased thermal stability. Thermal decomp. has been studied (*a*) by heating the dry ester alone, (*b*) by vac. distillation, and (*c*) by heating in various solvents. Menthyl methyl xanthate gives under these conditions (*a*) menthene, mercaptan, and COS ; (*b*) menthene ; (*c*) menthene, except in ethylene dibromide when there is some dimenthene. Bornyl methyl xanthate similarly affords (*a*) bornylene with some camphene, and the stable form of the ester; (*b*) similar to (*a*); (*c*) bornylene, except in ethylene dibromide when it is entirely dibornylene. Under all conditions the xanthates greatly exceed the sulphonates in thermal stability, but no explanation can be offered for these differences. F. R. SHAW.

Structure of terpin hydrate. P. J. CLAUS (Natuurwetensch. Tijds., 1931, **13**, 69—74).—No tri-replacement product results when terpin hydrate is treated with PCl_3, and, contrary to literature, BzCl is without action; terpin hydrate cannot be esterified by Chablay's method. In $COMe_2$ solution it is about 25% dissociated. Therefore, terpin hydrate is a true hydrate and is cyclic. H. F. GILLBE.

Carene. (MLLE.) M. JOFFRE (Bull. Inst. Pin, 1931, 79—85, 109—114).—Head and middle fractions of carene yield on ozonisation approx. equal amounts of CH_2O (weighed as CO_2 after oxidation to formic acid). The fraction, b. p. 60—105°/12 mm., of the non-acid products of reduction of the ozonide in each case gives a semicarbazone, m. p. 210—211°, probably of a cyclic ketone, whilst from the higher fractions are obtained mono- and di-semicarbazones of the aldehyde-ketone, $CMe_2<{CH\cdot CH_2Ac \atop CH\cdot CH_2\cdot CHO}$, and aldehyde-alcohol. The acid fractions appear to be derived normally from carene (J.C.S., 1923, **123**, 550). The production of CH_2O and of a cyclic ketone indicates the presence of a β-carene, $CMe_2<{CH\cdot CH_2\cdot C\!:\!CH_2 \atop CH\cdot CH_2\cdot CH_2}$. C. HOLLINS.

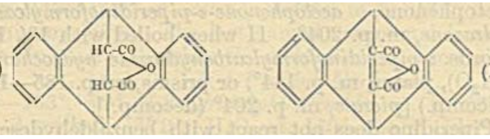
Dependence of optical rotatory power on chemical constitution. X. Rotatory dispersion of stereoisomeric phenyl and iodophenyl derivatives of iminocamphors and aminocamphors. B. K. SINGH, H. BASU-MALLIK, and B. BHADURI (J. Indian Chem. Soc., 1931, **8**, 95—117).—Condensation of camphorquinone (*d*, *l*, *dl*) with NH_2Ph and iodoaniline (*o*, *m*, *p*) yields iminocamphor derivatives from which the aminocamphors are obtained by reduction (cf. J.C.S., **95**, 1909, 949). The *o*-iodophenylaminocamphors give no hydrochlorides. *o*-Iodophenyliminocamphor exists in three polymorphic forms, of which the α and β can be converted into the γ; the rotatory power of each is identical. The following have been examined: *d*- and *l*-phenyliminocamphor, $M[\alpha]^{35}$ ±1622° in C_6H_6, ±1422° in MeOH; dl-*phenyliminocamphor*, m. p. 124°; *d*- and *l*-phenylaminocamphor, $M[\alpha]_D$ ±296·6° in $CHCl_3$, ±234·3° in MeOH (d- and l-*hydrochlorides*, m. p. 175°); dl-*phenylaminocamphor*, m. p. 104—105° (*hydrochloride*, m. p. 170—171°); d-o-*iodophenyliminocamphor*, m. p. 86° (α), 93° (β), 97° (γ), and l-o-*iodophenyliminocamphor*, m. p. 93°, $M[\alpha]^{35}_D$ ±809·5° in C_6H_6, ±634·4° in Et_2O; dl-o-*iodophenyliminocamphor*, m. p. 85°; d- and l-o-*phenylaminocamphor*, m. p. 147—148°, $M[\alpha]_D$ ±233·6° in $CHCl_3$, +133·2° in C_6H_6; dl-o-*iodophenylaminocamphor*, m. p. 144—145°; *d*- and l-m-*iodophenyliminocamphor*, m. p. 112—113°, $M[\alpha]^{35}_D$ ±1419° in C_6H_6, ±1163° in Et_2O; dl-m-*iodophenyliminocamphor*, m. p. 116°; d- and l-m-*iodophenylaminocamphor*, m. p. 109—110°, $M[\alpha]^{35}$ ±330·1° in Et_2O, ±248·4° in $COMe_2$; dl-m-*iodophenylaminocamphor*, m. p. 123° (*hydrochloride*, m. p. 162°); d- and l-p-*iodophenyliminocamphor*, m. p. 113—114°, $M[\alpha]^{35}_D$ ±1777° in C_6H_6, ±1520° in Et_2O; dl-p-*iodophenyliminocamphor*, m. p. 132°; d- and l-p-*iodophenylaminocamphor*, m. p. 113—114°, $M[\alpha]^{35}$ ±268·4° in $CHCl_3$, ±204·5° in MeOH (d-*hydrochloride*, m. p. 125—126°, d- and l-*Ac* derivatives, m. p. 117—118°, $M[\alpha]^{35}_D$ ∓20·24 in $CHCl_3$); dl-p-*iodophenylaminocamphor*, m. p. 160° (*hydrochloride*, m. p. 127°); *d*- and *l*-camphorquinone, $M[\alpha]^{35}$ ∓180·8° in C_6H_6, ∓113·75° in MeOH. The above mol. rotations are the highest and lowest mean values. The values for the yellow, green, and in some cases violet Hg lines are also given. The order of rotatory power of derivatives of phenyliminocamphor is *p*>unsubstituted>*m*>*o*, and of phenylaminocamphor *m*> unsubstituted>*p*>*o*. Acetylation of *p*-iodophenylaminocamphors reverses the sign of rotatory power. The physical identity of *d*- and *l*-enantiomerides is confirmed by the identical magnitude of their rotation. The rotatory powers bear no simple relation to the dielectric const. of the solvents.
D. A. FAIRWEATHER.

Two stereoisomeric derivatives of campholenic acid formed in unequal, but inverse, proportions by inverting the order of introduction of the groups. M. TIFFENEAU, J. LÉVY, and E. DITZ (Compt. rend. 1931, **192**, 955—957; cf. A., 1930, 470).—Camphenilonitrile with MgEtX and MgPhX gave *camphenilyl ethyl ketone*, $[\alpha]^{17}_{5461}$ +24·47°, and *camphenilyl phenyl ketone*, $[\alpha]^{1}_{5461}$ +37·33°. These with MgPhX and MgEtX respectively gave oils which with perbenzoic acid gave *α-oxidocamphenilylphenylethyl carbinol*, m. p. 92—93°, $[\alpha]^{13}_{5780}$ +17·90°, and its β-*isomeride*, m. p. 135°, $[\alpha]^{14}_{5780}$ −32·85°. A. A. LEVI.

Physical identity of enantiomerides. The camphoric acids. A. N. CAMPBELL (J. Amer. Chem. Soc., 1931, **53**, 1661—1666; cf. A., 1930, 1579). —The pure *d*- and *l*-acids differ slightly in m. p., solubility in H_2O, and numerical value of rotatory power in EtOH. The rotatory dispersions are identical. J. G. A. GRIFFITHS.

Syntheses in the hydroaromatic series. VIII. Di-"en"-syntheses with anthracene. Formula of anthracene. O. DIELS and K. ALDER [with S. BECKMANN] (Annalen, 1931, **486**, 191—202).—In conformity with the Armstrong–Hinsberg formula for anthracene which contains two pairs of conjugated double linkings ending in the 9 : 10 positions, anthracene easily adds on αβ-unsaturated esters and acids

to form stable anhydrides or esters of anthracenecarboxylic acids of the type I.

(I.)  (II.)

Anthracene combines with the appropriate anhydride or acid to give (*a*) 9 : 10-endo-*maleic anhydride*-, m. p. 262—263° [*dimethyl* ester, m. p. 150—151°; trans-*acid*, m. p. 241—242° (decomp.) (*dimethyl* ester, m. p. 106—107°)]; (*b*) 9 : 10-endo-*crotonic acid*-, m. p. 191—193°; (*c*) 9 : 10-endo-*citraconic anhydride*-, m. p. 182°; (*d*) 9 : 10-endo-*dibromomaleic anhydride*-, m. p. 246—247°, reduced catalytically to 9 : 10-endo-*acetylenedicarboxylic anhydride-anthracene* (II), m. p. 247° [also obtained by the action of Ac_2O on 9 : 10-endo-*acetylenedicarbomethoxyanthracene*, m. p. 160—161° (prepared from anthracene and methyl acetylenedicarboxylate)] Oxidation of II with $KMnO_4$ or O_3 affords anthraquinone. 9 : 10-Dibromoanthracene combines with maleic anhydride to give the corresponding *anhydride*, m. p. 261—262°.

F. R. Shaw.

Syntheses in the hydroaromatic series. IX. Synthesis of camphenilone and santene. O. Diels and K. Alder [with E. Peterson] (Annalen, 1931, **486**, 202—210).—Methylation of norcamphor with $NaNH_2$ and MeI gives 6-*methylnorcamphor*, b. p. 68—70°/15 mm. (*semicarbazone*, m. p. 185°), identical with that prepared by the action of O_3 on crotonaldehyde*cyclo*pentadiene, which is the *enol-acetate* of 3 : 6 - endo*methylene* - 2 - *methylhexahydrobenzaldehyde*, b. p. 112—115°/18 mm. Introduction of a second Me group in a similar manner affords 6 : 6-dimethylnorcamphor or camphenilone, from which camphene and camphor may be synthesised.

MgMeI and 6-methylnorcamphor yield *γ-santenol*, m. p. 63—65°, not identical with Aschan's β-santenol, m. p. 101—102°, γ-Santenol is converted by loss of H_2O into santene and by AcOH–H_2SO_4 into α-santenol, m. p. 85—86°. Hence it follows that β- and γ-santenols are *cis–trans*-isomerides. F. R. Shaw.

Nitrofuran. I. J. Rinkes (Rec. trav. chim., 1931, **50**, 590).—The decarboxylation of 5-nitropyromucic acid to 2-nitrofuran (cf. this vol., 626) may be effected by heating with twice its wt. of quinoline and copper powder at 200—230°. H. A. Piggott.

Nitrofurfuryl alcohol. H. Gilman and G. F. Wright (J. Amer. Chem. Soc., 1931, **53**, 1923—1924).—Nitration of furfuryl acetate in Ac_2O at —20° gives 5-*nitrofurfuryl acetate*, m. p. 40°, hydrolysed by 5% H_2SO_4 to 5-*nitrofurfuryl alcohol*, b. p. 157°/8 mm., m. p. 32°. Oxidation of this with MnO_2 and 50% H_2SO_4 at 40—50° affords 5-nitrofurfuraldehyde (A., 1930, 1045, 1592). H. Burton.

Cellulose furoate. K. A. Kobe [with R. E. Montonna] (J. Amer. Chem. Soc., 1931, **53**, 1889—1891).—Standard cellulose and furoyl chloride in presence of pyridine and tetrachloroethane give a fibrous insol. product (65% yield) containing 2·1—2·9 furoate residues per C_6 unit, and a small amount of sol. material containing rather more than 3 furoate residues per C_6 unit. Considerable degradation of the cellulose occurs. H. Burton.

Mechanism of the pyrrole syntheses of von Miller and Plochl. S. Bodforss (Ber., 1931, **64**, [*B*], 1111—1115).—Evidence is adduced in favour of the view that reaction between α-anilinophenylacetonitrile and cinnamaldehyde under the influence of KOH in MeOH occurs by condensation of the double linking of the aldehyde with the nitrile giving primarily $NHPh{\cdot}CPh(CN){\cdot}CHPh{\cdot}CH_2{\cdot}CHO$, which immediately passes into 2-*cyano-5-hydroxy*-1 : 2 : 3-*triphenyltetrahydropyrrole*, m. p. 183° (decomp.). When boiled in EtOH it loses HCN and yields 5-*hydroxy*-1 : 2 : 3-*triphenyldihydropyrrole*, m. p. 160°, which passes when distilled into 1 : 2 : 3-triphenylpyrrole, m. p. 178°. β-Naphthylaminophenylacetonitrile similarly yields 2 - *cyano* - 5 - *hydroxy* - 2 : 3 - *diphenyl* - 1 - β-*naphthyltetrahydropyrrole*, m. p. 191—195° (decomp.), and 2 : 3-*diphenyl*-1-β-*naphthylpyrrole*, m. p. 184°. 1 : 2 : 5-Triphenylpyrrole is almost quantitatively obtained from diphenacyl in hot NH_2Ph in presence of NH_2Ph,HCl. H. Wren.

General method of synthesis for 2-substituted pyrrolines and pyrrolidines. L. C. Craig, H. Bulbrook, and R. M. Hixon (J. Amer. Chem. Soc., 1931, **53**, 1831—1835; cf. Cloke, A., 1929, 703).—The additive compound from MgPhBr and γ-chlorobutyronitrile is heated in xylene giving a 55% yield of 2-phenylpyrroline, reduced by Sn and HCl (cf. A., 1908, i, 274; 1928, 1256) to 2-phenylpyrrolidine. 2-Ethylpyrroline, b. p. 140° (picrate, m. p. 87°; *chloroaurate*, m. p. 122°), and 2-benzylpyrroline, b. p. 126—128°/15 mm. [*picrate*, m. p. 89°; *chloroaurate*, m. p. 125° (decomp.)], are prepared similarly in 46 and 13% yield, respectively. 2-Phenylpyrrolidine is also obtained when phenyl γ-chloropropyl ketimine acetate is reduced catalytically (Adams), the resulting product basified, and subsequently distilled with steam. H. Burton.

Syntheses in the hydroaromatic series. X. Di-" en "-syntheses with pyrrole and its homologues. O. Diels and K. Alder (with D. Winter) (Annalen, 1931, **486**, 211—225).—Pyrrole reacts readily with 2 mols. of maleic anhydride in aq. solution to give, after removal of precipitated fumaric acid, γγ′-diketosebacic acid (I) (cf. A., 1929, 819). A small quantity of pyrrole-2 : 5-dipropionic acid is also formed, identical with that obtained by Kehrer (A., 1897, 214) by the direct action of NH_3 on the acid I. The acid is reduced by Clemmensen's method to sebacic acid, and reacts with HNO_3 to give an *acid*, $C_{10}H_{11}O_6N$, m. p. 166—167°, and succinic acid.

Aq. maleic anhydride and 2-methylpyrrole produce 2-*methylpyrrole-5-succinic acid*, m. p. 134° (*dimethyl* ester, m. p. 71°), decarboxylated to 2-methylpyrrole-5-propionic acid, the ester, m. p. 50—51°, of which is identical with that obtained by the action of $AcONH_4$ solution on the Me ester of acetonyl-lævulic acid.

N-Methylpyrrole reacts with 2 mols. of maleic acid to form N-*methylpyrrole*-2 : ɒ-*dipropionic acid*, m. p. 197—198° (the dimethyl ester being also prepared by the action of $NH_3Me{\cdot}OAc$ solution on the dimethyl ester of dilævulic acid), which is hydrolysed to the acid I, with loss of NH_3. In C_6H_6 solution, 2 : 4-dimethyl-

pyrrole condenses with maleic anhydride to give 2 : 4-*dimethylpyrrole-5-succinic anhydride*, m. p. 102—103°, and with citraconic anhydride to yield 2 : 4-*dimethylpyrrole-5-(β)-methylsuccinic anhydride*, m. p. 160°. 2-Methylpyrrole condenses with methyl acetylenedicarboxylate to form 5-2-*methylpyridylethylene-αβ-dicarboxylic acid*, m. p. 111°. F. R. SHAW.

Phenyl α-piperidinostyryl ketone. E. P. KOHLER and W. F. BRUCE (J. Amer. Chem. Soc., 1931, **53**, 1994—1998).—The red compound formed from phenyl α-bromostyryl ketone and piperidine is phenyl α-piperidinostyryl ketone (I) (A., 1927, 571) and not a piperidinoethylene oxide (A., 1930, 1436). Catalytic reduction (Adams) of I gives *phenyl α-piperidino-β-phenylethyl ketone*, m. p. 81° [stable *oxime*, m. p. 141—142° (*formate*, m. p. 177—178°)], also obtained from phenyl α-bromo-β-phenylethyl ketone and piperidine, which with MgPhBr affords *β-piperidino-ααγ-triphenylpropyl alcohol*, m. p. 148—149°. This alcohol at 260—280° gives $COPh_2$ and 1-β-phenylethylpiperidine. MgPhBr and I furnish *phenyl α-piperidino-ββ-diphenylethyl ketone*, m. p. 163° (*i.e.*, a 1 : 4-additive compound), converted by further treatment with MgPhBr into *β-piperidino-ααγγ-tetraphenylpropyl alcohol*, m. p. 137° (*chloride hydrochloride*, m. p. 162—164°), oxidised to $COPh_2$ (2 mols.). H. BURTON.

Cinchona alkaloids and substances related to them. I. Some piperidinomethylcarbinol hydrochlorides. (MISS) R. V. HENLEY and E. E. TURNER (J.C.S., 1931, 1182—1188).—The synthesis, by treatment of 1-phenacylpiperidine with the appropriate Grignard reagent, of a number of compounds of the type $OH\cdot CRPh\cdot NC_5H_{10}$ which bear pictorial resemblance to the cinchona alkaloids is described: *phenyl-*, m. p. 192—194°; *phenylmethyl-*, m. p. 140—141°; *phenylethyl-*, m. p. 171—173°; *phenyl-*n*-propyl-*, m. p. 185—187°; *phenyl-*n*-butyl-*, m. p. 166—169°; *diphenyl-*, m. p. 214—218°; *phenylbenzyl-*, m. p. 238—244°; *phenyl-β-phenylethyl-*, m. p. 211—216°; *phenyl-γ-phenylpropyl-*, m. p. 209—210°; *phenyl-δ-phenylbutyl-*, m. p. 173—174°; *phenyl-α-naphthyl-ω-piperidinomethylcarbinol hydrochloride*, m. p. 114—115°. None of these compounds possesses antimalarial activity. 1-Phenacylpiperidine does not react normally with magnesium *cyclo*hexyl bromide, *n*-hexyl iodide, or *n*-heptyl iodide.

Phenyl β-phenylethyl ketone is readily converted into *phenyl α-bromo-*, m. p. 50—51°, which reacts with piperidine to give *phenyl α-piperidino-β-phenylethyl ketone*, m. p. 77—78·5°, also obtained by the action of CH_2PhCl on the Na derivative of phenacylpiperidine. This synthesis has been applied to the prep. of piperidinodeoxybenzoin (cf. A., 1912, i, 718). F. R. SHAW.

Action of piperidine on acetonesemicarbazone. (MISS) J. M. STRATTON and F. J. WILSON (J.C.S., 1931, 1154—1159).—The reaction between acetonesemicarbazone and piperidine in toluene under anhydrous conditions yields *acetonepiperidinoformylhydrazone* (I), m. p. 101°, unstable to H_2O and giving $COMe_2$ on hydrolysis. When H_2O is not rigidly excluded the reaction results in *acetone-ε-piperidinoformylcarbohydrazone hydrate* (II), m. p. 145°, the structure being determined by hydrolysis as $OH\cdot CMe_2\cdot NH\cdot NH\cdot CO\cdot NH\cdot NH\cdot CO\cdot NC_5H_{10}$. With PhCHO, II gives *benzaldehyde-*, m. p. 211°, and with acetophenone, *acetophenone-ε-piperidinoformylcarbohydrazone*, m. p. 204°. II when boiled with 1% HCl affords *ε-piperidinoformylcarbohydrazide hydrochloride* ($1H_2O$), plates, m. p. 144°, or prisms, m. p. 185—186° (decomp.) [*picrate*, m. p. 204° (decomp.)].

Piperidine does not react with benzaldehydesemicarbazone, but with acetophenonesemicarbazone, *acetophenonepiperidinoformylhydrazone*, m. p. 168°, is formed, hydrolysed to *piperidinoformylhydrazide hydrochloride* (III), m. p. 189°, which reacts with PhCHO to give *benzaldehydepiperidinoformylhydrazone*, m. p. 179° (also obtained from I and PhCHO), and with $COMe_2$ to give II. III is smoothly decomposed into piperidine hydrochloride and 4-aminourazole. When II is boiled with water, $COMe_2$ and *ε-piperidinoformylcarbohydrazide* ($1H_2O$), m. p. 106—108°, anhydrous, m. p. 106—107°, is obtained. F. R. SHAW.

Catalytic dehydrogenation of cyclic bases. I. M. EHRENSTEIN (Ber., 1931, **64**, [*B*], 1137—1140).—Enlargement of the ring is not observed during the catalytic dehydrogenation of *N*- and *C*-methylpyrrolidines. A method is thus afforded for discriminating between a piperidine and a methylated pyrrolidine ring, since the former loses 3 and the latter 2 mols. of H. 2-Phenylpiperidine is converted by passage over platinised asbestos at 320—330° into 2-phenylpyridine, b. p. 141—143°/20 mm. (picrate, m. p. 176—177·5°). 4-Phenyl-2-methylpyrrolidine gives 4-phenyl-2-methylpyrrole, b. p. 175°/25 mm., and 2 mols. of H. H. WREN.

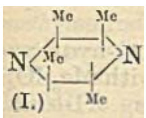
Subsidiary reaction of the Hantzsch pyridine synthesis. S. BODFORSS (Ber., 1931, **64**, [*B*], 1108—1111).—Gradual addition of PhCHO followed by AcOH to a boiling mixture of ethyl acetoacetate and NH_2Ph in EtOH results in the formation of (?) *ethyl 6-methyl-1 : 2 : 3 : 4-tetraphenyldihydropyrimidine-5-carboxylate*, m. p. 173°, converted by Na in boiling EtOH into 1 : 4-diphenyl-2 : 6-dimethyldihydropyridinecarboxylic acid, m. p. 165° (decomp.). Under similar conditions, the substitution of *p*-toluidine for NH_2Ph gives *ethyl 2 : 4-diphenyl-1 : 3-di-p-tolyl-6-methyldihydropyrimidine-5-carboxylate*, m. p. 193°, whereas with *m*-nitrobenzaldehyde and NH_2Ph *ethyl 1-phenyl-4-*m*-nitrophenyl-2 : 6-dimethyldihydropyridine-3 : 5-dicarboxylate*, m. p. 146°, is produced. Neither anisaldehyde nor cinnamaldehyde affords sparingly sol. products. Methyl acetoacetate, PhCHO, and NH_2Ph yield *methyl 1 : 4-diphenyl-2 : 6-dimethyldihydropyridine-3 : 5-dicarboxylate*, m. p. 197°. H. WREN.

4-Pyridylpyridinium dichloride and synthesis of 4-derivatives of pyridine. E. KOENIGS and H. GREINER (Ber., 1931, **64**, [*B*], 1049—1056).—Pyridine is converted by $SOCl_2$ rapidly at 100° or (preferably) slowly at room temp. into *4-pyridylpyridinium dichloride*, $C_5H_5N(Cl)\cdot C_5H_4NHCl$, m. p. (unstable) 151—152°, (stable) m. p. 172—174°, giving with alkali a brown ppt. which is not re-converted into the dichloride by HCl. The *dipicrate*, m. p. 180—181°, *chloroplatinate*, m. p. 272—274°, and additive *compound* with $HgCl_2$, m. p. 218—219°, are described.

The dichloride is converted by NH_2Ph in boiling EtOH into glutacondianil, m. p. 83—84° (hydrochloride, m. p. 143—144°), 4-*anilinopyridine*, m. p. 175°, and 4-aminopyridine. The last-named compound is prepared in good yield when the dichloride is heated with conc. NH_3 at 150°. N-4-*Pyridylphthalimide*, m. p. 232—233°, and N-2-*pyridylphthalimide*, m. p. 227°, are described. With H_2O at 150° the dichloride yields 4-hydroxypyridine, whilst with PhONa in boiling PhOH it affords 4-phenoxypyridine, m. p. 44—46°.
H. WREN.

Formation of 4-hydroxy-2-methylquinolines from β-arylaminocrotonic esters. L. LIMPACH (Ber., 1931, 64, [*B*], 969—971).—NH_2Ph is allowed to react with Et acetoacetate at room temp., and the product, after removal of water, is added to paraffin oil at 260—280°; after 15—20 min. at 240—250°, 4-hydroxy-2-methylquinoline is obtained in 90—95% yield. 4-Hydroxy-6-ethoxy-2-methylquinoline and 4-hydroxy-2-methylnaphthaquinoline are derived similarly from Et β-*p*-ethoxyphenylaminocrotonate and Et β-1-naphthylaminocrotonate, respectively.
H. WREN.

Stereoisomeric 2 : 3 : 5 : 6-tetramethylpiperazines. II. Configuration of the so-called β-isomeride. F. B. KIPPING (J.C.S., 1931, 1160—1165).—The so-called β-isomeride (A., 1930, 223) must have the configuration I for reasons (*a*) and (*b*). (*a*) It


(I.)

has been resolved into antimeric forms through the condensation product with *d*-hydroxymethylenecamphor; d-β-2 : 3 : 5 : 6-*tetramethylpiperazinebis*-d-*methylenecamphor*, m. p. 266°, $[\alpha]^{16}_{5461}$ +642° in $CHCl_3$, is decomposed to give d-β-2 : 3 : 5 : 6-*tetramethylpiperazine dihydrochloride*, $[\alpha]^{16}_{5461}$ +20·1° in water (*d*-nitroso-derivative, m. p. 108—109° $[\alpha]^{16}_{5461}$ +135° in EtOH). The *l*-base is obtained by crystallisation from $COMe_2$ of l-β-2 : 3 : 5 : 6-*tetramethylpiperazine mono*-d-α-*bromocamphor*-π-*sulphonate*, m. p. 129—130°, $[\alpha]^{15}_{5461}$ +65·5° in water, in the form of the dihydrochloride, $[\alpha]^{16}_{5461}$ —21·8° in water (*l*-dinitroso-derivative, m. p. 108—109°, $[\alpha]^{17}_{5461}$ —135·5° in EtOH). Attempts to resolve the base with *d*-camphor-10-sulphonic acid and by means of 1-*p*-toluenesulphonyl-β-2 : 3 : 5 : 6-tetramethylpiperazine *d*-camphor-10-sulphonate, m. p. 190°, $[\alpha]^{15}_{5461}$ +24·8° in EtOH; d-α-*bromocamphor*-π-*sulphonate*, m. p. 142—143°, $[\alpha]^{15}_{5461}$ +63·2° in EtOH; -d-*methylenecamphor*, m. p. 179°, $[\alpha]_{5461}$ +339° in EtOH, were unsuccessful. (*b*) The non-identity of compounds obtained by introducing two different groups in the 1 : 4- and 4 : 1-positions respectively. β-2 : 3 : 5 : 6-Tetramethylpiperazine is converted into 1-*benzenesulphonyl*-dl-β-2 : 3 : 5 : 6-*tetramethylpiperazine*, m. p. 132·5° (*hydrochloride*, m. p. 270—272°; *dibenzenesulphonyl* derivative, m. p. 177°), which when treated with *p*-toluenesulphonyl chloride affords 1-*benzenesulphonyl*-4-p-*toluenesulphonyl*-dl-β-2 : 3 : 5 : 6-*tetramethylpiperazine*, m. p. 186°. The corresponding 4-*benzenesulphonyl*-1-p-*toluenesulphonyl* derivative, m. p. 175—176°, is not identical with the compound described above.
F. R. SHAW.

Reciprocal reaction between piperazine and propylene oxide. K. A. KRASUSKI and G. T. PILIUGIN (Ukrain. Chem. J., 1930, 5, [Sci.], 349—351).—The reaction in aq. solution gives a 45% yield of 1 : 4-*di*-β-*hydroxypropylpiperazine*, m. p. 115—116° (*picrate*, m. p. 228—230°).
E. B. UVAROV.

Pyrimidines. CXXII. Synthesis of orotic acid. T. B. JOHNSON and E. F. SCHROEDER (J. Amer. Chem. Soc., 1931, 53, 1989—1994).—Improvements in the syntheses of 4-aldehydo-uracil and -2-thiouracil (A., 1915, i, 1002; 1916, i, 756) are described. Oxidation of either of these compounds or their acetals or 2-ethylthioluracil-4-aldehyde (or its acetal) with $Na_2Cr_2O_7$ in dil. H_2SO_4 gives orotic (uracil-4-carboxylic) acid. *Uracil*-4-*aldehyde diethylacetal*, m. p. 179°, is prepared by oxidising 2-thiouracil-4-aldehyde diethylacetal with alkaline H_2O_2.
H. BURTON.

Methylation of benziminazoles. M. A. PHILLIPS (J.C.S., 1931, 1143—1153).—Methylation of various 5(or 6)-methyl-, -bromo-, and -nitro-benziminazoles leads to the conclusion reached by Pyman (*ibid.*, 1922, **121**, 2616) on glyoxaline derivatives, that positive substituents in the benzene ring favour the formation of the 1 : 6-isomeride rather than the 1 : 5 when Me_2SO_4 is the methylating agent. In presence of aq. alkali the proportion of 1 : 6-isomeride is reduced. The effect of the NO_2 group is more powerful than that of Br. Methylation by (*a*) MeI, (*b*) Me_2SO_4 alone, or (*c*) Me_2SO_4 and alkali results as follows: 5(or 6)-methylbenziminazole, m. p. 114°, gives (*a*) an oil, b. p. 280°, probably 1 : 6-dimethylbenziminazole; (*b*) 1 : 6- and 1 : 5-derivatives in the ratio 10 : 1; (*c*) as (*b*) in the ratio 1 : 1; 2 : 5(or 2 : 6)-dimethylbenziminazole gives (*a*) 1 : 2 : 5-trimethyl- in 50% yield with some quaternary compound; (*b*) 6- and 5-isomerides in the ratio 10 : 1; (*c*) equal quantities of 1 : 2 : 5- and 1 : 2 : 6-trimethyl- and some unchanged material.

4-Bromo-2-nitroacetanilide is reduced to 4-*bromo*-2-*aminoacetanilide*, m. p. 154° (*Ac* derivative, m. p. 215°), the *hydrochloride* of which with $NaNO_2$ gives 4-*bromo*-1-*acetyl*-1 : 2 : 3-*benztriazole*, m. p. 112°, converted by alkali hydroxide into 4-*bromo*-1 : 2 : 3-*benztriazole*, m. p. 150°. 5(or 6)-Bromo-2-methylbenziminazole is methylated to give (*a*) 6-*bromo*-, m. p. 180° (also obtained from 5-bromo-2-aminomethylaniline and Ac_2O); (*b*) 6-bromo- and 5-*bromo*-1 : 2-*dimethylbenziminazole*, m. p. 141°, in the ratio 50 : 1; (*c*) as (*b*) in the ratio 2 : 1. Methylation of 5(or 6)-nitro-2-methylbenziminazole affords (*a*) with MeOH–HCl under pressure, 6-*nitro*-1 : 2-*dimethylbenziminazole*, m. p. 242°, also obtained by the action of AcOH and HCl on 5-*nitro*-2-*aminomethylaniline*, m. p 184°, (from 2-*chloro*-5-*nitromethylaniline*, m. p. 99°); (*b*) a mixture of the 6- and 5-isomerides in the ratio 100 : 1; (*c*) as (*b*) in the ratio 5 : 1. 2-Methylbenziminazole-5(or 6)-arsinic acid is converted by Me_2SO_4 into 1 : 2-*dimethylbenziminazole*-6-*arsinic acid*, m. p. above 300°.

5(or 6)-Methyl-, 2 : 5(or 2 : 6)-dimethyl-, 5(or 6)-bromo-2-methyl-, and 5(or 6)-nitro-2-methyl-benziminazoles form methiodides of the type $\left[C_6H_3R\left\langle{}^{NMe}_{NMe}\right\rangle CR'\right]\cdot\cdot\bar{I}$, which are converted by moist Ag_2O into the corresponding non-ionised carbinols, and a study of the rates of fission of these

is described. 5(or 6)-*Amino-2-hydroxy-*1 : 2 : 3-*trimethyl-*2 : 3-*dihydrobenziminazole* (*dihydrochloride*, m. p. 130°; *monohydrochloride*, m. p. 295°), obtained from the NO_2-compound, is transformed by the Bart reaction into 2-*hydroxy-*1 : 2 : 3-*trimethyl-*2 : 3-*dihydrobenziminazole-*5 (or 6)-*arsinic acid.* F. R. SHAW.

Formation of 4-*d*-arabinotetrahydroxy-*n*-butylglyoxaline, at low temperature, from dextrose and lævulose in ammoniacal copper hydroxide solution. J. PARROD (Compt. rend., 1931, **192**, 1136—1138).—Oxidation of either dextrose or lævulose by passing air through a solution in ammoniacal $Cu(OH)_2$ (A., 1930, 480) affords 4-d-*arabinotetrahydroxy-*n-*butylglyoxaline*, m. p. 164°, $[\alpha]_D$ —19·5° (*X*-ray diagram), identical with a specimen synthesised by the action of CH_2O and NH_3 on glucosazone. A mechanism for the reaction is suggested. J. W. BAKER.

Cyclic ammono-ketones and acid chlorides of the quinoxaline series. R. A. OGG, jun., and F. W. BERGSTROM (J. Amer. Chem. Soc., 1931, **53**, 1846—1853).—Evidence is given confirming the view that 2 : 3-dichloro-, 2 : 3-dimethyl-, and 2 : 3-diphenylquinoxalines are substitution products of an ammono-oxalyl chloride, an ammonodiacetyl, and an ammonobenzil, respectively. 2 : 3-Dichloroquinoxaline reacts with ethylenediamine at 150° giving o-*phenylene ethylene oxamidine*, m. p. above 350°, with MgMeI forming 2 : 3-dimethylquinoxaline, and with MgPrI yielding 2 : 3-*di-*n-*propylquinoxaline*, m. p. 42·9° (corr.). Treatment of 2 : 3-dimethylquinoxaline with KNH_2 in liquid NH_3 gives the *dipotassium* derivative, $C_6H_4{<}^{NK\cdot C:CH_2}_{NK\cdot C:CH_2}$ hydrolysed to 2 : 3-dimethylquinoxaline and converted by EtI into 2 : 3-di-*n*-propylquinoxaline. 2 : 3-Diphenylquinoxaline undergoes a "benzilic acid" rearrangement when treated with KNH_2 in liquid NH_3 forming (probably) 3-*amino-*2 : 2-*diphenyl-*1 : 2-*dihydroquinoxaline*, m. p. 287° (corr.). H. BURTON.

Constitution of pyracridone. C. RATH (Annalen, 1931, **486**, 284—294).—Anthranilic acid and 2-chloropyridine give pyracridone (*hydrazone*, m. p. 202°) identical with that obtained by Reissert (A., 1895, i, 244) but different from that of Seide (A., 1925, i, 159); 2-anilinopyridine is formed as by-product. Nitration of pyracridone gives (*a*) bz-*mononitropyracridone*, m. p. 252° [*sulphate*; corresponding *amine*, m. p. 267° (*hydrochloride*, m. p. above 300°)]; (*b*) bz-*mononitro-*(3-*nitropyracridone*) (I), m. p. 282° (*monobromo-*, m. p. 185°; *dibromo-*, m. p. 200°; *tribromo-*, m. p. 220°, derivatives), reduced to the *diamino-*derivative, m. p. 297° [*dihydrochloride*, m. p. 299—300° (decomp.)].

Pyracridone is oxidised with alkaline $KMnO_4$ to 2-*oxalylamido-*, m. p. 210—212°, hydrolysed to 2-*amino-pyridine-*3-*carboxylic acid* ($0{\cdot}5H_2O$), m. p. 217° (*hydrochloride*, m. p. 275°). Oxidation of I similarly affords oxalic acid, HNO_3, and 5-*nitro-*2-*amino-pyridine-*3-*carboxylic acid*, m. p. 233°, but when a large excess of alkali is used, 5-*nitro-*2-*hydroxypyridine-*3-*carboxylic acid*, m. p. 265°, is obtained. The results of oxidation indicate that the formula suggested by Reissert, $C_6H_4{<}^{CO\cdot C\cdot CH:CH}_{NH:C-N:CH}$, correct and that Seide's compound is isomeric. F. R. SHAW.

Triazole compounds. IV. Constitution of the methyl-1 : 2 : 3-benztriazole *N*-oxides and action of methyl sulphate on nitro-1-hydroxy-1 : 2 : 3-benztriazoles. O. L. BRADY and C. V. REYNOLDS (J.C.S., 1931, 1273—1281).—*N*-Methyl-*N*-oxides, obtained in some cases in the methylation of hydroxybenztriazoles, have the constitution $C_6H_4{<}^{NO}_{NMe}{>}N$ (A., 1928, 308), since reduction affords 3 : 6-dimethyl-1 : 2 : 3-benztriazole and not the 1 : 6-dimethyl compound as previously stated. 6-Nitro-1-hydroxy-1 : 2 : 3-benztriazole and aq. alkaline Me_2SO_4 give only the *O*-methyl ether, but when warmed with Me_2SO_4 alone yield first a compound which is slowly decomposed by water to give 6-*nitro-*3-*methyl-*1 : 2 : 3-*benztriazole* 1-*oxide* (II), m. p. 196° (decomp.). When the reaction is more prolonged the yield of this compound falls and the water-sol. product is decomposed by alkalis to give CH_2O and 6-nitro-3-methyl-1 : 2 : 3-benztriazole. This in turn slowly disappears, and heating for 8 hr. causes the formation of 6-*nitro-*1-*methoxy-*1 : 3-*dimethyl-*1 : 2 : 3-*benztriazolinium methyl sulphate*. The course of the reaction is formulated. Reduction of II with $Na_2S_2O_4$ affords the corresponding *amino-*derivative, m. p. 225° (decomp.), deaminated to give 3-methyl-1 : 2 : 3-benztriazole 1-oxide.

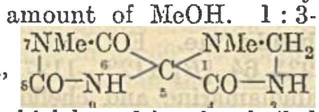
Similar results are obtained when 6-nitro-1-hydroxy-5-methyl-1 : 2 : 3-benztriazole is heated with Me_2SO_4. 6-*Amino-*3 : 5-*dimethyl-*1 : 2 : 3-*benztriazole* 1-*oxide*, m. p. 279° (decomp.), obtained from the corresponding NO_2-derivative, is deaminated to give 3 : 5-dimethyl-1 : 2 : 3-benztriazole. F. R. SHAW.

***isoapo*Caffeine.** H. BILTZ and L. LOEWE (Ber., 1931, **64**, [*B*], 1019—1025).—*isoapo*Caffeine is transformed by alcoholic NH_2Me into 5-*methylamino-*3-*methylhydantomethylamide*,

${}^{CO\cdot NH}_{NMe\cdot CO}{>}C(NHMe)\cdot CO\cdot NHMe$, m. p. 187° (*hydrochloride*, m. p. 208°), converted by Ac_2O into (?)di-acetyl*iso*caffuric acid, m. p. 195° (decomp.). Trimethylcaffolide under similar conditions affords *allo*-caffuric acid and dimethylcarbamide, whilst 1 : 7- and 1 : 3-dimethylcaffolides do not give 5-NHMe-compounds. 5-*Ethylamino-*3-*methylhydantmethylamide*, m. p. 187°, is described. 1-Acetyl*isoapo*caffeine and aq. NH_3 yield CO_2, 5-*amino-*3-*methylhydant-amide*, m. p. 186° (decomp.), and -*methylamide*, m. p. 147°. 5-Methylamino-3-methylhydantmethylamide with $COCl_2$ gives a *substance*, $C_9H_9O_5N_4Cl$, m. p. about 260° after softening at 230°, but does not react smoothly with $CSCl_2$ or $Cl\cdot CO_2Et$. The methylamide is converted by *s*-dimethylcarbamide at 150° into tetramethyl*spiro*dihydantoin and 3 : 6 : 8-*trimethylallantoin-*5-*carboxylmethylamide*, decomp. 220° (produced also from the methylamide and methylcarbimide or, preferably, from *isoapo*caffeine and *s*-dimethylcarbamide at 130—150°). 8-*Phenyl-*3 : 6-*dimethylallantoin-*5-*carboxylmethylamide* has m. p. 200° (decomp.). The 3 : 6 : 8-trimethyl compound is converted by evaporation with HCl or by heating at 220—225° into

1 : 3 : 7-trimethyl*spiro*dihydantoin, $\frac{NMe \cdot CO}{CO \cdot NMe} > C < \frac{NH \cdot CO}{CO - NMe}$, m. p. 183°, transformed by diazomethane into tetramethyl*spiro*dihydantoin. 3 : 7-*Dimethyl*spiro*dihydantoin*, m. p. 298°, is obtained from *isoapo*caffeine and carbamide at 130—170°.
H. WREN.

Application of diazomethane to the determination of constitution. H. BILTZ [with L. LOEWE and H. PARDON] (Ber., 1931, **64**, [*B*], 1146—1150).—Replacement of Ac groups during methylations with diazomethane is avoided if the reagent is free from MeOH and H_2O, as obtained by the action of conc. KOH on nitrosomethylcarbamide and dissolving the product in Et_2O. Replacement of Ac is achieved by the addition of a small amount of MeOH. 1 : 3-Dimethyl*spiro*dihydantoin,

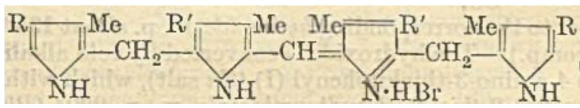


gives a diacetyl derivative which loses 1Ac when boiled with water. The monoacetyl compound is converted by diazomethane into 9-*acetyl*-1 : 3 : 7-*trimethyl*spiro*dihydantoin*, m. p. 185°, hydrolysed to 1 : 3 : 7-trimethyl*spiro*dihydantoin, m. p. 183°. The Ac group of the monoacetyl derivative is therefore present in position 9. With diazomethane containing MeOH the monoacetyl compound affords mainly tetramethyl*spiro*dihydantoin. 9-Methyluric acid glycol and boiling Ac_2O yield a compound shown to be 1 : 9-*diacetyl*-3-*methyl*spiro*dihydantoin*, m. p. 167—170°, since it is methylated to 1 : 9-diacetyl-3 : 7-dimethyl*spiro*dihydantoin, m. p. 178°. With diazomethane and MeOH it gives tetramethyl*spiro*dihydantoin. *spiro*-Dihydantoin and Ac_2O afford 1 : 9-*diacetyl*spiro*dihydantoin*, since the compound is sol. in NaOH and converted by pure diazomethane into 3 : 7-dimethyl-1 : 9-diacetyl*spiro*dihydantoin. With diazomethane containing MeOH the dimethyldiacetyl compound is formed initially and subsequently converted into tetramethyl*spiro*dihydantoin.
H. WREN.

Oxidation of theobromine; caffolides. H. BILTZ and L. LOEWE (Ber., 1931, **64**, [*B*], 1014—1019).—Methylalloxan and methylcarbamide, formed by the oxidation of theobromine by $KClO_3$ and HCl, slowly react in the acid medium with production of 3 : 7-dimethyluric acid glycol and *isoapo*caffeine. The first-named compound is produced in greatest yield when the action takes place rapidly, the last-named substance, m. p. 165—168° (decomp.) from H_2O or EtOH, decomp. 175—177° when recryst. from AcOEt, when the operation is slowly performed. Prolonged action of boiling H_2O on 1 : 7- and 1 : 3-dimethyl- and 1 : 3 : 7-trimethyl-caffolide leads to loss of the CO group in position 8 and production of 5-hydroxyhydantamides, whereas 3 : 7-dimethylcaffolide is transformed into 5-hydroxy-3 : 7-dimethylhydantamide, which loses approx. an additional mol. of CO_2. 1-*Acetyl*isoapo*caffeine*, m. p. 115°, 3-*acetyl*apo*caffeine*, m. p. 123°, and 7-acetyl-1 : 3 -dimethylcaffolide, m. p. 104°, are described.
H. WREN.

Bile pigments. IV. Bilirubinoid dyes and coproporphyrin. IV. H. FISCHER and A. KURZINGER (Z. physiol. Chem., 1931, **196**, 213—240).—*Methyl* 3 : 3′-*dimethyl*-5 : 5′-*di*(*methoxymethyl*)*pyrromethene*-4 : 4′-*dipropionate hydrobromide* (I), m. p. 172—173° [free *base*, m. p. 71° (*Cu* salt, m. p. 114°)], is obtained by boiling a MeOH solution of 3 : 3′-dimethyl-5 : 5′-dibromomethylpyrromethene-4 : 4′-dipropionic acid. The corresponding -5 : 5′-*di*(*ethoxymethyl*) derivative, m. p. 56° (*hydrobromide*, decomp. 182°), and 3 : 3′-*dimethyl*-4 : 4′-*diethyl*-5 : 5′-*di*(*methoxymethyl*)-, m. p. 85° (*hydrobromide*, decomp. 178°; *Cu* salt, m. p. 168°), and -5 : 5′-*di*(*ethoxymethyl*)-*pyrromethene* (*hydrobromide*, decomp. 180°) are similarly prepared. The OMe groups in these compounds are labile; thus by interaction with mercaptans in MeOH *methyl* 3 : 3′-*dimethyl*-5 : 5′-*di*(*ethylthiolmethyl*)-, m. p. 186°, and -5 : 5′-*di*(*methylthiolmethyl*)-, m. p. 180° (decomp.) -*pyrromethene*-4 : 4′-*dipropionate hydrobromides*, and 3 : 3′-*dimethyl*-4 : 4′-*diethyl*-5 : 5′-*di*-(*ethylthiolmethyl*)*pyrromethene hydrobromide*, m. p. 184°, are prepared. Fusion of the -5 : 5′-di(methylthiolmethyl) compound with 5 : 5′-dibromo-4 : 4′-dimethylpyrromethene-3 : 3′-dipropionic acid and succinic acid at 170—175° with the object of preparing a porphyrin with two of its methine groups substituted by the SMe group gave only coproporphyrin IV.

The $OMe \cdot CH_2 \cdot$ derivatives also condense with pyrroles having a free α-position with elimination of MeOH; *e.g.*, the interaction of I with 3-acetyl-2 : 4-dimethylpyrrole in C_6H_6 gives an intensely red *compound* (II; R=Ac, R′=$\cdot CH_2 \cdot CH_2 \cdot CO_2Me$), m. p. 204° (free *base*, yellow, m. p. 183°); the *substance* (II;

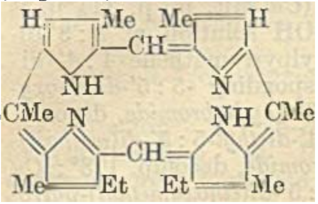


(II.)

R=Ac, R′=Et), m. p. 242° (*base*, m. p. 206°), is similarly prepared. With 2 : 3 : 4-trimethylpyrrole the *substance* (II; R=Me, R′=$\cdot CH_2 \cdot CH_2 \cdot CO_2Me$), m. p. 168—172° (*base*, m. p. 119—125°), is obtained in admixture with 3 : 4 : 5 : 3′ : 4′ : 5′-hexamethylpyrromethene and coproporphyrin; similarly, by the use of cryptopyrrole the *substance* (II; R=Et, R′=$\cdot CH_2 \cdot CH_2 \cdot CO_2 \cdot Me$), m. p. 185° (indef.), cryptopyrrolemethene, and coproporphyrin result, whilst opsopyrrole and its carboxylic acid give only ætioporphyrin and coproporphyrin (probably I and III), respectively. The formation of these porphyrins, involving disruption of the OMe group, thus occurs with extreme ease. Compounds of type II have the spectroscopic characteristics of both urobilin and the pyrromethenes, give the Gmelin reaction, and in extremely dil. solution give, on the addition of alcoholic $Zn(OAc)_2$, a marked urobilin fluorescence; on account of their resemblance to the biliary pigment the name "bilirubinoid dye" is suggested.

4-Methyl-2-ethylpyrrole is obtained by condensing oximinoacetone with $COEt_2$, and hydrolysing with boiling 40% H_2SO_4 the 3-*propionyl*-4-*methyl*-2-*ethylpyrrole*, m. p. 98°, produced. Condensation with its 5-*formyl* derivative, m. p. 66° (prepared by Gattermann's method), gives 3 : 3′-dimethyl-5 : 5′-diethylpyrromethene hydrobromide (cf. A., 1915, i, 309), which on fusion with 5 : 5′-dibromo-4 : 4′-dimethyl-3 : 5′-diethylpyrromethene hydrobromide (III) gives

a *porphyrin* (annexed formula), m. p. above 300° (*sulphone*), and an unidentified porphyrin. A similar



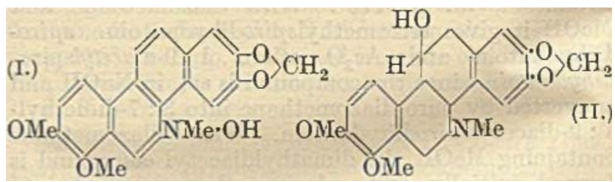
fusion of III with 3 : 3'-*dimethyl*-4 : 5 : 4' : 5'-*tetraethylpyrromethene hydrobromide*, m. p. 190° (from 4-methyl-2 : 3-diethylpyrrole, $H\cdot CO_2H$, and HBr) gives ætioporphyrin and a *porphyrin* of above type (Et replaces H in the β-position); the non-formation of a sulphone by the last suggests that this is a property of the unsubstituted β-position.

Coproporphyrin IV [*hydrochloride*, m. p. 285°; tetramethyl ester, m. p. 183—184° (cf. A., 1929, 940); *hæmin*, m. p. 300°; *Cu* salt; *rhodin* (*tetramethyl* ester, m. p. 183—184°)], is prepared by fusion of 5 : 5'-dibromo-3 : 3'-dimethyl-4 : 4'-dipropionic acid (improved prep. described) with 4 : 4'-dimethyl-5 : 5'-dibromomethyl- or 4 : 5 : 4' : 5'-tetramethyl-pyrromethene-3 : 3'-dipropionic acid, and methylsuccinic acid at 150°, or succinic acid at 175°, respectively. It gives a small amount of *OH*-derivative on oxidation with H_2O_2 in conc. H_2SO_4. H. A. PIGGOTT.

Heterocyclic derivatives of diphenyl. J. M. F. LEAPER (J. Amer. Chem. Soc., 1931, 53, 1891—1896). —Treatment of 4-aminodiphenyl hydrochloride with S_2Cl_2 first at 20° and then in presence of C_6H_6 at 75—80° gives *phenylphenylene thiazthionium chloride*, $Ph\cdot C_6H_3{<}{}^{N-}_{SCl}{>}S$, chars about 130°, hydrolysed by water to the corresponding *hydroxide*, m. p. about 135° (decomp.). The hydroxide is converted by cold alkali into 4-amino-3-thioldiphenyl (I) (*Zn* salt), which with CS_2 gives 2-*thiol*-6-*phenylbenzthiazole*, m. p. 220° (*Pb* and *Zn* salts; corresponding *disulphide*, m. p. 163°). 4-*Aminodiphenylyl*-3-*thiolacetic acid*, m. p. 212—212·5°, from I and sodium chloroacetate, gives a red *dye* when diazotised and coupled with alkaline β-naphthol. 2-*Amino*-6-*phenylbenzthiazole*, m. p. 227—228°, prepared from 4-aminodiphenyl, NaCNS, and Br in AcOH, is converted by conc. alkali into I. H. BURTON.

Lengthened *o*-di-derivatives of benzene and their ring-closure. VI. Synthesis of heptathiodiazines and triazoles. T. N. GHOSH (J. Indian Chem. Soc., 1931, 8, 71—76).—Substituted 1-*o*-aminophenylthiocarbamides, $NH_2\cdot C_6H_4\cdot NH\cdot CS\cdot NHR$, are condensed with phenacyl bromide. When R=Ph or $\cdot C_6H_4Me$ the product is 2-*phenyl*-2-*bromomethyl*-4 : 5-*benzo*-7-*ketotetrahydro*-1 : 3 : 6-*heptathiodiazine*, $C_6H_4{<}^{NH\cdot CO\cdot S}_{NH——CPh\cdot CH_2Br}$, m. p. 230° (decomp.), aniline and toluidine respectively being liberated from an intermediate compound. When $R=C_3H_5$, only 2-*phenyl*-2-*bromomethyl*-4 : 5-*benzo*-7-*allylaminodihydro*-1 : 3 : 6-*heptathiodiazine*, m. p. 201—202°, is formed. Condensation with $COCl_2$ yields compounds of the form $C_6H_4{<}^{N{=\!=}C{-}NHR}_{NH\cdot CO{-}S}$ viz., (R=Ph) 2-*keto*-4 : 5-*benzo*-7-*phenylaminodihydro*-1 : 3 : 6-*heptathiodiazine*, m. p. 175—176° (*Me* derivative, m. p. 126—127°), (R=*p*-tolyl) 2-*keto*-4 : 5-*benzo*-7-p-*tolylaminodihydro*-1 : 3 : 6-*heptathiodiazine*, m. p. 184—185°, and (R=1 : 3 : 4-xylyl) 2-*keto*-4 : 5-*benzo*-7-(1 : 3 : 4)-*xylylaminodihydro*-1 : 3 : 6-*heptathiodiazine*, m. p. 173—174° (*Ac* derivative, m. p. 202—204°). Treatment with HNO_2 gives triazoles, viz., (R=Ph) 1-*phenylthiocarbamyl*-4 : 5-*benzo*-1 : 2 : 3-*triazole*, m. p. 87—88° (liberates phenylthiocarbimide on keeping), (R=*p*-tolyl) 1-p-*tolylthiocarbamyl*-4 : 5-*benzo*-1 : 2 : 3-*triazole*, m. p. 115°, and (R=*m*-tolyl) 1-m-*tolylthiocarbamyl*-4 : 5-*benzo*-1 : 2 : 3-*triazole*, m. p. 94°. 1-o-*Aminophenyl*-3-m-*tolylthiocarbamide* has m. p. 144°. *o*-Phenylthiocarbamidophenylurethane heated with 15% KOH solution gives *o*-phenylenethiocarbamide and 2-anilino-4 : 5-benzo-1 : 3-thiazole. D. A. FAIRWEATHER.

Constitution of chelerythrine and homochelidonine. E. SPÄTH and F. KUFFNER (Ber., 1931, 64, [*B*], 1123—1127).—The technical mixture of sanguamarine and chelidonium bases is freed considerably from the former by crystallisation of the nitrates from water. The residual bases are transformed into the ψ-cyanides from which chelerythrine ψ-cyanide, m. p. 260—261° (decomp.), is isolated by crystallisation from $COMe_2$. It is transformed into the chloride, which is oxidised by $KMnO_4$ under mild conditions to hemipinmethylimide, whilst under more energetic conditions hydrastic acid is also produced. (The oxidation of chelidonine to 3 : 4-methylenedioxyphthalmethylimide is recorded.) When distilled with Zn dust, chelerythrine chloride gives α-naphthaphenanthridine. To chelerythrine and to homo-



(I.) (II.)

chelidonine on account of its transformation into chelerythrine the constitutions I and II are assigned. H. WREN.

Occurrence of sparteine in *Chelidonium majus*. E. SPÄTH and F. KUFFNER (Ber., 1931, 64, [*B*], 1127—1131).—Sparteine has been isolated in considerable amount from technical chelidonine residues. It is improbable that its presence can be accidental, since Gadamer and Winterfeld (A., 1924, i, 1227) have isolated from residues of *C. majus* an alkaloid $C_{19}H_{24}ON_2$ which is not similar to the other chelidonium alkaloids.

Reply is made to Leuchs (this vol., 500). H. WREN.

New *Corydalis* alkaloids; *d*-tetrahydrocoptisine, *d*-canadine, and hydrohydrastinine. E. SPÄTH and P. L. JULIAN (Ber., 1931, 64, [*B*], 1131—1137).—The non-phenolic bases of *C. cava* are separated as the hydrogen tartrates in EtOH into two main groups, the sparingly sol. salts being derived from *d*-tetrahydropalmatine and small amounts of similar bases, the freely-sol. from corydaline and other bases. From the sparingly sol. salts a base $C_{19}H_{17}O_4N$, m. p. (vac.) 203—204°, $[\alpha]_{D}^{15}$ +310° in $CHCl_3$, characterised by very sparing solubility in EtOH, has been isolated. It contains a methylene-

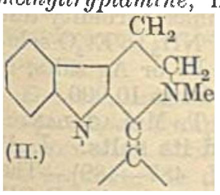
dioxy- but no OMe group. Dehydrogenation with I in EtOH gives a yellow quaternary salt reduced to *dl*-tetrahydrocoptisine, m. p. 227—228°. The conclusion that the base is d-*tetrahydrocoptisine* is confirmed by direct comparison with the *d*-base obtained by the resolution of *dl*-tetrahydrocoptisine with *d*-bromocamphor-π-sulphonic acid in dil. AcOH, whereby the l-*base*, m. p. 203—204°, $[\alpha]_D^{15}$ −310·5° in $CHCl_3$, is isolated from the sparingly sol. salt, its antipode being derived from the filtrate by crystallisation of the basic mixture from $CHCl_3$ and finally of the *d*-tartrate. The formation of a very sparingly sol. hydrochloride facilitates the isolation of *d*-canadine, m. p. 131—132°, $[\alpha]_D^{15}$ +299° in $CHCl_3$, from the sparingly sol. tartrate fraction; reduction of the dehydrogenated compound affords *dl*-tetrahydroberberine. Hydrohydrastinine, m. p. 66°, is isolated from the most strongly basic fraction of the alkaloids remaining after removal of *d*-tetrahydropalmatine and corydaline by fractional extraction of the ethereal solution with dil. HCl followed by distillation.

H. Wren.

Strychnos **alkaloids. LIX. Degradation of brucidine to diketonucidine, $C_{17}H_{20}O_3N_2$, and *apo*nucidine, $C_{15}H_{22}ON_2$.** H. Leuchs and H. S. Overberg (Ber., 1931, **64**, [*B*], 1007—1014; cf. A., 1929, 1320, 1470).—Brucidine is oxidised by CrO_3 in acid solution to diketonucidine, m. p. 275—278° after softening, with small amounts of a *compound*, $C_{19}H_{22}O_4N_2$, m. p. 286—288° (decomp.) after softening at 260°, $[\alpha]_D$ +132·8°/*d* in H_2O (*perchlorate*, $[\alpha]^{20}$ +88·2°/*d* in H_2O), and an isomeric *substance*, not molten below 315°, $[\alpha]_D^{17}$ +12·0°/*d* in H_2O. Oxidation of diketonucidine with H_2O_2 affords *carboxy*apo*nucidine*, m. p. (hydrated) 59—90°, solidifying at 140° and not re-melting below 290°, $[\alpha]_D^{20}$ +165°/*d* in H_2O (*hydrobromide*; *dipicrate*; *dihydroperchlorate*; *Ac* derivative, decomp. about 300°, $[\alpha]_D^{18}$ −197·1°/*d* in H_2O; *methiodide*, decomp. 255—260°, $[\alpha]_D^{18}$ −56·1°/*d* in H_2O). *apo*Nucidine, m. p. (anhyd.) 123—124°, (hydrated) 74—76°, $[\alpha]^{20}$ −84°/*d* in H_2O [*perchlorate*; *dipicrate*, m. p. about 175° (decomp.) after softening at 155° and m. p. 196—198°], N-*acetyl*apo*nucidine* (*perchlorate*), and apo*nucidine dimethoperchlorate*, decomp. 300° after darkening at 280°, are described. *apo*Nucine perchlorate has $[\alpha]_D^{17}$ +218·7°/*d*.

H. Wren.

Calycanthine. II. Degradation of calycanthine to *N*-methyltryptamine. R. H. F. Manske (Canad. J. Res., 1931, **4**, 275—282).—Benzoylation of calycanthine affords a viscous oil which with alcoholic KOH regenerates the base almost quantitatively, and in one experiment gave a *substance*, $C_{36}H_{34\text{ or }36}O_2N_4$, m. p. 235° (corr.). The crude derivative oxidised with $KMnO_4$ followed by alcoholic KOH gives *benzoyl*-N-*methyltryptamine*, m. p. 202° (corr.) (I). Similarly m-*chlorobenzoyl*-, m. p. 153° (corr.), and p-*nitrobenzoyl*-N-*methyltryptamine*, m. p. 134°, are obtained. The latter was also isolated directly from the crude *p*-nitrobenzoylation product. The constitution of I was established by synthesis from tryptamine by treatment with excess of MeI, a mixture of the quaternary *salt* and *N*-methyltryptamine being obtained, followed by benzoylation. For comparison, *benzoyl*-1-*methyltryptamine*, m. p. 117° (corr.), was synthesised. II is suggested as a partial representation of the formula for calycanthine.



(II.)

B. Levin.

Organic derivatives of silicon. XLIV. Formation of trichlorosilicane or of silicon dichloride from phenylsilicon trichloride. F. S. Kipping, J. C. Blackburn, and J. F. Short (J.C.S., 1931, 1290—1298).—The volatile silicon halide, obtained together with other products by heating $PhSiCl_3$ with Na (A., 1930, 939), is hydrolysed with water to give mainly $H_2Si_2O_3$, formed either by the hydrolysis of $HSiCl_3$ or from $SiCl_2$. The properties of this compound have been examined, and since they differ considerably from those of dioxodisiloxane (obtained from $HSiCl_3$), it is concluded that the substance is a condensation product of $[Si(OH)_2]_n$ formed from $SiCl_2$.

F. R. Shaw.

Organo-antimony compounds. V. Preparation of some substituted benzylbenzoates and their antimony derivatives. S. C. Niyogy (J. Indian Chem. Soc., 1931, **8**, 59—69).—5-Nitro-2-aminobenzoic acid, m. p. 267—268° (lit. 263—264°), and 5-*nitro-2-aminobenzyl alcohol*, m. p. 157—158°, are made from 5-nitro-2-acetamidobenzaldehyde by Cannizzaro's reaction. The Ac derivative of the first, m. p. 216—217° (lit. 152° and 221°), is treated as its Ag salt with CH_2PhCl to give *benzyl 5-nitro-2-acetamidobenzoate*, m. p. 175—176°, which is reduced by Al–Hg couple to *benzyl 5-amino-2-acetamidobenzoate*, m. p. 219—220° (decomp.). This is converted in the usual manner into *sodium 3-carbobenzyloxy-4-acetamidophenylstibinate*. 2-Propionamidobenzoic acid and 2-iso*butyramidobenzoic acid*, m. p. 129—130°, are nitrated, giving 5-*nitro-2-propionamidobenzoic acid*, m. p. 199—200°, and 5-*nitro*-2-iso*butyramidobenzoic acid*, from which are prepared as above *benzyl 5-nitro-2-propionamidobenzoate*, m. p. 122—123°, *benzyl 5-amino-2-propionamidobenzoate*, m. p. 187—188° (decomp.), *sodium 3-carbobenzyloxy-4-propionamidophenylstibinate*, *benzyl 5-nitro*-2-iso*butyramidobenzoate*, m. p. 129—130°, *benzyl* 5-*amino*-2-iso*butyramidobenzoate*, m. p. 207—208° (decomp.), and *sodium 3-carbobenzyloxy*-4-iso*butyramidophenylstibinate*. 5-Nitro-2-acetamidotoluene, m. p. 197—198° (previously 102—103°), when brominated and boiled with water gives 5-*nitro-2-acetamido*-m-*cresol* (?), m. p. 141—142°).

D. A. Fairweather.

Structure of proteins. A. Bernardi and M. A. Schwarz (Gazzetta, 1931, **61**, 169—177).—The Ac derivative of the substance, $C_{51}H_{91}O_{24}N_{14}S$ described previously (A., 1930, 628) was distilled under reduced pressure. The residue contained a brown substance, which softened at 210° and blackened at 240°, and gave reactions characteristic of *NN'*-diacetyldiketopiperazine.

O. F. Lubatti.

Mol. wt. of casein. III. D. C. Carpenter (J. Amer. Chem. Soc., 1931, **53**, 1812—1826).—The S, P, cystine, tryptophan, tyrosine, and histidine contents of the protein (*M* 75,000—100,000) previously separated (A., 1930, 356, 488) from casein are found to be 0·785, 0·856, 0·488, 1·237, 5·55, and 1·776%,

respectively. The mol. wt. of the protein calc. from these results is 98,000. H. BURTON.

Protein structure. C. RIMINGTON (Trans. Faraday Soc., 1931, **27**, 222—228).—A general discussion of recent work. F. L. USHER.

Electrolyte-free proteins. IX. Protein salts of various acids. W. PAULI and J. SAFRIN (Biochem. Z., 1931, **233**, 86—112).—The sp. conductivity of glutose from electrodialysed glutin increases and the a_H values slightly decrease with the time of hydrolysis. The dry wt. and the sp. conductivity of these samples of glutose decrease, but the a_H values increase during electrodialysis. Electrodialysed glutose binds less acid (trichloroacetic, H_2SO_4, HCl, HNO_3) than before electrodialysis. The binding of alkali is much greater with glutose than with glutin. Similar measurements are recorded for egg- and serum-albumin and pseudoglobulin.
P. W. CLUTTERBUCK.

Formation of acetaldehyde by alkaline fission of proteins. O. RIESSER [with A. HANSEN and R. NAGEL] (Z. physiol. Chem., 1931, **196**, 201—212).—MeCHO is slowly produced by action of boiling aq. alkalis on proteins in amounts varying from 3·63% (mucin) to 0·096% (keratin). The yield is unaffected by the concentration of NaOH (0·5—10%), but is somewhat better in a stream of N_2. It is not produced by acid hydrolysis, which gradually destroys the property; hydrolysis with pepsin is without action, but subsequent treatment with pancreas almost completely destroys the property. The MeCHO, after purification from H_2S, NH_3, etc., is determined by Ripper's method; the amount of the dimedon derivative of MeCHO agrees sufficiently with this to indicate that MeCHO is the sole aldehydic product. The method of Stepp and Fricke is found insufficiently accurate for the low concentrations dealt with.
H. A. PIGGOTT.

Pregl's method for the micro-determination of nitrogen. F. GOVAERT (Natuurwetensch. Tijds., 1931, **13**, 127—130).—An arrangement of apparatus, using magnesite as source of CO_2, is described. Details are given of a method of cooling the tube containing the sample by surrounding it with an Al block immersed in a freezing mixture; air can thus be rapidly removed by evacuation without loss of material and without using large quantities of CO_2.
H. F. GILLBE.

Centigram determination of halogens in organic substances. B. BOBRANSKI (Rocz. Chem., 1931, **11**, 301—326, and Z. anal. Chem., 1931, **84**, 225—240).—The substance (0·2—0·4 g.) is burned, using Pt catalyst in O_2, passed at the rate of 5 c.c. per min. for Cl or Br derivatives, and 10 c.c. per min. for I derivatives. Cl_2 and Br_2 are absorbed by $BaCO_3$ heated at a dull red heat at the end of the combustion tube, whilst I is absorbed by a 25% solution of Na_2SO_3 containing a trace of $SnCl_2$. The absorbed halogens are titrated with 0·05N-$AgNO_3$ in presence of adsorption indicators (uranin for Cl, and sodium eosinate for Br and I), and adding starch paste to prevent flocculation of colloidal silver halides. The mean error of the method is about 0·2%.
R. TRUSZKOWSKI.

Determination of phosphorus in organic compounds. W. C. DAVIES and D. R. DAVIES (J.C.S., 1931, 1207—1211).—The difficulty of determining P in tertiary alkylphosphines has been overcome by using a micro-quantity of the phosphine for oxidation with H_2O_2 and conc. H_2SO_4 and determining the H_3PO_4 produced colorimetrically with $(NH_4)_2MoO_4$ and quinol, comparison being made against a known amount of KH_2PO_4. The colorimetric determination depends on the quantitative reduction of the phosphomolybdic acid to the blue acid, $22MoO_3,2MoO_2,P_2O_5,H_2O$. The method is recommended for other organic P compounds.
F. R. SHAW.

Identification of the components of a mixture of hydrocarbons which gives, on combustion, a formula with fractional indices. G. SCHULTZE (Z. anal. Chem., 1931, **84**, 14—24).—Mathematical formulæ are derived for determining the components of a mixture of gaseous hydrocarbons from the results obtained by differential absorption, fractional distillation, and total combustion of the fractions.
A. R. POWELL.

Use of benzyl-alcoholic alkali for the determination of acetyl groups in substituted acetamides. S. SABETAY and J. SIVADJIAN (J. Pharm. Chim., 1931, [viii], **13**, 530—531).—The amide (0·5 g.) is boiled with 0·5N-benzyl-alcoholic KOH (25 c.c.) for 1½ hrs., the mixture cooled, and, after adding EtOH (20 c.c.), is titrated with 0·5N-HCl in presence of phenolphthalein. 8 satisfactory examples are given. E. H. SHARPLES.

Iodo-oxybenzoate as a reagent for free phenolic hydroxyl groups in organic compounds. C. D. LEAKE (Proc. Soc. Exp. Biol. Med., 1930, **28**, 148—150).—When treated with aq. NH_4 iodo-oxybenzoate, morphine salts give a straw-yellow to garnet-red colour; no other opium alkaloid except *apo*morphine gives a colour reaction. The effect is an oxidising reaction dependent on the presence of a free phenolic OH group; the compounds are not decomposed by the reagent, which may be employed to differentiate adrenaline from ephedrine and acetarsone from other As^V arsenicals. CHEMICAL ABSTRACTS.

Colour test for *o*-dihydroxyphenols. J. H. QUASTEL (Analyst, 1931, **56**, 311).—Addition of AcOH and $(NH_4)_2MoO_4$ to an aq. solution gives an intense reddish-brown colour, probably sp., the limit of sensitivity varying from 1 in 60,000 for adrenaline to 1 in 200,000 for gallic acid. The limit for salicylic acid is 1 in 3000. T. MCLACHLAN.

Detection of benzoic acid. A. N. LEATHER (Analyst, 1931, **56**, 299—304).—Apparatus is described for extraction of benzoic and other aromatic acids. For detection, a modification of Hinks' turbidity test (cf. A., 1914, ii, 439) on addition of NH_3 to Et_2O solution, confirming by formation of Fe or Ag salts, is used. The test has a sensitivity of 1 in 10,000.
T. MCLACHLAN.

Determination of cocaine and its salts. J. A. SANCHEZ (Semana Med., 1931, I, 487—489).—The cocaine hydrochloride (0·1 g.) is boiled with EtOH (5 c.c.) and 0·1N-NaOH (10 c.c.) for 15 min., BzONa

being formed. The diluted liquid is titrated with $0{\cdot}1N$-H_2SO_4 (phenolphthalein).

CHEMICAL ABSTRACTS.

Identification of organic compounds. III. Use of the "iodine tetrachloride" reagent for microchemical identification of alkaloids. L. ROSENTHALER (Pharm. Ztg., 1931, **76**, 524—526).—The reagent is prepared by saturating a suspension of I in 6 parts of conc. HCl with gaseous Cl_2. It gives cryst. *ppts.* with the hydrochlorides of the following: *apo*morphine, cocaine, caffeine, eumydrine, hexamethylenetetramine, hydrastinine, mezcaline, nicotine, pilocarpine, piperazine, strychnine, theophylline (drawings of the crystalline forms of these are given), aniline, antipyrine, atroscine, brucine, codeine, and physostigmine. Amorphous ppts. are given by a number of other alkaloids, and a deep violet coloration by berberine.

H. A. PIGGOTT.

Biochemistry.

Iron content of the liver and spleen of different kinds of animals in normal and rarefied air. A. LOEWY and G. CRONHEIM (Biochem. Z., 1931, **234**, 283—301).—The wt. and Fe contents of the liver and spleen of guinea-pigs, rats, rabbits, and mice under atm. pressure and after living 4—7 days under reduced pressure are determined. The decrease in wt. of the liver on reducing the pressure is small with guinea-pigs and rats and large with mice. An increase in wt. of the spleen is obtained with guinea-pigs and rats, a considerable decrease with rabbits, and little change with mice. The Fe content (%) is decreased when the wt. is increased. In the spleen of guinea-pigs and rats an abs. decrease of Fe is obtained. Change of the ratio blood-Fe : hæmoglobin under reduced pressure could not be established.

P. W. CLUTTERBUCK.

Oxygen consumption of blood at high altitudes. F. MÜLLER, G. CRONHEIM, and M. MÜLLER-MUNK (Biochem. Z., 1931, **234**, 302—306).—In rats, under reduced pressure, substances are present both in whole blood and plasma which consume O. In man after living at high altitudes, the presence of such substances may be demonstrated by addition of reduced glutathione to the blood sample.

P. W. CLUTTERBUCK.

Carbon dioxide content of the blood in the new born. H. F. KANE and J. KREISELMAN (Amer. J. Obstet. Gyn., 1930, **20**, 826—827).—Consistently high values increase with the degree of asphyxia.

CHEMICAL ABSTRACTS.

Carbon dioxide absorption curve of infants fed lactic acid, hydrochloric acid, and boiled cow's milk. D. C. DARROW (Amer. J. Dis. Children, 1930, **40**, 1016—1023).—Normal values for CO_2 absorption, p_H, $[HCO_3']$, and lactic acid concentration are obtained. Venous blood in infancy has p_H $7{\cdot}37 \pm 0{\cdot}05$, and the venous CO_2 tension is $41 \pm 5{\cdot}0$ mm.

CHEMICAL ABSTRACTS.

Carbon dioxide and oxygen tensions of the mixed venous blood of man at rest. D. W. RICHARDS, jun., and M. L. STRAUSS (J. Clin. Invest., 1930, **9**, 475—532).—A discussion. Equilibrium can be regularly established for CO_2 with certain high-O_2 mixtures and for both CO_2 and O_2 with certain low-O_2 mixtures.

CHEMICAL ABSTRACTS.

Determination of ethyl iodide in alveolar, inspired, and expired air. H. R. OLIVIER and J. BRETEY (Bull. Soc. Chim. biol., 1931, **13**, 458—465).—An apparatus is described by means of which the EtI is decomposed by a hot Pt spiral and the change in vol. determined.

C. C. N. VASS.

Individual differences in human blood. K. LANDSTEINER (Science, 1931, **73**, 403—409).—A lecture.

L. S. THEOBALD.

Optical activity of hæmoglobin. S. SIMONOVITS (Biochem. Z., 1931, **233**, 449—459).—Horse oxyhæmoglobin, once cryst., has $[\alpha]_{6440}$ $+12°$ to $+15°$ in 1% aq. solution, but this value decreases when the material is repeatedly recryst. In dil. aq. NH_3 (0·1—0·2%) seems to be lower than in water, but increases to about $1\frac{1}{2}$ times its original value as the concentration of the pigment is increased from 0·5 to 4·0%. In dil. aq. NH_3 the $[\alpha]_{6440}$ of ox oxyhæmoglobin is about $+5°$ and likewise increases greatly with increase in the concentration of the pigment. Horse oxyhæmoglobin, reduced with $Na_2S_2O_4$, has $[\alpha]_{6440}$ $+23°$ to $+27°$ in about 0·5% solution.

W. MCCARTNEY.

Catalytic action of blood-pigment. F. HAUROWITZ (Z. physiol. Chem., 1931, **198**, 9—17).—Synthetic hæmoglobin (cf. A., 1927, 67), methæmoglobin, and repeatedly cryst. horse oxyhæmoglobin catalyse the decomp. of H_2O_2 to about the same extent as protohæmin containing an equiv. amount of Fe. Gelatin restricts the catalytic effect of hæmin to the same extent as globin.

The conversion of mesoporphyrin ester in butyric acid into mesohæmin ester (this vol., 633) is attributed to a trace of Fe^{II} salt formed from the Fe^{III} salt at the high temp. of the reaction. Using Haurowitz's method (A., 1927, 1100) 3% of porphyrin is converted into hæmin by heating on the water-bath for a short time and 67% by heating for 1 hr. If a Fe^{II} salt replaces the Fe^{III} salt a short boiling effects quant. conversion.

A. RENFREW.

Have hæmoglobin and its derivatives a catalytic activity? M. RIGONI (Biochim. Terap. sperim., 1931, **16**, 489—494; Chem. Zentr., 1931, i, 1630).—The activity depends chiefly on the Fe content, and only slightly on catalase present as impurity.

A. A. ELDRIDGE.

Production of methæmoglobin and increased respiration by organic dyes. L. MICHAELIS and K. SALOMON (Biochem. Z., 1931, **234**, 107—115).—That treatment of oxyhæmoglobin with $K_3Fe(CN)_6$ yields methæmoglobin and liberates the whole of the O is confirmed. Org. dyes can oxidise hæmoglobin to methæmoglobin. The reaction in presence of excess O_2 is not complete, but comes into equilibrium sooner or later, according to the range of potential of the pigment. The equilibrium is not thermodynamic, but

consists of a kinetic inhibition. The action of those dyes which increase the respiration of non-nucleated red cells increases the more positive is their potential and the greater is their power to form methæmoglobin. P. W. CLUTTERBUCK.

Metallised food in the regeneration of hæmoglobin in the rat and in man. J. L. McGHEE (Science, 1931, **73**, 347—348).—Metals such as Fe, Cu, Mn, and Co are sufficiently sol. in milk to ensure rapid regeneration of hæmoglobin in man and in the rat. Cu alone is effective, but the presence of other metals, especially Fe, increases its effectiveness. Among rats mortality is reduced when metallised milk replaces milk to which a metallic salt has been added. L. S. THEOBALD.

Action of catalase of thrombocytes. K. IGLAUER and S. WEBER (Biochem. Z., 1931, **234**, 489—495).—Thrombocytes contain a catalase similar in its properties to that of leucocytes. The view that the catalase action is a function of the granula has received further confirmation. W. McCARTNEY.

Blood-lipins and hydrogen-ion concentration. B. PAUL (Magyar orvosi Arch., 1931, **30**, 359—362; Chem. Zentr., 1931, i, 1630).—The cholesterol/lecithin quotient increases with increase in p_H and *vice versa.* A. A. ELDRIDGE.

Cholesterol and bilirubin contents of blood of mother and child. H. HINGLAIS and J. GOVAERTS (Gynec. et Obstet., 1930, **22**, 137).—Maternal hypercholesterolæmia at term is frequent, whilst the blood-cholesterol of the infant at birth is low, and increases markedly in the first few days. No relation was found between the excess blood-bilirubin at birth and the lower cholesterol value. CHEMICAL ABSTRACTS.

Micro-determination of total fat and total cholesterol in blood. S. KATSURA and T. HATAKEYAMA (Biochem. Z., 1931, **234**, 462—477).—In Bloor's method (A., 1929, 837) the oxidation of the fatty acids is incomplete. In the process now described, which is based on the methods of Bloor and Bang (A., 1919, ii, 85), this difficulty is overcome and satisfactory determinations can be made in 0·2—0·3 c.c. of blood. W. McCARTNEY.

Determination of serum-proteins by the acetone method of Piettre and Vila. Comparison of the results with those of the salt method. A. ARCAND (J. Pharm. Chim., 1931, [viii], **13**, 518—528).—With normal blood-serum Piettre's method (A., 1926, 635) gives results which are comparable with those obtained by Howe's salt method. E. H. SHARPLES.

Unity of serum-albumin fractions. D. VON KLOBUSITZKI (Kolloidchem. Beih., 1931, **32**, 382—402).—A lecture. E. S. HEDGES.

Determination of non-protein-nitrogen in 0·1 c.c. of blood. A. K. ANDERSON and S. F. HOWELL (J. Lab. Clin. Med., 1930, **16**, 183—186).—Folin and Wu's method is applied to 0·1 c.c. of blood; precipitation is effected by a mixture of Na_2WO_4 and H_2SO_4. CHEMICAL ABSTRACTS.

Does normal blood contain acetylcholine? H. H. DALE and H. W. DUDLEY (Z. physiol. Chem., 1931, **198**, 85—99).—Contrary to Kapfhammer and Bischoff (A., 1930, 1464) fresh ox (and horse) blood contains no detectable amount of acetylcholine. A. RENFREW.

Determination of uric acid in blood. F. MONTEQUI (Anal. Fís. Quím., 1931, **29**, 264—266).—The method depends on the formation of Prussian-blue by the ferrocyanide resulting from the reduction of ferricyanide by the uric acid in presence of Na_2CO_3. Protein is first removed from the blood (2 c.c.) with Na_2WO_4 and H_2SO_4, and the uric acid is precipitated as Ag urate by addition of 5% Ag lactate solution. The washed ppt., corresponding with 1 c.c. of blood, is treated with 10% HCl to liberate the free acid, and the solution is rendered alkaline with 1 c.c. of sat. Na_2CO_3 solution, and centrifuged. Four drops of freshly-prepared aq. $K_3Fe(CN)_6$ are added and the mixture is heated at 50—60° for 5 min.; 2 c.c. of 10% HCl, 1 c.c. of 5% gelatin solution, and 4 drops of 10% $FeCl_3$ are added to the cooled solution, and the resulting coloration is compared with that produced with a known amount of uric acid. H. F. GILLBE.

Spectrographic detection of uric acid in blood-serum and in cerebrospinal fluid. A. KRUPSKI and F. ALMASY (Naturwiss, 1931, **19**, 461—462).—The absorption spectrum of serum (horse) has a marked band (max. 2750—2800 Å.) which is due to the uric acid present. It is displaced 75 and 145 Å. towards shorter wave-lengths relative to that of conc. aq. solutions of uric acid and Na urate, respectively. The band at 2800 Å. in the spectrum of cerebrospinal fluid (Opitz) is probably due to uric acid and indicates the large increase in uric acid content which occurs in diseases of the central nervous system. J. W. BAKER.

Distribution of uric acid between blood-cells and plasma. M. JACOBY and H. FRIEDEL (Biochem. Z., 1931, **234**, 46—53).—The more acid is the reaction of blood, the greater is the amount of uric acid found in the cells. Tables summarise the distribution of added uric acid between cells and plasma in a number of diseases. P. W. CLUTTERBUCK.

Action of blood-serum on morphine hydrochloride in presence of hydrogen peroxide. A. LEULIER and B. DREVON (Compt. rend., 1931, **192**, 1129—1131).—In presence of blood-serum and H_2O_2 morphine hydrochloride is converted into hydroxydimorphine. C. C. N. VASS.

Action of blood on morphine hydrochloride. A. LEULIER and B. DREVON (Compt. rend., 1931, **192**, 1283—1284).—Morphine hydrochloride is converted into ψ-morphine or dihydroxymorphine by whole or hæmolysed blood, either in contact or with the passage of O_2 or air through the mixture. Dihydroxymorphine is isolated through the sol. trichloroacetate. The transformation cannot be effected by carboxyhæmoglobin. C. C. N. VASS.

Rotatory power of blood-sugar. J. THOMAS (Bull. Soc. Chim. biol., 1931, **13**, 377—394).—The reducing and rotatory powers of dialysates of the blood of the ox, dog, rabbit, and horse have been determined. Isotonic saline, $Na_2C_2O_4$, NaF, or Na_2HPO_4 exert no effect on the rotatory power of blood-

sugar. The sp. rotation of blood-sugar is much smaller than that of the equilibrium mixture of α- and β-dextrose. No mutarotation was observed in the neutral dialysates kept at 5—7° for 3 days. The non-fermentable substances cannot account for the difference in the sp. rotation nor is the dextrose in the dialysate combined with H_3PO_4 or glycuronic acid. The sp. rotation of blood-sugar is a function of the p_H of the solution. The isoelectric point of dialysed blood-sugar is approx. p_H 2·4. Blood-sugar is considered to be an isomeric form of dextrose with a marked ampholytic character. C. C. N. VASS.

Distribution of blood-sugar between erythrocytes and plasma. H. KAHLER and K. MACHOLD (Z. ges. exp. Med., 1930, **74**, 162—179; Chem. Zentr., 1931, i, 1307).—By addition of NaCl solution to blood, sugar passes from the erythrocytes into the plasma; the change is unaffected by insulin. The reverse change is caused by addition of dextrose solution. In diabetic blood only the magnitude of the change differs from the normal. In hypoglycæmia the plasma-sugar is first passed into the tissue. The distribution of sugar in blood is not a purely physical phenomenon. A. A. ELDRIDGE.

Blood-sugar in elderly people. F. W. MARSHALL (Quart. J. Med., 1931, **24**, 257—284).—Five types of dextrose-tolerance curve are distinguished. The renal threshold in healthy old age is about 0·200%. CHEMICAL ABSTRACTS.

Peculiarities of glycæmic reaction in early infancy. V. L. STYRIKOVICH (Okhr. Mat. Detst., 1929, **1**, 28—42).—Three main types, with sub-types, are differentiated. CHEMICAL ABSTRACTS.

Course of blood-sugar curve after intravenous administration of sugar. H. STAUB (Arch. exp. Path. Pharm., 1931, **160**, 120—123).—Criticism of the results and conclusions of Juttemann (this vol., 110). W. O. KERMACK.

Course of blood-sugar curve after intravenous administration of sugar. H. FREUND (Arch. exp. Path. Pharm., 1931, **160**, 124—126).—A reply to criticism (preceding abstract). W. O. KERMACK.

Effect of calcium chloride injections on blood-sugar of normal and jaundiced dogs. A. G. REWBRIDGE and E. ANDREWS (Proc. Soc. Exp. Biol. Med., 1930, **28**, 126—127).—Intravenous injection of 10% aq. $CaCl_2$ causes a rise in blood-sugar nearly as marked as that following the injection of sugar itself; the effect tended to last longer. CHEMICAL ABSTRACTS.

Glycolysis in blood and formation of lactic acid. O. JERVELL (Acta med. Scand., 1930, **74**, 221—234; Chem. Zentr., 1931, i, 1631).—Glycolysis experiments with citrated blood buffered with 0·05N-phosphate to p_H 8·3 disclosed no difference between normal and pathological conditions except in cancer, when no glycolytic enzymes could be found in the serum. Insulin does not affect glycolysis. The production of lactic acid is much smaller than corresponds with the dextrose deficit. After glycolysis for 6 hrs. a slight increase in dextrose was observed, suggesting the presence of a glycosynthetic enzyme. A. A. ELDRIDGE.

Determination of blood-sugar. H. C. HAGEDORN, B. N. JENSEN, and F. LARSEN (Acta Med. Scand., 1929, **34**, Suppl., 182—183; Chem. Zentr., 1931, i, 1489).—The method of Hagedorn and Jensen is simplified by the use of tablet reagents. A. A. ELDRIDGE.

Modification of the Hagedorn–Jensen method for the determination of blood-dextrose. R. C. LÓPEZ (Anal. Fis. Quím., 1931, **29**, 306—309).—Proteins are removed from the blood by addition of an equal vol. of 10% trichloroacetic acid solution instead of by $Zn(OH)_2$. The reagent has no disturbing influence on the reduction of ferricyanide by dextrose in alkaline solution. The reagent should contain 3·3 g. $K_3Fe(CN)_6$ and 3·3 g. cryst. Na_2CO_3 per litre, and the method is then applicable to blood of high dextrose content. The modified method is applicable also to the determination of dextrose in cerebro-spinal fluid, which should be neutralised with Na_2CO_3 prior to the reduction. H. F. GILLBE.

[Micro-determination of blood-sugar.] H. J. JEGHERS and V. C. MEYERS (J. Lab. Clin. Med., 1930, **15**, 982—984).—Folin's micro-method is applied to 0·025 c.c. of blood. CHEMICAL ABSTRACTS.

Simultaneous determination of inorganic phosphate, sugar, and lactic acid in blood. S. MORGULIS and S. PINTO (J. Lab. Clin. Med., 1930, **16**, 60—64).—The methods of Kuttner and Cohen (inorganic phosphate), Hagedorn and Jensen (sugar), and Friedemann (lactic acid) are applied to the filtrate after treatment of 3 c.c. of blood with trichloroacetic acid. CHEMICAL ABSTRACTS.

Phosphorus metabolism. I. Blood-phosphorus analysis. G. E. YOUNGBURG and M. V. YOUNGBURG (J. Lab. Clin. Med., 1930, **16**, 158—166).—The colorimetric method, depending on the reduction of phosphomolybdate with $SnCl_2$, is applied to the determination of total, inorg. phosphate, total acid-soluble, and lipin-P in whole blood, corpuscles, and plasma. CHEMICAL ABSTRACTS.

Phosphorus partition in normal whole blood. B. S. WALKER and M. E. HUNTSINGER (J. Lab. Clin. Med., 1930, **16**, 247—252).—The total P content of normal whole blood is 39·2 mg. per 100 c.c. The inorg. P forms 9·7% of the total P, the acid-sol. P 68·1%, the ester-P 58·3%, and the lipin- or lecithin-P 36·0%. CHEMICAL ABSTRACTS.

Organic and inorganic phosphorus content of blood in children. P. FEDOROV (Vrach. Delo, 1930, **13**, 505—510).—The average blood-inorg. P of boys and girls (7—15 yrs.) is about 3·97 mg. per 100 c.c., and the org. P 6·02 mg. per 100 c.c. No seasonal changes in org. P were observed. CHEMICAL ABSTRACTS.

Determination of calcium in serum. L. BRULL (Bull. Soc. Chim. biol., 1931, **13**, 466—469).—Serum can be kept at 0° for 3 days without affecting the Ca content. Neither phosphate or Mg nor precipitation with trichloroacetic acid influences the direct or indirect determination of Ca. C. C. N. VASS.

Relation between blood-sugar and -coagulation time. V. Blood-sugar, -coagulation time, and glycolysis. A. PARTOS (Pflüger's Archiv, 1930,

226, 347—353; Chem. Zentr., 1931, i, 1631).—Adrenaline- or morphine-hyperglycæmia is associated with increased and insulin-hypoglycæmia with decreased glycolysis. Novirudin causes a fall in blood-sugar, diminished glycolysis, and retarded coagulation. In alimentary (dextrose) hyperglycæmia glycolysis is not increased, whilst the coagulability is enhanced.
A. A. Eldridge.

Relation between blood-sugar and -coagulation time. VI. Behaviour of blood-sugar and -lactic acid during glycolysis. A Partos and A. Herzog (Pflüger's Archiv, 1930, **226**, 464—471; Chem. Zentr., 1931, i, 1631—1632).—No regular relation between the sugar disappearing during glycolysis and the lactic acid formed was observed. The lactic acid increased, however, after 7 min. and decreased after 12 min. owing to oxidative degradation, but the sugar exhibited no regularity. In addition to glycolysis, autolysis plays a part in liberating bound carbohydrate from protein and lecithin complexes.
A. A. Eldridge.

Dietary protein and blood-clotting function. I. N. Kugelmass and E. L. Samuel (Amer. J. Dis. Children, 1931, **41**, 48—52).—Prolonged feeding of a protein-rich diet increases the coagulability of the blood. The production of fibrinogen is increased by surgical injury of tissues and (transiently) by introduction of heterologous proteins into the vascular system. Chemical Abstracts.

Bile-salt hæmolysis in new-born infants and its inhibition by the blood-serum. H. N. Sanford, M. M. Crane, and E. I. Leslie (Amer. J. Dis. Children, 1930, **40**, 1039—1044).—The erythrocytes are more resistant to hæmolysis by bile salts than those of adults. Chemical Abstracts.

Hæmolytic action of salicin. A. Busacca (Arch. Farm. sperim., 1931, **52**, 141—148).—No hæmolytic action was detected. R. K. Callow.

Relationship between the isoelectric points of human serum and its alexic power. F. Vles, M. Prager, and N. Bernstein (Compt. rend., 1931, **192**, 1506—1508).—Sera with high alexic powers have low isoelectric points (about p_H 5). H. W. Dudley.

Chief absorption bands of MacMunn's histohæmatins. O. Warburg and E. Negelein (Biochem. Z., 1931, **233**, 486).—If the long-wave portion of the spectrum is excluded by means of a suitable filter the chief absorption bands of Fe–porphyrin compounds can be made visible. The following bands, of which the first is weaker than the second and third, have been observed in the spectrum of MacMunn's histohæmatins: 446—452 mμ, 430—435 mμ, and 414—420 mμ. W. McCartney.

Specificity and chemical structure. H. Bierry (Compt. rend., 1931, **192**, 1284—1286).—Theoretical. It is suggested that the nature of the carbohydrate group in the protein mol. and its mode of combination determine the chemical individuality and zoological specificity. C. C. N. Vass.

Spectrophotometric analysis of the colouring matter of egg-yolk. R. Kuhn and A. Smakula (Z. physiol. Chem., 1931, **197**, 161—166).—The absorption curves of lutein and zeaxanthin were plotted, and from the figures the composition of the xanthophyll of egg-yolk was determined as 30% zeaxanthin and 70% lutein. This agrees with the polarimetric determination. J. H. Birkinshaw.

[Muscle- and yeast-adenylic acids.] G. Embden and G. Schmidt (Z. physiol. Chem., 1931, **197**, 191—192; cf. A., 1929, 591).—In the previous paper the reaction constants were wrongly calc. The corrected values are of the same order as those obtained by Yamagawa (A., 1920, i, 773) for inosic acid.
J. H. Birkinshaw.

Preparation of adenosinepyrophosphoric acid from muscle. K. Lohmann (Biochem. Z., 1931, **233**, 460—469; cf. A., 1929, 1098).—A method for the isolation from muscle of adenosinepyrophosphoric acid (adenylpyrophosphoric acid) and of the "pyrophosphate fraction" from other cells and tissues is described. Adenosinepyrophosphoric acid is a triphosphoric acid (viz., adenine nucleotide pyrophosphoric acid). The ratio of easily to difficultly hydrolysable P in the acid is exactly 2 : 1. On acid hydrolysis it yields 1 mol. adenosine, 1 mol. pentosephosphoric acid, and 2 mols. (inorg.) phosphoric acid. Neutral hydrolysis of its Ba salt yields adenosinephosphoric acid (adenylic acid) and pyrophosphoric acid. W. McCartney.

Muscle extract. I. A. Hahn, E. Fischbach, and W. Haarmann (Z. Biol., 1931, **91**, 315—321).—The isolation from muscle extract of adenylic acid and lactacidogen is described. Pyruvic acid is formed from adenylic acid, in the presence of methylene-blue, in extracted muscle. Lactacidogen and adenylic acid separately excite respiration in extracted muscle. Lactacidogen in untreated muscle is converted into pyruvic acid by a water-sol. enzyme.
C. C. N. Vass.

Occurrence of anserine and carnosine in *Selachii* and *Teleostei*. D. Ackermann and F. A. Hoppe-Seyler (Z. physiol. Chem., 1931, **197**, 135—140).—Anserine was present in dogfish, cod, and conger-eel, but absent from herring, river eel, and perch. Carnosine was found only in the river eel.
J. H. Birkinshaw.

Determination of glutathione in normal and pathological tissues. III. Relationship between development and glutathione content in chick embryos. IV. Glutathione content of various organs of pigeons fed on polished rice and subjected to starvation, and also of starved rabbits. V. Relationship between glutathione content and neurotomy in muscles of pigeons fed on polished and unpolished rice. T. Kamiya (Nagoya J. Med. Sci., 1930, **5**, 1—5, 6—17, 18—23).—III. The glutathione content reaches a max. in 12—14 days, and then decreases; the liver, brain, heart, muscle, and eye contain the largest amount.

IV. Pigeons fed on polished rice showed a decreased glutathione content in the liver, heart, and muscle; the adrenals, spleen, and blood showed an increase. Starvation produced a similar, but more marked, result.

V. After section of the right sciatic nerve the glutathione content of the muscle increased; in pigeons

fed on polished rice the glutathione content of control muscles (left leg) decreased more rapidly.

CHEMICAL ABSTRACTS.

Chitin from fungi and from crab-shells. G. RAMMELBERG (Bot. Archiv, 1931, **32**, 1—37).—The nature of the chemical and bacterial decomp. products of chitin from fungi and from crab-shells indicates the two materials to be almost, if not quite, identical.

A. G. POLLARD.

Acid formation in purified and neutral wool-fat. C. H. MOLLERING (Arch. Pharm., 1931, **269**, 225—228).—The acidity of purified wool-fat exposed to light in an unclosed vessel was doubled in 1 month and in 11 it rose from 0·11% to 1·64% (as oleic acid); after 1 year the acidity was 9·31%, 0·94%, and 0·16%, respectively, in the uppermost, middle, and lowest of three equal sections. Hg-lamp irradiation at 30 cm. increased the acidity from 0·14% to 0·55% in 8 hrs. The rise in acid val., especially as it is largely superficial, has little injurious effect.

C. HOLLINS.

Composition of bone skeletal substance and its formation. R. KLEMENT (Z. physiol. Chem., 1931, **196**, 140—154; cf. A., 1930, 237).—$CaHPO_4$ was shaken with a frequently renewed phosphate buffer solution in a thermostat at 37°. Ca and PO_4''' determinations on the solid showed that in 2 days at p_H 7·7 the greater part consisted of Ca_3PO_4 (Ca : PO_4, 1 : 0·667). The complete conversion occupied about 3 weeks, then the product gradually lost further phosphate, yielding $3Ca_3(PO_4)_2,Ca(OH)_2$ (Ca : PO_4, 1 : 0·60). When the change is almost complete (about 40 days) the product is a "semibasic" phosphate, $6Ca_3(PO_4)_2,Ca(OH)_2$. This product was also obtained starting from the pure basic phosphate. At p_H 4·5—5·9 the same stages were observed, although the time taken was different.

$CaHPO_4$ treated with Tyrode solution at 37° gave the same products as before; the CO_3'' content of the solid was very small until the Ca_3PO_4 stage was passed, and then increased slightly. Pure basic phosphate treated with $NaHCO_3$ or with Tyrode solution removed very little CO_3''. The constituents of bone skeletal substance are semibasic calcium phosphate and a small amount of $CaCO_3$.

J. H. BIRKINSHAW.

Iron in normal and pathological tissues and its biological significance. I. Iron content of the organs of various classes of animals. II. Relationship of the iron content of the organs and growth of animals. III. Effect of the time of year on the iron content of *Bufo vulgaris japonicus*. K. KOJIMA (Nagoya J. Med. Sci., 1930, **5**, 34—38, 49—61, 62—70).—I. In mammals and fishes the Fe content of the spleen is greater, and in birds, reptiles, and amphibians smaller, than that of the liver; the reverse holds for the glutathione content. In birds the lungs are richest in Fe and glutathione.

II. The Fe content of growing honey-bees and silk-worms varies with the cytochrome content; in chick embryos it is maximal later than the glutathione and cytochrome. For chickens the Fe content (mg. per g. dry wt.) is: liver, 0·1806, heart 0·1317, leg muscle 0 0879, brain 0·1444, kidney 0·4920, lung 0·0525, blood 0·1468; for egg-yolk 0·0314; for egg-white 0.

III. The Fe and glycogen contents are greatest in winter and least in spawning time; the reverse holds for glutathione. The liver contains twice as much Fe as the spleen.

CHEMICAL ABSTRACTS.

Occurrence of zinc in the mink. E. REMY and A. MÜLLER (Deut. tierärztl. Woch., 1931, **39**, 17—18; Chem. Zentr., 1931, i, 1465).—The kidneys and lungs are particularly rich in Zn; the Zn content of the liver only occasionally exceeds that of man and rabbits.

A. A. ELDRIDGE.

Determination of the albumin : globulin ratio in cerebrospinal fluid. W. G. EXTON and A. R. ROSE (J. Amer. Med. Assoc., 1931, **96**, 36—37).—For the determination of total protein 1 c.c. each of the fluid and Exton's reagent are mixed and the turbidity is measured in a scopometer. Globulin is salted out with $(NH_4)_2SO_4$, dissolved in water, and reprecipitated with phenol; the turbidity is determined 15—20 min. after precipitation. Albumin may be determined by precipitation with phenol in the filtrate from the salting out of globulin.

CHEMICAL ABSTRACTS.

Precipitation with cerebrospinal fluids. A. M. MALLOY, R. L. KAHN, and L. WESTALL (J. Infect. Dis., 1931, **48**, 203—211).—The colloidal Au and mastic reactions depend on the globulin fraction. The precipitation substances in the globulin solution, or the conditions of this solution, responsible for the Kahn reaction are not identical with those responsible for the colloidal Au and mastic reactions. Heating the globulin for 24 hrs. reduces the sensitivity in the Kahn reaction.

CHEMICAL ABSTRACTS.

Detection of semen [on fabrics] for forensic purposes. J. PELTZER (Chem.-Ztg., 1931, **55**, 70).—The suspected spots are moistened with 3% H_2O_2 solution, which produces a foam loosening the secretion from the fabric. Samples of the froth are squeezed out, scraped off, and examined microscopically for spermatozoa: some may be stained with 2% aq. eosin; other unstained samples, after fixing by rapid passage through a flame, are tested with aq. I–KI for the formation of Florence's crystals.

E. LEWKOWITSCH.

Micro-determination of bile acids in bile. S. NAGAKAWA and H. FUJIKAWA (J. Biochem., Japan, 1930, **12**, 399—410).—The red coloration produced when 0·5 c.c. of an aq. solution of bile salts is heated for 2 min. at 100° with 2 c.c. of H_3PO_4 and 2 drops of 0·6% abs. alcoholic furfuraldehyde is proportional to the concentration of bile salts within the range 5—20 mg. per 100 c.c. The coloration is probably due to cholic acid. A synthetic red solution is used for comparison.

CHEMICAL ABSTRACTS.

Gastric secretion. II. Criteria of acidity. F. HOLLANDER (J. Biol. Chem., 1931, **91**, 481—492; cf. this vol., 757).—Micro-methods of p_H determination with a quinhydrone electrode and of micro-titration, using bromophenol-blue at p_H 3·5, are described. With the pure gastric juice obtained under controlled conditions from stomach-pouch dogs the values obtained by the two methods are in close agreement.

R. K. CALLOW.

Gastric and duodenal contents of normal infants and children. Duodenal enzyme activity

and gastric and duodenal reactions. T. G. KLUMPP and A. V. NEALE (Amer. J. Dis. Children, 1930, **40**, 1215—1229).—In children under 2 yrs. the p_H of the gastric contents is approx. 4·1; at 9—12 yrs. it is 2·8. The histamine test must be employed for true achlorhydria. The p_H of the duodenal contents during fasting is about 7·0. During the first year the amylolytic enzyme activity of the duodenal contents is very low; it then increases abruptly. The lipolytic activity is low through infancy and childhood. The proteolytic activity is high. The gastric acidity and the lipolytic and amylolytic activity are slightly increased after ingestion of the test meal of cream.

CHEMICAL ABSTRACTS.

Determination of pancreatic enzyme in duodenal juice. R. MORACCHINI and A. ALLODI (Arch. Sci. med., 1928, **52**, 29 pp.; Chem. Zentr., 1931, i, 1489).—Lipase is most readily recognised, and indicates changes in the activity of the pancreas. In biliary disease (slight diminution), diabetes, and pancreatic disease, but not in gastric disease, the activity of the gland was diminished.

A. A. ELDRIDGE.

Flow of intestinal juice with milk ingestion. F. POKROVSKY (Acta Univ. Voronegiensis, 1930, **6**, 75—86).—The isolated small intestine of dog secretes juice more abundantly when stimulated by milk than by meat. Hence milk contains a substance which excites the secretion of the glands of the fundus ventriculi. This substance is found in the whey on coagulation, is thermostable, and is extractable by 96% EtOH and by H_2O but not by abs. EtOH. Et_2O extracts are also active. F. O. HOWITT.

Number and nature of proteolytic enzymes of pancreatic juice. E. LEBRETON and F. MOCOROA (Compt. rend., 1931, **192**, 1492—1494).—The juice contains prokinase, inactive proteinase, and an active carboxylopolypeptidase. Aminopolypeptidase and dipeptidase are present only in glycerol extracts of the whole gland. C. C. N. VASS.

Trypsin-like protease in the secretion of the human parotid gland. O. VOSS (Z. physiol. Chem., 1931, **197**, 42—54).—Human parotid secretion contains an enzyme which hydrolyses caseinogen. Yellow viscous and cloudy secretions are the most active. After centrifuging, the activity is found in the clear liquid and not in the sediment, in contrast with mouth saliva. The p_H optimum of the enzyme is 8·0, indicating that it is of tryptic nature.

J. H. BIRKINSHAW.

Permeability of the cells. XV. Permeation of dyes through the salivary glands. H. MATHYS (Biochem. Z., 1931, **234**, 419—440; cf. Jeangros, A., 1928, 1393).—In the saliva of rabbits into which indigo-carmine, fluorescein, or erythrosin has been injected the dye is never to be found even when salivary flow is stimulated by administration of pilocarpine and a sp. diuretic has also been given. Accompanying administration of thyroxine enables very small amounts of fluorescein but not of the other two dyes to pass through the salivary glands. In all cases the dyes pass easily and rapidly into the urine, the dye content of which is increased when thyroxine is given.

W. MCCARTNEY.

Phosphatides of cow's milk. R. SASAKI and E. HIRATSUKA (Proc. Imp. Acad. Tokyo, 1931, **7**, 99—100).—Methods are outlined for the isolation and separation of the phosphatides of dried milk. The fatty acid constituents are saturated, and the phosphatide content of milk containing 3·5% of fat is: myristolaurolecithin 0·003%, and palmitolaurocephalin 0·007%. A. COHEN.

Occurrence of peptidases in milk. A. HEIDUSCHKA and E. KOMM (Z. physiol. Chem., 1931, **196**, 187—194).—In sterile or nearly sterile samples of human, cow's, and goat's milk no peptolytic enzyme was detected. Positive results obtained by other observers are probably due to micro-organisms present in the milk. J. H. BIRKINSHAW.

Effects of high-fat and low-fat palm-kernel and cocoa residues on the fat content of milk. F. HONCAMP, H. HELMS, and P. MALKOMESIUS (Bied. Zentr., 1930, **60A**, 16).—The fat content of milk was not increased by the feeding of palm-kernel cake containing 0·93% of fat, but samples having 7% and 16% of fat produced proportionate increases in milk yield and fat content. Similar results were obtained with cocoa-waste, samples containing 2—3% of fat sufficing to affect the milk yield. With both foodstuffs considerable variations in the effects on individual cows were observed. A. G. POLLARD.

Effect of feeding Menhaden (fish) oil on the secretion of milk and the composition of butter-fat in the dairy cow. J. B. BROWN and T. S. SUTTON (J. Dairy Sci., 1931, **14**, 125—135).—Milk production percentage and total butter-fat in the milk were reduced by feeding Menhaden oil. Resumption of normality on a normal diet was slow with a tendency to drying off. Characteristic highly unsaturated acids of the fish oil passed in small amounts into the butter-fat and the analytical constants of the butter were characteristic of a mixture of butter and oil. Several specimens of normal butter contained unsaturated acid (up to 0·3%) similar to arachidonic acid.

A. G. POLLARD.

Optimum conditions for the precipitation of casein from human and from cow's milk. C. C. WANG and A. A. WOOD (Amer. J. Dis. Children, 1930, **40**, 787—790).—Fat-free human milk (100 c.c.) is treated with rennin (33 mg.) suspended in N-HCl (1 c.c.) for 15—30 min. at 38°, centrifuged, and filtered. Max. precipitation occurs at p_H 4·97 and represents 50% of the milk-N. Max. precipitation of cow's milk by lactic acid occurs at p_H 4·61 and represents 80% of the total N; max. precipitation by rennin and HCl occurs at p_H 6·53, and represents 73% of the total N.

CHEMICAL ABSTRACTS.

Serological studies on the proteins found in caseinogen. D. C. CARPENTER and G. J. HUCKER (J. Infect. Dis., 1930, **47**, 435—442).—Extraction with 70% EtOH and fractionation with $K_2C_2O_4$ led to the separation of proteins having mol. wts. 98,000, 188,000, and 375,000, respectively. Osborne and Wakeman's EtOH-sol. protein is not identical with that of mol. wt. 375,000. CHEMICAL ABSTRACTS.

Peroxidase reaction. XXVIII. Sensitive peroxidase reagent for human milk. XXIX, XXX. Determination of human milk-peroxidase.

XXXI. Approximate determination of milk-peroxidase. XXXV. Micro-determination of peroxide by means of milk-peroxidase. Preservation of milk-peroxidase. T. ARAKAWA (Tohoku J. Exp. Med., 1930, **16**, 83—89, 90—96, 97—106, 107—111, 232—235).—The composition and use of benzidine and guaiacol reagents are specified with reference to qual. and quant. tests. Milk-peroxidase can be preserved indefinitely by shaking 100 c.c. of milk with 10 c.c. of $CHCl_3$, 10 c.c. of 95% EtOH, and 1 c.c. of guaiacol; 0·5 c.c. of glacial AcOH is added and the mixture filtered after 24 hrs.

CHEMICAL ABSTRACTS.

Agglutinin, complement, and chemical composition of the colostrum of the cow. M. SATO, K. OGURA, and H. IKEJIMA (J. Dairy Sci., 1931, **14**, 156—172).—Wide fluctuations in $[H^{\cdot}]$, colour, coagulation, total and relative proportion of proteins, lactose and fat contents occur in colostra from different cows. The total ash and density are fairly constant.

A. G. POLLARD.

Lysolecithin formed by snake venom. M. IWATA (Proc. Imp. Acad. Tokyo, 1931, **7**, 96—98).—The lysolecithin formed by the action of Formosan cobra venom (0·1 g.) on egg-yolks (300) in phosphate solution is extracted with 95% EtOH and isolated as a $CdCl_2$ complex. After removal of Cd, 22 g. of lysolecithin are obtained, which, on recrystallisation from pyridine, is identical with lysolecithin from polished rice (A., 1930, 1324), and possesses the same physiological properties. A. COHEN.

Sweat and sweating. A. G. R. WHITEHOUSE (Proc. Roy. Soc., 1931, **B**, **108**, 326—339).—In a subject at rest, the [Cl] of the sweat increases with time, whilst a moderate amount of work is accompanied by a slight rise in [Cl]. A progressive decrease in the proportion of org. matter to ash in sweat is observed as sweating continues. The [Cl] in sweat varies in different individuals. B. LEVIN.

Glomerular elimination of urea in frogs. A. M. WALKER and K. A. ELSOM (J. Biol. Chem., 1931, **91**, 593—616).—By an adaptation of the hypobromite method, in which the reaction is carried out in capillary tubes, as little as 0·000003 mg. of urea in 0·05 cu. mm. of fluid may be determined with an error usually less than 10%. The urea content of the glomerular urine of frogs, determined by this method, and the urea content of the plasma, determined by the urease method, are identical. This confirms the assumption that the glomerular function is filtration. The concentration of urea in the bladder is accounted for by resorption of water from the renal tubule, and the assumption of tubular secretion is unnecessary.

R. K. CALLOW.

Determination of protein in urine. P. HORKHEIMER (Pharm. Ztg., 1931, **76**, 668—669).—The use of albuminometers (Esbach or Aufrecht) results in low values. The "ring" test of Heller is better, but gives values approx. 15% too low. The method recommended is precipitation of the protein by AcOH–AcONa mixture at 100°, washing the ppt. with H_2O, EtOH, and Et_2O, drying, and weighing; for greater accuracy the wt. of the residue on ashing is subtracted. F. O. HOWITT.

Urinary pigments. VIII. Approximate determination of porphyrin in urine, fæces, and bile. M. WEISS (Biochem. Z., 1931, **233**, 354—360).—A method by which the porphyrins of urine, fæces, and bile which are sol. in amyl alcohol can be spectrometrically determined is described. The material is mixed with AcOH and the mixture extracted with amyl alcohol. From the amyl alcohol solution the porphyrins are extracted with 30% H_3PO_4. In some cases coproporphyrins and protoporphyrins can be separately determined. These are found together in fæces, but only coproporphyrin has been found in bile. It is not possible to distinguish spectroscopically between coproporphyrins I and III.

W. MCCARTNEY.

Methylene-blue, a sensitive reagent for the detection of bilirubin. K. FRANKE (Med. Klinik, 1931, **27**, 94—96; Chem. Zentr., 1931, i, 1489).—The bilirubin content of urine (5 c.c.) is determined by the change in colour from green to blue; 2 drops correspond with 1 mg. of bilirubin. A. A. ELDRIDGE.

Detection of bilirubin in urine. G. HUNTER (Can. Med. Assoc. J., 1930, **23**, 823—824).—Urine (5 c.c.) is mixed and centrifuged with 10% $BaCl_2$ solution (2 c.c.), the ppt. being washed and centrifuged with a few c.c. of H_2O. Diazo-reagent (0·5 c.c.) is added, the ppt. is stirred, and then 96% EtOH (2 c.c.) and 6% $Na_2HPO_4,12H_2O$ solution (0·3 c.c.) are added. If bilirubin is present the same colour as is obtained with icteric serum is produced. Alkaline urine is slightly acidified with AcOH. With highly pigmented urine precipitation with $BaCl_2$ is followed by stirring with 96% EtOH (2 c.c.) to which has been added 10% H_3PO_4 (1 drop); after centrifuging, the liquid is transferred to a second tube with H_2O (4 c.c.), 10% $(NH_4)_2SO_4$ solution (2 drops) and $BaCl_2$ solution (2 c.c.) being added to reppt. the bilirubin. The above procedure is then followed. CHEMICAL ABSTRACTS.

Approximate determination of urobilin in urine by the spectroscopic method. E. ADLERCREUTZ (Acta Med. Scand., 1929, **34**, Suppl., 369—374; Chem. Zentr., 1931, i, 1489).—The spectroscopic method, compared with Adler's method, gives low values, but suffices for clinical purposes. The urine (3 c.c.), if not acid, is acidified with HCl, treated with I to convert urobilinogen into urobilin, and examined spectroscopically. A. A. ELDRIDGE.

Micro-determination of lead in urine. M. SETTIMJ (Annali Chim. Appl., 1931, **13**, 129—137).—Urine (1 litre) is evaporated to dryness, the residue is heated just to redness in a muffle furnace for 2 hr., treated with 3—5 c.c. Pb-free HNO_3, and the vol. made up to 50 or 100 c.c., warmed to boiling, and filtered through an ashless filter. The excess of acid is removed by treatment with 20% AcONa solution until a cloudiness appears, which is removed by a drop of dil. HNO_3. The solution is treated with H_2S, a cloudiness indicating 0·2 mg. of Pb; if the Pb is present in the colloidal state it is adsorbed by 0·1—0·3 g. of animal charcoal. The charcoal is collected and boiled with 2—3 c.c. HNO_3 and the Pb precipitated from this extract by $(NH_4)_2S$. The ppt. is dissolved in dil. HNO_3 and the solution treated with 20% Na_2SO_3 solution. Pb is precipitated as a white

substance insol. in AcOH, in which the corresponding salts of Bi and Cu are sol. C. C. N. VASS.

Liver extract, liver ash, and iron in the treatment of anæmia. C. S. KEEFER, K. K. HUANG, and C. S. YANG (J. Clin. Invest., 1930, **9**, 533—534).—With liver extract increased hæmoglobin regeneration was shown in anæmias; the effect was increased in some cases by Fe, particularly as $FeCO_3$. Liver ash (∼300 g. of liver daily) had little effect. CHEMICAL ABSTRACTS.

Average daily elimination of urobilinogen in health and in disease, with special reference to pernicious anæmia. C. J. WATSON (Arch. Int. Med., 1931, **47**, 698—726).—An aliquot part of a 48-hr. specimen of the fæces or urine is titurated with dil. aq. NaOH and the extract reduced with $FeSO_4$ under diminished pressure. If the absorption band of urobilin persists after 1 hr., reduction is continued with Na–Hg. The filtrate is acidified with 20% AcOH and extracted with Et_2O. The extract is treated with a saturated ethereal solution of *p*-dimethylaminobenzaldehyde, a few drops of conc. HCl, and a saturated solution of AcONa. The red colour is matched with 1 c.c. of 0·05% EtOH solution of phenolphthalein and 5 c.c. of saturated aq. Na_2CO_3 in 100 c.c. of H_2O; this solution has a colour equiv. to that given by 0·4 mg. of mesobilirubinogen. The upper limit for normal males is 250 mg. of urobilinogen *per diem*, for females 175 mg. These values are reduced in secondary anæmia and greatly increased in pernicious anæmia. C. C. N. VASS.

Serum- and plasma-bilirubin. M. JACOBI, R. FINKELSTEIN, and R. KURLEN (Arch. Int. Med., 1931, **47**, 759—763).—Plasma instead of serum may be used in the determination of bilirubin. C. C. N. VASS.

Proportion of certain constituents in dying heart muscle. L. C. SCOTT (J. Clin. Invest., 1930, **9**, 463—474).—No relation between (human) disease and the H_2O, ash, Ca, Mg, K, or Na content was observed. A high Ca content is not present in arteriosclerosis. CHEMICAL ABSTRACTS.

Fæces of patients with chronic arthritis. R. T. MONROE and F. C. HALL (Arch. Int. Med., 1931, **47**, 764—770).—64% of 142 fæces from 40 arthritic patients gave an acid reaction to litmus; 79% contained an abnormal amount of starch compared with 26·8% of the control group. I-Staining organisms were found in 90% of arthritic cases compared with 22% in the control group. A positive fermentation test was obtained in 82·5% of the arthritic cases compared with 24% in the control group. C. C. N. VASS.

Composition of the "nucleus" of urinary calculi. S. RANGANATHAN (Indian J. Med. Res., 1930, **18**, 613—617).—The nuclei of vesical calculi contain uric acid, urates, and only traces of phosphates; their composition usually, but not necessarily, is parallel with that of the surrounding stone. CHEMICAL ABSTRACTS.

Composition of urinary calculi in rats. S. RANGANATHAN (Indian J. Med. Res., 1930, **18**, 599—613).—Stones rich in Ca develop on a diet rich in Ca; they contain $CaCO_3$ and/or $Ca(OH)_2$, are low in P and N, and contain no uric acid. $MgNH_4PO_4$ stones develop on diets containing no added Ca. CHEMICAL ABSTRACTS.

Induced oxidation of lactic acid and the carcinoma problem. W. P. JORISSEN (Chem. Weekblad, 1931, **28**, 337).—In presence of Na_2SO_3, buffered with phosphate to p_H 6·8, lactic acid undergoes induced oxidation by air, CO_2 being produced. A solution of P in castor oil also acts an inductor. H. F. GILLBE.

Phosphorus metabolism. II. Distribution of phosphorus in normal and cancer blood. G. E. YOUNGBURG and M. V. YOUNGBURG (J. Lab. Clin. Med., 1930, **16**, 253—259).—In blood of cancer patients the ester-P of the corpuscles is increased 20·5%, the lipin-P is increased 17·2%, and the inorg. P is decreased 15·6%. CHEMICAL ABSTRACTS.

Carcinogenetic agent of the Rous chicken-sarcoma. E. MASCHMANN and B. ALBRECHT (Z. physiol. Chem., 1931, **196**, 241—275).—The tumours are extracted with physiological salt solution in presence of a little PhMe, the extract is freed from suspended matter by filtration, and, preserved under PhMe at 0°, it maintains its carcinogenetic activity for 10 days. Consistent results are not obtained with sarcoma dried over P_2O_5 in a vac. or by Me_2CO and Et_2O; in the majority of cases the extracts are inactive. The crude extract has 6·5—7·2, and gives the biuret, tryptophan, ninhydrin, and Millon's reactions. Evaporation or distillation under reduced pressure gives a dry prep. which maintains its activity for several months; precipitation with EtOH or $COMe_2$ destroys the activity, but addition of AcOH to p_H 4·6 yields an active ppt., and does not destroy the residual activity of the solution. A glycerol extract, prepared similarly to the aq. extract, may be preserved at 0° for 30 days. The active principle in aq. solution does not diffuse through animal membranes. It is adsorbed by $Al(OH)_3$, $Fe(OH)_3$, and kaolin at p_H 6 without loss of activity, and may be re-extracted by alkaline phosphate solutions or by very dil. aq. NH_3. H. A. PIGGOTT.

Human body-fluids. II. Ovarian cyst liquid. O. FLOSSNER (Z. Biol., 1931, **91**, 291—296).—The fluid from a multilobular cyst was chocolate-coloured and contained mucin (0·2%), pseudomucin (0·06%), a small quantity of purine bases, arginine, formic, propionic, and lactic acids. C. C. N. VASS.

Alkalinity of the blood in eczema. B. S. BIKKENIN and N. N. YASNITSKY (Kazan. Med. J., 1930, **26**, 703—708).—The p_H of the urine was normal; that of the blood was 0·1—0·5 above the average value. CHEMICAL ABSTRACTS.

Epilepsy. XI. Calcium content of the blood and cerebrospinal fluid. W. G. LENNOX and M. B. ALLEN (Arch. Neurol. Psych., 1930, **24**, 1199—1205).—Average concentrations and cerebrospinal fluid : serum ratios were normal, but the values were widely distributed, and the cerebrospinal fluid values tended to be low. CHEMICAL ABSTRACTS.

Ossification. I. Callus formation and calcification. I. N. KUGELMASS and R. N. BERG (Amer. J. Dis. Children, 1931, **41**, 236—248).—Union of bone

fractures, a local process, may be retarded by local injection of an alkaline solution of trypsin or accelerated by that of tissue-fibrinogen. The local production of fibrous tissue is not affected by high-protein diet. During bone repair the blood-Ca is higher and the -phosphate lower. CHEMICAL ABSTRACTS.

Carbohydrate metabolism in hypertension. M. WISHNOFSKY and C. S. BYRON (Arch. Int. Med., 1931, **47**, 790—798).—In 6 of the 10 cases investigated the fasting blood-sugar was higher than the normal, and all showed high blood-sugar curves on ingestion of dextrose. The R.Q. curves were normal in 9 subjects. C. C. N. VASS.

Influence of di-iodotyrosine on hyperthyreotic metabolism. I. ABELIN (Biochem. Z., 1931, **233**, 483—485).—Administration of di-iodotyrosine to rats restricts development of hyperthyroidism or, if toxic symptoms of the disease have appeared, moderates them and retards the loss of power of the liver to produce glycogen. Hence a correlation exists between the actions of di-iodotyrosine and thyroxine. W. MCCARTNEY.

Iron and copper in various tissues in acute myeloid leucæmia. K. KOJIMA and S. KOSAKA (Nagoya J. Med. Sci., 1930, **5**, 71—74).—The spleen was richest in Fe, and the renal cortex and brain contained more Fe than the marrow. The liver was richest in Cu, and the cerebral cortex contained nearly 3 times as much Cu as the marrow. CHEMICAL ABSTRACTS.

Chloræmia in malaria patients. S. MANCA (Arch. Farm. sperim., 1931, **52**, 67—72).—Blood-chloride decreases markedly during attacks of fever and slightly during sweating, but is normal at other times. Most elimination of chloride occurs by way of the kidney, but perspiration and fæces also contribute. R. K. CALLOW.

Reducing substances in nephritic urine. A. HILLER (J. Biol. Chem., 1931, **91**, 735—744).—The fermentable reducing substance in the urine of two patients with nephritis is dextrose. R. K. CALLOW.

Alkalosis of vomiting and the acidosis of advanced renal disease. T. G. H. DRAKE, P. MARSH, and J. L. GAMBLE (Amer. J. Dis. Children, 1930, **40**, 705—717).—Cl′ lost by vomiting can be restored by intravenous injection of physiological NaCl solution. Except in advanced impairment of renal control, lowered concentration of HCO_3' associated with nephritis can be corrected by intravenous injection of $NaHCO_3$. CHEMICAL ABSTRACTS.

Inorganic blood chemistry in the osteochondritides. J. BUCHMAN and I. F. GITTLEMAN (Amer. J. Dis. Children, 1930, **40**, 1250—1256).—The serum-Ca, Na, K, Mg, and inorg. P are normal. CHEMICAL ABSTRACTS.

Serum-calcium and plasma-cholesterol in health and disease ; blood chemistry in osteomalacia. T. A. HUGHES, D. L. SHRIVASTAVA, P. N. SAHAI, and K. S. MALIK (Indian J. Med. Res., 1930, **18**, 517—526).—The serum-Ca of inhabitants of the Punjab is higher than that of inhabitants of temperate climates. Oral administration of vitamin-*D* or -*A* caused a rise in serum-Ca in osteomalacia, but indefinite changes in serum-P or plasma-cholesterol. CHEMICAL ABSTRACTS.

Pentosuria in children. A. E. FISCHER and M. REINER (Amer. J. Dis. Children, 1930, **40**, 1193—1207).—Pentosuria in children is not associated with an increased amount of non-fermentable reducing substances in the blood or with changes in tolerance for dextrose. It results from a metabolic defect, and not from an increased permeability of the kidney for pentoses. CHEMICAL ABSTRACTS.

Blood-lipins in splenectomised animals. S. MARINO (Arch. Farm. sperim., 1931, **52**, 73—100).—Determinations of lipins in blood from the femoral artery of dogs at various periods after splenectomy show that the following changes occur in the first few days, during the next 1—2 months, and finally, respectively: cholesterol, fall, rise, normal; total fatty acids, rise, irregular, normal; phosphatides, rise, irregular, below normal; non-phosphatic acids, rise, fall, above normal; phospholipins, rise, fall, normal. The spleen does not appear to produce cholesterol, but acts as a store. When it is removed other organs take over this function. R. K. CALLOW.

Precipitation test for syphilis. E. WEISS (J. Infect. Dis., 1930, **47**, 355—358).—The prep. of an improved antigen is described. CHEMICAL ABSTRACTS.

Gallium: therapeutic properties in experimental syphilis and trypanosomiasis. C. LEVADITI, J. BARDET, A. TCHAKIRIAN, and A. VAISMAN (Compt. rend., 1931, **192**, 1142—1143).—Ga tartrate in doses of 0·03—0·045 g. per kg. orally or 0·15 g. per kg. intravenously exerts a curative action after 4 days on syphilitic rabbits. In the mouse, guinea-pig, and the monkey Ga tartrate acts as a protective and curative agent against trypanosomiasis. C. C. N. VASS.

Acetone substances in normal pregnancy and in the toxæmias of pregnancy. H. J. STANDER and J. F. CADDEN (Bull. Johns Hopkins Hosp., 1930, **47**, 382—390).—The free $COMe_2$, acetoacetic acid, and β-hydroxybutyric acid in the blood of normal, non-pregnant women corresponded with 11—18 (average 15·8) mg. $COMe_2$ per litre (corr. for lactic acid); for normal pregnant women the values were 11—24 (16·6) mg., in pregnancy with nephritis 8·6—48·8 mg., and in eclampsia 50·2 mg. CHEMICAL ABSTRACTS.

Resistance and blood-sugar of animals infected with *Trypanosoma evansi*. M. A. TUBANGUI and L. M. YUTUC (Philippine J. Sci., 1931, **45**, 93—107).—No evidence was obtained in rats, guinea-pigs, dogs, or horses infected with *T. evansi* of any progressive hypoglycæmia proportional to the number of parasites in the peripheral circulation. In the case of two cats which did show such hypoglycæmia, there was present also a coccidial infection. P. G. MARSHALL.

Creatinuria in tuberculosis. I. J. T. THOMPSON (J. Lab. Clin. Med., 1930, **16**, 5—11).—Creatinuria is often associated with pulmonary tuberculosis. CHEMICAL ABSTRACTS.

Hæmoglobin resistance in pulmonary tuberculosis. S. MANCA (Arch. Farm. sperim., 1931, **52**,

113—120).—The hæmoglobin resistance in cases of pulmonary tuberculosis decreases with increasing severity of the type of disease in the order sclerotic, proliferative, exudative, ulcerative.

R. K. CALLOW.

Relation of life to electricity. III. Stainability and electromotive forces of proteins; influence of water-soluble acids. R. BEUTNER and J. LOZNER (Protoplasma, 1931, **12**, 145—160).—Increasing aq. acidity changes the p.d. of gelatin cells in a negative direction and diminishes basophilic (nuclear) stainability. Cells containing fats or fat solvents as central conductors between two aq. phases show similar effects. A. G. POLLARD.

Oxygen and the central nervous system. M. MITOLO (Atti R. Accad. Lincei, 1930, [vi], **12**, 472—476).—The indispensability of O to the proper function of the central nervous system is explained by its continuous oxidation of metabolic products. This protective effect is exercised, not only while the system is resting, but also during the reflex activity accompanying the action of convulsant poisons (strychnine) and during alcoholic narcosis. T. H. POPE.

Degree of oxidation within the animal body under different conditions. H. KIMURA (J. Biochem., Japan, 1930, **12**, 351—369).—For the determination of the amount of O needed to oxidise the org. substances excreted through the urine the latter is oxidised with H_2SO_4 and HIO_3 during 2 hr. at 180°, and the I liberated by addition of KI to an aliquot portion is determined. N and Cl are also determined. Removal of the thyroid gland causes a diminution in O consumption, but the degree of oxidation is not altered. Feeding thyroid gland increases the amount of oxidation, whilst the degree is subnormal. Adrenalectomy diminishes the N, and the total, metabolism, but the degree of oxidation is not affected.

CHEMICAL ABSTRACTS.

Gaseous metabolism in muscular work after removal of the suprarenal glands in rats. A. VON ARVAY and F. VERZAR (Biochem. Z., 1931, **234**, 186—204).—Rats after removal of the suprarenal glands utilise ingested sugar and the R.Q. is increased as in normal rats. The gaseous metabolism and the R.Q. of normal rats are greatly increased by causing the animals to do work (tread-mill), but are not increased with animals 8 days after removal of the suprarenal glands. The normal reaction is again obtained with these animals about 4 weeks after extirpation of the glands. P. W. CLUTTERBUCK.

Gaseous metabolism of the mechanically perfused stomach. T. C. SHEN, T. G. NI, C. T. LOO, and R. K. S. LIM (Chinese J. Physiol., 1931, **5**, 103—112).—The dog stomach mechanically perfused consumes $0{\cdot}0138 \pm 0{\cdot}0012$ c.c. O_2 per g. per min., in agreement with the result previously found for the viviperfused stomach (cf. A., 1929, 719). Blood consumes approx. $0{\cdot}00025$ c.c. O_2 per c.c. blood per min., but excess O_2 consumption accompanies hæmolysis (cf. Quart. J. Exp. Physiol., 1930, **20**. 213—229).

W. O. KERMACK.

Metabolic rate and respiratory quotient of rats on a fat-deficient diet. L. G. WESSON and G. O. BURR (J. Biol. Chem., 1931, **91**, 525—539).—Determinations have been made on rats suffering from fat-deficiency (A., 1930, 810) and on normal rats. The R.Q. of the diseased rats is in many cases above unity in the first hrs. after carbohydrate feeding, indicating the formation of fat from carbohydrate. Since this self-formed fat does not cure the rat, it evidently does not form linoleic or linolenic acids. The basal and assimilatory metabolic rate in rats showing the early symptoms of the disease was above normal, whilst in the later stages it was normal or subnormal. The relation of thyroid activity to the fat-deficiency disease is discussed. R. K. CALLOW.

Specific dynamic action of foodstuffs. V. Action of foodstuffs on the isolated lung. G. MANSFELD and Z. HORN (Biochem. Z., 1931, **234**, 257—273).—A method is described for determination of the gaseous metabolism of the isolated perfused lung of dogs. Dextrose and lævulose in presence of insulin added to the perfusing blood considerably increased (in 3 or 5 experiments) the O utilisation, whereas neither sugar nor insulin alone has any effect. Addition of glycine did not but of alanine did increase the O utilisation. P. W. CLUTTERBUCK.

Determination of the residual air of the lungs. G. MANSFELD and I. SCHEFF-PFEIFER (Biochem. Z., 1931, **234**, 274—277).—In dogs, the residual air per 100 g. lung varied from 176 to 370 c.c.

P. W. CLUTTERBUCK.

Oxygen consumption of frog muscle in chemical contractures. W. O. FENN (J. Pharm. Exp. Ther., 1931, **42**, 81—97).—The contraction of the frog sartorius brought about by acids, alkalis, hypertonic NaCl, H_2O, isotonic solutions of K_2SO_4, KCl, and KCNS, by $Na_2C_2O_4$ and Na_2SO_4, and by caffeine, quinine, acetylcholine, and nicotine is accompanied by increased O consumption. In these contractions the ratio of the excess O used to the contraction time is greater than, but of the same order of magnitude as, that calc. from the literature for electrical stimulation. The ratio decreases with fall of temp.

W. O. KERMACK.

Lactic acid formation in contractures. A. H. HEGNAUER (J. Pharm. Exp. Ther., 1931, **42**, 99—105).—An increase in the lactic acid content of frog's muscle occurs as the result of contraction produced by acetylcholine or HCl. Muscles poisoned by iodoacetic acid and then placed in a solution containing caffeine or KCl exhibit normal contractions and increases of O consumption, but no increase in lactic acid concentration. W. O. KERMACK.

Formation of lactic acid in muscular contraction. E. LEHNARTZ (Klin. Woch., 1931, **10**, 27—28; Chem. Zentr., 1931, i, 1476).—A considerable proportion of the lactic acid is formed, not during convulsion or tetany, but later. A. A. ELDRIDGE.

Recovery heat in muscular contraction without lactic acid formation. McK. CATTELL, T. P. FENG, W. HARTREE, A. V. HILL, and J. L. PARKINSON (Proc. Roy. Soc., 1931, **B**, **108**, 279—301).—The existence of recovery heat in muscle poisoned with iodoacetic acid has been demonstrated by several different methods. In normal muscle stimulated to extreme exhaustion, the recovery heat has only one fourth its usual value.

B. LEVIN.

Subsequent lactic acid formation in tetanus and on the stimulation of isolated frog's muscle. E. Lehnartz (Z. physiol. Chem., 1931, **197**, 55—89).—In tetanic stimulation of frog's semimembranosus, the increased lactic acid formation persists long after the tetanus and is accompanied by a resynthesis of some of the phosphocreatine hydrolysed during the tetanus. When the intervals between successive stimulations were more prolonged, the subsequent lactic acid formation was increased. After stimulation by successive impulses the resynthesis of phosphocreatine during the pauses was not observed. J. H. Birkinshaw.

Relationship of glycogen to creatine and creatinephosphoric acid in rabbit muscle. T. Masayama and O. Riesser (Biochem. Z., 1931, **234**, 323—340).—The percentage ratio phosphagen · glycogen for the different white and red skeletal muscles is the same although the abs. values differ considerably. Isolated muscles stimulated in oxygenated Ringer's solution lose glycogen and phosphagen in such a way as to maintain the ratio const. Isolated muscle anaerobically loses phosphagen more rapidly than glycogen and the ratio decreases, whilst muscle of fasting animals and especially on treatment with adrenaline loses glycogen more quickly than phosphagen and the ratio increases. Tetrahydro-β-naphthylamine and caffeine cause considerable loss of glycogen but little loss of phosphagen.

P. W. Clutterbuck.

Dynamics of anaerobic muscular contraction. E. Lundsgaard (Biochem. Z., 1931, **233**, 322—343).—Anaerobic muscular contraction, considered as a mechanical process, is discussed in the light of the facts that the energy involved is derived from the degradation of phosphagen and that the energy concerned in the production of lactic acid serves only for the resynthesis of phosphagen. W. McCartney.

Possible significance of *l*-xyloketose (urinary pentose) in normal metabolism. I. Greenwald (J. Biol. Chem., 1931, **91**, 731—734).—After subcutaneous injection of *l*-xyloketose into dogs the urinary excretion of sugar rises only slightly, whilst *d*-xylose causes a large rise. *l*-Xyloketose can, therefore, be metabolised in the body. R. K. Callow.

Pyruvic acid in the metabolism of animal cells. B. Mendel, M. Bauch, and F. Strelitz (Klin. Woch., 1931, **10**, 118—119; Chem. Zentr., 1931, i, 1476).—Under anaerobic conditions pyruvic acid more than doubles the fermentation of body-cells. Sections of Jensen sarcoma form in 1 hr. 4% of their dry wt. of pyruvic acid in saccharine Ringer solution saturated with O_2. Minute quantities of pyruvic acid prevent the inhibitory action of glyceraldehyde on the anaerobic fermentation of Jensen sarcoma. The acid is also present in the serum of mammals.

A. A. Eldridge.

Conversion of fat into carbohydrate. I. Phosphatides as precursors of fat oxidation. H. Jost (Z. physiol. Chem., 1931, **197**, 90—134).—Livers rich in glycogen and low in fat obtained from fasting dogs and livers rich in fat from phloridzinised animals were isolated and perfused. Phosphatide added to the perfusion liquid was readily absorbed, in contrast to that present in blood-corpuscles. H_3PO_4 was readily eliminated from the phosphatide of the fatty liver; this hydrolysis was not observed in the case of the glycogen-rich liver, but addition of phosphatide in the latter case induced an increased O uptake and acetoacetic acid formation, whilst the R.Q. decreased. With the fatty liver ketone formation was not altered, but the O uptake and R.Q. were affected in the same manner as with glycogen liver. The main effect was a large increase in sugar production. The conversion of higher fatty acids into sugar probably takes place by way of intermediate phosphatide formation.

J. H. Birkinshaw.

Fat transfer. E. Wertheimer (Arch. exp. Path. Pharm., 1931, **160**, 177—188).—Section of the spinal cord above the fourth dorsal vertebra has little effect on the rise in blood-sugar of dogs (0·100—0·130 mg. per 100 c.c.) which have received subcutaneously 1·5 g. of dextrose per kg. body-wt. The limiting point at which section of the spinal cord inhibits the fat transfer occurring in phloridzin diabetes, P poisoning, etc. is not very sharp, but such transfer is definitely under nervous control. The fat migration, which is the result of venesection in the rabbit, can be inhibited by section of the thoracic region of the spinal cord, but not by insulin even in large doses. Fat transfer in anæmia or under reduced pressure is not influenced either by insulin or by dextrose, but only in those cases where primary changes in carbohydrate metabolism occur. P. G. Marshall.

Nutritive values of the hardened oils. IV. Nutritive value of hardened coconut oil and some vegetable oils. S. Ueno, Y. Ota, S. Yokoyama, and K. Koizumi (J. Soc. Chem. Ind. Japan, 1931, **34**, 132—133B; cf. A., 1928, 324; B., 1929, 26).—Hardened coconut oil proved inferior to the natural oil in rat-feeding tests: oils hardened at low temps. have the better nutritive value. Xerophthalmia developed in all cases (hardened coconut, soya, and arachis oils). E. Lewkowitsch.

Metabolic action of cholesteryl esters and fats. A. Cruto (Biochim. Terap. sperim., 1930, **17**, 97—108; Chem. Zentr., 1931, i, 1476).—Almond oil, administered parenterally, causes mobilisation of reserve carbohydrate. Addition of cholesteryl esters diminishes this action; the cholesterol content of the blood, liver, and adrenals is increased.

A. A. Eldridge.

Influence of nutrition on the general condition of animals. E. Abderhalden (Biochem. Z., 1931, **234**, 142—169).—The effect of feeding pigeons and rats exclusively on particular diets over a long period of time is investigated. Pigeons are much more resistant to lack of vitamins than rats. Lack of vitamin-*A* caused the greatest, of vitamin-*B* less, and of vitamin-*C* and -*D* least disturbance. When pigeons are fed on white bread, symptoms of *A*- and *B*-avitaminosis are, but on rye-bread are not, obtained; on cow's milk symptoms of *B*-avitaminosis and on milk in the winter months of *A*-, *B*-, *C*-avitaminosis are occasionally obtained; on raw and cooked horse-liver skin diseases result, whilst on a diet of cooked potatoes disturbances generally result in 4—16 months. With pigeons, goat's milk is better than cow's milk when given with polished rice. With

rats, administration of milk-rice frequently results in tumours, of white bread in *A*- and *B*-avitaminosis, of rye bread in occasional cases of keratomalacia, of raw horse-flesh in skin diseases, whilst with bread and milk (the milk was autoclaved for 30 min. at 100°) keratomalacia and *C*-avitaminosis were observed. With scorbutic guinea-pigs, ulcers of the gastro-intestinal tract were repeatedly observed and quickly healed on administration of fruit juices.

P. W. Clutterbuck.

Calculating rations for dairy cows. T. E. Woodward (J. Dairy Sci., 1931, **14**, 173—176).—Rapid methods of calculation giving sufficient accuracy are given. A. G. Pollard.

Skim milk as a feed for dairy cows. C. H. Eckles and E. N. Shultz (J. Dairy Sci., 1931, **14**, 189—197).—In rations for dairy cattle, skim milk is a satisfactory substitute for linseed meal (8 lb. of skim milk=1 lb. of linseed meal) as a protein supplement. A. G. Pollard.

Determination of the apparent digestibility of protein by modified procedures. W. S. Gallup and A. H. Kuhlman (J. Agric. Res., 1931, **42**, 665—669).—In large-animal trials the apparent digestibility of protein may be calc. from determinations of the ratios protein : Fe or protein : SiO_2, both in the feed and in the fæces. Values agree well with those of prior methods. The SiO_2 naturally present in the foods was a better index of the digestibility of the other constituents than was Fe artificially added for the purpose. A. G. Pollard.

Utilisation of milk-protein in feeding with carbohydrate. R. Scholz (Tierernahr., 1930, **1**, 502—538; Chem. Zentr., 1930, ii, 2400).—Feeding of sucking calves with potato parings resulted in a higher increase of body-wt. with no deterioration in the quality of flesh at death; supplementary feeding lessens this increase. L. S. Theobald.

Nutritive value of caseinogen and of albumin autoclaved in alkaline solution at a high temperature. A. Marletta (Biochim. Terap. sperim., 1930, **16**, 297—316; Chem. Zentr., 1931, i, 1471).—Caseinogen or ovalbumin, when autoclaved in alkaline solution, becomes less readily absorbed and digested, and less readily hydrolysed *in vitro* by pancreatic juice. The deficiency is due to chemical or stereochemical change, and not to decomp. of vitamin.

A. A. Eldridge.

Nutritive value of potato protein and of gelatin. D. B. Jones and E. M. Nelson (J. Biol. Chem., 1931, **91**, 705—713).—Young rats failed to grow on a diet in which 9% of potato protein was the sole source of N. Addition of 20% of gelatin, alone, or with cystine (0·2%), tyrosine (2·0%), and tryptophan (0·5%), was ineffective, but 10% of caseinogen or lactalbumin induced normal growth. The latter materials appear to contain some essential factor other than the known amino-acids. R. K. Callow.

Biological value of mixed proteins in omnivorous and vegetarian diets. S. Wan and W. Y. Lee (Chinese J. Physiol., 1931, **5**, 163—179).—The biological value as determined by Mitchell's method (A., 1924, i, 453) of proteins fed to rats is greater when the diet is omnivorous than when it is vegetarian.

W. O. Kermack.

Nutritive value of vegetarian diets from an economic viewpoint. K. H. Lin (Nat. Med. J. China, 1931, **17**, 200—209).—Such diets are cheaper than omnivorous diets for the growth and maintenance of rats. P. G. Marshall.

Proteinogenesis of the small intestine. C. Gautier (Bull. Soc. Chim. biol., 1931, **13**, 395—402).—The proteins of the intestine of the frog which are precipitated by 20% trichloroacetic acid show a marked increase after feeding with a mixed diet which gives no ppt. with the acid. C. C. N. Vass.

Physiological action of mineral waters. I. Influence of Anticolan water on nucleoprotein and nitrogen metabolism. U. Sammartino (Arch. Farm. sperim., 1931, **52**, 121—140).—Drinking the hypotonic waters of the Fiuggi source does not increase but rather diminishes the elimination of uric acid (endogenous and exogenous), decreases the urinary and fæcal N, but increases appreciably the excretion of NH_3. R. K. Callow.

Is the protein utilised in cell metabolism split into amino-acids before conversion into end-products? E. Abderhalden and E. Wertheimer (Z. physiol. Chem., 1931, **198**, 18—24).—Tissue-protein breaks down in the organism with the formation of amino-acids. If no protein, but PhBr, is given with food, mercapturic acid is generally formed.

A. Renfrew.

Tryptophan metabolism. I. Production of kynurenic acid from tryptophan derivatives. C. P. Berg (J. Biol. Chem., 1931, **91**, 513—524).—The excretion of kynurenic acid by rabbits after administration *per os* or subcutaneously of tryptophan has been used to test the ability of the body to split various tryptophan derivatives. Equal amounts of kynurenic acid were excreted in the urine after administering tryptophan or its Et ester hydrochloride. The Ac derivative, on the other hand, yielded only small amounts of kynurenic acid, some deacetylation evidently occurring, whilst the methylene and Bz derivatives yielded no kynurenic acid. The Ac and Bz derivatives were detected in the urine unchanged. R. K. Callow.

Effect of fasting on the creatine and nitrogen content of the body and muscle of the white rat. A. Chanutin and L. D. Shearer (J. Biol. Chem., 1931, **91**, 475—480).—During fasting the percentage of Et_2O extract and total solids in the eviscerated rat decreases, whilst the ash increases. The creatine in dry, fat- and ash-free tissue is const., whilst in fresh tissue, *e.g.*, muscle, it increases slightly. The N content is const. until just before death, when it rises. R. K. Callow.

Production of urea [in the animal organism]. II, III. K. Kase (Biochem. Z., 1931, **233**, 258—270, 271—282).—II. Production of urea takes place in preps. of livers from dogs and rabbits; the amount is increased if amino-acid is added and still more so if amino-acid anhydride or peptide is added. The optimal [H˙] in the first two cases is 5·9. The liver,

but no other organ, contains an enzyme which influences the production of urea from amino-acids but does not convert NH_4 salts into urea.

III. The production of urea in the livers is increased if O_2 is supplied, but is not if defibrinated blood is added. Urea is not produced from added amino-acid by organs other than liver. During the production of urea from amino-acids in the liver the decomp. of the arginine present is not affected. Enzymes other than that assumed to be involved do not share in the process of urea-production. The liver preps. do not convert NH_4 salts into urea.

W. McCartney.

Urea formation in the animal body. III. B. Perfusion experiments. S. Salaskin and J. Krivsky (Z. physiol. Chem., 1931, **196**, 121—139; cf. A., 1930, 1619).—Dog's liver perfused with Ringer–Locke solution alone or with the addition of $(NH_4)_2CO_3$ showed no urea formation. Serum alone or diluted with Ringer–Locke solution produces urea in small amount. Urea is formed when erythrocytes (intact or hæmolysed) or oxyhæmoglobin are added to the perfusion fluid. A sufficient supply of O_2 is necessary for the formation of urea. J. H. Birkinshaw.

Ammonia formation in the isolated frog's heart. J. K. Parnas and P. Ostern (Biochem. Z., 1931, **234**, 307—322).—Further work (cf. this vol., 255) was carried out in order to ascertain the precursor of the NH_3 and the mechanism of its formation. The total adenine content is insufficient to account for the whole of the NH_3 formed. A number of diagrams show the effect of various concentrations of adenine nucleotide on the beating frog's heart. The reaction of heart-muscle to adenine nucleotide consists of at least two processes, one in which the heart becomes able to reassume its normal frequency (in which the nucleotide concentration is unaffected) and a second in which the nucleotide action completely disappears. The latter cannot be wholly accounted for in terms of deamination. P. W. Clutterbuck.

Metabolism of women. V. Components concerned in the cyclic variations in the level of total non-protein-nitrogen in the blood of normal women. S. E. Erikson and R. Okey (J. Biol. Chem., 1931, **91**, 715—722).—An extension of previous work (A., 1926, 973) in which the means of a larger number of observations have been plotted on composite curves which show that, whilst marked individual divergences occur, there is a rise in the total non-protein-N of blood at the onset of menstruation which cannot be accounted for by known constituents. The uric acid content falls 2 days after the onset of menstruation. R. K. Callow.

Metabolism of women during the reproductive cycle. IV. Calcium and phosphorus utilisation in late lactation and during subsequent reproductive rest. E. Donelson, B. Nims, H. A. Hunscher, and I. G. Macy (J. Biol. Chem., 1931, **91**, 675—686; cf. A., 1930, 635).—There was a continued loss of Ca by three women during prolonged, intense lactation in contrast to the resumption of storage observed in immediately preceding periods of lactation of normal type. This loss continued for 12 months after lactation ceased. Storage of P occurred before the end of the lactation period and continued after it. R. K. Callow.

Calcium and phosphorus metabolism in dairy cows. IV. Assimilation of calcium fed as calcium gluconate. W. A. Turner, E. A. Kane, W. S. Hale, and H. G. Wiseman (J. Dairy Sci., 1931, **14**, 268—275).—Supplements of Ca gluconate were of little value in improving the Ca–P balance of cows giving 4—4½ gals. of milk daily. Supplements of limestone gave inconclusive results. A. G. Pollard.

Effect of calcium fluoride and phosphate rock on the calcium retention of young growing pigs. I. J. McClure and H. H. Mitchell (J. Agric. Res., 1931, **42**, 363—373).—Mineral supplements, containing 5 g. Ca daily, derived from $Ca_3(PO_4)_2$ and CaF_2 or rock phosphate, exert a deleterious effect on food consumption and growth of the pigs when the F content reaches 2%. Rock phosphate is more noxious than a mixture of the two first-named salts. It was impossible to demonstrate the effect of F on Ca utilisation during intermittent feeding of fluorides. C. C. N. Vass.

Distribution of lactic acid and calcium in tissue cultures. F. Demuth (Biochem. Z., 1931, **234**, 247—256).—The lactic acid formed by cells grown *in vitro* accumulates in the neighbourhood of the small pieces of culture, the concentration becoming with malignant tissue 15—53 times and with normal heart tissue 3—7 times as great as in the rest of the medium, and by increasing the concentration of Ca, Ca lactate separates in rings.

P. W. Clutterbuck.

Physiological variations in blood-inorganic phosphorus at different age periods. J. K. Bullock (Amer. J. Dis. Children, 1930, **40**, 725—740).—The serum-inorg. P in new-born infants is 4·82 mg. per 100 c.c., increasing to 5·66 mg. at the 7th month, and diminishing to constancy at the 19th or 20th year. Chemical Abstracts.

Resorption of iron. H. Sullmann (Biochem. Z., 1931, **234**, 241—246).—Fe of food, so long as it remains in the ionised form after digestion, can be absorbed in the small intestine as the diffusible $FeH_2(CO_3)_2$. P. W. Clutterbuck.

Sodium chloride and diuresis. H. Hirsch (Arch. exp. Path. Pharm., 1931, **160**, 220—237).—For determination of Na, it is first precipitated in AcOH solution as $NaMg(UO_2)_3(OAc)_6$. The washed and dried ppt. is dissolved in H_2O and a slight excess of a standard solution of KH_2PO_4 added. After removal of uranium phosphate, the excess of P in solution is determined colorimetrically and the Na content deduced. Where serum is used the liquid is first deproteinised with trichloroacetic acid. Na and Cl often show opposite changes in the amounts present in any tissue following diuresis. Both the Na and Cl of rabbits' muscle are lowered by administration of a diuretic, whilst the serum is unaffected in this respect.

P. G. Marshall.

Physiology of glands. XXV. Mode of action of diuretics. L. Asher and H. W. Buchler (Biochem. Z., 1931, **234**, 441—461).—Changes as small as 0·03% (such as may occur under physiological con-

ditions) in the concentration of NaCl in the liquid with which the kidneys (frog) are perfused have a diuretic effect which is not less than that produced by a sp. diuretic. W. McCartney.

Toxicity of "complete salt." H. Zimmermann (Munch. med. Woch., 1931, **78**, 52—55; Chem. Zentr., 1931, i, 1629).—The uncontrolled general use of iodised salt is undesirable, since the repeated administration of small quantities of I may lead to severe disturbances in sensitive individuals. Thymol has a similar effect. A. A. Eldridge.

Mechanism of the action of calcium. W. Heubner (Biochem. Z., 1931, **234**, 221—240).—The toxic action of intravenously injected Ca salts to cats is increased by addition of phosphate. Colloidally dispersed or suspensions of finely-powdered Ca, Fe^{III}, or Ba phosphates and of silicic acid act in the same way as the solution of Ca salt, and it is suggested that the supposed toxic effect of Ca is due not to increase of $Ca^{\cdot\cdot}$ but to the separation of fine particles. P. W. Clutterbuck.

Role of copper in the setting and metamorphosis of the oyster. H. F. Prytherch (Science, 1931, **73**, 429—430).—Cu as metal, carbonate, sulphate, or chloride initiates the setting process and is apparently the sp. element necessary for the attachment, metamorphosis, and survival of the oyster. L. S. Theobald.

Pharmacology of thallium and its use in rodent control. J. C. Munch (U.S. Dept. Agric. Tech. Bull., 1931, No. 238, 28 pp.).—The min. lethal dose of Tl_2SO_4 when fed to rats, or when injected intravenously into rabbits, is 25 mg. per kg. body-wt., death occurring 2—3 days later from respiratory failure. Tl affects the sympathetic nervous system, causing alopecia and muscular and glandular disturbances. The Ca metabolism is affected and rickets results. A. G. Pollard.

Properties of complexes between soaps and heavy metals. M. Renaud (Compt. rend. Soc. Biol., 1930, **105**, 365—367; Chem. Zentr., 1931, i, 1626).—The toxic effect of heavy metal salts, *e.g.*, $HgCl_2$, is markedly diminished (to 25%) by complex formation with soaps, *e.g.*, oleates. The complexes are sol. in the excess of soap, and give no ppt. with KI. A. A. Eldridge.

Chemical toxicological investigations. Schellbach (Chem.-Ztg., 1931, **55**, 456—457).—The distribution of the poison amongst the various tissues of human beings dying from administration of As_2O_3, $K_2C_2O_4$, veronal, and morphine has been determined. F. O. Howitt.

Action of iodoacetic acid on cellular metabolism. H. A. Krebs (Biochem. Z., 1931, **234**, 278—282).—If tissue (grey matter of brain, rat sarcoma, etc.) is suspended in Ringer's solution containing dextrose and 0·0003N-iodoacetic acid is added, both fermentation and respiration cease, whereas if lactate is also added fermentation only is inhibited. P. W. Clutterbuck.

Effect of drugs on the electrostatic charge of the tissues. E. Starkenstein and H. Weden (Biochem. Z., 1931, **234**, 205—220).—The action of atophan (2-phenylquinoline-4-carboxylic acid) and of $CaCl_2$ on the distribution of fluorescein in tissues is investigated. With atophan, the effect is due exclusively to the increased negative charge of the tissues relative to the body-fluids and is quite different from that with $CaCl_2$, which restricts the diffusion of fluorescein as a result of constriction of the vascular system. P. W. Clutterbuck.

Excretion curve of blood-iodine after [intravenous] administration of sodium tetraiodophenolphthalein. H. Eitel and A. Loeser (Klin. Woch., 1931, **10**, 109—111; Chem. Zentr., 1931, i, 1636).—In the healthy dog the amount of I excreted falls continuously. The effect of ligatures is described. A. A. Eldridge.

Uroselectan. A. Binz and C. Rath (Klin. Woch., 1930, **9**, 2297—2298; Chem. Zentr., 1931, i, 1637).—Relative toxicities are recorded for pyrid-2-one-5-arsinic acid, 5-iodo-2-hydroxypyridine (selectan), and Na 5-iodopyrid-2-one-N-acetate (uroselectan); the effect of structure on toxicity is discussed. Uroselectan in aq. solution does not liberate I. When heated with H_2O in a sealed tube at 130° for 30 min., p-hydroxyphenylarsinic acid decomposes (58%), forming H_3AsO_4; with pyrid-2-one-5-arsinic acid only slight decomp. occurs in 8 hrs. at 150°. A. A. Eldridge.

Comparative toxicity of merbaphen and salyrgan. B. I. Johnstone (J. Pharm. Exp. Ther., 1931, **42**, 107—121).—When administered intravenously to rabbits merbaphen (novasurol) is only slightly more toxic than salyrgan. W. O. Kermack.

Toxic principle (andromedotoxin) from Nao-Yang-Hua, *Rhododendron Hunnewellianum*. I. Effect on circulation and respiration. H. P. Chu and G. K. How (Chinese J. Physiol., 1931, **5**, 115—123).—The compound $C_{19}H_{31}O_6$ (A., 1927, 600) agrees in its pharmacological as well as in its chemical properties with andromedotoxin of Hardikar (J. Pharm. Exp. Ther., 1922, **20**, 17—44). W. O. Kermack.

Toxicity of toxicarol, deguelin, and tephrosin using the goldfish as the test animal. W. A. Gersdorff (J. Amer. Chem. Soc., 1931, **53**, 1897—1901).—The toxicities of toxicarol (A., 1930, 967, 1223), deguelin (this vol., 357), and tephrosin (this vol., 491) are determined by the method previously described (A., 1930, 1316) to be 65, 56, and 23%, respectively, of that of rotenone (this vol., 260). H. Burton.

Pollen and pollen extracts. IV. Allergically active constituent in pollen oil. M. B. Moore, H. W. Cromwell, and E. E. Moore (J. Allergy, 1931, **2**, 6—10).—The non-dialysable, anhydrous, EtOH-sol. fractions of pollens possess skin-reacting activity. The active constituent in pollen oil is believed to be identical with one or more of the antigens extracted by aq. solvents. The non-dialysable constituent may be glucosidic. Chemical Abstracts.

Toxic agent of the pollen of *Ambrosia div.* sp. M. Bouillenne and R. Bouillenne (Bull. Acad. roy. Belg., 1931, [v], **17**, 318—338).—"Atopene," the active principle of *Ambrosia*, acts in quantities too

small to be detected chemically. Its activity is destroyed by prolonged heating at 75°, and it is hydrolysed by prolonged treatment with a proteolytic enzyme. It does not appear to be a carbohydrate.

C. W. GIBBY.

Chemotherapy of paludism. Experiments on rice finches. E. FOURNEAU, J. TRÉFOUEL, D. BOVET, and G. BENOIT (Ann. Inst. Pasteur., 1931, **46**, 514—541).—The antimalarial action of chemical compounds may with advantage be tested on the rice finch (*Orizonis orizivora*). Of numerous quinoline derivatives allied to plasmoquin, 6-methoxy-8-γ-diethylaminopropylaminoquinoline gave the most promising results. W. O. KERMACK.

Mechanism of the action of sympathomimetic amines. M. RAYMOND-HAMET (Compt. rend., 1931, **192**, 1291—1294).—When the nicotine-like effect of NHPhEt and tyramine on the plain muscle of the small intestine *in situ* is abolished by sparteine, then the adrenaline-like action of these amines can be demonstrated. C. C. N. VASS.

The hydroxyephedrines. O. SCHAUMANN (Arch. exp. Path. Pharm., 1931, **160**, 127—176).—Of the three monohydroxyephedrines, the *m*-isomeride exerts the greatest effect on the capillaries of the isolated cat's heart and on the blood-pressure and the *o*-isomeride the least, the former resembling adrenaline and the latter ephedrine. In their action on the rabbit's uterus the *o*- and *p*-isomerides cannot be distinguished from ephedrine, whilst the *m*-isomeride is 15 times as active. All three arrest intestinal peristalsis to a similar degree in a concentration of 1 : 5000. In less than the toxic doses neither they nor ephedrine affect the blood-sugar of starved rabbits. *l*-Ephedrine in most cases has double the activity of its racemate, whilst, as regards the effect on the isolated rabbit's uterus, the *l*-hydroxyephedrines are 1·6 times as active as their racemates and are less toxic than ephedrine.

Dihydroxyephedrine (β-methyladrenaline) has an effect on the capillary circulation similar to that of ephedrine. The lowering of blood-pressure which it produces is greatly intensified by previous injection of ergotamine, whilst it is reduced by cocaine; the opposite obtains when these two drugs are injected prior to the administration of adrenaline. It has 50 times as great an effect on the rabbit's uterus as adrenaline, but only one fifth of its effect on the gut. Its toxicity does not distinguish it from related compounds. The contraction of the capillaries caused by dihydroxy*nor*ephedrine is more marked than that produced by the methylamino-compound (β-methyladrenaline). Amongst all these related compounds there is a striking parallel between the action on the heart and the oxidisability, the extremely active dihydroxyephedrine being the most readily oxidised.

P. G. MARSHALL.

Pharmacological actions of harmol. J. A. GUNN and R. C. MACKEITH (Quart. J. Pharm., 1931, **4**, 33—51).—Harmol is less toxic for mammals and protozoa than harmine, but more toxic for frogs. They differ particularly in their action on the central nervous system. The effect of the exchange of the OMe group in harmine by OH in harmol is thus similar to that observed in harmaline and harmalol (A., 1930, 1315). R. K. CALLOW.

Alkaloids of gelsemium. I. Gelsemine and gelsemicine. T. Q. CHOU. **Physiological properties.** K. K. CHEN, C. PAK, and H. C. HOU (Chinese J. Physiol., 1931, **5**, 131—139).—From the rhizome and roots of American gelsemium, gelsemine, $C_{20}H_{22}O_2N_2$, m. p. 178°, $[\alpha]_D^{24}$ +10° in 1% $CHCl_3$ solution, inactive in EtOH, and *gelsemicine*, $C_{20}H_{25}O_4N_2$, m. p. 171°, $[\alpha]_D^{24}$ −140° in 1% EtOH solution, have been isolated and examined pharmacologically. W. O. KERMACK.

Relative activity of ergotoxine and ergotamine. E. LOZINSKI, G. W. HOLDEN, and G. R. DIVER (J. Pharm. Exp. Ther., 1931, **42**, 123—131).—Experiments by the method of Broom and Clark (J. Pharm. Exp. Ther., 1923, **22**, 59) and colorimetric observations by the method of Smith (A., 1930, 1471) on ergotoxine ethanesulphonate, ergotoxine ditartrate, ergotamine methanesulphonate, and ergotamine tartrate indicate that ergotoxine has a biological activity of approx. 1·66 times that of ergotamine, whilst ergotamine is more chromogenic than ergotoxine.

W. O. KERMACK.

Stimulation of spermatozoa by drugs. J. R. BAKER (Nature, 1931, **127**, 708).—Strychnine and brucine hydrochlorides and chloral hydrate stimulated the activity of guinea-pig sperms which had fallen below the normal. L. S. THEOBALD.

Relation between structure and action of morphine and its derivatives. R. ZIFFERER (Pharm. Presse, 1931, 1—2; Chem. Zentr., 1931, i, 1637).—A discussion. A. A. ELDRIDGE.

Relationship between vomiting-, blood-sugar-, and uric acid-regulating centres from a pharmacological viewpoint. II. Influence of emetics on the excretion of uric acid. M. MUN (Folia Pharmacol. Japon., 1931, **11**, 359—369).—Compared with morphine, *apo*morphine, emetine, antimonial wine, $CuSO_4$, and erycon increase the excretion of uric acid. Na salicylate and antipyrin lower the blood-sugar and increase the formation of uric acid.

CHEMICAL ABSTRACTS.

Correction concerning the hypoglycæmic action of *p*-aminophenylguanidine hydriodide. T. B. PARKS and C. E. BRAUN (J. Biol. Chem., 1931, **91**, 629—632).—Hypoglycæmic activity previously observed (this vol., 82) with a discoloured specimen of *p*-aminophenylguanidine hydriodide is not observed with colourless specimens of the hydriodide, hydrochloride, or sulphate. No active fraction can be separated by crystallisation, nor does discoloration by deliberate oxidation evoke activity.

R. K. CALLOW.

Hypoglycæmic properties of white snakeroot (*Eupatorium urticaefolium*). G. F. CARTLAND, F. W. HEYL, and E. F. NEUPERT (J. Amer. Pharm. Assoc., 1931, **20**, 448—453).—White snakeroot on extraction with 70% EtOH yields a principle which, when administered orally, exerts a very slight hypoglycæmic effect on alimentary hyperglycæmia in dogs E. H. SHARPLES.

Hypoglycæmic action of the bulbs of *Allium cepa*, L. J. Laurin (Compt. rend., 1931, **192**, 1289—1291).—Extracts of the bulbs retain their hypoglycæmic action on starving rabbits in the absence of fats and ether-sol. oils or after removal of the glucosides by dialysis. The sugars appear, however, to disturb the carbohydrate metabolism.

C. C. N. Vass.

The three major hypoglycæmic syndromes. G. Monasterio (Arch. Farm. sperim., 1931, **52**, 33—52).—The hypoglycæmic symptoms produced by insulin, guanidine, and trypaflavine are similar, and the peculiarities observed with the last two are epiphenomena due partly to their toxicity.

R. K. Callow.

Depressor action of pancreas extract free from insulin. H. Alessandri (Compt. rend. Soc. Biol., 1930, **105**, 247—248; Chem. Zentr., 1931, i, 1779).—Histamine, choline, and peptone do not cause the depressor effect. Extracts of the liver or brain prepared like insulin contain the same depressor substance as pancreas extract. The effects on man of subcutaneous injection resemble those caused by acetylcholine.

A. A. Eldridge.

Reversible coagulation in living tissue. II. W. D. Bancroft and J. E. Rutzler, jun. (Proc. Nat. Acad. Sci., 1931, **17**, 186—192; cf. this vol., 649).—NaCNS is shown to minimise the physiological action of morphine, whilst Na tartrate has a contrary effect. These results are correlated with the peptising properties of the salts in connexion with Bernard's theory of anæsthesia. It is suggested that NaCNS can be used to cure drug addiction. A. A. Levi.

Reversible coagulation in living tissue. III. W. D. Bancroft and G. H. Richter (Proc. Nat. Acad. Sci., 1931, **17**, 294—301).—Two types of insanity, *C* due to over-coagulation, and *D* due to over-peptisation, of brain-colloids are differentiated. Insanity *C* can be ameliorated by administration of NaBr and NaCNS, whilst *D* can be ameliorated by cocaine and Na amytal. Insanity *D* can be induced in normal people by suitable treatment with NaCNS.

P. W. Clutterbuck.

Brain-water movement during anæsthesia. H. G. Barbour (Science, 1931, **73**, 346—347).—Results obtained with rats and rabbits support the view that anæsthesia is associated with dehydration of nerve-cell substance; the ratio H_2O in the medulla/H_2O in the cerebrum is increased. L. S. Theobald.

Disturbance of carbohydrate economy in narcosis. II—V. H. Fuss (Z. ges. exp. Med., 1930, **73**, 506—523, 524—531, 532—539, 540—556; Chem. Zentr., 1931, i, 1637—1638).—During Et_2O-narcosis of the dog hyperglycæmia appears owing to removal of sugar from the liver; it is not affected by administration of O_2. The acetone substances in the blood and urine are unaffected. The alkali reserve is diminished, but not owing to increase in lactic acid. The changes in the fasting, phloridzinised dog are smaller than in the normal animal.

A. A. Eldridge.

Duration of narcosis and narcotic range in relation to the mode of administration of non-specific narcotics. H. Tunger (Arch. exp. Path. Pharm., 1931, **160**, 74—91).—The narcotic actions of amylene hydrate, paraldehyde, avertin, and pernocton have been investigated with reference to depth and duration of anæsthesia. The route of administration affects the activity chiefly through its influence on the rate of absorption of the narcotic.

W. O. Kermack.

Pantocaine, a new local anæsthetic of the novocaine series. R. Fussgänger and O. Schaumann (Arch. exp. Path. Pharm., 1931, **160**, 53—65).—Pantocaine (dimethylaminoethyl *p*-*n*-butylaminobenzoate) is $2\frac{1}{2}$—3 times as toxic as cocaine, but it has more than 10 times the anæsthetic action of the latter when applied to the rabbit's cornea. The toxicity following subcutaneous injection can be largely reduced by means of adrenaline.

W. O. Kermack.

Pharmacology of some compounds allied to chloral and to urethane. K. J. Franklin (J. Pharm. Exp. Ther., 1931, **42**, 1—7).—The compounds $CHCl_2{\cdot}CH_2{\cdot}NH{\cdot}CO_2R$ (R=Me, Et, Pr, and Bu), $CHCl_2{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}NHAc$, and $CCl_3{\cdot}CH(OAc){\cdot}NH{\cdot}CO{\cdot}NHAc$ exert a hypnotic action on mice, rabbits, and frogs resembling that of urethane and chloral hydrate, but tend to be relatively more toxic. W. O. Kermack.

Chloroform poisoning during narcosis. A. Sartori (Chem.-Ztg., 1931, **55**, 222).—Examination of the organs of an 11-months'-old child 13 days after death under $CHCl_3$ failed to reveal whether an overdose had been administered. Hofmann's test showed qualitatively the presence of $CHCl_3$.

E. Lewkowitsch.

Mechanism of action of alcohols and narcotics on the frog's heart ventricle. A. J. Clark (Ar. Int. Pharmacodyn. Ther., 1930, **38**, 101—110; Chem. Zentr., 1931, i, 1477).—The action of aliphatic alcohols increases regularly with increase in the number of C atoms; the relation is not observed from dodecyl alcohol onwards. A. A. Eldridge.

Effect of radiation on the acidity of the blood. H. Q. Woodward and H. R. Downes (Amer. J. Roentgenol. Radium Ther., 1931, **25**, 271—275).—No change was observed in man or rabbits.

Chemical Abstracts.

Metabolic changes produced by irradiation. VII. Changes in catalase content [of blood and organs]. L. Pincussen and F. Tanino (Biochem. Z., 1931, **234**, 478—483).—In rats which have been irradiated with light from a Hg-vapour or Na-vapour lamp the catalase content of the liver decreases, but returns to normal after 90 min., whilst that of the spleen increases. In the blood and heart also alterations in the catalase content occur as a result of the irradiation. The change which occurs in the liver may be due either to increased oxidation or to decreased production of H_2O_2. W. McCartney.

Action of ultra-violet light on some odorous organic substances. S. Michael (Biochem. Z., 1931, **233**, 470—477).—Odours may be termed "light" or "dark" in the same sense as are colours and tones. Natural and artificial ultra-violet light alters the odour of many org. substances. The

extent of the alteration can be determined by measuring the amount of a substance with a " dark " (or " light ") odour which must be added to a compound the " light " (or " dark ") odour of which has been altered by exposure to ultra-violet light, in order to restore the odour to its original " lightness " (or " darkness ") as shown by a control. The odours of aliphatic and mixed aliphatic-aromatic ketones become " lighter " on exposure to ultra-violet light. Those of aromatic ketones, aromatic hydrocarbons, esters of ketonic acids, and lactones become " darker."

W. McCartney.

Influence of *X*-radiation on blood-sugar and -cholesterol equilibrium. E. Liverani (Arch. Farm. sperim., 1931, **52**, 53—66).—Localised *X*-irradiation of rabbits causes an increase of blood-sugar and cholesterol, most immediate and marked when the liver or abdomen is irradiated. It is considered that, as well as the direct action of *X*-rays on the organs regulating sugar and cholesterol, there exists an action on the tissues, either mobilising these substances locally or causing stimuli to be carried to the regulating organs. R. K. Callow.

Delayed lethal effect of radium on tissue cultures *in vitro*. Comparison of continuous and spaced radiation. F. G. Spear (Proc. Roy. Soc., 1931, B, **108**, 190—195).—Tissue cultures are equally affected by γ-rays whether exposed for 6 hr. on 1 day or for 1 hr. on each of 6 consecutive days.

W. O. Kermack.

Factors influencing the activity of peroxidase. R. W. Getchell and J. H. Walton (J. Biol. Chem., 1931, **91**, 419—433).—The activity of peroxidase from horseradish under various conditions has been measured by colorimetric determination of purpurogallin formed in a 12-min. period. Using phosphate and carbonate buffer solutions over the range p_H 3·3—10·6, the activity is maximal at p_H 7·8. Increased concentration of the enzyme causes increased formation of purpurogallin. With increased concentration of pyrogallol the activity reaches a max. and then falls. The effect of a number of inorg. salts has been examined. Some catalyse the oxidation; all reduce the activity of the enzyme in sufficient concentration, and F′, CN′, and S″ ions are markedly toxic. In 50% EtOH the activity is reduced to 0·5% of normal. Certain glucosides and alkaloids are without effect. Nicotine increases the activity. Ultra-violet irradiation causes total inactivation. Bubbling air, O_2, or CO_2 through the solution reduces the activity by 15%. Dialysis causes partial inactivation owing to adsorption by the membrane. The temp. coeff. of the activity is 1·4 and 1·2 in the ranges 0—10° and 10—20°, respectively. R. K. Callow.

Action of ultra-short electromagnetic waves (λ=2—3 m.) on amylase. G. Mezzadroli and E. Vareton (Atti R. Accad. Lincei, 1931, [vi], **12**, 594—598).—If barley is exposed to these waves for 30 min. prior to steeping, it attains its max. saccharifying power during germination 0·5—1 day earlier than the untreated control. If this exposure is continued each day during the germination period, about 2 days may be saved, and in addition the saccharifying power is increased by 15%. T. H. Pope.

Amylolytic fermentation. II. Effect of aliphatic amines and their hydrochlorides on the saccharification of starch by saliva. III. By malt extract. F. Caujolle and J. Molinier (Bull. Sci. pharmacol., 1930, **37**, 351—357; Chem. Zentr., 1931, i, 1303).—Methyl-, ethyl-, allyl-, propyl-, and *iso*amyl-amine inhibit the amylolysis of starch by human saliva, whilst the corresponding hydrochlorides increase it. The amines also inhibit the action of malt extract, whilst the hydrochlorides have no effect. The inhibition does not arise from destruction of the enzyme, since on addition of HCl the activity is regained. A. A. Eldridge.

Specificity of the α-glucosidases. R. Weidenhagen (Biochem. Z., 1931, **233**, 318—321; cf. Karstrom, this vol., 654).—Since Karstrom used very impure enzyme solutions and since experiments with the strain of *B. coli* which he employed confirm the author's results, the findings and conclusions of the former must be rejected. W. McCartney.

Influence of mineral waters or salt solutions on the diastatic action of the pancreas. F. C. Gaisser (Chem.-Ztg., 1931, **55**, 299).—The accelerating effect of various chlorides on the diastatic action is in decreasing order, NaCl, KCl, $MgCl_2$, $CaCl_2$. NaCl is active over a wider range of dilution than the others, but is less active in its optimum concentration (0·5%) than the others are in theirs (KCl 5%, $MgCl_2$ 5%, $CaCl_2$ 0·1%). Na_2SO_4, K_2SO_4, and $MgSO_4$ are inactive. $NaHCO_3$ is active only at approx. 0·5% and weakly so. A solution of several chlorides is much more active than one of a single chloride in the same concentration. The presence of more than one anion further increases the activity. W. J. Boyd.

Production of α-hydroxyglutaric acid by the enzyme of germinated peas. Conversion of methylglyoxalylacetic acid into α-ketoglutaric acid. P. Mayer (Biochem. Z., 1931, **233**, 361—370).—By the action of the enzyme in the cells and juice of germinated peas methylglyoxalylacetic acid is almost quantitatively converted into *d*-α-hydroxyglutaric acid. Aq. Br oxidises the former acid to α-ketoglutaric acid. Like malic acid (A., 1898, ii, 149) *d*- and *l*-hydroxyglutaric acids form complex compounds with uranyl salts. The optical rotations of these compounds are very much greater than are those of the free acids. W. McCartney.

Production and decomposition of methylglyoxal in muscles of cold-blooded animals. E. Sym (Biochem. Z., 1931, **233**, 251—257).—The best yields of methylglyoxal obtained by the action of extracts of pike-muscle on Mg hexosediphosphate are similar to those obtained from the muscle of mammals (cf. Vogt, A., 1929, 1338). The remainder of the hexose liberated is converted into lactic acid.

W. McCartney.

Emulsin. IV. B. Helferich and A. Schneidmuller (Z. physiol. Chem., 1931, **198**, 100—104).—Aq. solutions of emulsin (β-glucosidase val. 7·0) were mixed with various buffer solutions and kept for periods up to 36 days, the β-glucosidase values being determined at intervals. The reaction const. is of the first order. The inactivation velocity of the enzyme

is greatest at the outset. The enzyme is most stable at neutrality. A. RENFREW.

Synthetic action of emulsin on a propyl alcohol solution of dextrose. J. GULLAN (Bull. Soc. Chim. biol., 1931, **13**, 403—416).—At room temp. the greater the concentration of PrOH the more synthesis is effected. Rise in temp. reduces synthesis except in the highest concentrations of the alcohol, in which equilibrium is rapidly attained.

C. C. N. VASS.

Action of strychnine on the configuration-specificity of human liver-esterase. R. AMMON and H. FISCHGOLD (Biochem. Z., 1931, **234**, 54—61).—That strychnine influences the sp. action of human liver-esterase or racemic Me mandelate (A., 1930, 499) is confirmed. Activity–p_s curves for the hydrolysis of Me *l*- and *d*-mandelates with and without strychnine show that the rate of hydrolysis of the *l*-ester is accelerated by strychnine, but that of the *d*-ester is unaffected. Strychnine does not change the affinity of the enzyme for the *l*-ester, but accelerates the decomp. of the enzyme–*l*-ester complex by 1·5 times. Brucine also accelerates the hydrolysis of the racemic ester and influences the specificity of the esterase in the same way, but *l*- and *d*-ψ-cocaine have no such effects. P. W. CLUTTERBUCK.

Enzymic esterification of geometrically isomeric acids. W. FABISCH (Biochem. Z., 1931, **234**, 84—100).—The following pairs of geometrical isomerides, fumaric and maleic, oleic and elaidic, erucic and brassidic acids, were enzymically esterified with alcohols containing 1—6 C atoms, the enzymes used being for the first pair an acetone–ether-dry preparation of pig's kidney, liver, and pancreas and for both the remaining pairs only the pancreatic preparation. In all cases maleic acid was esterified twice as quickly as fumaric and both acids were toxic to the enzyme preparation. The esterification velocity of oleic acid was very slightly greater than that of elaidic acid and those of erucic and brassidic acids were equal. $CaCl_2$ inhibits esterification of oleic, elaidic, and erucic acids with *iso*amyl alcohol.

P. W. CLUTTERBUCK.

Asymmetric hydrolysis of esters by enzymes. VI. Influence of the products of fission on the optical selectivity of an esterase. E. BAMANN and P. LAEVERENZ (Ber., 1931, **64**, [*B*], 897—909; cf. A., 1930, 499).—Addition of EtOH in amounts of the order of those produced by hydrolysis influences the optical selectivity of the decomposition of Et *r*-mandelate by human liver-esterase in such a manner that the reaction of the (+) esters is favoured. Thus, for approx. equal degrees of fission the isolated mandelic acid was found to have $[\alpha]_D$ −10° and +15° in absence and presence of EtOH, respectively. The sense of the optical selectivity remains positive during the hydrolysis, since increase in the concentration of EtOH involved the diminution of the concentration of the ester. It appears probable that EtOH becomes added to the enzyme, giving a complex with different catalytic properties. The alteration of stereochemical selectivity may be due to a change of the affinities of this complex towards the antipodes of the racemate or to the velocities of decomp. of the enzyme–alcohol–(+)-ester or enzyme–alcohol–(−)-ester compound. The latter explanation is regarded as the more probable. H. WREN.

Multiple nature of the enzyme-carrier in the hydrolysis of polypeptides by yeast macerates. II. Method of enabling solutions which hydrolyse polypeptides only to hydrolyse dipeptides. A. FODOR and L. FRANKENTHAL (Biochem. Z., 1931, **233**, 283—295; cf. this vol., 392).—Since the extent of preferential hydrolysis exhibited by liquids prepared as previously described can be altered by treating them with ultra-filtrates from autolysed yeast, it is concluded that the hydrolysis of the dipeptides is due, not to special enzymes (dipeptidases), but to special enzyme-carriers. Indications of the nature and behaviour of these carriers have been obtained.

W. McCARTNEY.

Autolytic activity of animal-tissue proteinases and the effect of heavy metals. K. G. STERN (Biochem. Z., 1931, **234**, 116—138).—The early stages of degradation of dissolved organ-proteins by tissue-proteinases are studied nephelometrically. In extracts of kidney, spleen, and liver only one true proteinase, cathepsin, is found, the p_H optimum of which is 3·2—4·5. Fe^{III} and Mn ions accelerate, Hg^{II}, Cu^{II}, and Se ions inhibit, whilst Zn ions sometimes accelerate and sometimes inhibit the autolysis. The hydrolysis–time curve is at first linear, then rounds off and becomes asymptotic. Milk is clotted by a number of organ extracts. P. W. CLUTTERBUCK.

New substrates for use in detecting proteolytic activity. R. L. JONES (Ind. Eng. Chem. [Anal.], 1931, **3**, 149—151).—Since fibrin is insol. in H_2O the prep. of carmine–fibrin and Congo-red–fibrin depends solely on an adsorption system in which the dye is largely held on the surface of the protein. It is better to use a protein which may be dispersed with the dye and subsequently coagulated, and as examples the prep. of ovalbumin–iodoeosin and ovalbumin–basic fuchsin is described. T. McLACHLAN.

Dyed denatured ovalbumin for testing pepsin and trypsin. C. C. CHEN (Chinese J. Physiol., 1931, **5**, 159—161).—Nile-blue is added to an alkaline solution of ovalbumin which has been allowed to denature by keeping over-night with 0·05*N*-NaOH, and the ppt. which is obtained when the neutralised solution is boiled is collected and washed. The dyed ovalbumin is a convenient substrate for testing the activity of trypsin solutions, the dye being liberated as the protein is dissolved. Ovalbumin dyed with Prussian-blue prepared in a similar way is suitable for testing the activity of pepsin solutions.

W. O. KERMACK.

Enzymic degradation of histidine. E. MISLOWITZER and F. KAUFFMANN (Biochem. Z., 1931, **234**, 101—106).—Further experiments were made to discover the cause of the differences between the authors' results (A., 1930, 1619) and those of Edlbacher (A., 1926, 1171). Low results were again obtained with the authors' sample of histidine and higher results with Edlbacher's samples. In every case in addition to a considerable deamination, some NH_3 resulted from ring opening. P. W. CLUTTERBUCK.

Urease. I. Toxicity of soya-bean urease. II. Protective action of the liver in urease poisoning. III. Urease in gastric mucosa of man and animals. VI. Change in the ammonia content of circulating blood caused by urease. M. RIGONI (Arch. Sci. biol., 1930, **14**, 203—214; **15**, 29—36, 37—46, 342—345; Chem. Zentr., 1931, i, 1461).—I. In rabbits, endovenous administration of urease causes ureolysis with NH_3 poisoning owing to enrichment of the blood and organs with NH_3-N.

II. Administration of non-lethal doses leads to an increase of urease in the blood and liver, but increase in blood-NH_3 is not observed.

III. Human gastric mucosa contains urease in amount depending on the activity of the organ.

IV. Nash and Benedict's is preferred to Folin and Denis' method for the determination of blood-NH_3.

A. A. ELDRIDGE.

Enzymic degradation of chondroitinsulphuric acid. C. NEUBERG and E. HOFMANN (Biochem. Z., 1931, **234**, 345—346).—Sodium chondroitinsulphate is almost quantitatively hydrolysed by a bacterial culture of an organism resembling but not identical with, *B. fluorescens*, the H_2SO_4 being set free and the org. residue utilised. If, however, an alcohol–ether-dry prep. of the bacteria is used, an almost quant. yield of H_2SO_4 and a substance which reduces Fehling's solution strongly are obtained. Similar enzyme preps. are obtained using *B. pyocyaneus* and *B. proteus*. Chondrosulphatase is without action on the PhOH–H_2SO_4 esters, but attacks K myronate.

P. W. CLUTTERBUCK.

Influence of catalytic elements on alcoholic fermentation. M. ROSENBLATT and O. MARCH (Ukrain. Chem. J., 1930, **5**, [Tech.], 127—138).—The inhibitive action on the alcoholic fermentation of dextrose increases in the order 0·01% $MnSO_4 < CoSO_4 < FeSO_4 < Fe_2(SO_4)_3 < NiSO_4$, whilst for 1% solutions the order is $MnSO_4 < CoSO_4 < FeSO_4 < NiSO_4 < Fe_2(SO_4)_3$.

R. TRUSZKOWSKI.

Specific inhibition of alcoholic fermentation of yeast without arresting respiration, Pasteur–Meyerhof reaction, or growth. J. CAYROL and L. GENEVOIS (Compt. rend., 1931, **192**, 1494—1496).—Bromoacetic acid (14 mg. per litre) inhibits fermentation without inhibition of respiration, growth, or the Pasteur–Meyerhof reaction. After contact for a few hrs. in aerobic or anaerobic conditions the reaction is reversible; after longer periods the inhibition is irreversible.

C. C. N. VASS.

Action of poisons on living and dried yeast and on pressed yeast juice. S. KOSTYTSCHEV and V. BERG (Bull. Acad. Sci. U.S.S.R., 1930, 631—659).—Buchner's gravimetric method is unsuitable for the study of the action of poisons on extracellular fermentation, it being impossible to suppress fermentation by living yeast entirely even by excess of toluene. The sensitivity of dried yeast and, especially, that of yeast maceration juice towards poisons is as great as or even greater than that of living yeast. In some cases min. quantities of poison, particularly Et_2O, $CHCl_3$, or strychnine, exert a stimulating effect on so-called enzymic fermentation.

T. H. POPE.

Components of activator-*Z*. H. VON EULER and T. PHILIPSON (Z. physiol. Chem., 1931, **198**, 1—8).—Bottom yeast is saturated with Z_1, that part of activator-*Z* precipitated by $Fe(OH)_3$ from autolysed yeast, and is therefore only activated by Z_2, that part of *Z* remaining in the filtrate after removal of Z_1. Top yeast requires Z_1 and Z_2 for complete activation. The *Z*-activity of Swedish (Pilsner) beer is about 10% of that of the dialysate of autolysed yeast, but the beer can restore the original activity of "Fe-filtrate." The beer contains at least twice as much Z_1 as autolysed yeast. The dialysate of conc. beer often contains at least one Z_1-equiv. The activity of the dialysate of autolysed yeast is increased by adding Z_2 in excess. The excess of one component does not influence the fermentation velocity, which is controlled by the component present in least amount. $Pb(OH)_2$ is a poorer adsorbent for Z_1 than is $Fe(OH)_3$. $Zn(OH)_2$ is a good adsorbent. Urine is a good source of activator-*Z*, which is also found in white cabbages and onions.

A. RENFREW.

Origin of energy available for micro-organisms during fermentation of hexoses. C. FROMAGEOT (Compt. rend., 1931, **192**, 1501—1502).—It is suggested that the energy available for micro-organisms, under anaerobic conditions, arises from the transformation of the hexose mol. into methylglyoxal; aldehydes and ketones activate the reaction by means of their availability as H acceptors.

C. C. N. VASS.

Culture media containing urea. IV. A. J. J. VANDE VELDE (Natuurwetensch. Tijds., 1931, **13**, 159—166; cf. A., 1930, 1318).—The influence of urea on the fermentation of milk by various types of bacteria has been studied. *B. lactis acidi* forms acid at first, but its effect is readily masked by that of alkali-forming bacteria, whilst *B. fluorescens liquefaciens* produces first acid and then alkali; in presence of urea and both species alkali alone is formed. The production of acid from lactose by *B. ureæ* is favoured by addition of urea. In mixed cultures the action of *B. lactis acidi* predominates, and if *B. fluorescens liq.* is present its influence predominates over that of *B. ureæ*. Experiments in which the urea is added to the milk before sterilisation show that *B. ureæ* favours the production of acid by *B. fluorescens liq.* and retards that by *B. lactis acidi*. Mixed cultures of lactic acid bacteria and *B. ureæ* act very readily on urea, but *B. fluorescens liq.* does not appear to favour this decomp.

H. F. GILLBE.

Hydrogen-ion concentration of culture media. J. GIBSON (Analyst, 1931, **56**, 312).—[H$^{\cdot}$] of McIntosh and Smart broth is not 7·6, as stated by Patterson and Frederick (cf. B., 1931, 419), but requires adjustment.

T. MCLACHLAN.

Physiology of moulds. II. Chemical composition and culture of moulds. G. E. ROCKWELL and F. O'FLAHERTY (J. Amer. Leather Chem. Assoc., 1931, **26**, 216—222).—*Aspergillus niger* contained (%): H_2O 84·62, salts (ash) 0·64, proteins 3·47, carbohydrates 6·24, fat 0·58, undetermined 4·45. Chlorides, phosphates, carbonates, and sulphates of Mg, Ca, Na, K, and Fe were present in the ash. A higher fat and lower ash were found in *Penicillium* and higher

H_2O, N, and fat contents but a lower ash figure in *Mucorineæ*. The general nutritive requirements of moulds are discussed. 3—25% of the total solids in Czapek's medium were removed as a consequence of mould growths. D. WOODROFFE.

Effect of manganese, copper, and zinc on the growth and metabolism of *Aspergillus flavus* and *Rhizopus nigricans*. J. S. MCHARGUE and R. K. CALFEE (Bot. Gaz., 1931, **91**, 183—193).—The rate and extent of growth of *Aspergillus* cultures were increased by Mn, Cu, and Zn salts, the optimum concentrations of these metals being 2·5, 5·0, and 1·0 p.p.m., respectively. Combinations of optimum concentrations of the respective metals produced qual. additive effects. The assimilation of mineral nutrients was increased by Cu and Zn and diminished by Mn. All three metals increased the fat content of *Aspergillus* and decreased its N content. A. G. POLLARD.

Enzymes and salt ions. II. Invertase of *Penicillium* lacking calcium, magnesium, and phosphate. G. VON DOBY and E. FEHÉR (Z. physiol. Chem., 1931, **196**, 89—107; cf. A., 1930, 1067).—The yield of mycelium of *Penicillium* is considerably depressed by absence of Mg or by reduction of P to 0·001% in the medium. In the absence of phosphate there is no growth; deprivation of Ca has little effect. The course of the reaction curve obtained by limiting the Mg or phosphate is similar to that obtained with the complete medium; the p_H optimum of the invertase remains const. under varied conditions of medium. In absence of Ca or in partial deprivation of phosphate, the effect of sugar concentration on invertase production is normal (rising curve), but absence of Mg or a larger reduction in phosphate has the reverse effect (falling curve), resembling the effect of absence of K. Small differences in the behaviour of the invertase when treated with various anions and cations are attributed to changes in degree of dispersion by ion adsorption. A short dialysis strengthens, longer harms, the invertase. Ions in dil. solution activate invertase dialysed for a short time and inhibit that dialysed for a longer period. Autolysis has a slight activating effect. J. H. BIRKINSHAW.

Discharge of invertase from mycelium of *Penicillium glaucum*. Z. I. KERTESZ (Plant Physiol., 1931, **6**, 249—264).—The invertase content of the mycelium and of the nutrient medium reached a max. after 4 days' growth. The enzyme passed into the medium more readily when the latter was alkaline. The proportion of invertase in the medium at no time exceeded ⅓ that of the whole culture. The invertase content both of mycelium and of the nutrient decreased as the inversion of the sucrose present approached completion. A. G. POLLARD.

Hydrolytic enzymes secreted by *Hymenomycetes*. Degradation of the constituents of the cellular membrane. L. LUTZ (Bull. Soc. Chim. biol., 1931, **13**, 436—457).—The destruction of the beech, *Gleditschia triacanthos*, and sea-pine proceeds through successive stages of hydrolysis. From the products of the action of *Stereum purpureum*, *S. hirsutum*, *Coriolus versicolor*, and *Polyporus pinicola*, xylose, traces of EtOH, $COMe_2$, pentoses, and a sol. and an insol. gum have been isolated. On hydrolysis with 2% H_2SO_4 the insol. gum gave xylose and traces of glycuronic acid, mannose, and lævulose. C. C. N. VASS.

Changes produced in nitrogenous compounds by *Rhizobium meliloti* and *R. japonicum*. G. G. POHLMAN (Soil Sci., 1931, **31**, 385—406).—In culture solutions NH_3 was produced by *R. meliloti* from glycine, *dl*-alanine, *dl*-amino-*n*-butyric acid, asparagine, and urea, and by *R. japonicum* from *dl*-alanine, asparagine, and urea. Both species utilised nitrates without the production of nitrites, which to a small extent were also utilisable. Differences in the changes produced by the two species were observed with glycine, *l*-tyrosine, *dl*-amino-*n*-butyric acid, and urea. In certain cases different strains of the same species produced different effects. A. G. POLLARD.

Bacterial decomposition of nicotine in tobacco. J. BODNAR and L. BARTA (Biochem. Z., 1931, **233**, 311—317).—The putrefactive bacteria which grow in tobacco suspensions during autolysis do not decompose nicotine (cf. Faitelowitz, A., 1930, 1484) and the only volatile base which is produced in appreciable amount during the process is NH_3. The changes which take place in putrefying tobacco are quite different from those which occur during fermentation. W. MCCARTNEY.

Proteolytic bacteria of milk. V. Action of proteolytic bacteria on milk-serum. W. C. FRAZIER and P. RUPP (J. Bact., 1931, **21**, 263—271). —Changes in the N constituents of milk during the growth of proteolytic organisms are recorded. For detection of caseolysis the Br test for tryptophan is more satisfactory than tests for NH_2- or NH_3-N. A. G. POLLARD.

Influence of bacteria on the oxidation–reduction potential of milk. I. Influence of pure cultures of milk organisms. II. Influence of associated cultures of milk organisms. W. C. FRAZIER and E. O. WHITTIER (J. Bact., 1931, **21**, 239—251, 252—262).—I. Changes in E_h of milk produced by pure cultures of bacteria are characteristic for each organism.

II. Corresponding effects of mixed cultures are recorded. A. G. POLLARD.

Decomposition of urea by *Proteus*. A. W. KAY, W. M. GIBBS, A. W. WALKER, and R. E. JUNG (J. Infect. Dis., 1930, **47**, 490—502).—Urea does not meet the N requirement of the organism; the action on urea is therefore incidental to the metabolism of the bacteria. The enzyme responsible for the destruction of urea is endocellular. CHEMICAL ABSTRACTS.

Effect of yeast on ammonia and indole production by bacteria in culture and in fæces suspensions. H. B. PIERCE (J. Bact., 1931, **21**, 225—235).—Addition of yeast cells, alive or dead, to cultures of *B. coli communis* increased the rate of formation of indole and NH_3, and deamination. Yeast destroyed the toxicity of brilliant-green and gentian-violet toward bacteria. Yeast cells probably contain a deaminase. A. G. POLLARD.

Energy consumption of nodule bacteria during nitrogen fixation. F. ALLAM (Z. Pflanz. Düng.,

1931, 20A, 270—301).—Nodule bacteria of soya bean utilised energy sources from the plant. Approx. 15 g. of dry matter were utilised in the fixation of 1 g. of N.
A. G. POLLARD.

Isolation and characterisation of *Nitrosomonas* and *Nitrobacter*. D. H. NELSON (Zentr. Bakt. Par., 1931, 83, II, 280—311).—In enrichment cultures the growth of *Nitrosomonas* and *Nitrobacter* was stimulated by Cu carbonate in the presence of $CaCO_3$. Low concentrations of org. matter retard or prevent the initial growth of *Nitrosomonas*, but additions of dextrose (up to 4%) to active cultures did not check oxidation nor destroy the organisms. The ability of the organisms to utilise a variety of carbonates (Na, K, Li, Pb, Zn, Fe, Mn, Sr, Cd, Ba, Co) alone or in admixture is examined. No NH_2OH or aldehyde was detected in any of the cultures. The ratio of N oxidised to C reduced was 14·3 for *Nitrosomonas* and 76 for *Nitrobacter*. A. G. POLLARD.

Oxidation and reduction relations between substrate and products in the acetone-butyl alcohol fermentation. M. J. JOHNSON, W. H. PETERSON, and E. B. FRED (J. Biol. Chem., 1931, 91, 569—591).—The anaerobic fermentations of dextrose, mannitol, Ca gluconate, and arabinose by *Clostridium acetobutylicum* have been studied in the light of oxidation-reduction balances; in general the relative amounts of oxidised and reduced products are related to the degree of oxidation of the substrate. Mannitol gives much H_2 and BuOH, little $COMe_2$, and almost as much butyric acid as AcOH. Dextrose gives relatively less H_2 and BuOH and more $COMe_2$; the ratio of butyric acid to AcOH is higher. Ca gluconate yields acids to a large extent, owing to the presence of the Ca ion; more $COMe_2$ than BuOH is formed, and the ratio of butyric acid to AcOH is low; the production of H_2, a corollary of acid production, is high. Arabinose gives an "oxidised" type of fermentation. Much $COMe_2$ and little BuOH are formed; the acid produced is largely AcOH; little H_2 is formed. The behaviour of arabinose is a result of the elimination of only 1 mol. of CO_2 per mol., leaving little H available for reduction. The CO_2 evolved is more, however, than corresponds with an initial splitting into two- and three-C compounds, followed by the usual type of fermentation.

Whilst the productions of H_2 and CO_2 are compatible with the mechanisms proposed for the butyl fermentation, the gas production and the oxidation-reduction balance indicate the presence in the dextrose fermentation of an unknown intermediate product, a precursor of CO_2 and H_2.

Measurements of E_h show a rapid fall during the induction period, but a H overvoltage is never developed, except perhaps in the Ca gluconate fermentation. R. K. CALLOW.

***Staphylococcus* bouillon-filtrate vaccines.** M. K. KOMISSAROV (Acta Univ. Voronegiensis, 1930, 6, 54—60).—Commercial multivalent bouillon-filtrates (prepared according to Besredka) had only a negligible action when tested on cultures of hæmolytic *Staphylococci*. F. O. HOWITT.

Diphtheria anatoxin. G. RAMON (Ann. Inst. Pasteur, 1931, 46, 483—513).—The peculiar properties of anatoxin prepared from diphtheria toxin by treatment with CH_2O distinguish this substance from other immunological principles.
W. O. KERMACK.

Growth and toxin production of *Corynebacterium diphtheriæ* in synthetic media. M. E. MAVER (J. Infect. Dis., 1930, 47, 384—398).—Modification of the N-bearing constituents of Braun and Hofmeier's synthetic medium leads to growth and toxin production by the bacteria.
CHEMICAL ABSTRACTS.

Influence of the physical constitution of the soil on the course of microbiological phenomena. A. DEMOLON and G. BARBIER (Soil Research, 1931, 2, 197—200).—The activities of micro-organisms are largely controlled by the moisture content and the rate of translocation of water in soils, their growth being influenced not only by the supply of moisture, but also by the removal by diffusion of metabolic products. Local inequalities in moisture supply within the soil mass serve to explain local variations in the soil p_H and the irregular distribution of nitrates.
A. G. POLLARD.

Carbon cycle in sphagnum, an alder-bush soil, and a garden soil. F. W. MÜLLER (Bot. Archiv., 1931, 32, 38—63).—In highmoor (sphagnum) soils cellulose decomp. is confined to the surface layer and is less rapid than in garden soil. Pentoses and, less rapidly, dextrose are decomposed with the production of acids. Neither org. acids nor their salts are affected. In an acid forest moor soil (alder), bacterial activity is greater, cellulose being decomposed in both upper and lower layers. Wood pentosans, araban, and salts of org. acids (but not the free acids) are rapidly decomposed. Organisms decomp. dextrose are rare in these soils. In garden soils all org. matter (except free acids) is decomposed more rapidly than in either type of moor soil. A. G. POLLARD.

Insect bacteriolysins. V. ZERNOFF (Ann. Inst. Pasteur., 1931, 46, 565—571).—Bacteriolysins appear in the blood of the larvæ of *Galleria mellonella* and *Pyrausta nubilalis* after the injection of heated cultures of various bacteria and to a less marked degree after injection of foreign proteins. W. O. KERMACK.

Carbon metabolism of organisms of the genus *Mycobacterium*. II. Utilisation of organic compounds in a synthetic medium. III. End-products of carbohydrate utilisation as determined in synthetic media cultures. M. H. MERRILL (J. Bact., 1931, 21, 361—374, 375—381).—II. All organisms of this genus can utilise carbohydrates, alcohols, and salts of org. acids as sole sources of C. When org. salts are used the medium first becomes alkaline and later changes towards neutrality. With carbohydrates and EtOH the change is progressively acid.

III. In dextrose media, all the C utilised and not retained by the organism appeared as CO_2. Acidity produced in the media was entirely due to the removal of NH_3. A. G. POLLARD.

Germicidal efficiency of *o*-phenylphenol against *Mycobacterium tuberculosis*. F. W. TILLEY, A. D. MACDONALD, and J. M. SCHAFFER (J. Agric. Res., 1931, 42, 653—656).—Solutions of

o-phenylphenol (0·5%) in coconut-oil soap (1·0%) were effective against *M. tuberculosis*. Alternatively, the phenol may be treated with just sufficient $Ca(OH)_2$ or NaOH to yield the neutral salt. A. G. POLLARD.

Disinfection. II. Manner of death of certain bacteria and yeasts when subjected to mild chemical and physical agents. III. Taking up of iodine by yeast cells. G. KNAYSI and M. GORDON (J. Infect. Dis., 1930, **47**, 303—317, 318—321).—III. The cells of *Saccharomyces cerevisiæ* take up I from aq. solutions according to the adsorption isothermal. Adsorbed $HgCl_2$ may be precipitated as HgS and the high adsorptive power of the membrane indicated. The mechanism of disinfection is closely related to that of dyeing and tanning.
CHEMICAL ABSTRACTS.

Increased bactericidal effect of inorganic compounds in presence of *X*-rays. R. J. NORRIS (Bull. Basic Sci. Res., 1931, **3**, 21—36).—When bacteria are *X*-irradiated in solutions containing NaBr, NaCl, NaI, $BaCl_2$, $HgCl_2$, $UO_2(NO_3)_2$, CsI, or $Th(NO_3)_4$ the resulting lethal action is greater than that of exposure to *X*-rays and salts separately. The synergistic action is independent of permanent chemical decomp. For the salts the action is greatest at the crit. voltage for the ejection of the *K* electrons. A tentative explanation is based on the theory that the toxicity of the ion is related to its potential.
CHEMICAL ABSTRACTS.

Chemotherapy of bacterial infections. III. Specific relation between chemical constitution and kind of bacterial infection. E. L. WALKER, M. A. SWEENEY, and B. L. FREEDLANDER (J. Pharm. Exp. Ther., 1931, **42**, 17—25; cf. A., 1927, 991).—The chemotherapeutic activity in mice suffering from acute experimental infection of various derivatives of PhHgX and $HgPh_2$ containing substituents in the benzene ring depends on the nature of the bacterium producing the infection. This sp. action is influenced not only by the nature but also by the position of the substituents. With particular bacteria certain compounds were more active than metaphen or mercurochrome, but in no instance was the chemotherapeutic index very large. W. O. KERMACK.

Physiology of glands. CXXIV. Mechanism of the action of "thymocrescin." L. ASHER and P. STOTZER (Biochem. Z., 1931, **234**, 1—18).—Thymocrescin solutions (cf. A., 1930, 1615) freed from protein accelerate strongly the growth of young rats. When EtOH is added to the protein-free solution, a ppt. is obtained which possesses the whole of the activity and gives a strong biuret reaction. Thymocrescin is therefore either a polypeptide or is adsorbed on a polypeptide. Thymocrescin accelerates the growth of bone and of glandular, especially sexual, organs.
P. W. CLUTTERBUCK.

Posterior pituitary preparation. C. G. MACARTHUR (Science, 1931, **73**, 448).—Extraction of ox posterior pituitary lobes with various solvents gives a product with an isoelectric point at p_H 5; it contains labile S, is apparently a polypeptide sol. in dil. acid or alkali (unstable), and is precipitated by Cu and Zn salts. Trypsin and strong acids destroy the activity and hydrolyse the substance. L. S. THEOBALD.

Effect of anterior pituitary extract on the chemistry of the liver. E. CRUZ-COKE and J. ALTAMIRANO (Compt. rend. Soc. Biol., 1930, **105**, 241—242; Chem. Zentr., 1931, i, 1777).—Injection of neutral aq. extracts into rabbits increased the H_2O, cholesterol, fatty acid, and lipolytic coeff., and doubled the lipase content, of the liver. A. A. ELDRIDGE.

Effects of growth-promoting and gonad-stimulating principles of the anterior pituitary lobe on basal gaseous metabolism in the rat. M. O. LEE and J. GAGNON (Endocrinol., 1930, **14**, 233—242).—Subcutaneous injection into rats of the gonad-stimulating principle caused no significant change in basal metabolism, but intraperitoneal injection reduced the metabolic rate.
CHEMICAL ABSTRACTS.

Separation of the antagonistic sexual hormones in the extract of the anterior lobe of the pituitary. P. LEPINE (Compt. rend., 1931, **192**, 1127—1129).—At p_H 6·4—6·8 extracts of the pituitary body of the ox cause mutarotation of the follicles in the rabbit, whereas at p_H 7·4—7·8 luteinisation of the follicles occurs. The hormones are partly separated by filtration of the extract at p_H 7·6—8·2 through a Chamberland filter or by extraction with sterilised olive oil after partial deproteinisation.
C. C. N. VASS.

Determination of sexual hormone. I. Sexual hormone in blood. II. Sexual hormone in urine during regular menstrual cycle. III. Sexual hormone in rare menstruation and in amenorrhœa. IV. Sexual hormone in urine and fæces in regular menstrual cycle, in menstrual disturbances, and in hormone therapy. H. SIEBKE (Zentr. Gynakol., 1929, 2450—2462; 1930, 1601—1618, 1618—1630, 1734—1747; Chem. Zentr., 1930, ii, 2396—2397).—I. The hormone content reaches a max. 3 days before menstruation. In circulating blood of normal women during the cycle less than 100 or, at most, 200 mouse-units are present. During the first weeks of metropathia the hormone content of the blood rises.

II. The greatest hormone concentration during the cycles of 9 women was between 50 and 150 mouse-units per litre. L. S. THEOBALD.

Relation between the œstrus-producing hormone and a corpus luteum extract on the growth of the mammary gland. C. W. TURNER and A. H. FRANK (Science, 1931, **73**, 295—296).—Growth characteristic of pregnancy has been produced in rabbits by the combined action of the œstrus-producing and the corpus luteum extracts. L. S. THEOBALD.

Hormonal pregnancy reaction of human and animal urine. Female sexual hormone (folliculin). B. ZONDEK (Klin. Woch., 1930, **9**, 2285—2289; Chem. Zentr., 1931, i, 1304—1305).—The urine of the gravid mare contains 10^5 mouse-units of folliculin per litre. It cannot be extracted directly with C_6H_6 or Et_2O; extraction with Et_2O frequently increases the hormonal activity by removing an inhibitor. The serum contains 800 mouse units per litre. The urine also contains 800 rat units per litre of the follicular ripening hormone, but no luteinising hormone. The pregnancy reaction is carried out by

injecting six 0·05—0·1 c.c. portions of mare's urine into infantile rats within 48 hr. If œstrus appears in only one rat the reaction is positive.

A. A. ELDRIDGE.

Folliculin and clupanodonic acid. E. CRUZ-COKE (Compt. rend. Soc. Biol., 1930, **105**, 251—252; Chem. Zentr., 1931, i, 1776).—Clupanodonic acid, which is chemically similar to folliculin, when administered (0·1—0·01 mg.) to castrated mice, produces œstrus.

A. A. ELDRIDGE.

Preparation of theelol. E. A. DOISY and S. A. THAYER (J. Biol. Chem., 1931, **91**, 641—645).—The estrogenic triol previously reported (Proc. Soc. Exp. Biol. Med., 1930, **28**, 88) is obtained by faintly acidifying the NaOH solution from which theelin has been removed (A., 1930, 1069), warming, and recrystallising the ppt. two or three times from 95% EtOH. The triol is called theelol.

R. S. CAHN.

Bioassay of theelol. J. M. CURTIS and E. A. DOISY (J. Biol. Chem., 1931, **91**, 647—651).—By subcutaneous injection into ovariectomised rats the potency of theelol is found to be 1500—2000 rat units per mg., about half that of theelin. Tested by the production of opening of the vagina of rats 18 days old, theelol, 6000 units per mg., is 6—7 times as active as theelin. Orally administered, the activity of theelol is halved, whilst that of theelin is unchanged.

R. K. CALLOW.

Effect of theelol on the blood-pressure, heart-rate, and respiratory rate. R. MELCHIONNA (J. Biol. Chem., 1931, **91**, 653).—No changes were observed in dogs.

R. K. CALLOW.

Characterisation of theelol. S. A. THAYER, L. LEVIN, and E. A. DOISY (J. Biol. Chem., 1931, **91**, 655—665).—The following data are recorded: $C_{18}H_{24}O_3$, m. p. 273·8° (uncorr., long stem), 281·2° (uncorr., short stem), $[\alpha]_{D}^{25}$ +61° in 95% EtOH; Ac_3 derivative, m. p. 126° (uncorr.), unchanged by distillation at 0·026 mm. (bath 210°), hydrolysed by aq.-alcoholic NaOH to theelol; treatment with Me_2SO_4 and alkali gave a *Me ether*, m. p. 154·8° (uncorr.), unchanged by distillation at 0·02 mm. (bath 220—230°), insol. in alkali, and a faintly yellow distillation *residue*, m. p. 251—252°. Theelol has an activity of 1500 rat units per mg., and is probably closely related to theelin, both containing a double linking and a benzene nucleus.

R. S. CAHN.

Relation between hypocalcæmia and tetany. F. HOLTZ, E. ISEMER, and H. STICHNOTH (Z. physiol. Chem., 1931, **197**, 12—16).—Phosphate given to rabbits *per os* produces no diminution in serum-Ca. A considerable hypocalcæmia is not necessarily followed by tetany. Parathyroid hormone can produce a post-hypercalcæmic hypocalcæmia which may give rise to tetanic convulsions.

J. H. BIRKINSHAW.

Hormonal control of the colloidal osmotic pressure. Colloidal osmotic pressure and diuresis. H. A. OELKERS (Arch. exp. Path. Pharm., 1931, **160**, 9—18; cf. Tada and Nakazawa, A., 1930, 1479).—Administration of "thyreoidin" to animals reduces slightly the concentration of proteins and the colloidal osmotic pressure of the serum. Administration of insulin usually has the opposite effect, whilst injection of "pituglandol" or "hypophysin" is without action in these respects. It appears improbable that diuretics act through their effect on the colloidal osmotic pressure of the serum.

W. O. KERMACK.

Cortico-adrenal hormone. S. W. BRITTON and H. SILVETTE (Science, 1931, **73**, 373—374).—Blood-sugar is increased by administration of the cortico-adrenal extract to normal cats and rats and to man. The action of insulin is practically unaffected and non-protein-N of blood is only slightly altered.

L. S. THEOBALD.

Cortin, the vital hormone of the adrenal cortex. F. A. HARTMAN (Endocrinol., 1930, **14**, 229—232).—Injection of cortin (an extract prepared from the adrenal cortex) into cats permits survival after adrenalectomy or in adrenal insufficiency, the blood-urea being lowered.

CHEMICAL ABSTRACTS.

Antagonism between sulphur and adrenaline. D. CAMPANACCI (Wien. klin. Woch., 1931, **44**, 79—81; Chem. Zentr., 1931, i, 1124).—Injection of a colloidal solution of S in glycerol increases the blood-pressure; the effect is diminished by injection of adrenaline.

A. A. ELDRIDGE.

Relation between insulin and adrenaline in the human organism. B. KUGELMANN (Klin. Woch., 1931, **10**, 59—62; Chem. Zentr., 1931, i, 1124—1125). —The intravenous injection of 40 units of insulin does not reduce the sugar of normal blood below the value attained by that of 5 units, but owing to the greater amount of adrenaline passed into the circulating blood the hypoglycæmic symptoms are much more marked.

A. A. ELDRIDGE.

Effects of insulin and adrenaline on the blood-acetone in fasting children. L. SALOMONSEN (Amer. J. Dis. Children, 1930, **40**, 718—724).—The antiketogenic effect of insulin is secondary to its influence on sugar metabolism. The administration of insulin to children whose blood-sugar has been reduced by fasting reduces the blood-$COMe_2$, the reduction being the less marked the lower is the sugar concentration. Adrenaline increases the blood-$COMe_2$, the increase being the more marked the lower is the blood-sugar; the blood-fatty acid is also usually increased.

CHEMICAL ABSTRACTS.

Mode of action of insulin. F. O. HOWITT (Nature, 1931, **127**, 743—744).—Using Svedberg's value for mol. wt. (this vol., 658), it is calc. that 1 mol. of insulin removes approximately 7×10^5 mols. of dextrose.

L. S. THEOBALD.

Effect of insulin on the rate of dialysis of diabetic blood-sugar. I. S. KLEINER, H. BIRNKRANT, and T. ROTHMAN (Endocrinol., 1930, **14**, 226—228).—The addition of insulin to hirudinised blood of a diabetic dog did not alter the rate of dialysis of sugar from it; hence the action of insulin does not depend on the production of a more readily diffusible form of dextrose.

CHEMICAL ABSTRACTS.

Blood-sugar curve after intravenous injection of insulin. T. E. H. THAYSEN (Acta Med. Scand., 1929, **34**, Suppl., 197—198; Chem. Zentr., 1931, i, 1469).—A marked fall, dependent on the pre-injection value, is followed by a slow recovery.

A. A. ELDRIDGE.

Formation of fat from carbohydrates under the influence of insulin. M. BURGER and W. RUCKERT (Z. physiol. Chem., 1931, **196**, 169—186).—Lactating goats injected with insulin show a decrease in the quantity, but an increase in the calorific val., of their milk. The latter is due chiefly to an increase in milk-fat. Milk-sugar decreases and protein increases slightly. The blood-sugar of fasting goats varies between 70 and 54 mg. per 100 c.c.; under insulin treatment this may sink to 24 mg. without any appearance of hypoglycæmic symptoms. The residual N, normally 56—67 mg., may rise to 80 mg. under insulin. The normal f. p. of the milk ($-0·59°$ to $-0·63°$) is depressed $0·02°$ by insulin treatment. A dose of 150 g. of dextrose administered to a fasting animal milked hourly increases the milk-fat to six times its previous value. J. H. BIRKINSHAW.

Provitamin-*A*. E. J. QUINN and J. G. HARTLEY (J. Biol. Chem., 1931, **91**, 633—639).—The factor in light petroleum extracts of dried carrots which promotes growth in rats and gives a blue colour with $SbCl_3$ is termed provitamin-*A*. It is absorbed, together with the pigment, from the extract by norit and by Lloyd's reagent. The pigment is extracted from norit readily by $CHCl_3$, but little is removed by Et_2O; from Lloyd's reagent more is removed by Et_2O than by $CHCl_3$. The $CHCl_3$ extracts rapidly lose activity. Peanut oil readily extracts the provitamin from norit, but little or none from Lloyd's reagent. Rats are able to utilise partly the vitamin adsorbed on norit, but not that adsorbed on Lloyd's reagent. In the latter case the vitamin may be destroyed at some stage of the treatment. R. K. CALLOW.

Relation of carotene to vitamin-*A*. B. AHMAD (J.S.C.I., 1931, **50**, 12—14T).—The examination of a number of samples of crude and hydrogenated palm oils showed that their physiological activity is due to carotene. The results of biological and colorimetric tests can be correlated with the amount of the pigment contained in each sample. Carotene apparently represents the whole of the pigment of the oil, as spectrographic study does not reveal the presence of any other coloured substance. The colourless oil obtained by hydrogenation has no growth-promoting properties. The oil has no physiological activity when the pigment is removed by adsorbents. A small portion of physiologically active pigment can be recovered from the adsorbent.

Treatment of solutions of carotene in simple and natural solvents, and of vitamin-*A* in cod-liver oil, with adsorbent charcoals showed that carotene is easily adsorbed and readily destroyed, presumably by oxidation on the surface of the adsorbent, whilst the vitamin-*A* of fish-liver oils is not so readily adsorbed and is much more resistant to oxidation. Cod-liver oil can be entirely decolorised in this manner without diminishing its vitamin-*A* value. In this respect there seems to be an essential difference between carotene, which is responsible for the activity of vegetable sources, and the classical vitamin-*A* of fish-liver oils.

Pure carotene and vitamin-*A*. D. VAN STOLK, J. GUILBERT, H. PENAU, and H. SIMONNET (Compt. rend., 1931, **192**, 1499—1501).—Crude carotene dissolved in anhyd. EtOH–PhMe mixture is boiled for 10 min. with an excess of NaOEt. The hydrolysate is treated with warm H_2O. After drying with Na_2SO_4 the PhMe is evaporated in N_2. The residue is dissolved in CS_2 and precipitated with EtOH. It is recrystallised from CS_2–EtOH, m. p. 179°. Carotene after 11 successive recrystallisations is still active in doses of 0·002 mg. against avitaminosis-*A* in the rat. C. C. N. VASS.

Vitamin-*A* content of oats. C. R. MEYER and R. A. HETLER (J. Agric. Res., 1931, **42**, 501—506).—Whole hull-less oats contain little if any vitamin-*A*; oat oil contains only traces. C. C. N. VASS.

Alfalfa as a source of vitamin-*A* in sorghum grain rations. M. C. SMITH and M. L. LYNOTT (J. Agric. Res., 1931, **42**, 421—432).—Incorporation of 5% of lucerne leaf-meal in the sorghum grain ration largely compensates for the lack of vitamin-*A*, but optimum results are obtained with 10% of lucerne-meal. C. C. N. VASS.

Quantitative measurement of vitamin-*A* values. H. C. SHERMAN and E. L. BATCHELDER (J. Biol. Chem., 1931, **91**, 505—511).—Following improvements in technique, the differences in response of rats to graded additions of whole-milk powder to a diet deficient in vitamin-*A* are more marked than previously. Statistical analysis indicates that with a gain of wt. of about 3 g. per week a difference of +25% or −33% in vitamin-*A* value is measurable with 9 rats on each dose. R. K. CALLOW.

Fat-soluble vitamins. XXXIII. Determination of vitamin-*A* and its stability in butter-fat to ultra-violet radiations. H. STEENBOCK and A. M. WIRICK (J. Dairy Sci., 1931, **14**, 229—249).—The Evans–Bishop method of determining vitamin-*A* has no advantage over methods involving renewal of growth or cure of ophthalmia. Destruction of vitamin-*A* by ultra-violet light occurs even when irradiation is carried out in an atm. of CO_2, N_2, or H_2, and is directly proportional to the time of exposure and inversely to the thickness of the fat layer. Irradiation necessary to secure max. activation involves some destruction of the vitamin. Activated butter-fat retained its activity for 7 months. A. G. POLLARD.

Antineuritic vitamin. IV. A. G. VAN VEEN (Rec. trav. chim., 1931, **50**, 610—616).—The silicotungstate ppt. obtained by Jansen and Donath's method is extracted with $Ba(OH)_2$, and the extract neutralised with H_2SO_4. Distillation with MgO under reduced pressure gives NH_3, $NHMe_2$, and NMe_3. A similar extract poor in volatile amines (the above are not normally precipitated by the acid) is precipitated by dil. aq. H_2PtCl_6 and the ppt. treated with $PhSO_2Cl$; from the unaltered residue nicotinic acid is isolated as Cu salt, and the benzenesulphonyl derivative on hydrolysis gives uracil, derived from cytosine, which may be isolated as picrate from the original ppt. Further precipitation with $HAuCl_4$ gives the substances previously found in the third Ag ppt. (cf. this vol., 530). Removal of Pt and Au by H_2S, and addition of $CdCl_2$ in EtOH removes the residual vitamin among other substances; from the filtrate arginine is isolated.

The accompanying poisonous impurities may also be removed by treatment with arylsulphonyl chlorides. Thus a solution after precipitation with silicotungstic acid, treated at a low temp. with excess of $PhSO_2Cl$ and $NaHCO_3$, and then again with silicotungstic acid, gives a solution containing 50—80% of the original vitamin in a proportion of 20—50% of the total org. matter. H. A. PIGGOTT.

Isolation of oryzanin crystals (antineuritic vitamin) from rice polishings. I. S. ODAKE (Proc. Imp. Acad. Tokyo, 1931, **7**, 102—105).—From an "active oryzanin" obtained from rice polishings, cryst. oryzanin hydrochloride is prepared by a method similar to that of Jansen and Donath (A., 1927, 382). The product has m. p. 253° (uncorr.) and approximates to the formula $C_6H_8O_2N_2$,HCl, but otherwise agrees in properties with the oryzanin of Jansen and Donath. Pigeons and rats fed on a vitamin-*B*-free diet may be cured and protected by 0·02 mg. of the hydrochloride per day. A. COHEN.

Production of vitamin-*B* by *B. Ellenbachensis*, Stutzer, and *B. prodigiosum* (Ehrenberg), Lehm. and Neum. M. SCHIEBLICH (Biochem. Z., 1931, **233**, 371—374).—Experiments on rats show that these micro-organisms can synthesise vitamin-*B*. W. MCCARTNEY.

Specific effect of vitamin-*B* on lactation, growth, and water metabolism. B. SURE, M. C. KIK, M. E. SMITH, and D. J. WALKER (Science, 1931, **73**, 285).—The sp. beneficient effect of vitamin-*B* on the organism is unrelated to intake of food. With a ration deficient in vitamin-*B* the sp. influence of the added vitamin on growth is definitely related to H_2O and food intake. L. S. THEOBALD.

Are the Williams-Waterman vitamin-B_3 and Randoin-Lecoq nutritional vitamin the same ? R. LECOQ (J. Biol. Chem., 1931, **91**, 671—674).—The nutritional factors for the pigeon described by Williams and Waterman (A., 1928, 1058) and by Randoin and Lecoq (A., 1926, 871; 1928, 925) are probably identical. R. K. CALLOW.

Brewer's yeast and unsuitable diet. F. NEGRI (Biochim. Terap. sperim., 1930, **16**, 510—519; Chem. Zentr., 1931, i, 1471).—Addition of small quantities of brewer's yeast to vitamin-free diet does not prevent the appearance of hyperglycæmia in pigeons. The liver and kidneys always contain appreciable quantities of glycogen, and the breast-muscles contain normal amounts of inorg. P and lactacidogen. A. A. ELDRIDGE.

Vitamin problem. F. NEGRI (Biochem. Terap. sperim., 1930, **17**, 445—460; Chem. Zentr., 1931, i, 1471).—Symptoms of avitaminosis following the feeding of autoclaved meat are prevented by addition of brewer's yeast. A. A. ELDRIDGE.

Variation of globulin and albumin content of blood-serum on a diet containing no vitamin-*C*. L. RANDOIN and A. MICHAUX (Compt. rend., 1931, **192**, 1276—1279).—In the guinea-pig, with onset of severe symptoms of scurvy, a marked decrease occurs in the total proteins and in the globulin; the decrease in the albumin content is not so marked. C. C. N. VASS.

Crystalline antirachitic substance. T. C. ANGUS, F. A. ASKEW, R. B. BOURDILLON, H. M. BRUCE, R. K. CALLOW, C. FISCHMANN, J. ST. L. PHILPOT, and T. A. WEBSTER (Proc. Roy. Soc., 1931, B, **108**, 340—359).—Using modifications of the method previously described (A., 1930, 1481), larger quantities of the highly antirachitic substance, $C_{27}H_{44}O$, m. p. 123—125°, $[\alpha]_{5461}^{20}$ +260° in EtOH, have been prepared, to which the name *calciferol* is given. Measurements of the absorption spectrum are given. Treatment with oxalyl chloride yields a substance which regenerates calciferol and oxalic acid on warming with NaOH in EtOH, whilst treatment with Ac_2O affords a substance which regenerates calciferol and AcOH on the same treatment. Irradiation of calciferol by ultra-violet light destroys its antirachitic activity, and lowers its absorption and optical activity at the same rate, showing that the antirachitic activity is an inherent property of the substance. The conclusion is reached that calciferol is a chemical entity containing an alcoholic OH group, and that there are not less than two compounds possessing intense antirachitic activity. B. LEVIN.

Stability of irradiated ergosterol. A. WINDAUS and E. AUHAGEN (Z. physiol. Chem., 1931, **196**, 108—120).—Ergosterol was irradiated and preserved in a vac. in a special apparatus constructed entirely of quartz and glass. A slow change occurs on keeping at room temp., marked by a change in rotation from — to and by an increase in absorption specially marked at 280 mμ. This change is hastened by raising the temp. to 100°. The substance undergoing the change is not the vitamin, since the decrease in antirachitic activity is small. At 100—200° new reactions appear, characterised by changes in the absorption (max. at 290 mμ) and corresponding with destruction of the vitamin. J. H. BIRKINSHAW.

Separation of the antirachitic and the toxic factor in the irradiation products of ergosterol. A. WINDAUS and E. AUHAGEN (Z. physiol. Chem., 1931, **197**, 167—172).—Various methods of separation (fractional precipitation from $COMe_2$ at −80°, extraction from petroleum by MeOH, different rate of reaction with maleic anhydride) were unsuccessfully tried. J. H. BIRKINSHAW.

Antirachitic activation of ergosterol by soft X-rays. E. SHELOW and J. R. LOVFBOUROW.—See this vol., 806.

Significance of photo-activity in examining the antirachitic properties of substances. L. URBANEK (Mezog. Kutat., 1930, **3**, 491—496; Chem. Zentr., 1931, i, 1472).—There is no connexion between photo-activity and antirachitic power. Many org. solvents exhibit photo-activity after ultra-violet irradiation. A. A. ELDRIDGE.

Vitamin content and composition of various fish oils. H. SEEL (Z. Vitamink., 1930, 174—179; Chem. Zentr., 1931, i, 1472).—Varying results for composition and vitamin content were obtained with shark- and cod-liver oil. A. A. ELDRIDGE.

Composition of bone. XII. Effect of inadequate amounts of "viosterol" on the healing of rickets. B. KRAMER, M. J. SHEAR, and J. SIEGEL

(J. Biol. Chem., 1931, **91**, 723—730).—Incorporation of " viosterol " in a rachitogenic diet produces either healing of rickets in rats, accompanied by high blood-P and Ca$\times$P values or, in inadequate amount, no healing and low P and Ca$\times$P values. Addition of non-irradiated dried milk to the diet produces atypical healing with deposition in the metaphysis. Contrary to Hess *et al.* (A., 1930, 949), rise of the product Ca$\times$P above the rachitic level is always accompanied by healing. The difference in results is attributed to deficiencies in the technique adopted by the other authors.

R. K. CALLOW.

Comparative antirachitic and calcifying properties of irradiated milk and milk derivatives. G. C. SUPPLEE, G. E. FLANIGAN, O. J. KAHLENBERG, and A. F. HESS (J. Biol. Chem., 1931, **91**, 773—789).—Fractions obtained from the unsaponifiable matter of fat from dried milk could not be activated by irradiation in air. The result is attributed either to oxidation during manipulation or to combination of the provitamin with non-fatty constituents.

A preventive method for assay of antirachitic activity with chickens is described. " Viosterol " failed to give the same degree of protection to chickens as cod-liver oil, although administered in twice the supposed equiv. dose determined with rats.

Irradiation of whole milk causes max. activation in a few secs.; the final activity increases with the fat content. Dried milk, butter-oil, skimmed milk, skimmed milk powder, and total unsaponifiable matter from milk-fat showed various degrees of activatability.

R. K. CALLOW.

Duration of the effect of winter sunlight on bone formation in the chicken. W. C. RUSSELL and C. H. HOWARD (J. Biol. Chem., 1931, **91**, 493—496; cf. A., 1929, 105).—Young chicks exposed to winter sunlight through " Cel-O-Glass " for 1 day showed increased bone formation lasting 2—3 weeks, and the onset of leg-weakness was delayed. The effect of 3 days' exposure was more marked.

R. K. CALLOW.

Solar irradiation and vitamin-*D*. A. VAN WIJK, E. H. REERINK, and W. MORIKOFER.—See this vol., 694.

Physico-chemical study of some economic seeds during germination with particular reference to weight and energy losses. R. C. MALHOTRA (Protoplasma, 1931, **12**, 167—189).—Oil seeds have the highest and starchy seeds the lowest calorific val. before germination. Heat energy lost during the germination of various types of seeds was in the general order starchy < proteinaceous < oily. Seedlings retain 50—90% of the initial energy of the seeds. A significant part of the energy of germination is obtained by the combustion of oils or fats. The R.Q. of seeds varied with type in the order, oily < proteinaceous < starchy. A. G. POLLARD.

Microchemical changes in soya beans during germination. F. W. VON OHLEN (Amer. J. Bot., 1931, **18**, 30—49).—The commencement of germination in soya bean is marked by the appearance of reducing sugar, an increased starch content of the cotyledons and hypocotyl, and the appearance of starch in the root cap. In the first three days of germination starch accumulated in the apex of the hypocotyl and reducing sugar in the base of the hypocotyl and root. Starch increased in the cotyledons until the 5th day, and after remaining stationary for 4 days, rapidly decreased. Starch disappeared from the various parts of the seedlings in the order root, hypocotyl, epicotyl, cotyledons, and reducing sugars followed in the same order, but 2 days later. Asparagine was detected in the hypocotyl on the 3rd day and subsequently in the root base and epicotyl, and increased in amount with the growth of the plant. None was found in the plumule, cotyledons, or root-tip. Depletion of oil from the cotyledons began at the base and proceeded to the opposite end. Org. P and Mg were steadily transformed into an inorg. form and although the latter moved rapidly to the growing points of the plant, the proportion in the cotyledons continued to increase. K was removed from the cotyledons more quickly than Mg and P. Starch, reducing sugar, asparagine, oil, and inorg. P were not detected in the meristematic tissue of the root-tip.

A. G. POLLARD.

Changes in the sugar, oil, and gossypol contents of the developing cotton boll. C. CASKEY, jun., and W. D. GALLUP (J. Agric. Res., 1931, **42**, 671—673).—The amount of gossypol and oil in cotton seed increased rapidly from the 21st to the 30th day of growth. The rate of increase of gossypol was the more rapid and continued at a slower rate until the boll matured (50 days). There was a gradual decrease in sugar during the 30 days' growth period. A. G. POLLARD.

Effects of mineral salts on the transpiration and water requirements of the cotton plant. B. S. MEYER (Amer. J. Bot., 1931, **18**, 79—93).—Addition to soil of the nitrates and chlorides of Na, K, and Ca (0·025—0·4% of dry soil) decreased the respiration rates and water requirements of cotton plants in proportion to the amount of salt added.

A. G. POLLARD.

Osmotic pressure of bananas during ripening. F. C. STRATTON (Plant Physiol., 1931, **6**, 361—365).—Osmotic measurements in a ripening banana bunch indicate a transference of water from peel to pulp and also from the stalk through the crown and neck to the peel and pulp. A. G. POLLARD.

Changes in the composition of oranges during ripening. P. R. v.D. R. COPEMAN (Trans. Roy. Soc. S. Africa, 1931, **19**, 107—167).—During the ripening of oranges, increases are observed in the wts. of the whole fruit and of the skin and pulp separately, in the concentration of sol. solids and sugars in the juice, and in the amounts of these constituents per fruit. The percentages of cell-wall material in the pulp and of acid in the juice decrease. During the final stage of ripening marked transpiration results in a decrease in the wt. of the fruit in consequence of loss of H_2O, whilst the concentration of sol. solids in the juice correspondingly increases. During ripening the N and ash contents of the juice do not significantly alter. Spraying with $Pb_3(AsO_4)_2$ mixtures results in a significant decrease in the acid content of the juice together with a slight increase in sucrose but not in reducing sugars, and a significant increase of cell-wall material in the pulp. W. O. KERMACK.

Electrodialysis in a study of apple tissue. J. R. NELLER (Plant Physiol., 1931, 6, 355—359).—Electrodialysis of apples showed no essential difference between normal fruit and those undergoing physiological breakdown. The cathode compartment contained mainly malic acid with traces of Cl′, SO_4'', and NO_3'. K and small amounts of Ca appeared in the cathode compartment. A. G. POLLARD.

Relation of catalase activity to physiological breakdown in Jonathan apples. J. R. NELLER (Plant Physiol., 1931, 6, 347—354).—A method and apparatus for catalase determinations are described. The catalase activity of apples undergoing breakdown is greater in the early stage and less in more advanced stages than that of normal fruit. During the storage of apples not developing breakdown the catalase activity increased at first and subsequently declined. Catalase activity may be used as an index of the rate of metabolic activity. A. G. POLLARD.

Energy value of apples and pears in storage. K. MEIER (Landw. Jahrb. Schweiz, 1930, 44, 589—597; Chem. Zentr., 1931, i, 1299).—The H_2O and mineral content and the energy val. vary with the season, soil, and fertilisation; in storage the energy val. changes reciprocally with the H_2O content and proportionally to the dry matter. For dried apples it is about 3538 g.-cal. per kg. (10% H_2O) and for fresh apples 3930 g.-cal. per kg. of dry substance. A. A. ELDRIDGE.

Changes in composition of picked and shelled peas. Z. I. KERTÉSZ (Mezog. Kutat., 1930, 3, 450—455; Chem. Zentr., 1931, i, 1535).—The sugar content falls rapidly and the residue insol. in 80% EtOH rises. Drying inhibits all biochemical activity. In crushed peas under toluene-water the invert sugar and non-protein-N increase, whilst the sucrose, starch, and protein-N decrease. When ripe peas are kept, immediately after gathering, at −20° for 24 hr. the changes, although marked, are much smaller than at room temp. A. A. ELDRIDGE.

Relation between initial root length and subsequent growth in *Zea mais* seedlings. F. S. HAMMETT, J. ANDERSON, and E. JUSTICE (Protoplasma, 1931, 12, 190—195).—The general parallelism between initial root length and subsequent growth is not attributable to differences in the concentration of the growth-stimulating SH compounds (cf. this vol., 400), but to variations in the amount of cell nutrient made available (*e.g.*, by enzymes) within the germinating seed. A. G. POLLARD.

Relation between growth and intake of nutrients by the Cholam plant. C. N. ACHARYA (Madras Agric. J., 1931, 19, 1—12).—The intake of N by the Cholam plant is high in the early stages of growth. The rate of absorption of nutrients increases with growth up to the flowering stage, after which it declines. The total accumulation of nutrients is greatest at the flowering stage, and a return flow of nutrients to the soil follows. Application of N-manures partly at the time of sowing and partly just before flowering is suggested. A. G. POLLARD.

Nature and seasonal variation of the carbohydrates in *Laminariæ*. P. RICARD (Bull. Soc. Chim. biol., 1931, 13, 417—435).—Determinations of the dry wt., total salts, mannitol, laminarin, algin, and the cellulose residue, algulose, of *Laminaria flexicaulis* and *L. saccharina* have been made monthly for the years 1927 to 1929, and have been correlated with sea-temp. and the amount of sunshine. Neither dextrose nor fucose was detected at any time. No laminarin was present in the winter months, but its max. concentration coincided with that of the dry wt. and the min. concentrations of total salts, mannitol, and algin and the complete development of the spores. The accumulation of laminarin showed a marked relationship to the sea-temp. and the amount of sunshine. C. C. N. VASS.

Variation of the carbohydrate composition of the root of herb bennet (*Geum urbanum*, L.) during a year's growth. J. CHEYMOL (Bull. Soc. Chim. biol., 1931, 13, 470—476).—The distribution of the monosaccharides, disaccharides, and polysaccharides has been determined monthly. The mono- and di-saccharide, hydrolysable by emulsin, appear to accumulate when the activity of the chlorophyll is reduced; the polysaccharides vary directly with the quantity of the vegetation, whilst geoside accumulates chiefly in the spring. C. C. N. VASS.

Biochemical addition of water to fumaric acid by plant cells and yeast. K. P. JACOBSOHN (Biochem. Z., 1931, 234, 401—418).—By the action of preps. from peas or beans, or of yeast, either fumaric acid or *r*-malic acid is converted into an equilibrium mixture containing 20—40% of fumaric acid and 80—60% of *l*-malic acid. The conversions are probably brought about by a fumarase which exhibits stereochemical specificity, although it has not yet been possible so to treat the enzyme that *d*-malic acid is produced. W. MCCARTNEY.

Distribution of total nitrogen during regeneration of the willow. P. A. DAVIES (Bot. Gaz., 1931, 91, 320—326).—Cuttings of *Salix nigra* developed shoots from stem areas of high N content and roots from those of lowest N content. Initial changes prior to the generation of shoots are not dependent on the rapid translocation of N from the apex. A. G. POLLARD.

Solubility changes of inorganic constituents in citrus cuttings. F. F. HALMA and A. R. C. HAAS (Bot. Gaz., 1931, 91, 213—218).—Changes in the sol. Ca and K contents of stem and leaf cuttings of orange and lemon during the rooting process are recorded. In stem cuttings the sol. Ca content decreased in stems and increased slightly in leaves. In leaf cuttings (no stem) the sol. Ca content declined. Losses of sol. K occurred in the leaves of stem cuttings and in leaf cuttings. During the growth of rooted leaf cuttings in culture solutions the sol. K content increased considerably. There was no effect on the sol. Ca content. No appreciable changes occurred in the solubility of Mg during the rooting process or in subsequent water cultures. A. G. POLLARD.

Chemistry of the plant cell-wall. V. Microscopy of acid-treated sawdust as an index to some of the differences in the physical properties of hardwood and softwood lignin. W. M. HARLOW.

(Ind. Eng. Chem., 1931, **23**, 419—421).—In the determination of lignin by the hydrolysis of finely-divided woods by means of 72% H_2SO_4, it is noted that the lignin residues from hard and soft woods behave differently on settling and filtration. Microscopical examination shows that the lignin residue from hardwoods consists only of the middle lamella, whereas that of the softwoods contains in addition the secondary layers. The difference in form is held to account for the difference in physical properties.
T. T. POTTS.

Osmotic adaptation of *Nitella* in sucrose and dextrose solutions. L. S. WILDERVANCK (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 297—308).—Barger's method is suitable for the determination of the osmotic vals. of *Nitella* cells, quantities obtainable by pricking one cell being sufficient for testing. The changes occurring in these osmotic vals. in normal circumstances and the changes they undergo when cultivated in sucrose and dextrose have been investigated. J. W. SMITH.

Variations in the "*Og*" of plant tissues. W. A. BECK (Plant Physiol., 1931, **6**, 315—323).—The *Og* (osmotic value at incipient plasmolysis) of plant cells is characteristic for the kind of tissue examined, and shows seasonal variations. Sucrose solutions were used as the plasmolysing agent.
A. G. POLLARD.

Acidity of the cell sap of cultivated plants. W. P. SHYWAN (Pflanzenbau, **6**, 170—174; Bied. Zentr., 1931, **60**, A, 77).—Values for numerous crops are recorded. A. G. POLLARD.

Influence of hydrogen-ion concentration on the vacuole contraction in stained *Elodea* cells. R. KUNZE (Protoplasma, 1931, **12**, 161—166).—Vacuole contraction following the immersion in tap-water of *Elodea* leaf-cells stained with neutral-red is not the result of the Ca concentration of the tap-water, but of its p_H. A. G. POLLARD.

Influence of 0·7—0·1% chloroform solutions and of 7—1% ether solutions on the assimilation of *Elodea canadensis*. A. DE CLERCQ (Natuurwetensch. Tijds., 1931, **13**, 79—82).—In solutions of $CHCl_3$ of concentrations higher than 0·1% or of 1% $CHCl_3$ and 1% Et_2O the assimilation of *E. canadensis* is retarded and poisoning ensues; there is no evidence of any acceleration. In presence of 0·1% $CHCl_3$ and 1% Et_2O narcosis is produced slowly, but normal assimilation is subsequently restored if the plant is immersed in water. H. F. GILLBE.

Phycoerythrin and phycocyan. H. KYLIN (Z. physiol. Chem., 1931, **197**, 1—6).—Phycoerythrin appears to occur in *Rhodomelaceæ* in a strongly fluorescent (orange-yellow) and a weakly fluorescent (orange to orange-red) form. The presence of a phycoerythrin with only one absorption band in *Cyanophyaceæ* (A., 1922, i, 210) is confirmed. Blue-green, blue, and blue-violet modifications of phycocyan are described. J. H. BIRKINSHAW.

Occurrence of malic acid in a brown alga. H. KYLIN (Z. physiol. Chem., 1931, **197**, 7—11).—The strong acidity of aq. extracts of *Desmarestia viridis* is probably due to malic acid. J. H. BIRKINSHAW.

Composition of some marine algæ. M. R. BUTLER (Plant Physiol., 1931, **6**, 295—305).—The moisture, ash, K, I, protein, and crude fibre contents of several species of algæ are recorded.
A. G. POLLARD.

Fluorescence spectra of chromoproteins in solution and in a living alga. C. DHERE and M. FONTAINE (Compt. rend., 1931, **192**, 1131—1133).—The absorption and fluorescence spectra of phycocyanin obtained from *Aphanizomenon flos aquæ*, of phycoerythrin from *Ceramium rubrum*, of the living *Rhodymenia palmata* and of solutions of its pigments and the fluorescence spectrum of living *Ulva lactuca* have been examined. C. C. N. VASS.

Fluorescence spectrum of protochlorophyll. C. DHERÉ (Compt. rend., 1931, **192**, 1496—1499).—The absorption and fluorescence spectra of the protochlorophyll of wheat in MeOH solution alone and in the presence of chlorophyll are recorded.
C. C. N. VASS.

Possible relationship between hæmoglobin and chlorophyll as shown by the use of liver extract. O. RABER (Science, 1931, **73**, 457—458).—Liver extract increases the chlorophyll content of maize plants. L. S. THEOBALD.

Membranes of spores and pollens. V. Autoxidation of sporopollenins. F. ZETZSCHE and O. KALIN (Helv. Chim. Acta, 1931, **14**, 517—519).—The O content of pollen samples from *Picea orientalis* (C : H = 5 : 8) and from *Pinus* which had been kept over $CaCl_2$ in the light for 2·5 years had increased from 24·6 to 67·6 (C : H = 1 : 1) and from 23·9 to 64·9%, respectively, the decomp. point being considerably lowered and the behaviour towards various reagents also being changed. On the other hand, lycopodium sporonin similarly aged remained unchanged, as did also a sample of pollen of *P. orientalis* which had been stored in the dark. Thus the bleaching of the pollen previously observed (this vol., 536) appears to be due to autoxidation.
J. W. BAKER.

Organic acids of spinach, broccoli, and lettuce. E. K. NELSON and H. H. MOTTERN (J. Amer. Chem. Soc., 1931, **53**, 1909—1912).—Fresh spinach contains 0·31% of oxalic and small amounts of citric and *l*-malic acids. Complete analyses of the buds and leaves of broccoli (*Brassica oleraceæ*) are given; non-volatile acids present are *l*-malic, citric, and small amounts of oxalic and succinic. Fresh lettuce contains *l*-malic (0·065%), citric (0·048%), and oxalic acids (0·01%). H. BURTON.

Occurrence of coumarin in *Ficus radicans*. H. MOLISCH (Ber. deut. bot. Ges., 1931, **49**, 138—140).—Coumarin has been found in the withered leaves.
B. LEVIN.

Hemicelluloses. I. Evolution of carbon dioxide by plant materials and some hemicelluloses under the action of boiling 12% hydrochloric acid. E. ANDERSON (J. Biol. Chem., 1931, **91**, 559—568).—Determinations of the CO_2 evolved on boiling with 12% HCl (Lefevre–Tollens method) have been carried out with hemicellulose fractions from various materials. It is concluded that some hemicelluloses contain uronic acids, but others,

giving no CO_2, are true polysaccharides. Some materials, by successive extractions by different methods, appear to yield more than one hemicellulose. Certain hemicelluloses yield aldobionic acids and reducing sugars on partial hydrolysis, and thus resemble plant gums. An aldobionic acid has been isolated as the Ba salt from cottonseed hull hemicellulose. Material other than uronic acid hemicellulose may be extracted by 1% NaOH. R. K. CALLOW.

Modification of Pervier and Gortner's method for determination of pentosans in plant tissues. R. C. MALHOTRA (J. Indian Chem. Soc., 1931, 8, 51—58).—Improvements in detail have been made. Comparative figures obtained by other methods are shown. D. A. FAIRWEATHER.

Light and the carotenoid content of certain fruits and vegetables. L. L. W. SMITH and O. SMITH (Plant Physiol., 1931, 6, 265—275).—Carotenoid pigments may be extracted from fresh tissue by means of pyridine. Peaches, apricots, and nectarines developing in darkness from the flowering stage do not oxidise, when exposed to air, as fruits growing wholly in daylight. Irregular differences occur in the carotenoid content of fruits developed in darkness and those in daylight. No chlorophyll develops in tomatoes ripened in darkness, the fruits being quite white, changing to red as maturity approaches, and finally attaining the same colour as fruit ripened in daylight. In yellow-fleshed tomatoes the dark-ripened fruit has a higher carotenoid content than those ripening in daylight. The reverse was the case with red-fleshed varieties. Dark-ripened fruits have a higher p_H than those grown in light.
A. G. POLLARD.

Carotenoid of the spindle-tree (*Euonymus europœus*). II. L. ZECHMEISTER and P. TUZSON (Z. physiol. Chem., 1931, 196, 199—200; cf. A., 1930, 1323).—At least 75% of the zeaxanthin of *Euonymus europœus* is present in the free state. The remainder could not be separated from the lipin fraction.
J. H. BIRKINSHAW.

Xanthophylls. R. KUHN, A. WINTERSTEIN, and E. LEDERER (Z. physiol. Chem., 1931, 197, 141—160).—Xanthophylls from green leaves and yellow petals of various plants contain one main constituent which it is proposed to call *lutein*, m. p. 193° (corr.), $[\alpha]_{Cd}^{18}$ +160° ($CHCl_3$), +145° (EtOAc). Nettles, *Tagetes*, and horse-chestnut leaves contain in addition violaxanthin. Xanthophylls are extremely sensitive to acid. The colouring matter of egg-yolk is a mixture of lutein and zeaxanthin, the respective amounts of which can be determined polarimetrically. Lutein dipalmitate, hentriacontane, and a trace of a *ketone* (*oxime*, m. p. 55—59°, possibly palmitoneoxime) were isolated from *Tagetes*. J. H. BIRKINSHAW.

Water-soluble purgative from black alder bark, hydrolysable by rhamnodiastase. M. BRIDEL and L. CHARAUX (Compt. rend., 1931, 192, 1269—1271).—The parent substance of franguloside is obtained as an amorphous unstable powder in 10% yield on distillation in vac. of the EtOH extract of the pulverised bark. Hydrolysis with dil. H_2SO_4 gives a ppt. (40·3%) containing 59·73% of reducing sugars. Emodol is the chief constituent of the residue. Hydrolysis by rhamnodiastase gives a ppt. (26·52%), of which 21·79% is reducing sugars, and an anthraquinone substance $C_{17}H_{12}O_4$. Hydrolysis by yeast gives 1 mol. of franguloside to 2 mols. of dextrose. Distillation of an EtOH solution of the parent substance at ordinary pressures causes a partial hydrolysis. C. C. N. VASS.

Microscopy and histochemistry of some fruits and leaves. A. NIETHAMMER (Z. Unters. Lebensm., 1931, 61, 103—105, 217—221).—(1) The fruits of *Pirus malus*, *Prunus domestica*, *P. cerasus*, *P. persica*, and *P. armeniaca*, *Ribes grossularia*, *R. aureum*, *Vaccinium myrthillus*, *V. vitis idaea*, *V. uliginosum*, *Cucurbita Pepo*, and *Solanum lycopersicum* were examined. In general, the unripe fruits contain CaC_2O_4 crystals. These disappear as the fruit ripens, owing to resorption, with the production of MeCHO (cf. B., 1931, 43). Inclusion formations are characteristic of the over-ripe *Rosaceæ*, and are coloured deep-red by vanillin hydrochloride or diaminobenzaldehyde. The crystals are identified by dissolving in HCl or H_2SO_4 (but not AcOH), isolation of the oxalic acid by sublimation, and precipitation from solution as CaC_2O_4. Inclusions in the *Saxifragaceæ* are similar, but less abundant. *Zea mais* (large crystals in the endosperm cells, disappearing on ripening, which coincides with development of a cleft or hilum in the whole starch grains) and hazel nut (oxalate in the unripe fruit, but not in the cotyledon parenchyma) are examples of hard-husked fruits in which CaC_2O_4 disappears on ripening.

(2) In addition to CaC_2O_4 resorbed into the fruit on ripening, the fruits of *Vitis vinifera* and *Prunus spinosa* contain tubular trains of and single tannin cells, respectively (blue with $FeCl_3$), similar to those of the banana and giving, in the ripe fruits, a red colour with vanillin hydrochloride. In the parenchyma of the unripe fruits they are globular in shape, and probably of a fatty character, and are rapidly stained yellowish-red with Sudan III; they give no reaction with vanillin. Hesperidin, which occurs in orange and citrus fruits as sphæro-crystals (ripe) and cryst. strips (unripe), is in both cases sol. in EtOH and separable by sublimation for 2 hr. at 300° as double or single sword-shaped crystals. Both forms, and also the yellow globules observed in unripe citrus fruits, give yellow crystals similar to those of the sublimate with 20% KBr saturated with Br. The sublimation and bromide tests appear to be characteristic of glucosides, and behave similarly with saponin in beet and spinach leaves. J. GRANT.

[Constituents of] yellow [pine] buds. I. M. TOMEO and J. G. VIANA (Anal. Fís. Quím., 1931, 29, 300—305).—The yellow buds produced by certain species of pine contain an abnormally high quantity of resin acids, of which *n* and *d* are normal but the rotatory power is high; the mol. is smaller than that corresponding with the formula usually accepted.
H. F. GILLBE.

Isolation and properties of visammin, visammidin, visnaginin, visnagidin, khellinin, khellidin, and visnagan. K. SAMAAN (Quart J. Pharm., 1931, 4, 14—27).—Fractionation of the Et_2O extract of the fruit of *Ammi visnaga* yields the following cryst.

non-nitrogenous substances in the yields stated: *visammin*, $C_{11}H_{10}O_4$, m. p. 153° (0·31%); *visammidin*, m. p. 147—148° (0·02%); *visnaginin*, m. p. 125—132°, a glucoside: *visnagidin*, m. p. 145° (0·06%); and *visnagan*, an oil, d^{25} 1·012 (2·15%), with 19·4% of "fixed oil." The EtOH extract of the residue yields *khellinin*, $(C_3H_4O_2)_n$, m. p. 170·5°, a glucoside (0·38%), and *khellidin*, m. p. 167—168° (0·03%).

R. K. CALLOW.

***Monarda punctata*, L.** A. A. HARWOOD (J. Amer. Pharm. Assoc., 1931, **20**, 433—437).—The inorg. constituents of various parts of the plant have been determined. E. H. SHARPLES.

Oil content and presence of alkaloids in seeds of *Papaver somniferum*. A. CHISTONI (Arch. Farm. sperim., 1931, **52**. 29—32).—The oil content of seeds of *P. somniferum* v. *album* grown in Italy is 40—50%, equal to that of plants grown in the Orient. The seeds contain an alkaloid fraction, giving ppts. with general reagents, and toxic to mice, but not containing morphine. R. K. CALLOW.

Occurrence of benzylmethylamine in the extract of Ma Huang. A. L. CHEN, E. H. STUART, and K. K. CHEN (J. Amer. Pharm. Assoc., 1931, **20**, 339—345).—Benzylmethylamine has been isolated from the extract of Ma Huang after the removal of *l*-ephedrine. The following salts are described: hydrochloride, m. p. 180·5°; chloroaurate, m. p. 139—140°; chloroplatinate, m. p. 194—195°; sulphate, m. p. 144·2°; *nitrate*, m. p. 86·5°; *phosphate*, m. p. 162·5°; *oxalate*, m. p. 200·5—201° (all m. p. corr.). The base has practically the same physiological activity as benzylamine. It is slightly less toxic.

E. H. SHARPLES.

Occurrence of trigonelline in Guatemala coffee. A. HEIDUSCHKA and R. BRUCHNER (J. pr. Chem., 1931, [ii], **130**, 11—22).—Trigonelline (0·06—0·1%) was isolated from Guatemala coffee.

H. A. PIGGOTT.

Physiological action of cyanide. I. Effects of cyanide on the respiration and sugar content of the potato at 15°. C. S. HANES and J. BARKER (Proc. Roy. Soc., 1931, B, **108**, 95—118).—Respiration increases when the tubers are exposed to low concentrations of HCN (0·10—0·47 c.c. per litre of air), rising to a max., then falling slowly. When the tubers are exposed to air containing higher concentrations (0·71 c.c. per litre) for short periods (up to 9 days), the R.Q. remains unchanged, but for long periods the R.Q. increases. During rise in respiration in cyanide the sugar content increases, and during fall in respiration the amount of sugar decreases, and there is a linear relation between respiration and sugar content, suggesting that changes in respiration are due to changes in the amount of sugar. Cyanide activates barley-amylase *in vitro* and the authors conclude by analogy that the changes in sugar concentration are due to the effect of cyanide on the starch-hydrolysing system of the potato. B. LEVIN.

Dry-rot in wood. II. Products of decay of spruce wood rotted by *Merulius lachrymans*. E. C. BARTON-WRIGHT and J. G. BOSWELL (Biochem. J., 1931, **25**, 494—506).—The action of the fungus is first to remove the easily-hydrolysable fractions, mannan and galactan, and then to attack the cellulose. The latter is converted into dextrose and consumed as such. At the same time a small residue of oxycellulose is left. A homogeneous lignin *substance*, $C_{11}H_{33}O_9(OH)_4(OMe)_2{\cdot}CHO$, was extracted from the rotted wood with alcohol; it is similar to the lignins which have been isolated from woody tissues by the action of alkali hydroxides under pressure. The hemicellulose fractions of spruce wood are unaffected by the fungus. An unknown uronic acid, possibly a penturonic acid, was isolated from the hemicellulose-*A* fraction. The total lignin content of the wood was practically unaltered, but marked oxidation took place.

S. S. ZILVA.

Preparation of cellulose films of fossil plants. H. DUERDEN (Ann. Bot., 1931, **45**, 376—378).—By incorporating a "plasticiser" and a small proportion of high-boiling solvent into solutions of cellulose acetate or pyroxylin in low-boiling solvents, clear films are obtained which are not brittle and do not contract. Examples of the use of different ingredients are given. A. COHEN.

Chemical changes that occur during the curing of tobacco leaves. H. B. VICKERY and G. W. PUCHER (Science, 1931, **73**, 397—399).—Changes in H_2O content, carbohydrates, and N during curing are described. The main part of the changes occurs during the first 12 days of curing. L. S. THEOBALD.

Carbohydrate variations accompanying the mosaic disease of tobacco. A. A. DUNLAP (Amer. J. Bot., 1931, **18**, 328—336).—Tobacco plants infected with Mosaic disease contained less reducing sugars, disaccharides, starch, and pentosans than healthy controls, the greatest reduction being in the sugar and starch contents. A. G. POLLARD.

Positive gas and water pressure in oaks. C. A. ABELL and C. R. HURSH (Science, 1931, **73**, 449).—Insertion of a borer permitted the issue of an inflammable gas from *Quercus montana* and *Q. alba* in which the heart-wood was unsound.

L. S. THEOBALD.

Gas analysis by the method of Van Slyke. R. STURM (Arch. Exp. Path. Pharm., 1931, **160**, 117—119).—An improved type of tonometer with ground-in glass stopper suitable for use in the Van Slyke method and a modified Ostwald pipette for use in the apparatus are described. W. O. KERMACK.

Colorimetric method for the determination of magnesium. J. BEČKA (Biochem. Z., 1931, **233**, 118—128).—A colorimetric method for the determination of small amounts (0·015 mg.) of Mg in org. (0·1 c.c. of urine, 0·1—0·2 c.c. of blood, serum, or plasma) and inorg. substances is described. It depends on the comparison of colour tones obtained by the production of a colloidal complex of $Mg(OH)_2$ and Ti-yellow which is stabilised by agar.

P. W. CLUTTERBUCK.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

AUGUST, 1931.

General, Physical, and Inorganic Chemistry.

Relative intensities of the Balmer and Paschen lines. U. Doi (Sci. Rep. Tokyo Bunrika Daigaku, 1931, 1, 97—103).

Reversal-like phenomenon of the Balmer lines of hydrogen. H. Nagashima (Sci. Rep. Tokyo Bunrika Daigaku, 1931, 1, 133—143).—The H_β, but not the H_α and H_γ, lines were reversed in the spectra of the explosion in water vapour or in H_2 or under water of metallic wires (Pb, Al, Cu).
N. M. Bligh.

Spectrum of H_2. Bands ending on $2p^3$ II. levels. O. W. Richardson and P. M. Davidson (Proc. Roy. Soc., 1931, A, 131, 658—683).—A full description of the bands is given. The value of ν_e'' is estimated to be 29,307, in fair agreement with the value 29,503 extrapolated from the Rydberg–Ritz formula for the α, β, γ bands (A., 1927, 1).
L. L. Bircumshaw.

Intensity variations of the helium lines with voltage. J. Razek (Physical Rev., 1931, [ii], 37, 1252—1262).—Direct measurements were made by a new method. N. M. Bligh.

Anomalous dispersion of lithium vapour. A. Filippov (Z. Physik, 1931, 69, 526—547).—Anomalous dispersion of Li vapour in the visible and ultraviolet gives the relative transition probabilities for the first 12 terms of the principal series; the results agree with theory (cf. A., 1929, 1129). A. B. D. Cassie.

Spectrum of the cathode glow in nitrogen and other gases. K. G. Emeléus and (Miss) O. Hall (Proc. Roy. Irish Acad., 1931, 40, A, 1—10; cf. A., 1930, 835).—The appearance of the arc spectrum of N in the light from the cathode glow of a low-voltage d.c. glow discharge from a cold cathode is confirmed, and an explanation suggested which accounts for the cathode glow spectra in a number of polyat. gases and gas mixtures. Local plasma-type discharges were observed. N. M. Bligh.

Large displacements in the spectrum of singly-ionised oxygen. K. Asagoe (Sci. Rep. Tokyo Bunrika Daigaku, 1931, 1, 105—125).—The modes of appearance and displacements are tabulated for 82 lines of the doublet, 67 lines of the quadruplet, and 138 unclassified lines of O II for pressures of 3 cm., 7 cm., and 1 atm. N. M. Bligh.

Difference in the self-reversal of neon lines excited by direct and alternating currents. H. Nagaoka and T. Mishima (Proc. Imp. Acad. Tokyo, 1931, 7, 140—141).—The reversal is greater for d.c. than for a.c. W. E. Downey.

Origin of the light from the negative glow. R. H. Sloane and K. G. Emeleus (Phil. Mag., 1931, [vii], 12, 73—80).—The view of Druyvesteyn that the negative glow of the normal discharge in Ne and A gives an excitation light (cf. A., 1930, 1076) is in agreement with the similarity of the intensity distribution for A I lines in the negative glow and positive column, and with the electrical analysis of the negative glow. N. M. Bligh.

Oscillating arc: elements of group VI. E. Z. Stowell (Physical Rev., 1931, [ii], 37, 1452—1457; cf. this vol., 1).—The behaviour of S, Se, Te, Cr, Mo, W, and U as cathodes in an arc in H_2 was investigated.
N. M. Bligh.

Structure of the Cr I spectrum. M. A. Catalan and P. M. Sancho (Anal. Fis. Quím., 1931, 29, 327—366).—Existing data are summarised and reviewed, and more than 700 lines are classified in 202 levels belonging to triplet, quintuplet, and septet systems. The principal ionisation potential is 6·74 volts.
H. F. Gillbe.

Hyperfine structure in the spectrum of copper. J. B. Green and J. Wulff (Nature, 1931, 127, 891—892).—Each line of the doublet at 3248 and 3275 Å. consists of a sharp, narrow doublet of separation 0·043±0·001 Å. L. S. Theobald.

Absolute wave-lengths of the copper and chromium *K*-series. J. A. Bearden (Physical Rev., 1931, [ii], 37, 1210—1229).—In measurements by ruled gratings the periodic error of the grating and the geometrical divergence of the *X*-ray beam are corrected by a study of the intensities of the optical ghost lines, and by the disposition of apparatus, respectively. Satisfactory agreement among results from 5 glass gratings and with a calcite crystal are obtained, and values of e/m, N, Planck's constant, and the calcite crystal grating space are calc. N. M. Bligh.

Fine structure in the arc spectra of bromine and iodine. S. Tolansky (Nature, 1931, 127, 855).—Fine structure measurements have been extended for I (4700—8000 Å.) and Br. The most probable values of nuclear spin are F $\frac{1}{2}$, Cl 5/2, Br 3/2, and I 9/2; the isotopes of Br, 79 and 81, appear to possess the same nuclear spin. L. S. Theobald.

Hyperfine structure in the rubidium spectrum. D. A. Jackson (Nature, 1931, 128, 34).—Effects due to the isotopes Rb 85 and 87 are described and discussed. L. S. Theobald.

Near infra-red spectrum of iodine. T. Iwama (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, 15,

163—165).—Results of an examination of the I spectrum, obtained by discharge in a narrow quartz Geissler tube, are given. W. GOOD.

Absorption spectra of salt solutions. Metallic ions. S. KATO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, **15**, 161—162).—The absorption corresponding to the third term $^3P_2$ in $Tl^{\cdot}$ and $Pb^{\cdot\cdot}$ ions appears respectively at λ 1710 and λ 1570 Å. W. GOOD.

Nuclear moments of cæsium, rubidium, and indium. D. A. JACKSON (Nature, 1931, **127**, 924—925).—The probable values of i (the quantum no. of the nuclear rotation) for Cs, Rb, and In are 9/2 or more, ½ to 3/2, and 7/2, respectively. L. S. THEOBALD.

Effect of other metals on the secondary emission from platinum. T. I. CAMPAN (Bul. Fac. Stiinte Cernauti, 1929, **3**. 245—247; Chem. Zentr., 1931, i, 1570).

Hyperfine structure of the principal components of mercury lines 5770, 5791, 5461, and 4358 Å. H. NAGAOKA and S. MISHIMA (Proc. Imp. Acad. Tokyo, 1931, 7, 137—139). W. E. DOWNEY.

Isotope effect and hyperfine structure of the mercury resonance line. S. MROZOWSKI (Nature, 1931, **127**, 890—891).—A discussion. L. S. THEOBALD.

Emission bands in the mercury spectrum under low excitation. (LORD) RAYLEIGH (Nature, 1931, **127**, 854).—The "core effect" (this vol., 780) includes a band series identical with that obtained in electrically stimulated vapour (A., 1927, 1122). L. S. THEOBALD.

Molecular spectra of mercury, zinc, cadmium, magnesium, and thallium. H. HAMADA (Phil. Mag., 1931, [vii], **12**, 50—67).—Full details of work previously noted (this vol., 664) are given.

[Absorption of resonance lines by mercury vapour containing foreign gases.] E. A. NEUMANN (Z. Physik, 1931, **69**, 701—702).—A reply to Kunze (this vol., 541). A. B. D. CASSIE.

Displacement effect in the hyperfine structure terms of thallium isotopes. H. SCHULER and J. E. KEYSTON (Z. Physik, 1931, **70**, 1—9).—The hyperfine structure of some Tl I and Tl II lines is consistent with two isotopes of nuclear spin ½, and with masses 205 and 203 in the ratio of 2·3 to 1; the two isotopes have different nuclear fields. A. B. D. CASSIE.

Resonance potential of trebly-ionised bismuth. S. SMITH (Nature, 1931, **127**, 855).—A discussion. L. S. THEOBALD.

High-frequency behaviour of a plasma. L. TONKS (Physical Rev., 1931, [ii], **37**, 1458—1483; cf. A., 1929, 1359).—The formula for the sp. inductive capacity of a uniformly ionised gas is extended to two cases of non-uniform ionisation. Formulæ are derived for the conductivity and sp. inductive capacity of a cylindrical plasma (positive column of an arc). N. M. BLIGH.

Repulsive energy levels in band spectra. J. KAPLAN (Physical Rev., 1931, [ii], **37**, 1406—1411).—Theoretical. N. M. BLIGH.

Statistical equilibrium in the positive branch of the gas discharge. H. KOPFERMANN and R. LADENBURG (Naturwiss., 1931, **19**, 513—515).—The relatively simple optical phenomena noticed in the positive branch of the electric discharge through rare gases are investigated. A. J. MEE.

Temperature of the arc light. L. S. ORNSTEIN (Physikal. Z., 1931, **32**, 517—520).—A spectral method is used. In arc-light gas the temp. is very high, being highest in the centre and lowest at the edge. A. J. MEE.

Semi-silvering of interferometer plates by distillation in a high vacuum. R. RITSCHEL (Z. Physik, 1931, **69**, 578—585).—A means is described of depositing Ag simultaneously and at the same rate on to two plates, by distillation of the Ag in a high vac.; any density can be obtained. A. B. D. CASSIE.

***Kα* lines of the light elements.** E. RUDBERG (Phil. Mag., 1931, [vii], **11**, 1248—1250).—A comparison with, and discussion of, the results of Söderman (cf. A., 1930, 1502). N. M. BLIGH.

Absorption of the *Kα* line of carbon in various gases and its dependence on atomic number. E. DERSHEM and M. SCHEIN (Physical Rev., 1931, [ii], **37**, 1238—1245).—Absorption coeffs. in the elementary gases, CO_2, and Au leaf for the $K\alpha$ line of C were determined photographically, and values of some at. absorption coeffs. (μ_a) are deduced. Log μ_a is a linear function of log Z (where Z is the at. no.). N. M. BLIGH.

Reflexion of the *Kα* line of carbon from quartz and its relation to refractive index and absorption coefficient. E. DERSHEM and M. SCHEIN (Physical Rev., 1931, [ii], **37**, 1246—1251; cf. preceding abstract). N. M. BLIGH.

Fine structure of absorption edges of the Röntgen *K* series of elements with a medium atomic number. H. T. MEYER (Wiss. Veröff. Siemens-Konz., 1931, **10**, [2], 95—98).—Absorption spectra of the K series have been examined in Rb_2CO_3, $Sr(NO_3)_2$, $ZrOCl_2$, $Zr(NO_3)_4$, Y_2O_3, K_2NbF_7, Nb_2O_5, and MoO_3. The results are in agreement with the assumption that fine structure at the edges of the absorption bands in the Röntgen spectra are observed only in the higher valency states of those elements which have more than one valency. Thus fine structure is particularly well marked in bromates, selenates, and arsenates, but not in bromides or in salts of Rb and Sr. $ZrOCl_2$, K_2NbF_7, and Mo^{VI} compounds all have fine structure. A. R. POWELL.

Investigations of Röntgen spectra. I. *X*-Ray spark lines. II. *X*-Ray spectra and chemical combination. Sulphur. III. Fine structure of *K*-absorption edge of SiO_2. G. B. DEODHAR (Proc. Roy. Soc., 1931, **A**, **131**, 633—647, 647—653, 654—658).—I. A study of the $K\alpha$ and $K\beta$ satellites of Si, P, S, and Cl indicates that the structure of the satellites is complex and their nature highly dependent on the state of chemical combination of the atom which emits them.

II. Many S compounds have been studied. Considerable changes are found in the relative intensities

of β_1 and β_x lines for different compounds, and new lines are obtained for some compounds. The influence of the anticathode material is investigated. It appears that the substance of the anticathode reacts under cathodic bombardment on the mol. of the S compound, causing alteration in the electron distribution of the peripheral levels of the S atom.

III. The fine structure has been measured by using quartz as the analysing and absorbing crystal. The fact that the difference between the principal edge and the limit of the fine structure K_{m-2} is only 5·17 volts precludes the possibility of double ionisation.

L. L. BIRCUMSHAW.

Complexity of the *L* series of barium. V. DOLEJSEK and J. KUBIČEK (Compt. rend., 1931, **192**, 1369—1370; cf. A., 1929, 376).—Emission bands, $L\alpha_3$, $L\beta_2'$, and $L\gamma$, similar to $K\beta'$, occur near $L\alpha_1$, $L\beta_2$, and $L\gamma_1$ of Ba. For BaO the centres are at 2767·6, 2398·6, and 2235·4 X, respectively.

C. A. SILBERRAD.

Natural widths of the *X*-ray lines in the *L* series spectrum of uranium. J. H. WILLIAMS (Physical Rev., 1931, [ii], **37**, 1431—1442).—The half widths at half max. of the rocking curves in parallel positions of the double *X*-ray spectrometer are a linear function of the wave-lengths. N. M. BLIGH.

Plane grating spectroscopy in the ultra-soft *X*-ray region. J. A. PRINS (Z. Physik, 1931, **69**, 618—636).—Measurement of wave-lengths between 20 and 50 Å. with a grating of 50 lines per mm. is discussed theoretically and practically; wave-lengths are given for *K* lines due to O, N, C, B, Be, and *M* and *N* lines due to W. A. B. D. CASSIE.

Breadth of the Compton modified line with the double-crystal spectrometer. A. HOYT and J. DU MOND (Physical Rev., 1931, [ii], **37**, 1443—1451; cf. A., 1929, 747).—Using similar apparatus, the narrow structure reported by Davis (A., 1928, 1168), Bearden (A., 1930, 1491), and Gingrich (*ibid.*) is not confirmed. Concordant results are obtained by the single-, double-, and multi-crystal spectrometer.

N. M. BLIGH.

Atomic scattering factors. R. W. JAMES and G. W. BRINDLEY (Phil. Mag., 1931, [vii], **12**, 81—112).—A general account of the nature of, and methods of calculating, the scattering factors of atoms for *X*-rays is given. Two methods of calculating the factor for the atom at rest, with sufficient accuracy for use in crystal analysis, are discussed, and values are tabulated for many atoms and ions. N. M. BLIGH.

Photo-electric properties of gold. L. W. MORRIS (Physical Rev., 1931, [ii], **37**, 1263—1268).—Variations in photo-electric properties of Au filaments were investigated with regard to rise of temp. and progress of out-gassing up to a stable state.

N. M. BLIGH.

Photo-electric properties of silver. R. P. WINCH (Physical Rev., 1931, [ii], **37**, 1269—1275).—Investigations were made during out-gassing, and in the resulting stable state, of photo-emission as a function of temp. for fixed wave-lengths. N. M. BLIGH.

Recoil atoms in rare gases. L. GOLDSTEIN (Compt. rend., 1931, **192**, 1373—1376; cf. this vol., 279).—The yield of activation for voltages giving the saturation current is identical for A, He, and Ne, and independent of the ionisation potential. Results at both electrodes and at varying pressures are discussed. C. A. SILBERRAD.

Electron polarisation. G. O. LANGSTROTH (Nature, 1931, **137**, 891).

Interference of electron spin in crystals. H. HELLMANN (Z. Physik, 1931, **69**, 495—506).—Theoretical. Reflexion of electrons at crystal surfaces is governed by a potential barrier of finite thickness.

A. B. D. CASSIE.

Behaviour of electrons in homogeneous electromagnetic fields according to Dirac's relativistic theory. F. SAUTER (Z. Physik, 1931, **69**, 742—764).—Mathematical.

Angular distribution of photo-electrons ejected by polarised ultra-violet light in potassium vapour. M. A. CHAFFEE (Physical Rev., 1931, [ii], **37**, 1233—1237; cf. Anderson, A., 1930, 972).—The most probable direction of ejection was found to be that of the electric vector; results are in accord with wave-mechanical predictions for a spherically symmetrical atom. N. M. BLIGH.

Specific heat of quasi-free electrons. E. C. G. STUECKELBERG and P. M. MORSE (Z. Physik, 1931, **69**, 666—677).—Theoretical. Sommerfeld's conductivity law may be considerably modified for quasi-free electrons. A. B. D. CASSIE.

Microscopical determination of the position of an electron. K. F. VON WEIZSÄCKER (Z. Physik, 1931, **70**, 114—130).—Mathematical.

A. B. D. CASSIE.

Pictorial representations of the electron cloud for hydrogen-like atoms. H. E. WHITE (Physical Rev., 1931, [ii], **37**, 1416—1424).—The wave-equation probability density factors are represented graphically and discussed. N. M. BLIGH.

Elucidation of the wave nature of H particles by scattering measurements in hydrogen. C. GERTHSEN (Ann. Physik, 1931, [v], **9**, 769—786).—The scattering of H particles by H_2 has been observed for angles between 15° and 35°. The scattering of He^+ particles by He has also been studied.

W. R. ANGUS.

Mobility of aged ions in air in relation to the nature of gaseous ions. N. E. BRADBURY (Physical Rev., 1931, [ii], **37**, 1311—1319).—The change in mobility with age of ions formed under the conditions of recombination measurements was investigated, and results are discussed. N. M. BLIGH.

Relation between range of rapid protons in air and the ionisation produced: artificial disintegration of the elements. L. LEPRINCE-RINGUET (Compt. rend., 1931, **192**, 1543—1545).—The range of protons arising from the transmutation of Al by α-rays of Po in air at 15° and 760 mm. is about 60 cm., those of longest range forming a definite monokinetic group. The max. ionisation produced by such a proton is about one fourth the max. produced by an α-ray, and during the last 50 cm. of its range is about 2800 ions per cm. C. A. SILBERRAD.

Ionic and electronic collisions. E. Friedlander, H. Kallmann, and B. Rosen (Naturwiss., 1931, **19**, 510—512).—Multiply-charged ions can be formed directly by electronic collision, and have been produced in CO_2 and CO. The decomp. of mol. ions by collision with a gas mol., or with a surface such as the walls of a containing vessel, is also shown.

A. J. Mee.

Residual ionisation in air at new high pressures, and its relation to the cosmic penetrating radiation. J. W. Broxon (Physical Rev., 1931, [ii], **37**, 1320—1337).—The ionisation-pressure curve slope (up to 170 atm.) gradually decreased to zero. N. M. Bligh.

Influence of bromine vapour on the mobility of positive and negative ions in hydrogen and oxygen. H. Mayer (Bul. Fac. Stiinte Cernauti, 1928, **2**, 65—82; Chem. Zentr., 1931, i, 1573—1574).

Effective cross-sections of molecules on the basis of gas theory. H. E. Binkele (Ann. Physik, 1931, [v], **9**, 839—852).—Theoretical. Consts. calc. from viscosity measurements agree well with the value of b in van der Waals' equation. W. R. Angus.

Effective cross-section of extinction of light emitted from sodium by iodine molecules and atoms. A. Terenin and N. Prileshaeva (Z. physikal. Chem., 1931, **B**, **13**, 72—92; cf. A., 1930, 520).—The extinction by I mols. of the D lines emitted by excited Na atoms formed by optical dissociation of NaI is attributed to the reaction $Na'+I_2=NaI+I$, the effective cross-section in the collision between the Na atom and the I mol. falling from 7×10^{-14} to $1{\cdot}5\times10^{-14}$ sq. cm. as the speed of the Na atom is increased from 1×10^5 to 3×10^5 cm. per sec. The extinction by I atoms is ascribed to the reaction $Na'+I=NaI+h\nu$; the effective cross-section is $1{\cdot}5\times10^{-14}$ sq. cm. and does not vary with the speed of the Na atom. R. Cuthill.

Periodic classification of the elements. S. K. Mitra (Phil. Mag., 1931, [vii], **11**, 1201—1214).—The periodic table is modified and extended to show electron configurations. N. M. Bligh.

Spectrographic search for element 61. S. Takvorian (Compt. rend., 1931, **192**, 1372—1373; cf. this vol., 783).—Spectrographic examination of the fractions previously referred to showed nothing but Nd and Sm, of which some 50 and 40 new lines respectively were measured between 3150 and 3200 Å.

C. A. Silberrad.

Existence of the stable element of at. no. 84. J. Proszt and M. Vendl (Mitt. Berg- Huttenmänn. Abt. Sopron, 1930, 21 pp.; Chem. Zentr., 1931, i, 1893).—Attempts to obtain the element from tetradymite, crude Te, and a metallurgical Bi residue were unsuccessful. A. A. Eldridge.

At. wt. of xenon. R. Whytlaw-Gray, H. S. Patterson, and W. Cawood (Nature, 1931, **127**, 970—971).—The extrapolated limiting density of Xe obtained from measurements of the pressures at which O_2 and Xe are equal in density is 4·1020, giving an at. wt. 131·26(4) ±0·005 in agreement with Aston's value of 131·27±0·04. L. S. Theobald.

Radioactive disintegration according to the relativity wave equation. S. Gupta (Z. Physik, 1931, **69**, 686—698).—Mathematical.

A. B. D. Cassie.

New applications of the emanation method. F. Strassmann (Naturwiss., 1931, **19**, 502—504; cf. Hahn, A., 1929, 737).—The method is used to show the marked difference in emanation properties of a dry and a moist sample of $BaSO_4$, and its dependence on temp. The method was also used to show the different emanation properties of Ba glasses with different life histories, and their dependence on temp. The emanation power of org. Ba salts in relation to their mol. structure is also investigated. A. J. Mee.

Grouping of radioactive atoms in gases. (Mlle.) C. Chamie and L. Goldstein (J. Chim. phys., 1931, **50**, 228—232).—The formation of groups of radioactive atoms is probably due to ionisation of traces of gas in the emanation tube, forming centres for condensation of radioactive atoms.

E. S. Hedges.

Actinium problem. II. G. Elsen (Chem. Weekblad, 1931, **28**, 342—348).—A survey of the problem of the origin of the actinium family, in the light of recent work on isotopes. H. F. Gillbe.

Range of α-rays of polonium in different gases. Nahmias (Compt. rend., 1931, **192**, 1451—1452).—Using Curie's method (cf. A., 1925, ii, 834) the value of $\varphi=l/\alpha$, where l is the most probable range and α varies directly with l and inversely as the density of the gas, is for air, O_2, A, and CO_2, respectively, 0·0200, 0·0250, 0·0190, and 0·0280. l_{ThC}/l_{Po} in air at 15° and 760 mm. is 1·20—1·21. Short-range α-particles of Th-C form a notable percentage of the total emitted. C. A. Silberrad.

Analysis of the long-range α-particles from Ra-C. (Lord) Rutherford, F. A. B. Ward, and W. B. Lewis (Proc. Roy. Soc., 1931, **A**, **131**, 684—703).—The new counting methods (A, 1930, 1338) have been used to analyse the distribution of the long-range α-particles from Ra-C (7—12 cm. in air). Nine homogeneous groups have been detected varying in energy between 8·30 and $10{\cdot}62\times10^6$ volts. The mean range of the strongest group is 9·04 cm. The velocities and energies of the α-particles are deduced from the measured ranges. The emission of α-rays from Ra-C appears to be closely connected with the long-range α-particles. It is concluded that the γ-rays arise from transitions of the α-particle between the excited levels and the ground level.

L. L. Bircumshaw.

Nuclear deflexions of β-rays. J. M. Nuttall and H. S. Barlow (Mem. Manchester Phil. Soc., 1929—1930, **74**, 35—40).—Stereoscopic photographs of more than 900 tracks of β-rays deviated by passage close to the nucleus in O_2 and N_2 were examined. The variation in the no. of deflexions with scattering angle, and the calc. value of the at. no. of the scattering nucleus were in accordance with the simple Rutherford theory of nuclear deflexion. N. M. Bligh.

γ-Rays of potassium. F. Behounek (Z. Physik, 1931, **69**, 654—663; cf. A., 1930, 1233).—Ionisation due to 96 kg. of KCl suggests that γ-radiation due to

K is homogeneous and of wave-length 13·3 X; its intensity is $1·3\times10^{-10}$ times that of the hardest Ra-*C* γ-radiation. A. B. D. CASSIE.

Decay constant of uranium II. C. H. COLLIE (Proc. Roy. Soc., 1931, A, **131**, 541—553).—The half-life period of U II is shown to be not less than 10^6 years. L. L. BIRCUMSHAW.

Experimental technique preparatory to atom disintegration by means of high potentials. A. BRASCH and F. LANGE (Z. Physik, 1931, **70**, 10—37).—Apparatus necessary for utilising atm. p.d. of 8000—15,000 kv. is described. Using an impulse generator, discharge tubes were tested to 2000 kv., and *X*-rays, β-rays, and H canal rays were produced. A. B. D. CASSIE.

Ionisation probability for inner levels through rapid corpuscular radiation and a method for its proof. L. MEITNER (Naturwiss., 1931, **19**, 497—499).—The question of how far it is possible for rapid corpuscular radiation—electrons or α-rays—to ionise from the inner shell is discussed, and investigated for light elements in the gaseous state. A. J. MEE.

Conditions on Schrödinger's ψ. E. H. KENNARD (Nature, 1931, **127**, 892—893).—Theoretical. L. S. THEOBALD.

Transformation of light into heat in solids. II. J. FRENKEL (Physical Rev., 1931, [ii], **37**, 1276—1294; cf. this vol., 282).—Previous results are generalised for diatomic crystals. N. M. BLIGH.

Application of quantum mechanics to chemical kinetics. L. GOLDSTEIN (Compt. rend., 1931, **192**, 1536—1539; cf. this vol., 666).—A qual. study of the combination of two H atoms to H_2, all being in the fundamental state, and neglecting proton spin and rotation of the atoms, based on a Schrödinger equation, shows that for this to occur a de Broglie wave must affect the system while it is experiencing a collision of the second kind. C. A. SILBERRAD.

Formation of elements and cosmic radiation. M. VON LAUE (Naturwiss., 1931, **19**, 530—531).—Theoretical. A. J. MEE.

Identification of the Raffety spectrum. H. GRENAT (Compt. rend., 1931, **192**, 1553—1555).—Measurements of 20 lines, with their intensities, of the Raffety spectrum, observed in the pointed flame of an O_2-C_2H_2 blowpipe, show this spectrum to belong definitely to the hydrocarbon group. C. A. SILBERRAD.

Raffety bands and cometary spectra. F. BALDET (Compt. rend., 1931, **192**, 1531—1533).—Comparison between the lines of the Raffety band (cf. preceding abstract) and those of cometary spectra shows definitely that there is no connexion. C. A. SILBERRAD.

Transparency of sodium fluoride and lithium fluoride in the extreme ultra-violet. E. H. MELVIN (Physical Rev., 1931, [ii], **37**, 1230—1232).—Artificially prepared single crystals of NaF and LiF were transparent to 1320 and 1083 Å. (132 Å. below the limit of fluorite), respectively. N. M. BLIGH.

Visible halogen bands, with special reference to ICl. R. S. MULLIKEN (Physical Rev., 1931, [ii], **37**, 1412—1415; cf. A., 1930, 1328; this vol., 1).—Dissociation into normal atoms of excited ICl mols., after absorption of light in the visible bands, agrees with theory. The probable classification of these bands is discussed; previous views on the behaviour of the I_2 bands in magnetic fields are revised. N. M. BLIGH.

Vibrational levels of the iodine monochloride molecule. W. E. CURTIS and O. DARBYSHIRE (Trans. Faraday Soc., 1931, **27**, 77—87).—The effect of temp., up to 200°, on the intensities of the vibrational progressions of ICl has been investigated. F. G. TRYHORN.

Ultra-violet absorption spectrum of sulphur dioxide. W. W. WATSON and A. E. PARKER (Physical Rev., 1931, [ii], **37**, 1484—1492; cf. A., 1930, 1090).—Band assignments to the fundamental vibrational series are tabulated. The process $SO_2 \longrightarrow S+O_2$ for the two symmetrical vibrations and $SO_2 \longrightarrow SO+O$ for the asymmetrical vibration are indicated. N. M. BLIGH.

Ultra-violet absorption spectrum of hydrazine vapour. S. IMANISHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, **15**, 166—167).—A brief account of results obtained with small dispersion. W. GOOD.

Absorption spectra of complex salts of Fe, Co, Ni, Pd, and Pt. R. SAMUEL (Z. Physik, 1931, **70**, 43—73).—With a H_2 discharge tube absorption spectra were measured in the region 200—600 mμ for $[Co(NH_3)_6]Cl_3$, $[Co(NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)_2]Cl_2$, $[Co(NH_3)_6]Cl_3$ to $[Co(NH_3)_3(NO_2)_3]$, $Na_3[Co(NO_2)_6]$, $Na_2[Fe(CN)_5(NO)]$, $[Co(NH_3)_6]Cl_3$ to $[Co(NH_3)_4Cl_2]Cl$, $[Co\,en_2Cl_2]Cl$, K_3 and $K_4[Fe(CN)_6]$, K_3 and $K_4[Co(CN)_6]$, $K_2[Ni\,CN_4)]$, $K_2[Ni(CN)_4]$, $K_2[Pd(CN)_4]$, and $K_2[Pt(CN)_4]$. The results are inconsistent with a purely electrostatic theory of co-ordination, only the long-wave limit of absorption being influenced by the degree of ionisation of the metal atom. Observed bands do not belong to radicals such as NH_3, but are characteristic of the co-ordination group. A. B. D. CASSIE.

Organic acid iron solutions. I. Concentrations and colours. N. J. HARRAR and F. E. E. GERMANN (J. Physical Chem., 1931, **35**, 1666—1673).—The concentrations, colours, colours on dilution, and relative colour intensities of the solutions obtained by dissolving freshly-precipitated $Fe(OH)_3$ in HCl, H_2SO_4, and the commoner org. acids (mainly aliphatic, and approx. *N* where possible) are recorded. Colour is mainly determined by the strength of the acid concerned, strong acids giving green, and weak acids red, solutions. L. S. THEOBALD.

Absorption spectra of crystals at low temperatures as references in the measurement of stellar velocities. S. FREED (Nature, 1931, **128**, 33).—The absorption spectrum of dysprosium ethyl sulphate at the temp. of liquid N contains sharp lines between 4000 and 4800 Å., and, together with spectra of other rare earths at this temp., is suggested as reference for stellar velocities. L. S. THEOBALD.

Simple relations between molecular spectra and structure. H. DESLANDRES (Compt. rend., 1931, **192**, 1417—1421; cf. this vol., 544).—Further

examples are given, the submultiples of the fundamental frequency (1062·5) being 3, 6, 7, 8, and 9.

C. A. SILBERRAD.

Simple relations between molecular spectra and structure. H. DESLANDRES (Compt. rend., 1931, **192**, 1606—1610; cf. preceding abstract).—Similar relations are shown to exist as regards many infra-red bands of CO_2 and NH_3, the submultiples of the fundamental frequency 1062·5 varying from 2 to 108.

C. A. SILBERRAD.

Spectroscopy and chemical reactions. M. DE HEMPTINNE (Bull. Soc. chim. Belg., 1931, **40**, 220—233).—A lecture.

H. F. GILLBE.

Spectroscopic and photochemical research on the diazo-compounds. I. FUKUSHIMA and M. HORIO (Mem. Coll. Eng. Kyoto, 1931, **6**, 179—238).—The absorption spectra of C_6H_6, NH_2Ph,HCl, and diazobenzene chloride are similar, but different from NH_2Ph. This relationship persists if the groups NO_2, SO_3H, CO_2H, Me, and Cl are introduced into the nucleus, and suggests that diazobenzene chloride and its derivatives are structurally similar to NH_2Ph,HCl and its derivatives, the first N atom being quinquevalent in each case. The spectra of the diazo-compounds are radically changed by the introduction of the groups OH, OMe, and OEt.

Absorption spectra of 1 : 2 : 4-diazonaphtholsulphonic acid and diazobenzenesulphonic acid were obtained. The rate of photolysis of both compounds is independent of the concentration, and that of diazonaphtholsulphonic acid is independent of the temp., but reduced by addition of quinine sulphate. The rate of decomp. of diazobenzenesulphonic acid varies with the temp., for the photolysis is accompanied by a thermal reaction, the rate of which is proportional to the concentration of reactant. The two reactions are not entirely independent, but the effect of the thermal reaction is not perceptible below about 40°. The quantum efficiency of the photolysis of diazobenzenesulphonic acid by light of wave-length 366 mμ is 0·16.

R. CUTHILL.

Absorption spectra of plumbagin and naphthoquinones. N. GÓMEZ (Anal. Fís. Quim., 1931, **29**, 367—368).—The ultra-violet absorption spectra of naphthoquinone and 2-methylnaphthoquinone are almost identical, and it is not possible to ascertain the position of the OH group of plumbagin spectroscopically.

H. F. GILLBE.

Absorption spectra and constitution of azoxy-derivatives and analogous compounds. L. SZEGO and P. OSTINELLI (Atti III Cong. Naz. Chim. pura appl., 1929, 395—401; Chem. Zentr., 1931, i, 1444).—Ultra-violet absorption spectra of the following compounds were studied: deoxybenzoin, m. p. 56°; *p*-nitro-; *p*-amino-, m. p. 95°; β-*p*-hydroxy-; α-*p*-methyl-; β-*p*-chloro-, m. p. 102°, -deoxybenzoin; oxime, m. p. 117°. The singular behaviour of the β-compounds is discussed.

A. A. ELDRIDGE.

Absorption of infra-red radiation by water vapour. E. K. PLYLER and W. W. SLEATOR (Physical Rev., 1931, [ii], **37**, 1493—1507).—Using increased resolution, new lines of the 4 absorption bands of water vapour have been measured, and existing data for the strong lines corrected.

N. M. BLIGH.

Reflecting power of water and ice for infra-red radiation. M. WEINGEROFF (Z. Physik, 1931, **70**, 104—108).—The reflecting power of liquid water was measured for the wave-lengths 11—18 μ, and of ice for 6—16 μ; the latter suggests a residual-ray frequency in this region.

A. B. D. CASSIE.

Obtaining Raman spectra with small quantities of liquid. W. DEKEYSER (Natuurwetensch. Tijds., 1931, **13**, 230—231).—About 13 c.c. are enclosed in a small vessel covered with a microscope cover glass; the time of exposure in the spectrograph is reduced to about one seventh by using an Al electrically-heated plate holder.

H. F. GILLBE.

Monochromatic excitation of Raman spectra in the ultra-violet. H. HULUBEI and (MLLE.) Y. CAUCHOIS (Compt. rend., 1931, **192**, 1640—1643; cf. this vol., 667).—By interposing a quartz tube containing Cl under pressure and an arrangement for cooling in the apparatus previously described, the resonance line, λ 2535·32, is isolated, accompanied only by λ 4358 slightly diminished and the green and yellow lines. The blue Raman H_2O band (cf. A., 1930, 1091) is double, whilst that with max. at 2780—2782 Å. is simple (cf. this vol., 408). Six other bands were observed corresponding with Δν 7729, 8243, 8703, 9223, 10,151, 11,264 $cm.^{-1}$ EtOH showed lines corresponding with Δν 506, 880, 1038, 2741, 2876, 2929, and 2980, and two bands with Δν 9870 and 10,551 $cm.^{-1}$

C. A. SILBERRAD.

Raman effect and polymerisation of water at various temperatures. O. SPECCHIA (Atti R. Accad. Lincei, 1930, [vi], **12**, 659—662).—Raman spectra of water in the region 4108—5790 Å. have been measured at 17—91°. The results indicate changes in the state of polymerisation of water with temp.

O. J. WALKER.

Raman spectra of some substances containing SO or SO_2 group. H. NISI (Japan. J. Phys., 1930, **6**, 1—15; cf. A., 1930, 662).—Raman lines and wave-no. shifts are tabulated for SO_2 (liquid), H_2SO_4, $SO_2\cdot OH\cdot Cl$, SO_2Cl_2, $PhSO_3H$, $PhSO_2Cl$, $C_6H_4Me\cdot SO_3H$ (*p*), C_6H_6, PhMe, $SOCl_2$, S_2Cl_2, $POCl_3$, PCl_3, $SO(OEt)_2$, EtOH, and H_2SO_3. The structure of the last (non-ionised) is indicated as $H\cdot SO_2\cdot OH$. The polarisation states of the various lines are described.

N. M. BLIGH.

Raman effect in the ultra-violet region. J. C. GHOSH and B. C. KAR (J. Physical Chem., 1931, **35**, 1735—1744).—The Raman effects produced by ultra-violet light are recorded for a number of simple org. compounds. The frequency shifts between 1340 and 1405 given by $H\cdot CO_2H$, $H\cdot CO_2Na$, and NaOBz may be due to a C—(OH) vibration. Acids, except $CCl_3\cdot CO_2H$, but not the corresponding Na salts, give frequency shifts 1600—1700. The shifts diminish in passing from $CH_2Cl\cdot CO_2H$ and $CCl_3\cdot CO_2H$ to their Na salts. Formic acid undergoes decomp. and the halogeno-acids undergo hydrolysis when exposed to ultra-violet light of wave-length 2000—3000 Å.

L. S. THEOBALD.

Spectrum of radiation scattered by some simple open and closed hydrocarbon rings. J. Weiler (Z. Physik, 1931, 69, 586—596).—Raman spectra due to C_5H_{12}, amylene, *cyclo*pentane, *cyclo*hexane, *cyclo*hexene, and C_6H_6 are given in full, and are shown to be consistent with an intense line near 900 cm.$^{-1}$ characteristic of a closed ring, and with a line near 3000 cm.$^{-1}$ due to CH groups.

A. B. D. Cassie.

Ionic nature of the hydrogen linking. C. Kasper (J. Amer. Chem. Soc., 1931, 53, 2424—2425; cf. this vol., 670).—Raman effect data for hydrates and solutions afford strong evidence that the H linking is not of the extreme electron-pair type.

J. G. A. Griffiths.

The carbon-halogen linking as related to Raman spectra. W. D. Harkins and H. E. Bowers (J. Amer. Chem. Soc., 1931, 53, 2425—2427). —The frequency corresponding with the C–Br linking in MeBr is $1{\cdot}808\times10^{13}$ per sec., but with longer normal chains or with sufficiently remote *iso*-groups, the const. value $1{\cdot}688\times10^{13}$ is found. An adjacent double linking or side-chain or direct attachment of the Br to a *sec.* or *tert.* C atom decreases the frequency to $1{\cdot}61\times10^{13}$, except in the case of $Bu^{\beta}Br$. The results indicate that the CH_2 group, and not the whole org. radical linked to the Br atom, vibrates with respect to the Br, but the effective mass of the CH_2 is increased by constraints due to its union with the rest of the hydrocarbon chain. J. G. A. Griffiths.

Raman spectra of formaldehyde, trioxymethylene, ethylene glycol, and some viscous liquids. J. H. Hibben (J. Amer. Chem. Soc., 1931, 53, 2418—2419).—The similarity of the Raman spectra of 37% aq. CH_2O and ethylene glycol indicates the formation of methylene glycol by CH_2O in aq. solution. Lines typical of the C:O linking are absent, but that of C·O is strong in these spectra and in that of trioxymethylene.

Na silicate, H_3PO_4, potassium hydrogen phosphite, and glycol solutions afford strong continuous Raman spectra which decrease on dilution and on raising the temp., indicating that this property is probably common to viscous liquids (cf. A., 1928, 1170, 1306).

J. G. A. Griffiths.

Raman effect of some amino-compounds. A. S. Ganesan and V. N. Thatte (Z. Physik, 1931, 70, 131—139).—The Raman effect due to NHPhMe, $NPhMe_2$, and $NPhEt_2$, *o*-, *p*-, and *m*-toluidine and xylidine has been investigated. The displacement 3432 cm.$^{-1}$ is characteristic of the N–H linking.

A. B. D. Cassie.

Intensity and polarisation of Raman radiation due to polyatomic molecules. G. Placzek (Z. Physik, 1931, 70, 84—103).—Intensity and polarisation of Raman radiation is determined by variation of mol. polarisability with nuclear separations, whereas infra-red absorption depends on the effective permanent electric moment. This explains differences between the two, and indicates that the intensity of Raman lines increases from zero for ionic mols., where the resultant polarisability tends to be independent of nuclear separation, to a max. for homopolar mols. Symmetry properties lead to the selection rule that no normal frequency can appear as Raman radiation if a symmetry operator of the mol. (such as rotation of a symmetrical linear mol. through 180°) when applied to the corresponding normal co-ordinate changes its sign but not its magnitude. These results are applied to the spectra of CCl_4, CO_2, N_2O, CS_2, C_2H_2, and C_2H_4. A. B. D. Cassie.

Fluorescence and absorption of phosphorus vapour. A. Jakowlewa (Z. Physik, 1931, 69, 548—563).—Fluorescence and absorption spectra of P vapour indicate a 5·2 volt dissociation energy for the P_2 molecule. A. B. D. Cassie.

Phosphorescent substances. IV. Calcium, strontium, and barium sulphides. N. F. Shirov (Ukrain. Chem. J., 1930, 5, [Sci.], 365—382).—The intensivity and duration of phosphorescence of mixtures containing alkaline-earth sulphides are increased by ignition with MgO and, to a smaller extent, with BeO, CdS, or tungstates; BaO, CaO, SrO, and Al_2O_3 are unsuitable. The best activation temp. is 900—1000° for mixtures containing alkaline-earth carbonate, MgO, Mg tungstate, S, sugar, borax, Li_2O_3, K_2SO_4, CaF_2, and $Bi(NO)_3$.

R. Truszkowski.

Quenching of some alkali-halide phosphors and the quantum efficiency of quenching for the potassium chloride phosphor with admixed thallium. W. Bunger and W. Flechsig (Z. Physik, 1931, 69, 637—653).—Spectral distribution of radiation effective in quenching light from KCl, KBr, and NaCl phosphors was found to give a max. at the frequency equal to the difference between positions of absorption and emission max.; the abs. efficiency for the KCl–Tl phosphor suggests that quenching by irradiation is a quantum process. A. B. D. Cassie.

Connexion between photo-current and light intensity for gas-filled alkali cells. G. Kortüm (Physikal. Z., 1931, 32, 417—425).—The relationship $i^z=cj+$const. holds to a fair degree of accuracy for the cells investigated. The cell const., z, is rarely unity, and is then independent of charge and wavelength. In other cases it differs considerably from unity and varies with the intensity and the wavelength. A. J. Mee.

Photo-electric cells and formation of photo-electrons. S. E. Sheppard and W. Vanselow (Physikal. Z., 1931, 32, 454—455).—The mechanism of the photo-electric effect and formation of photo-electrons is discussed for Ag–AgBr–KBr cell.

A. J. Mee.

Spectral sensitivity of unidirectional layer photo-cells. B. Lange (Naturwiss., 1931, 19, 525—530).—The spectral sensitivity of several Cu_2O unidirectional photo-cells was determined. The cells differ markedly among themselves in their sensitivity, but in all cases the photo-current started at about 575 mμ, and reached a very sharp max. at about 630 mμ. The infra-red wave-length limit for all cells was about 1400 mμ. The course of the sensitivity curve appears to depend on the thickness of the Cu_2O layer. The very sharp increase in spectral sensitivity at the red end of the spectrum is explained by the considerable transparency of Cu_2O for light of this wave-length. A. J. Mee.

Photo-electric emission of thin films. N. R. CAMPBELL (Phil. Mag., 1931, [vii], 12, 173—185).—The nature of the film formed and the changes in emission during the heating of oxidised Ag in Cs vapour are described. The reaction is concluded to be $2Cs+Ag_2O=Cs_2O+2Ag$. The support for the Cs film is probably a mol. mixture of Cs_2O and Ag formed from an alloy of Cs and Ag. N. M. BLIGH.

External photo-electric effects in phosphors and its dependence on the state of excitation. H. GOTHEL (Ann. Physik, 1931, [v], 9, 865—886).—Curves are reproduced showing the effects produced by modifications of experimental procedure using Ca–Bi–Na, Sr–Bi–Na, and Ba–Bi–K sulphide phosphors; the effects are discussed. W. R. ANGUS.

Electrical discharge in rock-salt. L. INGE and A. WALTHER (Naturwiss., 1931, 19, 595).—The direction in which the electrical discharge takes place in rock-salt is investigated. A. J. MEE.

Conductivity of pure liquids [hexane]. A. NIKURADSE (Z. physikal. Chem., 1931, 155, 59—64).—An apparatus is described in which by drying with P_2O_5, filtration through sintered glass, cataphoresis, and fractional distillation, commercially pure hexane is purified until its conductivity is reduced from its original value of 10^{-12} to 10^{-13} mho to a limiting value of 10^{-19} mho. N. H. HARTSHORNE.

Electrical conductivity of single aluminium crystals in directions inclined at various angles to the crystal axes. M. FRASER (Phil. Mag., 1931, [vii], 12, 112—129).—The sp. resistance of a single crystal was independent of the orientation relative to the crystal axes, and was about 1% greater than for the annealed metal. N. M. BLIGH.

Conductance of zirconium oxide. H. SCHWEITZER (Z. angew. Chem., 1931, 44, 151—152).—The conductance of ZrO_2 has been measured over the range 200—800°. Slight differences appear in measurements made during heating or cooling. Traces of MgO considerably increase the conductance. Ohm's law is obeyed up to a potential gradient of 1500 volts per cm. F. G. TRYHORN.

Electrical conductivity of liquid hydrocarbons. L. BRUNINGHAUS (Ann. Office Nat. Combust. liq., 1929, 4, 515—527; Chem. Zentr., 1931, i, 1705).—The fact that benzine, when filtered through metal filings, becomes negatively, and the metal positively, charged is discussed theoretically.

A. A. ELDRIDGE.

Magnetic and electric moments of Dirac's electrons. T. TANAKA (Z. Physik, 1931, 69, 810—821).—Mathematical.

Experimental and theoretical foundations of the swarm theory. L. S. ORNSTEIN (Z. Krist., 1931, 79, 90—121).—A critical account of the theory.

C. A. SILBERRAD.

Oscillation method for determining the dielectric constants of conducting liquids. W. GRAFFUNDER and R. WEBER (Ann. Physik, 1931, [v], 9, 887—904).—A more detailed account of work already noted (this vol., 23). W. R. ANGUS.

Dipole moments of some inorganic compounds and a method for determining atomic distances and radii. E. BERGMANN and L. ENGEL (Physikal. Z., 1931, 32, 507—509).—Inorg. halides of the type AX_3 have a finite dipole moment. Hence the atoms cannot all be arranged in one plane, but must be arranged as a three-sided pyramid. The same conclusion is reached by considering the Raman effect. A calculation based on the work of Hund on the H_2O and NH_3 models shows that the plane model would be less stable than the pyramidal. In the series BCl_3–PCl_3–$AsCl_3$–$SbCl_3$ the radius of the central atom increases, and there is a gradually increasing distance between the central atom and the halogen atoms. Compounds of the type AX_4, such as $SnCl_4$, have also a finite moment. Hence the atoms must be arranged in the form of a four-sided pyramid. For $SiCl_4$ and $TiCl_4$ (as for CCl_4) the moment is zero, and the arrangement is tetrahedral. Compounds of the type AX_5 have also a finite moment. The moments of $SbCl_5$ and $Fe(CO)_5$ exclude the two configurations, plane (a regular pentagon with the central atom at the centre of gravity), and trigonal bipyramid, but allow the five-sided pyramid, and the four-sided pyramid with four atoms at the base and one atom at the point, and a central atom inside. The tetragonal cryst. structure of PCl_5 and $TaCl_5$ as well as the chemical properties are in favour of the latter. A. J. MEE.

Dielectric constant of air at high pressures. J. W. BROXON (Physical Rev., 1931, [ii], 37, 1338—1344).—The dielectric const. of aged, dry, dust-free air, measured up to 170 atm., increased linearly with the pressure. N. M. BLIGH.

Dielectric properties of methylamines. O. STEIGER (Physikal. Z., 1931, 32, 425—434).—The dielectric consts. of gaseous NH_2Me, $NHMe_2$, and NMe_3 have been determined. Several other consts. for these substances are also found. A. J. MEE.

Dielectric constant and chemical constitution: method. A. CHRETIEN (Compt. rend., 1931, 192, 1385—1387).—The method is Nernst's (cf. A., 1894, ii, 437) modified by using condensers with quartz plates, an indirectly excited oscillating circuit, a galvanometer in place of telephone, and a vertical condenser for the liquid under examination. Et_2O is the standard liquid. ε at 25° for C_6H_6, $CHCl_3$, hexane, and acetal is respectively 2·270—2·274, 4·721—4·726, 1·910—1·014, and 4·791—3·798 (cf. A., 1930, 729).

C. A. SILBERRAD.

Electric moments and molecular constitution. G. ALLARD (Compt. rend., 1931, 192, 1455—1457).—The principle of additivity of electric moments (cf. A., 1929, 980) is extended by assigning different moments to atoms attached to a C atom according as this latter is attached to another by a single or double linking. The results indicate three ethylenic linkings for C_6H_6, and a quinonoid structure for *p*-chlorophenol (cf. Smyth and Dornte, this vol., 669).

C. A. SILBERRAD.

Dielectric constants [of mesomorphic substances]. W. KAST (Z. Krist., 79, 146—160).—A crit. summary of recent work. C. A. SILBERRAD.

Dipole moments and structure of organic compounds. VII. Electric moments of stereo-

isomeric hydrobenzoins. A. WEISSBERGER and R. SANGEWALD. **VIII. Nature of simple linkings.** A. WEISSBERGER (Z. physikal. Chem., 1931, **B**, **12**, 399—407, 408—412; cf A., 1930, 1093).—VII. The dipole moments of hydrobenzoin and *iso*hydrobenzoin, measured in C_6H_6 solution at 25°, are respectively 2·1 and $2{\cdot}7\times10^{-18}$ e.s.u. Owing to small solubility, supersaturated solutions were used. The Me_2 esters of *d*-tartaric and racemic acid were examined in both unsaturated and supersaturated solution, and the same dipole moment, $2{\cdot}9\times10^{-18}$, was obtained in both cases and for both substances.

VIII. A general discussion of results. Reasons are given for believing that groups inclined at an angle to a single linking do not assume a rigid position of low symmetry. F. L. USHER.

Electric moment and molecular structure. IV. Glycols. C. P. SMYTH and W. S. WALLS (J. Amer. Chem. Soc., 1931, **53**, 2115—2122).—Density and dielectric const. data at 25° and 50° have been determined for solutions of BuOH and the glycols in 1 : 4-dioxan (cf. A., 1930, 849). The following electric moments at 25° are recorded: BuOH $1{\cdot}81\times10^{-18}$ e.s.u.; $HO{\cdot}[CH_2]_2{\cdot}OH$ 2·28; $OH{\cdot}CHMe{\cdot}CH_2{\cdot}OH$ 2·25; $HO{\cdot}[CH_2]_3{\cdot}OH$ 2·5; $HO{\cdot}[CH_2]_6{\cdot}OH$ 2·48; $HO{\cdot}[CH_2]_{10}{\cdot}OH$ 2·52. The results are discussed and indicate the absence of any pronounced bending of the C chain. J. G. A. GRIFFITHS.

Dielectric constant of formic, acetic, and propionic acids, and the electric moment of complex molecules. C. T. ZAHN (Physical Rev., 1931, [ii], **37**, 1516—1526; cf. A., 1930, 841).—The temp. and pressure variations of the dielectric const. of formic and propionic acids are similar to those for AcOH. For formic acid the amount of association into double mols. is calc.; values for the electric moment of the single and double mol. are $1{\cdot}51\times10^{-18}$ and $0{\cdot}99\times10^{-18}$ e.s.u., and for the single mol. of acetic and propionic acids $1{\cdot}73\times10^{-18}$ and $1{\cdot}74\times10^{-18}$ e.s.u., respectively. The electric moment of complex mols. is discussed and interpreted, and a structure for the double mol. of formic acid is suggested.

N. M. BLIGH.

Electric moments of the fixed vegetable oils. W. N. STOOPS (J. Physical Chem., 1931, **35**, 1704—1711).—The densities and dielectric consts. of tung, linseed, and castor oils have been measured at temp. between −70° and 100° and the polarisations at infinite dilution calc. from the Debye equation.

L. S. THEOBALD.

Optical activity dependent on co-ordinated nickel. G. T. MORGAN and F. H. BURSTALL (Nature, 1931, **127**, 854).—Pink, complex nickelous salts $[Ni3R]X_2,6H_2O$, where R is dipyridyl and X is Cl, Br, I, or NO_3, and $[Ni3R](CNS)_2,3H_2O$ have been prepared. Ammonium *d*-tartrate and the chloride give a soluble dextrorotatory tartrate $[Ni3R]C_4H_4O_6,6H_2O$ which on double decomp. with NH_4Cl furnished an optically active tris-$\alpha\alpha'$-dipyridyl nickelous chloride. The fall in optical activity corresponded with that for a unimol. reaction; max. activity corresponded with $[\alpha]$ +550°. Analogous complex salts of $Mn^{\cdot\cdot}$ have also been obtained. Tripyridyl (R′) gives rise to well-defined compounds of the type $[M2R']X_2$ with $Fe^{\cdot\cdot}$ and Ni. L. S. THEOBALD.

Optical activity in terms of the theory of coupled surfaces. K. SCHERINGA (Chem. Weekblad, 1931, **28**, 363—365).—Theoretical.

H. F. GILLBE.

Anomalous dispersion of active tartaric acid. K. SCHERINGA (Chem. Weekblad, 1931, **28**, 394—395).—A theoretical note. H. F. GILLBE.

Double refraction of thin layers of anisotropic liquids in a magnetic field, and the force orienting these layers. V. FREEDERICKSZ and V. ZOLINA (Z. Krist., 1931, **79**, 255—267).—Previous results (cf. A., 1927, 505; 1929, 743) are extended to acetoxybenzaldazine and anisaldazine and the existence of a layer in contact with the wall unaffected by the magnetic field is confirmed. C. A. SILBERRAD.

Optics of mesophases. H. ZOCHER (Z. Krist., 1931, **79**, 122—133).—A non-mathematical account of the phenomena observed. C. A. SILBERRAD.

Magneto-optical dispersion of organic liquids. III. Active *iso*amyl alcohol and *n*-propyl formate. E. THOMAS and E. J. EVANS (Phil. Mag., 1931, [vii], **11**, 1220—1232; cf. this vol., 411).—Data are recorded and expressions found for the magneto-optical and natural dispersion for various wave-lengths in the visible and ultra-violet. N. M. BLIGH.

Molecular and atomic volumes. XXXI. Low-temperature densities of certain elements. A. SAPPER and W. BILTZ [with (FRL.) WÜNNENBERG]. **XXXII. Zero volumes of the elements.** W. BILTZ and K. MEISEL (Z. anorg. Chem., 1931, **198**, 184—190, 191—203).—XXXI. Data are given for the halogens, Ca, Hg, S, and P (white). The extrapolated zero vols. of the halogens are in extremely close agreement with the calc. val. of Hertz, but for the other elements the discrepancies are considerable.

XXXII. Existing data for the densities, zero vol., at. vol., and expansion coeff. of the elements are summarised, and the regularities observed when the zero vol. are classified according to the periodic system are discussed. Calculation of the packing densities demonstrates the close packing of the metals compared with the definitely non-metallic elements, the inert gases and H being the sole exceptions.

H. F. GILLBE.

Problems in the theory of anisotropic liquids. C. W. OSEEN (Z. Krist., 1931, **79**, 173—185).—A mathematical treatment of the effects of temp. on anisotropic liquids. C. A. SILBERRAD.

Para- and ortho-hydrogen. A. BIJL and J. VAN HEININGEN (Chem. Weekblad, 1931, **28**, 359—363).—A survey. H. F. GILLBE.

Pseudopolar reaction between atoms of hydrogen. E. MAIORANA (Atti R. Accad. Lincei, 1931, [vi], **13**, 58—61).—Mathematical.

O. J. WALKER.

Paramagnetism of bivalent silver. G. T. MORGAN and S. SUGDEN (Nature, 1931, **128**, 31).—The magnetic susceptibility of $[Ag3R](ClO_3)_2$ (R= dipyridyl) at 20° gives χ $1\ 93\times10^{-6}$ and χ_M 1434×10^{-6}; the Weiss magneton no. is 9·1. L. S. THEOBALD.

Magnetic susceptibility [of mesomorphic substances]. W. Kast (Z. Krist., 1931, 79, 161—172).—A crit. summary of recent work.
C. A. Silberrad.

Influence of chemical combination on the absorption spectrum of the Röntgen series. R. Swinne (Wiss. Veröff. Siemens-Konz., 1931, 10, [2], 89—94).—From London's theory of non-polar valency linkings it follows that in the case of non-polar compounds of certain elements peripheral electronic arrangements and Röntgen terms would be expected which do not occur in polar compounds or with free neutral atoms. This conclusion is held to explain qualitatively the nature of the absorption observed by Meyer in the K series of elements with a higher at. no. than Fe. The special effect of rhombic S in causing displacement of the Röntgen absorption edges of elements and compounds is attributed to its powerful association action. A. R. Powell.

Two modifications of liquid carbon disulphide. M. Wolfke and J. Mazur (Nature, 1931, 127, 926—927).—The heating curve of CS_2 shows a break at $-90·03°$. The two modifications of CS_2 become visible on cooling. The heat of transformation is approx. 0·04 g.-cal./g. L. S. Theobald.

Viscosity, surface tension, and parachors of some cyclic hydrocarbons. M. Godchot and (Mlle.) G. Cauquil (Compt. rend., 1931, 192, 1560—1562).—These consts. have been determined for 12 cyclanes and 11 cyclenes (C_6 to C_8). The cyclanes have higher viscosities than the cyclenes, both very much higher than the corresponding paraffins. Surface tension increases with no. of C atoms in the ring, and is always much higher than in the corresponding paraffin. The parachors agree with the calc. values within 1%; the values for closure of a C_7 and a C_8 ring are respectively 4·6 and 2·37.
C. A. Silberrad.

Surface tension of saturated vapours and the equation of Eötvös. J. L. Shereshefsky (J. Physical Chem. 1931, 35, 1712—1720).—Theoretical. An expression connecting surface tension of saturated vapours with temp. is deduced and compared with experimental values for C_6H_6, PhCl, Et_2O, CCl_4, $H·CO_2Me$, and AcOEt. A new modification of Eötvös' law is developed and tested against observed data for the same compounds in the liquid state.
L. S. Theobald.

Methods and apparatus employed at the Bureau of Physico-Chemical Standards. IV. Surface tension of a number of organic compounds. (Mme.) H. Roland and Lek (Bull. Soc. chim. Belg., 1931, 40, 177—188).—An apparatus is described for the measurement of surface tension by the capillary-flow method; the results are accurate to within about 0·2%. Data are given for a large number of org. liquids for the interval 15—30°; results for C_6H_6 are compared with recorded results.
H. F. Gillbe.

Calculation of van der Waals forces. H. Margenau (Physical Rev., 1931, [ii], 37, 1425—1430).—Mathematical. N. M. Bligh.

Diffuse scattering of X-rays by solids. G. E. M. Jauncey (Physical Rev., 1931, [ii], 37, 1193—1202).—Theoretical. From the classical theory of X-ray scattering applied to that by the electrons in the atoms of one kind in a solid an expression is deduced for the scattered intensity per electron. N. M. Bligh.

Diffuse scattering of X-rays by simple cubic crystals. G. E. M. Jauncey and G. G. Harvey (Physical Rev., 1931, [ii], 37, 1203—1209).—The expression previously obtained (cf. preceding abstract) is modified for a cubic crystal of atoms of one kind.
N. M. Bligh.

Principles determining the arrangement of atoms and ions in crystals. M. L. Huggins (J. Physical Chem., 1931, 35, 1270—1280).—A review of fundamental principles. L. S. Theobald.

Electrical figures on photographic plates in liquids. K. Przibram (Physikal. Z., 1931, 32, 481—482).—The method of obtaining the figures is described.
A. J. Mee.

Causes of the broadening of the lines in X-ray powder and rotating-crystal diagrams. U. Dehlinger (Z. Metallk., 1931, 23, 147—149).—From a review of recent work on the effect of cold work on the broadening of the lines in rontgenograms of various metals it is concluded that this effect can be due only to the non-homogeneous distortion or bending of the grains remaining after slip has occurred, which is produced by pressure perpendicular to the direction of deformation by rolls or by dies in cold-working.
A. R. Powell.

X-Rays for the determination of small changes in the lattice constants of α-iron. A. E. van Arkel and W. G. Burgers (Z. Metallk., 1931, 23, 149—151).—Accurate results are obtained for the lattice consts. of α-Fe by using Co-$K\alpha$ radiation with an angle of incidence of 80—81°. Pure Fe has a 2·8614; after annealing in H_2 for 8 days at 100 atm. no change occurs. A. R. Powell.

Crystal structure of the compound Fe_2B. G. Hagg (Z. physikal. Chem., 1931, B, 12, 413—414).—Complete analogy exists between the structure of Fe_2B and that of $CuAl_2$. The space-group is most probably D_{4h}^{18}, and not V^{11} (cf. this vol., 151).
F. L. Usher.

Crystal structures of Cu_5Zn_8 and Cu_5Cd_8. A. J. Bradley and C. H. Gregory (Phil. Mag., 1931, [vii], 12, 143—161).—The structures are of the γ type, with 52 atoms in the unit cell; in Cu_5Cd_8 there are 16 Cu atoms in groups of 8 and 8, and 4 Cu and 32 Cd atoms distributed at random amongst groups of 12 and 24. In Cu_5Zn_8, similarity of X-ray scattering powers prevents a distinction of the atoms, and deductions on analogy with Ag_5Zn_8 and Au_5Zn_8 appear incorrect. Data obtained from interat. distance values and ternary Cu–Zn–Al alloys indicate a structure differing from that of Cu_5Cd_8.
N. M. Bligh.

Crystal lattice of anhydrous sodium sulphite. W. H. Zachariasen and H. E. Buckley (Physical Rev., 1931, [ii], 37, 1295—1305).—Four methods were employed. The hexagonal unit cell contains 2 mols., and has a 5·441, c 6·133 Å., requiring the assumption of twin crystals with the c-axis as twinning axis. The disposition of the atoms is described, and the presence of SO_3 groups shown. N. M. Bligh.

Crystal structure of potassium permanganate. R. C. L. MOONEY (Physical Rev., 1931, [ii], **37**, 1306—1310).—The unit cell is orthorhombic, contains 4 mols., and has *a* 9·09, *b* 5·72, *c* 7·41 Å. The observed intensity and calc. structure amplitude agree satisfactorily. The grouping of the atoms is described. N. M. BLIGH.

Crystal structure of the tetrahalides of the lighter elements. Structure of silicon tetraiodide. O. HASSEL and H. KRINGSTAD (Z. physikal. Chem., 1931, **B**, **13**, 1—12).—The structure is cubic, and the edge of the unit cell, which contains 8 mols., is 11·99 Å. in length. R. CUTHILL.

Crystal structure of molybdenum trioxide: a correction. N. WOOSTER (Nature, 1931, **128**, 35).—*c* should be 3·67 and *u* and *v* should be interchanged (this vol., 289). L. S. THEOBALD.

Structure of XO_3 groups in crystals. W. H. ZACHARIASEN (J. Amer. Chem. Soc., 1931, **53**, 2123—2130; cf. A., 1929, 1131).—The data indicate two classes of structure for the groups $(XO_3)^{-m}$, one coplanar and having 3×8 valency electrons and the other low pyramidal and having $3\times8+2$ valency electrons. The formation of asymmetrical groups is explained in terms of the polarisability of ions. The pyramidal groups consist of 3 O ions at 3 corners of a tetrahedron, the fourth corner being occupied by two displaced electrons and the centre by the core of the cation. Inter-atomic distances are tabulated. A rule relating the symmetry of the groups $(XY_2)^{-m}$ and $(XY_3)^{-m}$ with the number of valency electrons is given.
J. G. A. GRIFFITHS.

***X*-Ray investigation of orthotitanates.** S. HOLGERSSON and A. HERRLIN (Z. anorg. Chem., 1931, **198**, 69—78).—Orthotitanates of Mg, Co, Zn, and Mn, prepared synthetically, possess the spinel type of lattice. Mg_2TiO_4 has *a* 8·44, Co_2TiO_4 8·43, Zn_2TiO_4 8·44, and Mn_2TiO_4 8·67 Å. H. F. GILLBE.

Molecular symmetry of hexa-aminobenzene in the crystalline state and certain other properties of the substance. (MISS) I. E. KNAGGS (Proc. Roy. Soc., 1931, **A**, **131**, 612—620).—Powder photographs have been taken of hexa-aminobenzene The space-group is O_h^1 with a Γr lattice. There are 16 mols. in the unit cell (15·14 Å.), and they possess a threefold axis of symmetry. The coeff. of linear expansion between −183° and +15° is 0·000102. The *X*-ray evidence is in agreement with the view of Flürscheim and Holmes (A., 1929, 438) that the stability of hexa-aminobenzene is greater than has hitherto been supposed. A possible structure is suggested. L. L. BIRCUMSHAW.

***X*-Ray study of mannitol, dulcitol, and mannose.** (MISS) T. C. MARWICK (Proc. Roy. Soc., 1931, **A**, **131**, 621—633).—Mannitol has *a* 8·65, *b* 16·90, *c* 5·56 Å., space-group Q_4, 4 mols. per unit cell, (flotation) 1·497. Dulcitol has *a* 8·61, *b* 11·60, *c* 9·05 Å., β 113° 45′, space-group C_{2h}^5, 4 mols. per unit cell, *d* 1·466. Mannose has *a* 7·62, *b* 18·18, *c* 5·67 Å., space-group Q_4, 4 mols. per unit cell, *d* 1·501. In each case the long dimension of the mol. corresponds with the *a*-axis. The alcohol mols. appear to have the long-chain configuration, the sugar mol. that of the mannopyranose ring. The relationship is traced between the structures of mannitol and dulcitol, and those of mannose and other saccharides. The area of cross-section of the alcohol end-group $CH_2{\cdot}OH$ is found to be 22·1 Å. from measurements on docosanol. This is in very fair agreement with the value 21·5 Å. obtained by Adam using a widely different method of measurement (*ibid.*, 1922, **A**, **101**, 452).
L. L. BIRCUMSHAW.

Interferometric determination of molecular form. II. H. MARK (Z. angew. Chem., 1931, **44**, 525—531; cf. this vol., 413).—A survey, with special reference to long-chain and simple aromatic compounds. H. F. GILLBE.

***X*-Ray examination of liquid-crystalline substances. II. Allyl phenetoleazoxybenzoate.** K. HERRMANN and A. H. KRUMMACHER (Z. Krist., **79**, 134—145; cf. this vol., 290).—*X*-Ray examination of the ester [solid ⟶ fluid crystal I (smectic) 66° ⟶ fluid crystal II (nematic) 77° ⟶ amorphous liquid 95°] shows in the fluid crystal phases, with Cu-$K\alpha$ radiation, two rings, the inner due to white radiation (cf. A., 1930, 843), the outer corresponding with $d=$ 4·6 Å., a mean of the length 5·7 Å. and breadth 3·5 Å. of the mol. C. A. SILBERRAD.

***X*-Ray diffraction study of fractionated paraffin waxes.** G. L. CLARK and H. A. SMITH (Ind. Eng. Chem., 1931, **23**, 697—701).—Fractionated paraffin waxes were photographed (1) as very thin films, slowly cooled, by the oscillating method, (2) by the Laue method. The orders of diffraction due to oriented mols. varies directly with the m. p. of the fraction. From a consideration of the mol. refractions it is concluded that all the fractions contain both normal and *iso*-paraffins. In the 16 fractions studied 5 normal paraffin hydrocarbons were found that give an identity period diffraction. Two of these, $C_{38}H_{78}$ and $C_{42}H_{86}$, are new identifications. C. IRWIN.

Apparent crystallographic anomaly for choleic acid. R. O. HERZOG, O. KRATKY, and S. KURIYAMA (Naturwiss., 1931, **19**, 524—525).—The crystallographic investigation of choleic acid gives results which do not agree with the theory, so far as it requires the basic cell to be made up of a single mol., or a whole no. of mols. Reasons are put forward to explain the anomaly. A. J. MEE.

***X*-Ray studies of structure of hair, wool, and related fibres. I.** W. T. ASTBURY and A. STREET (Phil. Trans., 1931, **A**, **230**, 75—101).—All animal hairs give essentially the same *X*-ray diagram, the typical fibre diagram, presumably that of cryst. keratin. Only part of the hair substance is cryst. When the hair is stretched, this α-diagram is gradually replaced by another, the β-diagram. This transformation is reversible, and accounts quantitatively for various of the elastic properties of hair. It apparently depends on the elongation of an intramol. group of length 5·15 Å. to a group of length 6·64 Å. Hair in the β state is more readily attacked by Na_2S solution than it is in the α state, and it is likely that the β form is composed of mol. chains linked side to side by nuclei of cystine or cysteine. It is probable that unstretched fibrous keratin is built up of hexagonal ring systems

linked along the fibre axis by bridge atoms. The lattice units seem to be of relatively low mol. wt., and the primary mol. grouping may be based on equimol. proportions of leucine, glutamic acid, cysteine, and arginine. Cystine has a hexagonal lattice with three mols. per cell, and a 9·40, c 9·42 Å. R. CUTHILL.

Changes in X-ray spectrum through swelling of cellulose in aqueous lithium thiocyanate solutions. J. R. KATZ and J. C. DERKSEN (Rec. trav. chim., 1931, 50, 736—745).—The X-ray diffraction spectrum of cellulose is not changed by swelling in solutions of LiCNS containing less than 3·0 g. LiCNS per g. H_2O, but a new spectrum, due to a compound of cellulose and LiCNS, appears when cellulose swells in solutions containing more than 3·25 g. LiCNS per g. H_2O. E. S. HEDGES.

Lattice changes through swelling of cellulose acetate in aqueous lithium thiocyanate solutions. J. R. KATZ and J. C. DERKSEN (Rec. trav. chim., 1931, 50, 746—752).—The X-ray diffraction spectrum of cellulose acetate is changed by swelling in conc. solutions of LiCNS, but not in dil. solutions. The change is due to an alteration in the lattice structure with formation of a compound, and not to the formation of an adsorption layer at the surface of the micelle. Unlike the results obtained with cellulose under similar conditions, no change occurs in the identity period in the direction of the fibre axis. E. S. HEDGES.

Magnetisation curve in strong fields. N. S. AKULOV (Z. Physik, 1931, 69, 822—831).

Transverse effect of magnetostriction. A. ESAU (Physikal. Z., 1931, 32, 483—485).—The transverse effect of magnetostriction can readily be calc. from the longitudinal and vol. effects. A. J. MEE.

Magnetic after-effect. H. KÜHLEWEIN (Physikal. Z., 1931, 32, 472—480).—Two methods for determining the change of magnetisation with time are described. A. J. MEE.

Electrical resistance of nickel and iron wires as affected by longitudinal magnetic fields. O. STIERSTADT (Physical Rev., 1931, [ii], 37, 1356—1366; cf. A., 1930, 984).—Available data are applied to a consideration of change of resistance in small fields and the early saturation of the magneto-resistance effect. N. M. BLIGH.

Magnesium and magnesium alloys. E. SCHIEBOLD and G. SIEBEL (Z. Physik, 1931, 69, 458—482).—X-Ray and micrographical study of the relative motion, during strain of a single Mg and Al–Zn–Mg crystal, of the crystal planes, and a study of the anisotropy of chemical attack; the basic crystal plane was most readily attacked. A. B. D. CASSIE.

Elastic anisotropy of iron. E. GOENS and E. SCHMID (Naturwiss., 1931, 19, 520—524).—The elastic parameter of the Fe crystal is determined. Both the moduli of elasticity are greatly dependent on orientation of the crystal. A. J. MEE.

Impurities in metals. F. BITTER (Physical Rev., 1931, [ii], 37, 1527—1547).—Mainly mathematical. The distorting effect of impurities in the crystal lattice is investigated; applications to ferromagnetic solutions are discussed. N. M. BLIGH.

Physical properties and classification of mesomorphic stases. G. FRIEDEL and E. FRIEDEL (Z. Krist., 1931, 79, 1—60).—A proposed scheme of classification. C. A. SILBERRAD.

Chemistry of crystalline fluids. D. VORLÄNDER (Z. Krist., 1931, 79, 61—89).—An account of the author's views on the connexion between the properties of cryst. fluids and mol. constitution. C. A. SILBERRAD.

Symmetry groups of the amorphous and mesomorphic phases. C. HERMAN (Z. Krist., 1931, 79, 186—221).—The 18 structure types intermediate between those of a truly amorphous and of a truly cryst. substance are described. C. A. SILBERRAD.

Mesomorphic and colloid systems. Wo. OSTWALD (Z. Krist., 1931, 79, 222—254).—A discussion of the relations between these systems with reference to the varieties of mesomorphic systems, their forms, arrangements, and the size of the component elements, the effects of varying conditions, the degree of dispersion, viscosity, and electrophoresis. C. A. SILBERRAD.

Allotropy of phosphorus. V. N. IPATIEV, A. FROST, and A. V. VEDENSKI (Bull. Soc. chim., 1931, [iv], 49, 670—680).—The ignition temp. and density of red P are independent of the pressure (1—200 atm.) at which the transition from the white form is effected. When white P is heated in N_2 at 330°/160 atm. a violet and a red modification are formed. The density of red P varies from 2·13 to 2·34 when the temp. of formation is raised from 210° to 590°. It is suggested that red P consists of extremely small particles of violet P (d 2·34) on which is adsorbed a more volatile and less dense variety; this view is supported by the increase of density observed when red P is heated at low temp. in vac. H. F. GILLBE.

Superheating of crystal nuclei. R. BLOCH, T. BRINGS, and W. KUHN (Z. physikal. Chem., 1931, B, 12, 415—426).—Regarding fusion as a process of dissolution of a solid in its own liquid, it is shown from kinetic considerations that at const. temp. the linear dimensions of a crystal should decrease exponentially with time, so that extremely small crystals (nuclei) may have a comparatively long life. The duration of nuclei of salol at 23° above its m. p. is calc. to be 7 min., in approx. agreement with the observed time, 10 min. F. L. USHER.

Loss of recrystallising power by re-moulding. P. BECK and M. PÓLÁNYI (Naturwiss., 1931, 19, 505—506).—The phenomena of recovery and recrystallisation are distinguished and discussed. A. J. MEE.

Refraction in hydrogen, oxygen, argon, and nitrogen. J. TAUSZ and H. GÖRLACHER (Z. tech. Physik, 1931, 12, 19—24; Chem. Zentr., 1931, i, 1571—1572).—The following values of x (where $n=1+x\times10^{-8}$) are recorded for 6564, 5876, 5461, and 4358 Å., respectively: H_2 13869, 13963, 14018, 14188; O_2 27008, 27151, 27227, 27627; A 28110, 28237, 28314, 28611; N_2 29729, 29842, 29914, 30226. A. A. ELDRIDGE.

B. p. of water as a function of pressure. A. Bonhoure and A. Zmaczynski (Rocz. Chem., 1931, **11**, 354—361).—The b. p. of water determined by means of Swientoslawski's ebullioscope, and resistance thermometers, at 683—832 mm. Hg is $\theta=57{\cdot}2587+79{\cdot}3722\times10^{-3}p-35{\cdot}5273\times10^{-6}p^2+6{\cdot}695\times10^{-9}p^3$, where p is the pressure in mm. Hg.

R. Truszkowski.

F. p. of naphthalene for standardisation of mercury thermometers. P. de Beule (Bull. Soc. chim. Belg., 1931, **40**, 195—200).—$C_{10}H_8$, purified by recrystallisation from Et_2O, has m. p. 80·21—80·23°; considerable irregularities occur among the individual measurements, as a result of slow solidification and other factors. $C_{10}H_8$ is unsuitable as a thermometric standard.

H. F. Gillbe.

Calculation of heats of dissociation from electrolytic conductivity. J. Zirkler (Z. Physik, 1931, **69**, 515—525).—Using Nernst's method of calculating heats of dissociation from the chemical const., heats of dissociation can be deduced from the temp. coeff. of the conductivity of electrolytes. The conductivities of KI, KBr, KCl, KNO_3, $AgNO_3$, $TlNO_3$, $CuSO_4$, $ZnSO_4$, and $MgSO_4$ were accurately determined between 0° and 26° and for concentrations between $0{\cdot}1N$ and $0{\cdot}001N$, and from them were determined heats of dissociation and of dilution; the results show a general deviation, but no sp. error, due to the Debye effect.

A. B. D. Cassie.

Variation of the specific heats (C_p) of oxygen, nitrogen, and hydrogen with pressure. E. J. Workman (Physical Rev., 1931, [ii], **37**, 1345—1355; cf. A., 1930, 1508).—Data are recorded and plotted for the pressure range 10—130 kg. per sq. cm.

N. M. Bligh.

M. p. and heats of crystallisation of the normal long-chain hydrocarbons. W. E. Garner, (Miss) K. Van Bibber, and (Miss) A. M. King (J.C.S., 1931, 1533—1541; cf. A., 1929, 1225).—Heats of crystallisation, Q, of the α and β forms of the following hydrocarbons are, respectively, $C_{22}H_{46}$, 11·7, 18·6; $C_{26}H_{54}$, 14·04, 22·41; $C_{30}H_{62}$, 16·45, 25·17; $C_{34}H_{70}$, 19·11, 30·59; $C_{35}H_{72}$, 20·65, 30·47 kg.-cal. per mol. Q and Q/T are linear functions of the no. of C atoms. An empirical expression is found for the f. p. of the hydrocarbons, giving good agreement with observed values between C_{20} and C_{70}; the convergence temp. is 135°. The increment of Q for the Me group is 0·608 for the α- and 1·0 kg.-cal. for the β-forms. The heat of transition (α—β) is 6—11 kg.-cal., and varies with chain length.

N. M. Bligh.

Thermal energy of hydrogen-charged palladium, iron, and palladium–silver alloys. R. Nübel (Ann. Physik, 1931, [v], **9**, 826—838).—The thermal energy depends on the amount of H_2 adsorbed and on the nature of the electrolytes. With Pd and Pd–Ag alloys the thermal energy increases with the concentration of the electrolyte and has its peak value at N-H_2SO_4.

W. R. Angus.

Change of density of nitrobenzene with temperature. J. Mazur (Nature, 1931, **127**, 893—894; cf. this vol., 148).—$PhNO_2$ has d^{20} 1·1916, rising to $d^{9\cdot8}$ [?$d^{9\cdot5}$] 1·2134; a sharp change then occurs in the slope of the density–temp. curve. At the f. p., 5·5°, d is 1·2569.

L. S. Theobald.

Thermodynamical studies. A. Press (Z. Physik, 1931, **69**, 483—494).—Theoretical. A new general equation of state is deduced from classical considerations, and from this equation is deduced a more general entropy expression for the Willard Gibbs transformation for the (p,v) plane.

A. B. D. Cassie.

Densities of *iso*propyl and *n*-butyl alcohols at low temperature. T. Tonomura and K. Uehara (Bull. Chem. Soc. Japan, 1931, **6**, 118—124).—Data are given for $Pr^{\beta}OH$ and BuOH for the temp. intervals 0° to −106° and 0° to −80°, respectively, together with interpolation formulæ.

H. F. Gillbe.

Lithium hydride. H. Bode (Z. physikal. Chem., 1931, **B**, **13**, 99—104).—The values of $0{\cdot}70_5\pm0{\cdot}02$ and 1·615 have been obtained for d and n_D, respectively. The value of 4·21 Å. is deduced for the lattice const.

R. Cuthill.

Coefficient of expansion of gallium and the value of αT_s for the elements. W. Klemm (Z. anorg. Chem., 1931, **198**, 178—183).—Specimens of Ga and Bi, after being maintained at a low temp. (−78°) for several months, underwent no vol. change, and therefore no transition. The temp. coeff. of expansion of Ga, α, is $5{\cdot}3(\pm0{\cdot}5)\times10^{-5}$ for the interval 18° to −78·3°. The relationship between the m. p. (abs.) and values of α for the elements is discussed.

H. F. Gillbe.

Compressibilities of the permanent gases. W. Wild (Phil. Mag., 1931, [vii], **12**, 41—49).—Data for the coeff. p_0v_0/p_1v_1, required in determining at. wt. by the limiting density method, obtained from high- and low-pressure experiments on H_2, N_2, O_2, He, and A are compared.

N. M. Bligh.

Explicit formulæ for slip and fluidity. M. Mooney (J. Rheology, 1931, **2**, 210—222).

Law of elasticity for isotropic and quasi-isotropic substances by finite deformations. H. Hencky (J. Rheology, 1931, **2**, 169—174).

Inner friction and the liquid state. N. Gerasimov (Physikal. Z., 1931, **32**, 444—450).—Theoretical.

A. J. Mee.

Calculation of critical viscosity and applicability of Stokes' law [with Tausz ball viscosimeter]. A. Rabl and F. Geiger (Petroleum, 1931, **27**, 439—442).—A new formula indicates the extreme limit of Stokes' law. It is analogous to Reynolds' data for concentric cylinder and capillary systems.

E. Doctor.

Viscosities of *iso*propyl and *n*-butyl alcohols at low temperatures. T. Tonomura (Bull. Chem. Soc. Japan, 1931, **6**, 124—126).—Data obtained by the modified Ostwald viscosimeter are given for the temp. interval 0° to −60°. For $Pr^{\beta}OH$, $\log\eta=5{\cdot}4727+1127{\cdot}09t$ and for BuOH $\log\eta=5{\cdot}0562+1051(t-5{\cdot}2)$.

H. F. Gillbe.

Diffusion problem for a solid in contact with a stirred liquid. T. E. W. Schumann (Physical Rev., 1931, [ii], **37**, 1508—1515).—Mathematical.

N. M. Bligh.

Specific heat of binary liquid mixtures. K. M. STACHORSKI (Ukrain. Chem. J., 1930, **5**, [Sci.], 317—331).—The association factor of alcohols in C_6H_6 solution, as deduced from sp. heat measurements, varies from 1·24 in 3·52% to 3 in 100% MeOH, and from 1·37 in 3·62% to 2·5 in 100% EtOH. The association factor of H_2O in $CaCl_2$ solutions is similarly calc. to be 3. R. TRUSZKOWSKI.

Method of calculating [the partial vapour pressures of liquid mixtures] by means of distillation experiments. G. BOZZA (Atti R. Accad. Lincei, 1930, [vi], **12**, 675—681).—Mathematical (cf. A., 1914, ii, 766). O. J. WALKER.

Dielectric constants of binary mixtures. XII. Dipole moment data for (A) naphthalene and its derivatives, (B) α- and β-benzene hexachlorides. J. W. WILLIAMS and J. M. FOGELBERG (J. Amer. Chem. Soc., 1931, **53**, 2096—2104).—Dielectric const. and density data at 25° for C_6H_6 solutions are tabulated, and the following electric moments are recorded: $C_{10}H_8$ and 2 : 6-dichloronaphthalene 0 (cf. A., 1928, 229); α-$C_6H_6Cl_6$ $2·15\times10^{-18}$; β-$C_6H_6Cl_6$ $0·7\times10^{-18}$ e.s.u. The results indicate an extended rather than a folded arrangement of the C_6H_6 rings in the $C_{10}H_8$ derivatives, and further that in the hexachlorides there is a strong interaction between the Cl atoms accounting for the unpredicted moment of β-$C_6H_6Cl_6$ (cf. this vol., 24). J. G. A. GRIFFITHS.

Diamagnetism of liquid mixtures. S. P. RANGANADHAM (Nature, 1931, **127**, 975).—Mixtures of C_6H_6 and CCl_4 show no deviation from the additive law, and those of $COMe_2$ and $CHCl_3$ only a slight deviation at the concentration for which density deviation is greatest (cf. this vol., 676). L. S. THEOBALD.

Interatomic forces in binary liquid alloys. Determination from thermodynamic data. N. W. TAYLOR (J. Amer. Chem. Soc., 1931, **53**, 2421—2423; cf. A., 1929, 398, 1374).—Existing data for Zn–Cd, Cd–Pb, Cd–Sn, and Tl–Sn liquid alloys support Langmuir's theory. The discrepancies in the Zn–Sn system are attributed to factors inhibiting random orientation of the mols. (A., 1924, ii, 89). J. G. A. GRIFFITHS.

Periodic phenomenon for alcoholic, aqueous, and other mixtures. J. PLOTNIKOV and S. NISHIGISHI (Physikal. Z., 1931, **32**, 434—444).—The Plotnikov light-scattering effect affords a very sensitive method of showing the variation in complexity of large mol. complexes. By using this method periodic phenomena connected with mol. complexity were observed for aq. solutions of MeOH, EtOH, PrOH, $COMe_2$, glycerol, CH_2O, H_2O_2, sucrose, and various salt and acid solutions. The amplitude and wave period of the periods are functions of temp. and concentration. For pure H_2O, the higher the temp. the smaller is the amplitude, whilst there is a characteristic change in the type of scattering in the range 28—44°. The importance of these periodic phenomena in biological processes is discussed. A. J. MEE.

Equilibrium diagram of copper–tin alloys. M. HAMASUMI and S. NISHIGORI (J. Study Met., 1930, **7**, 535—551).—The change in electrical resistance on heating and the thermal dilatation have been measured, and the quenched bars subjected to thermal and microscopical examination. The compounds Cu_3Sn_8 (δ) and Cu_3Sn (η) exist; at 675° η affords the solid solution γ. There are 3 eutectoid transformations at 510° (α+δ ⇌ β), 570° (δ+η ⇌ ε), and 630° (β+η ⇌ γ), and 2 peritectic transformations at 580° (δ ⇌ β+ε) and 625° (ε ⇌ β+η). The existence of the new phase ε is proved microscopically. CHEMICAL ABSTRACTS.

Structure analogies of intermetallic phases. A. WESTGREN and W. EKMAN (Arkiv Kemi, Min., Geol., 1931, **10**, *B*, No. 11, 6 pp.).—Recent research has shown that many binary intermetallic compounds have structures analogous to those of β- and γ-brass; in all these alloys one of the constituents is always a metal of the transition group or Cu, Ag, or Au, and the atoms of these metals do not appear to contribute any of their electrons to those common to the lattice, but act as if they had a valency of zero. Phases having the β-brass structure are NiAl and CoAl. Further investigation of the phase previously formulated as Fe_3Zn_{10} shows that it has the γ-structure and should therefore be more correctly formulated as Fe_5Zn_{21}. Phases of the same structure and composition have been prepared by heating Zn or Cd with the transition elements in sealed quartz tubes at 1000°; Co_5Zn_{21}, Ni_5Zn_{21}, Rh_5Zn_{21}, and Pd_5Zn_{21} have a body-centred cubic lattice, Ni_5Cd_{21} has a simple cubic lattice, and Pt_5Zn_{21} a face-centred cubic lattice with a parameter double that of the others. A. R. POWELL.

Equilibrium diagram of calcium–sodium alloys. E. RINCK (Compt. rend., 1931, **192**, 1378—1381).—Using Ca distilled in vac. (m. p. 848°), the data obtained in an atm. of A afford no evidence of compound formation. The liquidus is horizontal at 710° from 7 to 86% Ca, Ca being sol. in Na to the extent of 7% and Na in Ca to 15%. Complete miscibility occurs at 1185° (cf. A., 1930, 1252). Caβ changes to Caα at 450° (cf. this vol., 416). C. A. SILBERRAD.

Change in the elastic modulus of Au–Cu alloys with transition to single crystal form. H. RÖHL (Z. Physik, 1931, **69**, 309—312).—Young's modulus for the Au–Cu alloy diminishes as the atoms assume a regular structure. A. B. D. CASSIE.

Lead alloys. B. GARRE and A. MÜLLER (Z. anorg. Chem., 1931, **198**, 297—309).—Alloys of Pb, Cd, and Sb harden considerably on quenching from about 200°, and the hardening continues at room temp. The effect, which is independent of cold-working, is a max. in alloys containing 2·5% CdSb, and increases with rise of the quenching temp. With alloys of certain composition hardening occurs even on slow cooling. The corrosion-resistance of the alloys towards H_2SO_4 is scarcely altered by hardening, but the electrical resistance of the quenched alloys diminishes with time. The presence of Sn tends to prevent hardening of Pb alloys. Cold-working causes Pb–Sn alloys to become softer, the max. hardness being at 8% Sn and the max. softening effect at the eutectic point (64% Sn), whereas the hardness of the cast alloys is a max. when the composition is that of the eutectic. The brittleness which appears in com-

mercial Pb on heating to just below the m. p. is the result of the melting of the Pb–Sb eutectic, but pure, coarsely crystalline Pb also exhibits brittleness under certain conditions. H. F. GILLBE.

Crystal structures of electrodeposited alloys. Silver–cadmium. C. W. STILLWELL (J. Amer. Chem. Soc., 1931, **53**, 2416—2417).—In contrast to results with thermal alloys (A., 1928, 1175), the *X*-ray structure of electrodeposited alloys, containing 20—96% Cd, shows that with 40% Cd the α, β', and γ phases, and possibly β, are present, whilst with 46—75% of Cd, only ε (apparently metastable between 46 and 66% of Cd) is deposited. With 89—96% Cd, ε and η are deposited. J. G. A. GRIFFITHS.

Ternary eutectic in aluminium–silicon–beryllium alloys. W. KROLL and E. JESS (Wiss. Veroff. Siemens-Konz., 1931, **10**, [2], 25—28).—The eutectic composition, determined by micrographical examination of specimens annealed for long periods at 500—520°, is 13·4% Si and 0·75% Be. A. R. POWELL.

Crystalline form in the formation of solid solutions. VII. Thermal analysis of the anhydrous systems $SrCl_2$–$FeCl_2$, $SrCl_2$–$CoCl_2$, $ZnCl_2$–$FeCl_2$, and $ZnCl_2$–$CoCl_2$. A. FERRARI and A. INGANNI (Atti R. Accad. Lincei, 1930, [vi], **12**, 668—675; cf. A., 1930, 285).—The first two systems show no miscibility in the solid state; eutectics occur at 541° (50 mol.-% $FeCl_2$) and 564° (40·5 mol.-% $CoCl_2$), respectively. In the $ZnCl_2$ systems there is also no miscibility, and the eutectic temp. is the same as the m. p. of $ZnCl_2$ (300°). Complete miscibility would be expected if $ZnCl_2$ had a rhombohedral structure of the $MgCl_2$ type. O. J. WALKER.

Crystalline form in the formation of solid solutions. VIII. Thermal and *X*-ray analysis of the anhydrous system Li_2Br_2–$MgBr_2$. A. FERRARI and C. COLLA (Atti R. Accad. Lincei, 1931, [vi], **13**, 78—80).—Two series of mixed crystals are formed, one having the $MgBr_2$ structure (up to 35 mol.-% $MgBr_2$), the other of the Li_2Br_2 type (up to 60 mol.-% $MgBr_2$) with a small region of incomplete miscibility between the two. O. J. WALKER.

Mixed crystal formation in molecular lattices by irregular exchange of molecules. L. VEGARD (Naturwiss., 1931, **19**, 443).—Substances with analogous mol. lattices form mixed crystals by the interchange of mol. groups. A. J. MEE.

F. p. and b. p. of the ternary system ethyl alcohol–methyl alcohol–water. E. W. ALDRICH and D. W. QUERFELD (Ind. Eng. Chem., 1931, **23**, 708—711).—Mixtures of MeOH and EtOH in various proportions were diluted with H_2O and the f. p. and b. p. of solutions of different concentrations determined. Each of these for a given aq. solution falls uniformly as the EtOH is gradually replaced by the MeOH. As a rule the b. p. differences are only small. C. IRWIN.

Electrical energy of dipole molecules in solution, and the solubilities of ammonia, hydrogen chloride, and hydrogen sulphide in various solvents. R. P. BELL (J.C.S., 1931, 1371—1382).—Existing data for the solubility of Hg halides in various solvents support the hypothesis that the energy of transference of a dipole mol. from one continuous medium to another is equal to the change of energy of the electrical field of the dipole. The solubilities of HCl, H_2S, and NH_3 in hydrocarbons and halogenated hydrocarbons tend to increase with increase of the dielectric const. of the solvent, but the measurements indicate that the media cannot be regarded as homogeneous, probably because of displacement of the solvent mols. by those of the solute and not because of deformation of the latter. Nevertheless, even for solvents of low dielectric const., the energy of the dipoles may influence the solubility considerably. H. F. GILLBE.

Water content of benzene. A. W. C. MENZIES (J. Physical Chem., 1931, **35**, 1655—1659).—The H_2O content of C_6H_6 at its b. p. has been determined by the author's apparatus for measuring the v.-p. lowering of a solvent and by determining the v. p. corresponding with the equilibrium $ZnSO_4,(NH_4)_2SO_4,6H_2O \rightleftharpoons ZnSO_4,(NH_4)_2SO_4,2H_2O + 4H_2O$. When one fourth of a sample of ordinary, undried C_6H_6 is distilled at 1 atm. the residue contains less H_2O than that which changes the b. p. by 0·1°. C_6H_6 dried by Na contains less H_2O than that which alters the b. p. by 0·01°. The bearing of the results on work with intensively dried C_6H_6 is discussed. L. S. THEOBALD.

Solubility of barium sulphate in sulphuric acid. N. R. TRENNER and H. A. TAYLOR (J. Physical Chem., 1931, **35**, 1336—1344).—The system $BaSO_4$–H_2SO_4–H_2O, investigated at 25° for 83—100% H_2SO_4, has only two solid phases, $BaSO_4$ and probably $BaSO_4,H_2SO_4$, with a transition at approx. 85% of acid. The solubility in abs. H_2SO_4 is 15·89 wt.-%. Compound formation has been distinguished from solid solution and adsorption by a conductance method. κ for abs. H_2SO_4 is 1045×10^{-6} ohm^{-1} (cf. A., 1909, ii, 38). L. S. THEOBALD.

Solubility of picric acid and naphthalene picrate. L. PIATTI (Z. angew. Chem., 1931, **44**, 519—520).—The solubilities of picric acid and naphthalene picrate in C_6H_6 and tetrahydronaphthalene have been measured at different temps. The solubility rises steeply with rise of temp. The results are discussed in connexion with the determination of picric acid. E. S. HEDGES.

Solubility of naphthalene in some derivatives of furfuraldehyde. A. S. SUNIER (J. Physical Chem., 1931, **35**, 1756—1761).—Solubility data obtained by the synthetic method for temp. between 20° and 75° are recorded in furfuryl alcohol, the acetate, and in Me, Et, Pr, and Bu furoates. Certain regularities are discussed. L. S. THEOBALD.

Solubilities of the soluble electrolytes. V. Estimation of the radii of ions in saturated solutions. A. F. SCOTT (J. Physical Chem., 1931, **35**, 1410—1417; cf. A., 1930, 1362).—The empirical relationship $V^{2/3} = \alpha N + \beta$ between the vol., V, of a saturated solution and the solubility, N, of the saturating salt is discussed, and the radii of individual ions for the limiting state when no H_2O is present are calc. The apparent radii thus found are, for certain

alkali salts, generally larger than the corresponding radii in the cryst. state and smaller than in dil. solution. In the saturated state, the effective vol. of the anions may be the same as in dil. solutions, whilst those of the cations may be approx. the same as in the cryst. state. L. S. THEOBALD.

Crystals of lower refractive index than the mother-liquor. E. GILTAY (Chem. Weekblad, 1931, **28**, 395).—The coloration observed when Na_2SiF_6 is precipitated from aq. solution is ascribed to the lower refractive index of the crystals compared with that of the solution. H. F. GILLBE.

Cyclic separation of two salts. A. V. RAKOVSKI (Trans. Inst. Pure Chem. Reag., 1931, **11**, 62—113).—From an examination of the theory of the separation by crystallisation from solution of two salts which do not form double salts a cyclic process giving any required degree of purification has been devised. Methods of washing are also considered. R. CUTHILL.

Influence of traces of water on solution equilibria. S. MIYAKE (Mem. Coll. Eng. Kyushu, 1931, **6**, 1—114).—The solubility of a number of org. compounds in a variety of completely anhyd. org. solvents has been determined. Traces of H_2O cause in general a marked increase of the solubility, and the results are therefore lower than those in the lit. The percentage increase rises at first with increasing dielectric const. and internal pressure of the solvent, and, after passing through a max., diminishes. It is suggested that the H_2O added, on account of its highly polar nature, causes deformation of the dipoles of the other components, and consequently an increase of the dipole moment; as a result the solvation, and therefore the solubility, of the solute is increased. If the solute mols. are associated when in solution, and addition of H_2O diminishes the degree of association, the decreased size of the solute mols. causes an increase of the forces of attraction between the solvent and solute, and the solubility again tends to increase. This view is confirmed by measurements of the mol. wt. by the f.-p. method for certain systems in which the increase of solubility is especially pronounced; addition of H_2O causes an increase of the number of smaller mols. Hildebrand's theory of solution is supported by the measurements. The influence of miscibility of the solvents on the distribution coeff. of various solutes between H_2O and C_6H_6 or CCl_4 has been studied. A method for the determination of traces of H_2O in org. solvents by measurement of the increase of solubility of a given solute is described. Results for H_2O and C_6H_6 yield for the heat of dissolution at 23° 8·016 kg.-cal. per mol. H. F. GILLBE.

Distribution of ammonia between chloroform and water at 25°. V. J. OCCLESHAW (J.C.S., 1931, 1436—1438).—The distribution coeff. K of NH_3 between $CHCl_3$ and H_2O at 25° for aq. solutions from 0·1388 to 1·022M is given by $K=24{\cdot}10-28{\cdot}45c$, where c is the concentration in the $CHCl_3$ layer. A const. is not obtained if correction is made for the equilibrium $NH_3+H_2O \rightleftharpoons NH_4^{\cdot}+OH'$, but K still decreases with rise of the NH_3 concentration. H. F. GILLBE.

Determination of sorption isothermals on charcoal by the retentivity technique. Experiments with carbon tetrachloride and water. A. J. ALLMAND and L. J. BURRAGE (J. Physical Chem., 1931, **35**, 1692—1703).—Details of the results previously reported (A., 1930, 1513) are given and the discontinuous nature of the isotherms is discussed. L. S. THEOBALD.

Rate of sorption of ammonia on meerschaum. M. G. EVANS (Trans. Faraday Soc., 1931, **27**, 333—340).—The form of the curves representing the progress of the sorption of NH_3 by meerschaum varies with the temp. at which the latter is initially outgassed, and is possibly a consequence of the presence of both a cryst. and a gel constituent. The Freundlich isotherm is applicable, except at the higher pressures, and the total amount of NH_3 sorbed decreases as the amount of H_2O present diminishes. R. CUTHILL.

Sorption of ammonia on chabazite. M. G. EVANS (J.C.S., 1931, 1556—1564).—The H_2O in chabazite is probably loosely held and not present in chemical combination, since the hydration and dehydration curves are smooth, and the processes are reversible and without hysteresis. The rate of sorption of NH_3 is greater for dehydrated than for hydrated chabazite. The sorption-pressure curves conform to the Langmuir isotherm, and the heat of sorption is a linear function of the sorption. H. F. GILLBE.

Adsorption of iodine on thin layers of sublimed calcium fluoride. J. H. DE BOER [with J. BROOS] (Z. physikal. Chem., 1931, **B**, **13**, 134—154).—The adsorption of I on CaF_2 sublimed in vac. may be represented by the isotherm previously deduced (A., 1929, 875). Adsorption apparently occurs on the F ions. R. CUTHILL.

Molecular and activated adsorption of hydrogen on manganous oxide surfaces. H. S. TAYLOR and A. T. WILLIAMSON (J. Amer. Chem. Soc., 1931, **53**, 2168—2180; cf. this vol., 421).—Data for the adsorption and rate of adsorption of H_2 by MnO and MnO–Cr_2O_3 surfaces between −78·5° and 450° are recorded. At the lower temps., the H_2 is reversibly and rapidly adsorbed by MnO–Cr_2O_3 with negligible energy of activation and a heat of adsorption of about 1900 g.-cal. per mol. ("molecular" adsorption). The second type of adsorption ("activated") becomes prominent above 0° and the energy of activation increases from 6000 to 10,000 as successive portions of the MnO–Cr_2O_3 surface are covered. At about 300°, the heat of adsorption is of the order 20,000. Thus, at const. pressure and with rise of temp. the adsorption passes through a min. at about 0° and then increases to a max. between 200° and 300°, finally decreasing again at still higher temp.

Both types of adsorption are exhibited by CO on MnO–Cr_2O_3 surfaces between −78·5° and 450°. J. G. A. GRIFFITHS.

Adsorption of hydrogen by nickel poisoned with carbon monoxide. T. A. WHITE and A. F. BENTON (J. Physical Chem., 1931, **35**, 1784—1789).—At 0°, small amounts of CO increase the quantity of H_2 adsorbed by Ni at all pressures up to 1 atm.;

larger amounts only decrease the rate of adsorption. At $-183°$, the H_2 adsorbed at pressures up to 1 atm. is decreased by an amount approx. equal to the amount of CO used. The poisoning action of CO in hydrogenations using Ni is discussed.

L. S. THEOBALD.

Effect of the ignition loss on the adsorptive power of decolorising clays. O. ECKART (Z. angew. Chem., 1931, **44**, 326—327).—Tests on numerous types of decolorising clays show that there is no relation between their decolorising power and the loss on ignition. This loss is due entirely to H_2O of constitution and not to adsorbed H_2O; prolonged cleaning of the clay with dil. acids or the use of too highly conc. acids results in partial decomp. of the hydrated silicates in the clay and a corresponding decrease in the decolorising power. A. R. POWELL.

Condition of the surface of platinised charcoal in the simultaneous presence of hydrogen and oxygen, and the mode of action of active centres. A. FRUMKIN, S. LEVINA, and O. ZARUBINA (Z. physikal. Chem., 1931, **155**, 41—50).—The alteration in the potential of platinised charcoal in an atm. of H_2 from positive to negative with increasing Pt content (A., 1929, 640) raises the question as to whether, in the intermediate neutral state, the surface (i) possesses an equal number of positive and negative centres, or (ii) is at the same potential throughout. Since positive charcoal adsorbs the anion and negative charcoal the cation from neutral salts, neutral charcoal will adsorb (i) both or (ii) neither. Experiments on the adsorption of $0\cdot01N$-NaCl solution by charcoals with different Pt contents show (ii) to be correct, as do experiments in which the composition of the charcoal ($0\cdot5\%$ Pt) and solution ($0\cdot01N$-NaCl) are fixed and the composition of the atm., H_2+O_2, is varied. In the former series the neutral charcoal contained $0\cdot002$—$0\cdot003\%$ Pt, which corresponds with a covering of only about $0\cdot002\%$ of the charcoal surface by the Pt even if the Pt is in a unimol. layer, which from X-ray photographs of more highly platinised charcoals seems doubtful. The ability of such a small covering of Pt to promote a uniform potential is discussed, and it is suggested that the results are of significance in the theory of heterogeneous catalysis.

N. H. HARTSHORNE.

Determination of the energy level of adsorbed hydrogen and oxygen by the method of electron bombardment. N. I. KOBOSEV and V. L. ANOCHIN (Z. physikal. Chem., 1931, **B**, **13**, 18—62).—The desorption of H_2 and O_2 from Pt as a result of ionisation caused by bombardment with electrons has been studied. The curve representing the relation between the energy of the electrons and their desorbing power towards H_2 shows three well-defined maxima. These represent the ionising potentials of H_2 adsorbed on the faces, edges, and corners of crystals: the adsorbed H_2 is apparently in the at. state. Adsorbed O_2 also exhibits definite ionisation potentials, but is in both the at. and mol. states. With both O_2 and H_2 the firmness with which the gas as a whole is held increases as the amount of adsorbed gas diminishes, and also, with O_2, as the roughness of the metal surface increases. At saturation with either H_2 or O_2, 12—15% of the surface is filled, the three types of adsorption occurring to approx. equal extents. This is of the same order as the value for the active surface calc. from kinetic data. With Pt the adsorption complex seems to be PtH_2. The rate of desorption of H_2 follows the unimol. law at the start, but ultimately becomes const. owing to the loss by desorption being compensated by diffusion from the interior of the metal. O_2 diffuses much less rapidly than H_2. H_2 is adsorbed more tenaciously than O_2 and readily displaces O_2. Nevertheless, adsorbed O_2 and H_2 can be present simultaneously. In this case, the H_2 is largely in the interior of the metal, whilst the O_2 is on the surface, and prevents the diffusion of the H_2 from the interior. The desorption of H_2 from Pd is essentially similar to that from Pt. The order of the desorption potentials of H_2 from a series of metals is exactly opposite to that of the H_2 overvoltages of the same metals, which confirms the theory of overvoltage previously advanced (A., 1930, 1254). R. CUTHILL.

Translational motion of molecules in the adsorbed phase on solids. D. H. BANGHAM and N. FAKHOURY (J.C.S., 1931, 1324—1333).—Comparisons of Schofield and Rideal's equation of state for two-dimensional adsorbed films with the equation relating the quantity adsorbed S with the linear expansion x of the adsorbent suggest that films of H_2O, CO_2, NH_3, and SO_2 behave as two-dimensional gases. The curves of Mx/S–x resemble the PV–P curves of imperfect gases, but those for C_6H_6 and pyridine are of a different form; in all cases they become linear at high surface concentrations. The hypothesis is supported by the agreement of the observed S–pressure curves with the curves derived by combining Gibbs' equation with the two-dimensional equation of state. The Langmuir isotherm cannot apply to a mobile phase, as it ignores the finite area of the min. space necessary for the condensation of a mol. H. F. GILLBE.

Influence of neutral salts on properties of solutions of non-electrolytes. I. Adsorption of phenol and benzoic acid by charcoal. P. P. KOZAKIEVITSCH and N. A. IZMAILOV. **II. Capillary activity of organic solutes.** P. P. KOZAKIEVITSCH and N. S. KOZAKIEVITSCH (J. Gen. Chem. Russ., 1931, 1, 105—120, 121—132).—I. The adsorption by charcoal of PhOH from aq. solution and of BzOH from alcoholic solutions is increased by addition of alkali halides; in H_2O and MeOH solutions the activity of ions diminishes in the order Cl>Br and Na>Li>K, whilst in EtOH Br>Cl. The action of salts is a function of their solvation.

II. The surface activity of PhOH, o-cresol, thymol, and menthol is augmented by ions in the order Cl>Br>I, and in the case of menthol Na>Li. Schofield and Rideal's (A., 1925, ii, 960) formula, $FA/RT-BF/RT-x$, is applicable to the surface layer of PhOH, o-cresol, and thymol, but not of menthol solutions. The relation between FA/RT and F, where F is the depression of surface tension and A the area occupied by 1 mol. of the surface-active substance on the surface of the solution, is unaffected by the presence of salts if the activity and not the concentration of the non-electrolyte is considered. The

above formula is applicable to the calculation of the activity of non-electrolytes in salt solutions.

R. TRUSZKOWSKI.

Adsorption in binary systems of electrolytes. (MLLE.) L. S. LÉVY (Ann. Chim., 1931, [x], 15, 85—200).—The adsorption of an electrolyte by MnO_2, in presence of a second electrolyte at various concentrations, can be represented by the Freundlich equation. The consts. depend on the nature of the second component and vary in a simple manner with its concentration, and since the isotherms intersect those obtained for the electrolyte when present alone, the second substance is able to depress or increase the adsorption according to its relative concentration. Hydrolysis plays an important role in the mechanism of the process, since if the hydroxide of the second component tends to enhance the stability of the colloidal hydroxide of the adsorbed salt the adsorption is increased, and *vice versa*. The influence of aq. NH_3 on the adsorption by $Fe(OH)_3$ of $Cu^{\cdot\cdot}$ and $Ni^{\cdot\cdot}$, present separately or simultaneously, is due partly to its influence on the p_H of the solution and partly to the formation of complexes, and at higher concentrations, to the stabilisation of such complexes. Measurements of the adsorption of $Mn^{\cdot\cdot}$ by MnO_2 demonstrate the existence of an adsorption equilibrium, and data for the replacement of the $Mn^{\cdot\cdot}$ by other metal ions indicate the existence of a displacement equilibrium.

H. F. GILLBE.

Adsorption equilibria on precipitated manganese dioxide. (MLLE.) L. S. LEVY (Compt. rend., 1931, 192, 1376—1378; cf. B., 1927, 205; A., 1927, 407).—In the adsorption of $Mn^{\cdot\cdot}$ from a solution of a $Mn^{\cdot\cdot}$ salt (0·001*N*) by MnO_2, equilibrium is reached in 1 hr., and remains const. for at least 50 hr. From a solution of p_H 1·4 it is about 2·4 times that from one of p_H 0·6. On addition of a $Cu^{\cdot\cdot}$ salt the ratio of $Mn^{\cdot\cdot}$ displaced to $Cu^{\cdot\cdot}$ adsorbed is a function of the initial concentration of $Mn^{\cdot}$, and for small additions is const. It is independent of the p_H.

C. A. SILBERRAD.

Relation between gas content and adsorption of electrolytes by activated charcoal. VI. B. BRUNS and A. PILOJAN (Z. physikal. Chem., 1931, 155, 77—83; cf. this vol., 34).—The adsorption of H_2SO_4 in dil. solution by activated charcoal in an atm. of O_2 is accompanied by adsorption of O_2 (cf. A., 1930, 684). Activated charcoal is oxidised by O_2 even at room temp., but this effect was satisfactorily controlled and allowed for by working at 0° and by previously determining the rate of disappearance of O_2 due to oxidation. More equivs. of electrolyte than of gas are adsorbed, as in the case of alkali and H_2, but the difference is here much greater. This is attributed to the supply of chemically bound or ionised O on the charcoal surface being greater than that of H_2, and also, possibly, to mol. adsorption of the H_2SO_4.

On addition of NaOH to activated charcoal carrying H_2SO_4 adsorbed as above, evolution of O_2 does not occur, owing not to the formation of CO_2 by the O_2, but to the formation of alkali-adsorbing oxides similar to those obtained when charcoal is heated to 300—400° in presence of O_2 (cf. A., 1929, 261).

N. H. HARTSHORNE.

Adsorption of solutes by crystals in relation to compatibility of space lattice. C. A. SLOAT and A. W. C. MENZIES (J. Physical Chem., 1931, 35, 2022—2025).—The amounts of the bromides of Li, Na, K, Rb, Cs, and NH_4 adsorbed by PbS at 25° depend mainly on the solubility of the bromide in H_2O. Adsorption does not appear to be related to lattice dimension or to orientation of the deposited salt on the substrate. L. S. THEOBALD.

Solubility as a complicating factor in adsorption measurements at gas-solid interfaces. E. W. R. STEACIE (J. Physical Chem., 1931, 35, 2112—2117).—Evidence supporting the hypothesis of an activation energy for adsorption processes (this vol., 421) is re-examined. It is concluded that the hypothesis is not of general applicability and that irreversible adsorption and slow effects accompanying adsorption processes can be explained by existing data for the solubility of gases in solids.

L. S. THEOBALD.

Heat of adsorption of hydrogen and carbon monoxide on zinc and chromium oxide catalysts. W. E. GARNER and F. E. T. KINGMAN (Trans. Faraday Soc., 1931, 27, 322—333).—The heat of adsorption of H_2 and CO on ZnO and Cr_2O_3 and ZnO-Cr_2O_3 catalysts is a max. in the initial stage of the process. Since the heat of adsorption of CO on a mixed catalyst is the same as that on ZnO, the promoter action of the Cr_2O_3 must be attributed to its increasing the internal surface of the catalyst; Cr_2O_3 has, however, considerable adsorptive power for CO. The mixed catalyst adsorbs H_2 more strongly than either oxide singly. At low temps. H_2 and CO are largely adsorbed without dissociation of the mols., and the adsorption is partly reversible, whereas at 100° or above adsorption is irreversible, and the gas is then released only at high temp. in the form of H_2O or CO_2. R. CUTHILL.

Reflexion of vapour molecules at a liquid surface. T. ALTY (Proc. Roy. Soc., 1931, A, 131, 554—564).—The rate of evaporation from a water surface is measured as a function of the b. p. above the surface and the actual temp. of the surface. Extrapolation to zero pressure enables the rate of evaporation into a vac. to be deduced, and this result is compared with the formula derived from the kinetic theory for the no. of vapour mols. striking a water surface per sec. from the saturated vapour. Extensive reflexion of water vapour mols. must occur, since only about 1% of the mols. incident on the surface enter the liquid.

L. L. BIRCUMSHAW.

Specific properties of surface molecular fields. V. V. ILJIN and J. P. SIMANOV (J. Gen. Chem. Russ., 1931, 1, 85—90).—The *X*-ray spectrum of charcoal activated by heating at 1000° in CO_2 is of the same type as that activated at 850° in air; these charcoals adsorb homologous hydrocarbons in the order of increasing and decreasing at. wt. respectively. The sp. properties of adsorbent charcoals are not connected with their crystal structure. R. TRUSZKOWSKI.

Spreading of some saponins [on aqueous surfaces]. F. GRENDEL (Pharm. Weekblad, 1931, 68, 610—615).—From surface tension measurements, the film thicknesses of various saponins on water

are found to be between 12·8 and 42×10^{-8} cm.; the films are thus of unimol. thickness. S. I. LEVY.

Investigation of specific surface of pulverised substances by optical methods. G. I. POKROVSKI (Kolloid-Z., 1931, **55**, 321—323).—Theoretical. E. S. HEDGES.

Capillary systems. X. Electro-osmotic behaviour of collodion membranes of graded porosity. E. MANEGOLD and K. SOLF (Kolloid-Z., 1931, **55**, 273—310).—A mathematical investigation is made of the application of Helmholtz' equation to capillary systems and of the relation between velocity of dialysis, ohmic resistance, and capillary structure, and the electro-osmotic transport of H_2O through capillary systems. Observations have also been made on the ohmic resistance of collodion membranes impregnated with various liquids, the electro-osmotic permeability of the membranes for pure H_2O, and the maximal osmotic flow. The quotient of the conductivity of the impregnated membrane and that of the impregnating liquid is greater than 1 for pure H_2O, and with increasing electrolyte concentration approaches a const. value, which is less than 1, the constancy being reached at the concentration 0·03*N*. The electrical conductivity of the capillary-bound H_2O is 10—12 times that of the free H_2O. The electro-osmotic permeability for H_2O increases with the size of the pores, but in electrolyte solutions more conc. than 0·03*N* the value is independent of the porosity. For equal current densities the max. electro-osmotic flow is independent of the porosity of the capillary system, a result which must be due to the variation of conductivity with the porosity. E. S. HEDGES.

Osmotic pressure of dilute benzene solutions by the porous disc method. W. C. EICHELBERGER (J. Amer. Chem. Soc., 1931, **53**, 2025—2036; cf. this vol., 423).—The author's apparatus has been modified for the measurement of the osmotic pressure of non-aq. solutions. With the temp. controlled to within 0·0005°, the osmotic pressures of solutions of 0·02—0·004*M*-tetraphenylethylene in C_6H_6 have been determined with an accuracy of 1%. J. G. A. GRIFFITHS.

Cellulose acetate solutions [viscosity]. H. BARTHÉLEMY (Chim. et Ind., 1931, **25**, 819—831).—The viscosities of 6% solutions of cellulose acetate in $COMe_2$–H_2O mixtures have been determined, and are discussed in relation to the composition of the solvent. Pure $COMe_2$ solutions containing up to 30% of cellulose acetate have also been examined. 99% MeOH depresses the viscosity of $COMe_2$ solutions of cellulose acetate more than H_2O or abs. EtOH. The high viscosities of cellulose acetate in methylene chloride, $CHCl_3$, dichloroethylene, and tetrachloroethane are greatly reduced by MeOH, the min. in 6% solutions being attained when 20 vol.-% is present. The viscosities of conc. solutions in $COMe_2$, *e.g.*, 25%, can be determined by the rate of fall of steel balls. The difference between the true and apparent viscosity of such a solution is a measure of its rigidity. A. RENFREW.

Apparent molar volumes of dissolved electrolytes. I. W. GEFFCKEN (Z. physikal. Chem., 1931, **155**, 1—28).—Priority for the equation $\phi_c = \phi_0 + Kc^{\frac{1}{2}}$ (this vol., 680) is now accorded to Masson (A., 1930, 31). The values of ϕ_c for solutions of all the alkali halides except the fluorides of Li, Na, Rb, and Cs, and for solutions of HCl and $BaCl_2$ at different temp. are tabulated, using the best data available. The equation holds over wide ranges of temp. and concentration. Redlich's equation (this vol., 560) $V = V_0 + K_2c^{\frac{1}{2}}$, where V and V_0 are the partial molar vol. of a dissolved electrolyte at the molar concentrations c and infinite dilution respectively, is shown to be related to Masson's equation by the approximation $K_2 - 1{\cdot}5/K$. Masson's equation affords a convenient means of calculating the densities of solutions of given concentration with great accuracy, and is suggested as an aid to the crit. examination of published tables. N. H. HARTSHORNE.

Partial molar volume of dissolved electrolytes. I. O. REDLICH and P. ROSENFELD (Z. physikal. Chem., 1931, **155**, 65—74).—Theoretical. On the basis of the Debye–Hückel theory, the dependence of the partial molar vol. of an electrolyte on its concentration is derived for high dilutions. N. H. HARTSHORNE.

Absorption spectra of the rare earths. Y UZUMASA and H. OKUNO (Bull. Chem. Soc. Japan, 1931, **6**, 147—152).—The absorption spectrum of $Nd(NO_3)_3$ in H_2O, glycerol, MeOH, EtOH, and $COMe_2$ is shifted toward the red in passing from H_2O to $COMe_2$. The same effect is observed with solutions of $Pr(NO_3)_3$. The addition of $Mg(NO_3)_2$ also produces the same displacement. The phenomenon is attributed to the deformation of the metallic ion. F. J. WILKINS.

Electrochemical and spectral investigations of nickel chloride solutions. II. M. PAVLIK (Coll. Czech. Chem. Comm., 1931, **3**, 302—313).—Addition of org. dehydrating agents such as glycerol or EtOH or of an excess of inorg. chlorides to $NiCl_2$ solutions causes an increase of absorption in the blue and a decrease in the red part of the spectrum; rise of temp. produces the same effect. The change of the absorption spectrum in the shorter wave-length region occurs with solutions of the same composition as those in which the polarographic current–voltage curves show reversible deposition at the dropping Hg cathode, and both phenomena are attributed to the formation of complexes of the type $[NiCl_n]^{(n-2)'}$ by replacement of the hydration H_2O mols. by the easily deformed Cl ions. H. F. GILLBE.

Varying magnetic state of the nickel ion in solutions of the chloride. G. FOEX and (MLLE.) B. KESSLER (Compt. rend., 1931, **192**, 1638—1640; cf. A., 1928, 454; 1930, 1095).—Ni^{++} (in $NiCl_2$ solution) when not heated above 90° has a magnetic moment of 17 Weiss magnetons with $\theta = -16°$ to $-29°$. When heated above 100° the moment diminishes and θ approaches zero, and after heating at 120° the respective values are 17 magnetons and $-3°$. C. A. SILBERRAD.

General limiting law of internal friction of strong electrolytes. H. FALKENHAGEN (Z. physikal. Chem., 1931, **B**, **13**, 93—98).—The relation previously deduced (A., 1929, 1389; 1930, 155)

between the viscosity and concentration of a solution of a uni-univalent electrolyte with ions of equal mobility has been generalised to include electrolytes of any type. The results are in satisfactory agreement with the experimental data. R. CUTHILL.

Constitution of nitric acid in aqueous solution. R. BRUNETTI and Z. OLLANO (Atti R. Accad. Lincei, 1931, [vi], **13**, 52—57).—A study of the Raman spectra of solutions of nitrates, nitrites, and HNO_3 of various concentrations. The results indicate that conc. aq. solutions of HNO_3, down to about 7·0*M*, contain the species $O_2N{\cdot}OH$ and also a hydrated form $O_2N{\cdot}OH,H_2O$. O. J. WALKER.

Preparation of gold sols by reduction with hydrogen. Influence of visible light on sol formation. A. SCHMIDT (Kolloid-Z., 1931, **55**, 333—341).—In order to prepare reproducible Au sols it is necessary to keep light intensity, temp., and alkali content const. Highly disperse Au sols can be prepared by reducing a dil. $AuCl_3$ solution, to which excess of NaOH has been added, irradiated with visible light. The light does not appear to be capable of promoting the formation of nuclei. $HAuCl_4$ has a coagulating effect on these Au sols. E. S. HEDGES.

Standardisation of gold sols for the Lange gold sol reaction. G. ETTISCH and O. EINSTEIN (Naturwiss., 1931, **19**, 506—510).—The prep. of a standard Au sol is described, and a method of standardisation based on coagulation is given. The mechanism of Lange's Au sol reaction with cerebrospinal fluid is discussed. A. J. MEE.

Colour of colloidal solutions of arsenic trisulphide. S. S. BHATNAGAR (J. Physical Chem., 1931, **35**, 1803—1804).—The view that the colour of colloidal solutions of As_2S_3 is due only to variations in the physical character of the precipitated substance is contested (cf. A., 1930, 721). L. S. THEOBALD.

Tyndall beam intensity of turbid coloured solutions. L. SATTLER and F. W. ZERBAN (Science, 1931, **73**, 641).—The turbidity in coloured raw sugar solutions can be measured with the Pulfrich photometer. Wells' formula (Chem. Reviews, **3**, 331) holds when certain adjustments are made.
L. S. THEOBALD.

Method for determination of mol. wt. of colloids from the dielectric constant. N. MARINESCO (J. Chim. phys., 1931, **50**, 233—235).—A theoretical exposition. The method gives the value 11,300 for gelatin. E. S. HEDGES.

Viscosity and rigidity in suspensions of fine particles. II. Non-aqueous suspensions. C. M. MCDOWELL and F. L. USHER (Proc. Roy. Soc., 1931, **A**, **131**, 564—576; cf. this vol., 681).—Measurements were made of the viscosity of starch suspended in amyl acetate and tetrachloroethane, the mixed liquids containing 0·05% of rubber and a 6% suspension of starch protected with 0·05% of rubber. Only the unprotected suspension showed an increase of viscosity at low rates of shear; in the others the viscosity was approx. const. Similarly a solution of 0·5% of cellulose nitrate in amyl acetate and a 0·13% gas black suspension protected with cellulose nitrate gave a const. viscosity, but a 0·13% gas black suspension unprotected in the liquid mixture gave rapidly increasing viscosity at low rates of shear. Microscopical examination related the latter phenomenon with the appearance of aggregates in the suspension. The extreme shear gradients were 114,000 : 1. Rigidity was detected in starch suspension $>8\%$. A suspension of this content was perfectly elastic for small strains (0·005). Neither the starch nor the gas black showed cataphoresis, from which it is inferred that the particles are unchanged. The results are discussed from the viewpoint of possible solvation.
L. L. BIRCUMSHAW.

Action of immiscible organic liquids on colloidal gold. T. R. BOLAM and J. CROWE (J. Physical Chem., 1931, **35**, 1448—1460).—Carefully purified CS_2, CCl_4, $CHCl_3$, Et_2O, C_6H_6, PhCHO, PhBr, *o*-, *m*-, and *p*-chlorotoluene, PhMe, PhEt, *m*-xylene, salicylaldehyde, and paraffin have no action on either Nordenson or Zsigmondy sols. Miscible alcohols are also without effect, but immiscible alcohols exert a sp. influence by causing the Au to collect at the liquid–liquid interface. The formation of red interfacial films under certain conditions shows, however, that coagulation is not essential for the transference of Au to the interface. With amyl alcohol film formation is generally promoted by the addition of electrolytes. The action of an immiscible alcohol may be due to its strong tendency to be adsorbed at the surface of the sol particle. L. S. THEOBALD.

Effect of aldehydes on solutions of molybdenum-blue. S. L. MALOWAN (Kolloid-Z., 1931, **55**, 342—343).—Aldehydes containing a double linking in the α-position (citral, cinnamaldehyde, and α-amylcinnamaldehyde) decolorise Mo-blue, a green reduction product being formed in the aldehyde layer. Other aldehydes and ketones examined had no effect on Mo-blue. The reaction is favoured by a high degree of dispersion of the Mo-blue sol.
E. S. HEDGES.

Dispersoid chemical acceleration of vaporisation. R. STUMPER (Kolloid-Z., 1931, **55**, 310—321).—Measurements of the rate of vaporisation of H_2O at the boiling temp. under the influence of various additions show that molecularly or ionically dispersed substances produce little effect, although substances of high mol. wt. (sucrose) or those which give colloidal hydrolysis products ($FeCl_3$) accelerate the rate of distillation. Colloids accelerate the rate of vaporisation, the effect increasing in the order dextrin, gelatin, tannin, soap. No relation was found between the diminution of surface tension and the acceleration of vaporisation. Coarsely disperse substances (C, $BaSO_4$, $CaCO_3$, MgO, etc.) have a much greater accelerating effect than colloids, the effect depending on particle size and adsorbent power.
E. S. HEDGES.

Difform systems. I. Stereometry and classification of difform systems. WO. OSTWALD (Kolloid-Z., 1931, **55**, 257—272).—The concepts of continuity and discontinuity, homogeneity and heterogeneity are discussed. Discontinuous systems may be made by dispersion or by "difformation" (an unsymmetrical alteration of form involving the relatively great reduction of 1 or 2 dimensions). The

forms produced from cubes or spheres are thus lamellæ or threads, which are regarded as simple difform systems, whilst multiple or disperse laminated or fibrillar systems, such as graphite and asbestos, constitute complex difform systems. Intermediate forms between disperse and difform systems are classified as reticular, spongoid, and porodin. Calculations are made of the increase of discontinuity resulting from the formation of various types of difform systems. E. S. HEDGES.

Triangular co-ordinates in colloid chemistry. II. Fehling's solution. A. DUMANSKI and A. A. DIKANOVA (J. Gen. Chem. Russ., 1931, **1**, 163—171).—The system $CuSO_4$–K Na tartrate–NaOH may contain both negatively- and positively-charged colloidal particles. Cryst. or amorphous black or blue ppts. may form. $Cu(OH)_2$ is peptised by both NaOH and Na tartrate. R. TRUSZKOWSKI.

Mechanism of the coagulation of sols by electrolytes. II. Hydrous alumina sols. H. B. WIESER (J. Physical Chem., 1931, **35**, 1368—1396).—The changes in chloride-ion concentration and p_H values accompanying the stepwise addition of various electrolytes to Al_2O_3 sols prepared by two different methods have been followed as with Fe_2O_3 sols (this vol., 425) and similar results have been obtained. Curves showing the displacement of chloride from the micelles when K_2SO_4, $K_2C_2O_4$, KNO_3, potassium citrate, and $AcONH_4$ are added to the sols are given. The chloride displacement curve is S-shaped with electrolytes containing multivalent precipitating ions which cause rapid coagulation above a crit. concentration, the amount of chloride displaced for a given increment in precipitating ion being proportionally greater as the point of rapid coagulation is approached. Above this point chloride is displaced by exchange adsorption and the curve follows the usual course of the adsorption isotherm. Univalent precipitating ions which do not cause rapid coagulation in a crit. zone give displacement curves resembling the adsorption isotherm, and this is attributed to exchange adsorption and gradual agglomeration. The chloride-displacing power and the coagulating power follow the order citrate $> SO_4'' > C_2O_4'' > OAc' > NO_3'$, and the order in which the salts increase p_H on addition to the sols is citrate $> C_2O_4'' > OAc' > NO_3' > SO_4''$; at the precipitation value this order is modified. An adsorption mechanism explaining the effect of electrolytes on the chloride displacement, the lowering of the charge, and the change in p_H is advanced. The prep. of Al_2O_3 sols with any required chloride content from $Al(OH)_3$ formed by the action of H_2O on Al–Hg is described. L. S. THEOBALD.

Influence of light on flocculation of colloidal sols in a fluorescent medium. Effect of coloured inhibitors and of viscosity. A. BOUTARIC and J. BOUCHARD (Compt. rend., 1931, **193**, 45—46).—The photo-sensitising effect of a fluorescent substance, *e.g.*, fluorescein (cf. this vol., 425), is diminished in presence of an electrolyte by the addition to the sol (*e.g.*, of As_2S_3) of a dye with absorption bands similar to those of the fluorescent substance, *e.g.*, eosin or erythrosin, although either alone increases the photo-sensitising power. The effect of rhodamine-*B* on the flocculating power of an electrolyte on a $Fe(OH)_3$ sol is also much diminished if the electrolyte is $KMnO_4$. Increased viscosity of a sol, by addition, *e.g.*, of glycerol or sucrose, has a similar effect (cf. A., 1930, 133). C. A. SILBERRAD.

Equivalent discharging and charging of lyophilic sols. H. G. B. DE JONG and J. LENS (Biochem. Z., 1931, **235**, 174—184).—Electro-equiv. concentrations of electrolytes sometimes neutralise the charge of lyophilic sols the more strongly the higher is the valency, but in some cases the effect is independent of the valency of the oppositely-charged ions. The latter is designated "equivalent discharging." The appearance or non-appearance of equiv. discharging depends on the type of the disperse phase, of the discharging ions, and of the medium. Often a mass equivalence is detected between the equiv. discharging ions and the colloidal substance. P. W. CLUTTERBUCK.

Optical study of secondary Liesegang rings. L. BULL and (MLLE.) S. VEIL (Compt. rend., 1931, **192**, 1314—1315; cf. this vol., 563).—The secondary rings occasionally exhibit a cryst. formation. C. A. SILBERRAD.

Periodic precipitation. F. E. LLOYD and V. MORAVEK (J. Physical Chem., 1931, **35**, 1512—1547; cf. A., 1929, 507).—Photographic and kinemaphotographic records are discussed. Every reaction may proceed periodically under the necessary conditions of space and concentration. Exceptions may occur when a reagent reacts with the medium or when the gel fails to act as a protective colloid for the ppt. The medium may act chemically or mechanically, but its nature is not of fundamental importance. Viscosity plays a minor role, but in higher concentrations of the medium there is more periodicity. Surface is of importance in capillary tubes, but not in larger tubes, and periodicity is often obtained in the former but not in the latter. The relative importance depends on the nature of the ppt. or on the degree of adsorption. Inhomogeneities such as occur in starch or agar affect the behaviour of the reagents and ppt. in any system. Periodicity is independent of the states in which the reaction product may occur and there may be at least two types of periodic precipitation in a single system. At high concentrations of internal reagent a plug tends to form near the mouth of the tube, and the entering reagent is more rapidly consumed, reducing the rate of diffusion throughout the tube. Effects produced by a rise of temp. are due to a change in the velocity of the reaction concerned. Exposure to light may induce periodicity or may disturb it if already established. The influence of foreign ions is described as well as experiments in U-tubes with $HgCl_2$ and KI. Diffusion, adsorption, recrystallisation, and polymorphic changes of the ppt. and the apparent and real absence of periodicity are discussed. A theory is elaborated in which backward diffusion of a complex formed between the reaction product and internal reagent plays an essential part. L. S. THEOBALD.

Desorption of electrolytes from colloidal particles on coagulation. II. S. A. VOSNESSENSKI and L. P. ARTEMOVA (J. Gen. Chem. Russ., 1931, **1**,

173—177).—Conductivity measurements of Au sols or dialysed Ag sols, to which increasing quantities of HCl are added, indicate that the electrolyte is in small concentrations adsorbed by the particles, and that desorption takes place on coagulation.

R. TRUSZKOWSKI.

Colloid chemistry of dyes. Aqueous solutions of benzopurpurin-4*B* and its isomeride prepared from *m*-tolidine. I. II. C. ROBINSON and H. A. T. MILLS (Proc. Roy. Soc., 1931, **A**, **131**, 576—595, 596—611).—I. Solutions of benzopurpurin-4*B* and the isomeride prepared from *m*-tolidine have been examined from a colloid viewpoint, and a method has been devised for purifying these and similar dyes. The phenomenon of ageing found by previous workers is not exhibited if the solutions are pure. The viscosity does not vary with the rate of shear, is the same for both dyes, and is of the order expected for a typical, unhydrated, lyophilic colloid. Flocculation experiments with NaCl, $CaCl_2$, $AlCl_3$, and NaOH show that the particle of the 4*B* dye is probably of colloidal dimensions (confirmed by ultra-filtration measurements), whilst that of the *m*-dye is more nearly in true solution. The latter is much more sol. than the former. On the addition of small quantities of electrolytes to the two dyes, non-spherical ultramicrons are obtained in the case of the 4*B* dye, but not in that of its isomeride. Similarly, the 4*B* dye showed streaming double refraction. Measurements over a wide range of concentrations showed the conductivities of the two dyes to be nearly the same; by subtracting the conductivity of the filtrate, that of the micelle is obtained.

II. The osmotic pressures of the two dyes are the same. It is shown how the errors arising from membrane equilibria can be reduced and the amount of alkali necessary to prevent membrane hydrolysis calc. The micelle of the *m*-dye consists of about 10 anions, whilst that of the 4*B* dye must contain considerably more. By the application of Donnan's membrane equilibrium theory attempts are made to measure the activity of the Na ions. It is concluded that both dyes exist in solution as completely dissociated colloidal electrolytes and that hydrolysis is negligible. L. L. BIRCUMSHAW.

Refraction of protein colloids. N. F. JERMOLENKO (J. Gen. Chem. Russ., 1931, **1**, 21—30).—Equiv. concentrations of various chlorides produce an equal change in the *n* of fish glutin, ovalbumin, and gelatin sols which is proportional to the concentration of the protein. The *n* of gelatin sols is const. during 33 hr. after preparation, and is probably unaffected by time. On keeping gelatin or glutin sols for varying periods at 0—90°, and allowing them slowly to attain 25°, the final value of *n* is the same in all cases. Min. refraction of gelatin is found at the isoelectric point.

R. TRUSZKOWKSI.

Relations between colloids and constitutive changes of some proteins. I. W. PAULI and R. WEISS (Biochem. Z., 1931, **233**, 381—443).—A detailed record of observations on the coagulation of egg-albumin, serum-albumin, and pseudoglobulin produced by acids, neutral salts, and alcohols, and by heating. Considerable attention has been paid to the reversibility of the processes and to changes in the optical rotation of the sols under the influence of various addition agents. E. S. HEDGES.

Colloid-chemical behaviour of typical hydrophilic phosphatide sols. H. G. B. DE JONG and R. F. WESTERKAMP (Biochem. Z., 1931, **234**, 347—366).—Both hydrophobic and hydrophilic sols of lecithin can be prepared from commercial lecithins by mixing the alcoholic solution with H_2O. Hydrophilic sols are favoured by high temp., low concentration of the original lecithin solution, and the use of higher alcohols (*e.g.*, $Pr^{\beta}OH$) as solvents. Hydrophilic sols prepared from egg- or soya-bean-lecithin are not flocculated by NaCl, $BaCl_2$, or HCl. Sols containing 5% of resorcinol behave as dehydrated sols and are coagulated by neutral salts, the effect increasing with the valency of the cation, whilst the anion is of little account. Sols containing 50% of EtOH behave similarly, except that the effects of ter- and sexa-valent cations are practically identical. In the presence of a sufficient quantity of neutral salt (the concentration decreasing with increasing valency of the cation) lecithin can be extracted from the hydrophilic sols by shaking with Et_2O. The hydrophilic sols are negatively charged; egg-lecithin sols have an isoelectric point at about p_H 2·7. The electroviscous effect is shown with small concentrations of neutral salts, but at high concentrations viscosity anomalies occur. E. S. HEDGES.

Complex coacervation. VI. Lecithin as a complex component. H. G. B. DE JONG and R. F. WESTERKAMP (Biochem. Z., 1931, **234**, 367—400).—Lecithin sols form complex coacervates with gelatin, ichthyocoll, casein, egg-albumin, and clupein. The formation of gelatin–egg-lecithin coacervates is confined to the p_H region between the isoelectric points of the components (4·8—2·7). In the neighbourhood of the isoelectric point of gelatin the complex coacervate is obtained in the form of liquid drops; in the middle part of the effective p_H region a flocculent ppt. of droplets is obtained, uniting with difficulty, but more readily in the presence of neutral salts. Higher concentrations of neutral salts destroy the coacervate. The droplets show the Büchner effect in the electric field. The resistance to neutral salts is zero at both isoelectric points, and passes through a max. in the intermediate p_H region. Measurements of viscosity and light absorption and observations of the morphological characters of the coacervate have established that a neutral salt is more effective the greater the difference between the valencies of the cation and the anion. The sp. effect of the cation is less important, but is in the following order: Li>Na>K>Ca>Mg>Sr>Ba. The resistance towards neutral salts depends on both of the components of the complex coacervate; complexes with clupein are more resistant than those with gelatin, and complexes of soya-bean-lecithin are more resistant than those of egg-lecithin. At p_H<2·7 egg-lecithin can act as a positive component and give complex coacervates with negatively-charged thymus-nucleic acid and gum arabic.

E. S. HEDGES.

Complex coacervation. VII. Autocomplex coacervation. H. G. B. DE JONG and J. LENS

(Biochem. Z., 1931, **235**, 185—204).—The coacervate of gum arabic sol with $[Co\{(OH)_2Co\ en_2\}_3](NO_3)_6$ shows towards neutral salts and also in an electric field the characteristics of a complex coacervate, although only colloidal substances are concerned. The opposite charges are taken up by particles of the same type or even on the surface of one and the same particle. The type is designated "autocomplex coacervation." An explanation of the phenomenon is discussed and further examples are given. P. W. CLUTTERBUCK.

Swelling minimum and isoelectric point of fibrin. H. J. VONK (Z. physiol. Chem., 1931, **198**, 201—218).—The swelling min. of fibrin, which must correspond with its isoelectric point, depends both on p_H and on the presence of other ions. If the p_H is attained by the use of HCl and NaOH the min. lies at about 7·1; if by the use of buffer mixtures it may be displaced as far as 3·7. J. H. BIRKINSHAW.

Distribution of hydrochloric acid in gelatin gels. L. HALPERN (J. Gen. Physiol., 1931, **14**, 575—581).—No evidence of a permanent ionic concentration gradient, such as that reported by Bigwood (this vol., 306) when NaOH solution diffuses into gelatin gel, is obtained when dil. aq. HCl is allowed to diffuse, when the concentration of the aq. liquid is unchanged; $d/\sqrt{t}$ is const. When an artificial gradient of protein concentration is set up the $[Cl']$ at equilibrium varies in the same direction as protein concentration, whilst the $[H^{\cdot}]$ varies in the opposite direction. These facts are in accordance with Donnan's theory. R. K. CALLOW.

Flocculation of gelatin at the isoelectric point. D. STRAUP (J. Gen. Physiol., 1931, **14**, 643—660).—Isoelectric gelatin solutions, after purification by electrodialysis, flocculate when cooled below 30°. The following observations have been made with stock solutions sterilised at 80° for 10 min., a treatment which does not affect flocculation properties. Solutions heated at 100° show a decrease in the rate and amount of flocculation. An equilibrium point with the same concentration in the liquid phase is reached by allowing a solution to flocculate at 25° or by redispersing a solution previously flocculated at a lower temp. The concentration of the liquid phase at equilibrium decreases with fall of temp., and the rate of attaining equilibrium is greater. At const. temp. the equilibrium concentration in the liquid phase is proportional to the initial concentration. Ppts. redissolved in H_2O give solutions which flocculate more rapidly and completely than the original solutions. When flocculation at low temp. is followed by warming, an opalescent solution is formed temporarily by disruption of the floccules and reflocculation then occurs. If the liquid phase is removed from the ppt. and concentrated, this may be flocculated, but only at a lower temp. The fraction of gelatin from the liquid phase is less readily salted out by $(NH_4)_2SO_4$ than that from the ppt. phase. Solutions of the liquid fractions have the same n as those of the ppt. fractions, but the viscosity is lower. It is concluded that gelatin is a mixture of mol. aggregates of widely differing degrees of association.

R. K. CALLOW.

Structure of silica gel. X-Ray study. L. KREJCI and E. OTT (J. Physical Chem., 1931, **35**, 2061—2064).—After heating at 1150° for 5 hr. precipitated SiO_2 gives the same X-ray pattern as cristobalite. Cryst. centres of colloidal dimensions have also been detected by means of X-rays in precipitated SiO_2 which has never been heated above 100°; the crystals appear to be cristobalite.

L. S. THEOBALD.

Cobalt sulphide bands in solid silica gel. E. R. RIEGEL (J. Physical Chem., 1931, **35**, 1674—1683).—Rhythmic bands of CoS are formed when SiO_2 gel containing Na_2S is placed on a solid SiO_2 gel containing $Co(NO_3)_2$; Na_2S solution forms similar bands, but produces collapse of the SiO_2 gel. The greater the concentration of Na_2S and the less that of $Co(NO_3)_2$ the more rapid is the advance of the rings, and generally, but not invariably, advance is slower the more conc. are the gels. The behaviour of air bubbles in a gel in which bands are being formed is described. Bands of CoS formed on a microscope slide have also been studied and a mechanism for both cases is discussed. L. S. THEOBALD.

Reduction reactions in silica gels. D. S. DEDRICK (J. Physical Chem., 1931, **35**, 1777—1783).—NH_2OH,HCl reduces $Cu^{\cdot\cdot}$ to $Cu^{\cdot}$ and Cu in SiO_2 gels made from Na_2SiO_3 and $CuSO_4$ in dil. H_2SO_4; a 1% aq. solution gives well-defined crystals in banded rings, but a 2% solution gives no banded structure. Gels made from Na_2SiO_3 of d 1·06 are more satisfactory than those made from Na_2SiO_3 of d 1·10. Variations in the concentration of $Cu^{\cdot\cdot}$ or the H_2SO_4 used in making the gel have little effect. A M-aq. solution of SO_2 diffuses rapidly into the alkaline gels, forming a ppt. of yellow, metastable Cu_2O which dissolves as more H_2SO_3 diffuses through the gel. In acid solution the oxide is reprecipitated as well-defined crystals of red Cu_2O. During the first 20 hr. the rate of diffusion of SO_2 solution in the more conc. gel (d 1·10) is greater than that in the more dil. gel (d 1·06). After this the rates become equal, indicating that at first the gels are structurally different. Variations of factors other than concentration have no effect. Diffusion of a 5% dextrose solution into the dil. but not into the conc. gel produces yellow Cu_2O. The mols. of dextrose are larger than the interstices of the conc. gel, but smaller than those of the dil. gel.

L. S. THEOBALD.

Alkali peptisation of stannic acid gels. R. WINTGEN and W. KEILHOLZ (Kolloid-Z., 1931, **55**, 323—330).—Experiments on the peptisation of precipitated SnO_2 by NaOH indicate that in sols prepared at 18° the average particles contain 40,000 mols. of SnO_2, 2,600,000 mols. of H_2O, and 900 atoms of Na in the kernel. In addition, there are 530 elementary charges, which are balanced by 530 $Na^{\cdot}$ ions. The radius of such a particle is 26 mμ. The size of particle increases with rise in the temp. of peptisation, the ratio SnO_2/H_2O also increasing. E. S. HEDGES.

Radiochemical equilibrium in ammonia synthesis. S. C. LIND (J. Amer. Chem. Soc., 1931, **53**, 2423—2424).—The observed low equilibrium concentration of NH_3 (this vol., 580), as compared with that calc., indicates that the intermediate steps

of the opposed reactions are not independent. The results are explained if an exchange of ionisation from H_2^+ (16 volts) or N_2^+ (17 volts) to give NH_3^+ (11 volts) occurs, assuming that H_2^+ and N_2^+ in some way cause synthesis and NH_3^+ decomp. J. G. A. GRIFFITHS.

Maximum concentration of endothermic compounds at elevated temperatures. Ozone and nitric oxide. E. BRINER and B. SUSZ (J. Chim. phys., 1931, **50**, 206—227).—Although the formation of endothermic compounds from the constituent elements is favoured by rise of temp., the elementary mols. tend to dissociate into atoms, resulting in a max. yield of the endothermic compound at a particular temp. The max. concentration is evaluated for O_3 and NO on the basis of the law of mass action and the Nernst theorem, using the known heats of dissociation of N_2 and O_2. The max. concentration of O_3 produced from O_2 at 1 atm. is 0·0000276% at 3750°, whilst the max. concentration of NO produced from air at 1 atm. is 10·9% at 4000°. The extremely small value of the concentration of O_3 shows that its production in electrical discharges is not a thermal effect.
E. S. HEDGES.

Cryoscopic study of paraldehyde in solutions of lithium and magnesium chlorides. F. BOURION and E. ROUYER (Compt. rend., 1931, **192**, 1724—1726; cf. this vol., 430).—The values of the cryoscopic consts. indicate the stability of paraldehyde in these solutions. C. A. SILBERRAD.

Ionisation constant of acetic acid [at 25°]. D. A. MACINNES and T. SHEDLOVSKY (J. Amer. Chem. Soc., 1931, **53**, 2419—2420).—From conductance measurements, the thermodynamic ionisation const., K, of AcOH in $0{\cdot}03—10\times10^{-3}N$ solution is computed to be $1{\cdot}746\times10^{-5}$. At higher concentrations, K decreases. J. G. A. GRIFFITHS.

Universal buffer solutions and the dissociation constant of veronal. H. T. S. BRITTON and R. A. ROBINSON (J.C.S., 1931, 1456—1462).—The dissociation const. of diethylbarbituric acid is $1{\cdot}1\times10^{-8}$ at 18°. A universal buffer solution, containing citric acid, Na diethylbarbiturate, H_3BO_3, HCl, and KH_2PO_4, exhibits a strictly linear change of p_H in relation to the quantity of strong acid or alkali added over the greater part of the range p_H 2—12. Below 16% neutralisation the deviation is slight, but above 64% a pronounced inflexion of the curve occurs as a result of the transition from the neutralisation of H_3BO_3 to that of the third stage of H_3PO_4. For the range p_H 3·85—12·0 the HCl may be omitted. The Prideaux–Ward buffer mixture has been further investigated (cf. this vol., 585). H. F. GILLBE.

Electrochemical method for approximate determination of the constitution of complexes in solution. Application to some complex ions of copper and nickel. F. K. V. KOCH (J.C.S., 1931, 1418—1421).—The method (A., 1930, 1372) has been extended to electrodes which do not give const. and reproducible potentials, and applied to $CuSO_4$ and $NiSO_4$ solutions containing NH_3 or pyridine. The results are in accordance with those obtained by the distribution coeff. method, and indicate the formation of $Cu(NH_3)_4^{\cdot\cdot}$, $Cu(C_5H_5N)_4^{\cdot\cdot}$, and $Ni(NH_3)_2^{\cdot\cdot}$.
H. F. GILLBE.

Determination of hydrolysis of zinc sulphate solutions with quinhydrone electrode. P. DUPONT (Compt. rend., 1931, **192**, 1643—1645).—The p_H–log concentration curve obtained with $ZnSO_4$, using the quinhydrone electrode, agrees with Kolthoff and Kameda's results (cf. this vol., 565). To obtain an accurate result pure N_2 was passed through the solution for 30 min., atm. CO_2 otherwise causing a diminution in the p_H. $ZnSO_4$ calcined at a red heat or agitated with ZnO probably contains some basic sulphate.
C. A. SILBERRAD.

Measurement of the hydrolysis of zinc and cadmium sulphates by means of the hydrogen and quinhydrone electrodes. V. ČUPR and O. VIKTORIN (Publ. Fac. Sci. Univ. Masaryk, 1931, No. 134, 18 pp.).—Measurements of the hydrolysis of Zn salts with the aid of the H electrode yield unsatisfactory results; the deviations depend more on the p_H of the solution than on its concentration. Since colloidal Pt does not reduce the p_H of the solution, and in absence of H_2 the solution becomes acid in presence of Pt-black, the reaction suggested by Denham and Marris, viz., $Zn^{\cdot\cdot}+H=Zn^{\cdot}+H^{\cdot}$, does not occur; the change of p_H is attributed to a replacement of H ions by Zn ions on the Pt surface. Measurements with the quinhydrone electrode indicate that the degree of hydrolysis in $1{\cdot}0-0{\cdot}1M$-$ZnSO_4$ is about 0·0023—0·0046%, and in $1{\cdot}0—0{\cdot}1M$-$CdSO_4$ 0·0006—0·0016%.
H. F. GILLBE.

Hydrolysis of salts of beryllium and aluminium with strong acids. II. V. ČUPR (Publ. Fac. Sci. Univ. Masaryk, 1931, No. 133, 3—50).—The salt error of simple quinhydrone electrodes increases for anions in the series $Cl<Br<NO_3<ClO_3<ClO_4$ and for cations $K<Na<Li$. The degree of hydrolysis of solutions of $BeCl_2$, $BeBr_2$, $BeSO_4$, $MgCl_2$, $MgSO_4$, $AlCl_3$, $AlBr_3$, and $Al_2(SO_4)_3$ is independent of the age of the solution. The apparent increase in the acidity of more conc. solutions of Be salts is due to their influence on the activity of $H^{\cdot}$. The influence of neutral salts on the hydrolysis of $BeCl_2$ and $BeBr_2$ is ascribed to hydration. R. TRUSZKOWSKI.

Hydrolysis of salts. V. CUPR (Z. anorg. Chem., 1931, **198**, 310—328).—Partly an account of work published elsewhere (see preceding abstracts). Slow hydrolysis does not occur with Be and Al salts. Deviations occur at high concentrations from the logarithmic law connecting the p_H of the solution with the concentration of the Be or Al ion, and these are ascribed to the change of activity of the H ion in presence of other ions; the min. in the concentration-degree of hydrolysis curve is due to the same cause.
H. F. GILLBE.

Potentiometric measurement of the acidity of acids, and its alteration by solvents. A. HANTZSCH (Helv. Chim. Acta, 1931, **14**, 665—669).—Polemical against Schwarzenbach (A., 1930, 1526). It is not possible to compare the acidity of acids in different solvents by means of the H electrode. In such solutions the complicated equilibria between free acids, solvates, and oxonium salts must be studied by as many different physical methods as possible, bearing in mind the purely chemical facts.

[With K. BERGER.] The sp. conductivity of practi-

cally anhyd. $HClO_4$ is $10{\cdot}7 \times 10^{-4}$ mho at 0°. This is of the same order as the sp. conductivities of abs. HNO_3 and H_2SO_4, and about 10^3 that of the common hydracids. Dissociation of a polymerised mol. into the ions $[(HO)_2ClO_2]^{\cdot}$ and $[ClO_4]'$ is suggested as the explanation, and the behaviour is thus similar to that of HNO_3 and H_2SO_4.

[With D. KARVÉ.] The heats of dissolution of 1 mol. of H_2SO_4 in 1, 2, 5, 10, 25, and 50 mols. of H_2O are 6200, 9000, 13,500, 15,200, 16,400, 16,800 g.-cal., respectively, whilst for $CCl_3{\cdot}CO_2H$ the heat of dissolution in 50 mols. of H_2O is only 800 g.-cal. Such results are difficult to reconcile with Schwarzenbach's conclusion that in 2*N*-ethereal solution $CCl_3{\cdot}CO_2H$ is as strong an acid as H_2SO_4. N. H. HARTSHORNE.

Existence of undissociated salt molecules in aqueous solutions of strong electrolytes. L. DEDE (Helv. Chim. Acta, 1931, **14**, 743—751).—The dilution–equiv. conductivity curves for conc. solutions of strong electrolytes show frequently a min. This can be correlated with Debye's view that the electrolyte acquires a dipole character as the concentration is increased, the dipoles being either ion-associations or undissociated mols. The curve for HBr shows no min., whilst that for KBr is very marked. This points to the existence of undissociated mols. of HBr which, owing to the small size of the H nucleus, should have a very weak dipole moment as compared with $OH_3^{\cdot}Br'$; the latter, from a comparison of the size of the $OH_3^{\cdot}$ and $K^{\cdot}$ ions, should have a greater dipole moment than $K^{\cdot}Br'$. This conclusion is borne out by the viscosity of HBr solutions, which is greater than that of water at all concentrations, whereas the viscosities of solutions of the halides of the heavier alkali metals are lower than that of H_2O except at low concentrations. This points to the presence of a weak dipole in the case of HBr, and of a strong dipole in the alkali halide solutions. N. H. HARTSHORNE.

Composition of acid boric acid–diol compounds. J. BOESEKEN and N. VERMAAS (J. Physical Chem., 1931, **35**, 1477—1489).—Bancroft and Davis' conclusions (this vol., 163) are criticised.

L. S. THEOBALD.

System metal–acid–reducible compound. H. J. PRINS (Chem. Weekblad, 1931, **28**, 390—393).—A lecture. The assumption that nascent H forms complexes with the metal and reducible compound is rejected. H. F. GILLBE.

Physico-chemical studies of complex acids. VI. Precipitation of molybdates. H. T. S. BRITTON and W. L. GERMAN (J.C.S., 1931, 1429—1435).—The ppts. resulting from the interaction of Na molybdate, paramolybdate, or metamolybdate with salts of Zr, Th, Al, Cu, Cr, Be, Ni, and Mg consist of either normal molybdate, sometimes contaminated with basic molybdate, basic molybdate, or the normal or basic salt accompanied by MoO_3. The precipitation is controlled largely by the relation between the resultant p_H, determined by the degree of neutralisation of H_2MoO_4, and that necessary to cause precipitation of the hydroxide.

H. F. GILLBE.

Aqueous salt solutions in equilibrium with solid secondary calcium phosphate at 40°. J. W. H. LUGG (Trans. Faraday Soc., 1931, **27**, 297—309).—The form of $CaHPO_4$ which is stable in contact with aq. solutions of NaCl at 40° is brushite, the solubility product, *s*, of which in aq. solutions of NaCl, KCl, Na_2SO_4, $CaCl_2$, and $MgSO_4$ at 40° has been determined. From p_H data at 23·5° for solutions of these salts containing primary and secondary alkali phosphates values for the second dissociation const., K_2, of H_3PO_4 have been obtained. Equations connecting the concentration of foreign salt with *s* and with K_2 have been derived by means of the Debye–Hückel theory. R. CUTHILL.

Molecular combination of aliphatic iodides. J. C. SMITH (Nature, 1931, **127**, 928).—The system hexadecyl iodide–octadecyl iodide has a eutectic at 19·3° and a non-congruent m. p. at 22·3°, showing the existence of an equimol. *compound.*

L. S. THEOBALD.

Theory of Löwig's process. V. I. SOKOLOV (J. Chem. Ind. Russ., 1931, **8**, 248—252).—The ferrite obtained by the combination of Na_2O with Fe_2O_3 in Löwig's process has the composition Na_2O,Fe_2O_3. The decomp. of ferrite by H_2O is endothermic (−55·14 g.-cal.) and the heat of formation of ferrite is +58 g.-cal. R. TRUSZKOWSKI.

Melting diagram of the system Al_2O_3–Cr_2O_3–MgO. K. J. A. BONTHRON and R. DURRER (Z. anorg. Chem., 1931, **198**, 141—156).—The system has been studied at 1900—2550°, but owing principally to evaporation losses and decomp. of the Cr_2O_3 the results involve large errors. Cr_2O_3 and Al_2O_3 form a eutectic at 30 mol.-% Cr_2O_3, and possibly another, resulting from the formation of a compound, at 90 mol.-% Cr_2O_3. The ternary system contains at least two ternary eutectics, but there is no evidence of the formation of ternary compounds.

H. F. GILLBE.

Use of rhodium vessels for investigation of oxide systems. G. TRÖMEL and F. WEVER (Naturwiss., 1931, **19**, 519—520).—The use of Rh vessels for the investigation of equilibria at high temps. is recommended. A. J. MEE.

System P_2O_5–CaO–H_2O and the recrystallisation of calcium dihydrogen phosphate. N. A. CLARK (J. Physical Chem., 1931, **35**, 1232—1238; cf. A., 1908, ii, 675).—The equilibrium relations have been examined and methods for the recrystallisation of $CaHPO_4$ are given. L. S. THEOBALD.

Equilibrium in the system potassium sulphate–sulphuric acid–water. A. V. BABAEVA (Trans. Inst. Pure Chem. Reag., 1931, **11**, 114—128).—The equilibrium data for 30°, 50°, and 75° indicate the formation of the *salts* $K_2SO_4,3KHSO_4$ and $K_2SO_4,6KHSO_4$. R. CUTHILL.

Equilibrium in the system sodium sulphate–sodium dichromate–water. A. V. RAKOVSKI and E. A. NIKITINA (Trans. Inst. Pure Chem. Reag., 1931, **11**, 5—14).—The isotherms for 0°, 15°, 25°, 40°, 60°, 80°, and 98° have been examined, the results showing that in practice pure $Na_2Cr_2O_7$ cannot be obtained by recrystallisation. The solid phases separating from the system $Na_2Cr_2O_7$–$NaHSO_4$–H_2O at 20° are

$Na_2Cr_2O_7,2H_2O$, Na_2SO_4, $Na_3H(SO_4)_2,H_2O$, and $Na_3H(SO_4)_2$. R. CUTHILL.

Equilibrium in the system potassium dichromate–potassium sulphate–water. A. V. RAKOVSKI and A. V. BABAEVA (Trans. Inst. Pure Chem. Reag., 1931, **11**, 15—19).—The isotherms for the above system at 0°, 20°, 40°, 60°, 80°, and 98° have been derived. R. CUTHILL.

Equilibrium in ternary systems of nitrites, nitrates, and chlorides of sodium and potassium. A. V. RAKOVSKI and D. S. SLAVINA (Trans. Inst. Pure Chem. Reag., 1931, **11**, 20—33).—The isotherms for $NaNO_2$–$NaNO_3$–H_2O at 15° and for KNO_2–KNO_3–H_2O, $NaNO_2$–$NaCl$–H_2O, and KNO_2–KCl–H_2O at 0°, 20°, 40°, 60°, 80°, and 98° have been derived. R. CUTHILL.

Equilibrium in the quaternary system sodium dichromate–ammonium chloride–water. J. GERASIMOV (Trans. Inst. Pure Chem. Reag., 1931, **11**, 34—61).—The isotherms for the above quaternary system and for the ternary systems $(NH_4)_2Cr_2O_7$–NH_4Cl–H_2O, $(NH_4)_2Cr_2O_7$–$Na_2Cr_2O_7$–H_2O, $Na_2Cr_2O_7$–$NaCl$–H_2O, and NH_4Cl–$NaCl$–H_2O have been obtained at 0°, 20°, 50°, and 75°. $(NH_4)_2Cr_2O_7$ and $Na_2Cr_2O_7$ exhibit slight miscibility in the solid state. R. CUTHILL.

Relationship of m.-p. energy to absolute temperature. Z. HERRMANN (Z. anorg. Chem., 1931, **198**, 204—205).—The "m.-p. energy" of an element, *i.e.*, the total heat content of the liquid phase at the m. p., bears a linear relation to the abs. temp. H. F. GILLBE.

Free energy of formation in fused salts. IV. Alkaline-earth halides. G. DEVOTO and G. JENY (Gazzetta, 1931, **61**, 305—311; cf. A., 1928, 135).—Further measurements of the decomp. potentials of the fused halides of Mg and of the alkaline-earth metals are in approx. agreement with the thermodynamically calc. values. The temp. coeff. of the free energy of formation of the halides of Ba, Sr, and Ca is higher than the theoretical value, and the anomaly is ascribed to the formation of sub-salts. O. J. WALKER.

Hydrogen exponent of water. A. KLING and A. LASSIEUR (Ann. Chim., 1931, [x], **15**, 201—227).—A more detailed account of work already noted (A., 1930, 1520).

Activity coefficients and heats of transfer of cadmium sulphate from electromotive force measurements at 25° and 0°. Application of the extended theory of Debye and Hückel. V. K. LA MER and W. G. PARKS (J. Amer. Chem. Soc., 1931, **53**, 2040—2061; cf. A., 1928, 241).—The activity coeff. and partial molal free energies of transfer of $CdSO_4$ have been calc. from the e.m.f. of the cell Pb–Hg (2 phase)|$CdSO_4$(0·000458—3·7M)|$PbSO_4(s)$|Pb–Hg(2 phase). The e.m.f. of the cell, E_0, when the ion activities of the $CdSO_4$ are hypothetically M, is 0·00142 volt at 25° and 0·0162 volt at 0°. The Gronwall, LaMer, and Sandved extension of the Debye–Hückel theory affords const. values of a—3·6 Å. in solutions between 0·0006 and 0·01M, whereas the Debye–Hückel approximation affords variable negative values for the distance of closest approach of the ions (a). $\partial a/\partial T$ is very small, and indicates that the hydration of ions is not involved in a. The mean heat of the cell reaction Cd (s, sat. with Hg)+$PbSO_4(s)$=$CdSO_4(m)$+Pb (s, sat. with Hg) at 12·5° is 8375 g.-cal. J. G. A. GRIFFITHS.

Heat of dissociation of fluorine. M. S. DESAI (Nature, 1931, **128**, 34).—The heat of dissociation of F_2 calc. from the absorption spectrum data for NaF and KF is 76±2 kg.-cal. L. S. THEOBALD.

Thermochemistry of fluorine; heat of formation of hydrogen fluoride, chloride fluoride, and fluorine oxide. O. RUFF and W. MENZEL (Z. anorg. Chem., 1931, **198**, 375—382).—Recalculation of existing data and correction for polymerisation yields for the heat of formation of HF 64·0 kg.-cal. per mol.; that of ClF then becomes 27·4 kg.-cal. per mol. Crit. comparison of various data relating to F_2O point to a value of -7 ± 2 kg.-cal. per mol. H. F. GILLBE.

Heat capacity and free energy of formation of ethane gas. V. R. THAYER and G. STEGEMAN (J. Physical Chem., 1931, **35**, 1505—1511).—The sp. heat of C_2H_6 between 2·20° and 64·40° has been measured using a const.-flow calorimeter; C_p— 5·981 +0·2193T. The free energy of C_2H_6 gas has been recalc.; $\Delta F = -18{,}789 + 16{\cdot}17T \log T - 0{\cdot}006T^2 - 63{\cdot}9T$. L. S. THEOBALD.

Heat of ionisation of water. F. D. ROSSINI (Bur. Stand. J. Res., 1931, **6**, 847—856).—From existing data for heats of dilution and heats of neutralisation the heat of the reaction $H_2O = H^{\cdot} + OH'$ at infinite dilution and over the temp. range 10—35° is calc. to be $\Delta H = 13{,}721 - 57{\cdot}9(t-18) + 0{\cdot}15(t-18)^2$ g.-cal. per g.-mol., where t is the temp. and the uncertainty is ±16 g.-cal. per g.-mol. This gives 57,370 abs. joules per g.-mol. for ΔH at 18°. R. CUTHILL.

Calorimetric determinations of thermal properties of methyl alcohol, ethyl alcohol, and benzene. E. F. FIOCK, D. C. GINNINGS, and W. B. HOLTON (Bur. Stand. J. Res., 1931, **6**, 881—900).—The heat contents of the liquids and saturated vapours referred to the values for the liquids at 0°, and also the latent heats of evaporation, have been determined from 40° to 110°. R. CUTHILL.

Heat of dissolution of benzoic acid in toluene. G. CHAPAS (Compt. rend., 1931, **192**, 1446—1448).—The sp. heat of a solution of BzOH in PhMe is identical with that of PhMe. The heat of dissolution varies but slightly with the concentration of the solution, viz., from —2880 to —3040 at 18°, and from —3160 to —3220 at 25°. Such solutions are not ideal. C. A. SILBERRAD.

Heat of dissolution of some potash minerals. L. T. RICHARDSON and R. C. WELLS (J. Washington Acad. Sci., 1931, **21**, 243—248).—Preliminary measurements of the heats of dissolution of polyhalite, langbeinite, kainite, carnallite, and anhydrite have been made. C. W. GIBBY.

Heat content values for aqueous solutions of the chlorides, nitrates, and hydroxides of hydrogen, lithium, sodium, and potassium at 18°. F. D. ROSSINI (Bur. Stand. J. Res., 1931, **6**, 791—806).—Published data for the heats of dilution

of the above compounds have been used to calculate the relative apparent molal heat content of the solute, the relative partial molal heat content of the solute, and the relative partial molal heat content of the H_2O at 18° from infinite dilution to a concentration of about 2 molal. R. CUTHILL.

Viscosity isotherms and differential heats of dilution in aqueous solutions. Z. V. VOLKOVA and V. S. TITOV (Z. physikal. Chem., 1931, **155**, 51—58).—The differential heats of dilution, U, of a number of solutions have been compared with their $1/\eta - V$ isotherms (η being the coeff. of viscosity, and V the sp. vol.), the data being drawn from a variety of sources. For solutions of, *e.g.*, N-KI+HgI_2, $AgNO_3$, NH_4NO_3, CsCl, and carbamide $U<0$, and the isotherms are convex to the $1/\eta$ axis. For solutions of $ZnCl_2$, $AlCl_3$, $MgCl_2$, and sucrose $U>0$, and the isotherms are convex to the V axis and may also have a straight portion. In the latter series the relation U/η=const., previously found for glycerol–water mixtures (A., 1930, 679), holds within the probable limits of accuracy imposed by errors in the determination of U. N. H. HARTSHORNE.

Thermal expansion and the Debye–Hückel heat of dilution. G. SCATCHARD (J. Amer. Chem. Soc., 1931, **53**, 2037—2039).—Heats of dilution calc. from the Debye–Hückel theory by differentiation at const. vol. are incorrect. A complete equation is derived for one case, and it is shown that neglect of thermal expansion leads to errors in the limiting law. J. G. A. GRIFFITHS.

Thermochemistry of the system ammonia–sulphuric acid. W. A. ROTH and H. ZEUMER (Z. angew. Chem., 1931, **44**, 559—565).—The heat of formation of cryst. $(NH_4)_2SO_4$ from NH_3 (gas) and 100% H_2SO_4 at 20° is 65·44 kg.-cal. per mol. and from the 96·6% acid is 63·89 kg.-cal. per mol. The values obtained for the heat of dissolution of $(NH_4)_2SO_4$ differ considerably from those of Thomsen. The heat of formation of the salt from the saturated solution containing 10% of free H_2SO_4 and NH_3 diluted with air is not altered if H_2O vapour or CO_2 be present separately in the gas phase, but if both are present it is depressed. Thus although NH_4OH or NH_4 carbamate is not present in the vapour phase, $(NH_4)_2CO_3$ or NH_4HCO_3 is formed therein. When moist NH_3 containing the same quantity of CO_2 as is present in the technical gas is used the heat of formation is 58—59 kg.-cal. per mol. H. F. GILLBE.

Thermal properties of cellulose and its derivatives. E. HEISENBERG (Cellulosechem., 1931, **12**, 159—162).—The heat of formation of a cellulose ester, calc. from its heat of combustion, increases with the no. of C atoms in the esterifying acid (triacetate, -600 ± 1000; 2·9-hexoate, $20{,}000\pm1000$; and 2·73-laurate, $26{,}500\pm4000$ g.-cal. per mol. of acid). Cellulose monoacetate is formed exothermically (heat of formation of 0·43-acetate, $21{,}000\pm6000$ g.-cal.), but further esterification is endothermic. The energy contents of viscose and acetate silks, measured by their heats of combustion, increase with the spinning tension. A. RENFREW.

Galvanometric method of measuring an electrolytic resistance. J. A. C. TEEGAN (Phil. Mag., 1931, [vii], **11**, 1250—1252; cf. A., 1930, 1375).—Results obtained by the telephone and galvanometric methods are compared. N. M. BLIGH.

Calculation of the equivalent conductivity of strong electrolytes at infinite dilution. A. FERGUSON and A. I. VOGEL (Trans. Faraday Soc., 1931, **27**, 285—294; cf. A., 1925, ii, 1163).—Arguments are put forward to justify the method of calculation previously adopted. J. W. SMITH.

Conductivity of aluminium bromide in non-aqueous solution. E. WERTYPOROCH (Ber., 1931, **64**, [*B*], 1369—1380).—The molar conductivity of $AlBr_3$ in ethereal solution is const. for concentrations between 0·5 and 0·4M, but diminishes to 0·1 of this value between 0·4 and 0·1M, subsequently remaining const. Addition of substances containing O or N (MeCN, PhCHO, phenylthiocarbimide, BzOEt, allyl alcohol, anisole), or of amylene, CS_2, or C_6H_6 usually increases the conductivity of ethereal solutions of $AlBr_3$; marked exaltation of K is not caused, however, by amounts equiv. to the dissolved $AlBr_3$, but by such as cause a greater or less displacement of the solvent into the solvates. In EtBr the conductivity of $AlBr_3$ increases with the concentration up to about 20%. At room temp., the final value for the conductivity is not immediately reached, particularly in dil. solution. Addition of C_6H_6 to a solution of $AlBr_3$ in EtBr causes very marked increase in the conductivity, the max. value being observed after 5—6 hr. The solution becomes golden-yellow and finally reddish-brown; HBr is rapidly evolved, but its presence is not the cause of the increased conductivity. With trimethylethylene the considerable increase in conductivity is partly masked by polymerisation of the hydrocarbon. Increase is observed also with tetramethylethylene and $C_{10}H_8$. Dimethylpyrone and $AlBr_3$ in EtBr yield a *ppt.*, $5C_7H_8O_2,HAlBr_4,2H_2O$, m.p. 205°; similar ppts. are obtained with NH_2Ph, *p*- and *m*-nitroaniline, NHPhMe, $NPhMe_2$, $NHPh_2$, cineole, and quinoline. Electrolysis of solutions of $AlBr_3$ in EtBr causes accumulation of Al at the anode, indicating the presence of a salt $Al[AlBr_4]_3$, the existence of which is confirmed by observations in solutions in hexaethylbenzene. The conductivity of C_6H_6 is not increased by dissolution of $AlBr_3$ (up to 20%). Addition of C_6H_6, $C_{10}H_8$, or diphenyl to $AlBr_3$ in Et_2O diminishes the conductivity. The occurrence of a primary compound, *e.g.*, $(PhAlCl_3)^-H^+$, appears excluded. The existence of a compound C ...$ClAlCl_2$ is improbable, since solutions of $AlBr_3$ in C_6H_6 do not appreciably absorb Br, do not add H in presence of spongy Pt more rapidly than in the absence of Al halide, and do not react with HNO_2. Complex formation between C_6H_6 and Al salts appears actually to restrict the reaction, which progresses only so far as the Al complex is transformed into the ternary compound by partial displacement of C_6H_6 by the compound containing halogen or O. The conductivity per mol. of $AlBr_3$ is increased by the addition of hydrocarbons to such an extent that the solutions have an equiv. conductivity of the same order as that of normal salts

(measurements of NEt_4Br and ethyltriamylammonium bromide in EtBr are recorded). Migration experiments show that the Al atoms wander to anode and cathode in the approx. ratio 3 : 1, and that formed or added hexaethylbenzene becomes about five times as highly conc. at the cathode as at the anode, thus indicating a complex $[Al(EtBr)_n(C_{18}H_{30})_4][AlBr_4]_3$. In $COMe_2$ the conductivity of $AlBr_3$ immediately attains its final value, and is diminished by C_6H_6 or EtBr. Solutions of $AlBr_3$ in ethylene bromide do not conduct; addition of C_6H_6 causes slight conductivity. BF_3, BCl_3, and $TiCl_4$ in benzotrichloride are inactive.

H. Wren.

Conductivity of fused sodium tungstates. V. Spitzin and A. Tscherepnev (Z. anorg. Chem., 1931, **198**, 276—286).—The conductivity of Na_2O–WO_3 melts has been determined at temp. from 750° to 900° as a function of the composition; it falls as the ratio $WO_3 : Na_2O$ is increased from 1 to 4·5, and thereafter becomes const., and for a given mixture increases linearly with rise of temp. The curves demonstrate the existence of di- and quadri-tungstates, and the non-formation of $Na_2W_8O_{25}$: the existence of $Na_2W_5O_{16}$ is doubtful. H. F. Gillbe.

Electro-endosmosis. V. Electro-endosmosis and surface conductivity against a glass surface of solutions of hydrogen chloride in benzene and other solvents. F. Fairbrother and M. Balkin (J.C.S., 1931, 1564—1578).—Solutions of dry HCl in C_6H_6 exhibit marked electro-endosmosis through a sintered glass membrane, which increases with increase of the HCl concentration. In *cyclo*hexene the electro-endosmosis is very small, and in CCl_4 and *cyclo*hexane it is not measurable. In contact with glass powder all the solutions exhibit surface conductivity; this effect is not a result of the electro-endosmosis, but may be due to ionisation caused by extreme deformation of the HCl mols. at the polar glass surface or by a surface film of adsorbed H_2O. The solubility of HCl in the 4 solvents has been determined; the sp. conductivity of the solutions is less than 7×10^{-13} mho.

H. F. Gillbe.

Null point of the charge of silver. M. Proskurnin and A. Frumkin (Z. physikal. Chem., 1931, **155**, 29—40).—Measurements of the adsorption on an etched Ag surface in contact with dil. solutions of Ag ions have been made by two methods. From the concentration at which no adsorption occurs the null point of the charge of the Ag surface is calc. to correspond with $\varepsilon_h=+0{\cdot}51$ volt, the charge being defined as the quantity of electricity which the surface must send into the solution in order to keep const. the concentration of the Ag ions, when the surface is increased by 1 sq. cm. This value agrees well with those obtained from electrokinetic measurements by Billitzer and Bennewitz. N. H. Hartshorne.

Quinhydrone electrode. III. [Effect of electrode materials.] J. L. R. Morgan and O. M. Lammert (J. Amer. Chem. Soc., 1931, **53**, 2154—2168; cf. this vol., 456).—Au electrodes, from whatever source, afford erratic results when the area is less than 1 sq. cm. Sufficiently large electrodes of Pt, Au, and lead-pencil graphite, but not lamp-carbons, produce equal p.d. in 0·1*N*-HCl, but the current capacity of the half-cell with Pt is greater than with a Au electrode of equal area. Au-plated and Pt-alloy electrodes give different p.d., but these differences are eliminated by stirring with N_2. The reproducibility of Pt, Pt–Rh and Pt–Ir alloy, but not of Au and graphite electrodes, is improved by stirring with N_2.

J. G. A. Griffiths

Problem of the Haber glass electrode. J. Zirkler (Z. physikal. Chem., 1931, **155**, 75—76).—When the same solution of HCl is placed inside and outside the bulb of a glass electrode a potential drop is set up across the glass which is independent of the HCl concentration within the range *N* to 0·001*N*, but varies with the kind of glass, being about 30—60 mv. with "Violax," and about 90—110 mv. with "Jena Normalglas 16'''." The phenomenon is not shown by quartz bulbs. It is not influenced by the addition of small quantities of surface-active substances, nor by the replacement of HCl by H_2SO_4, nor by the use of bulbs blown with O_2 or CO_2 instead of with air. N. H. Hartshorne.

Polarographic studies with the dropping mercury cathode. XIX. Effect of some organic dyes on the current maxima due to absorption of oxygen. B. Rayman (Coll. Czech. Chem. Comm., 1931, **3**, 314—327).—The suppressive effect produced by org. dyes on the current max. caused by the electro-reduction of dissolved O_2 is due to preferential adsorption of the dye and consequent removal of O_2 from the electrode–solution interface. The dilutions of the dyes at which the max. in 0·001*N*-KCl is reduced to one half may be regarded as a measure of the extent to which each dye is adsorbed; data are given for a number of substances. The less readily adsorbed acid dyes suppress the max. at cathode potentials which are more positive than the electrocapillary zero, and cause a discontinuity on the curve; this effect is ascribed to adsorption of anions at the interface and preferential adsorption of O_2 mols. in the neighbourhood of the electrocapillary zero.

H. F. Gillbe.

Electrochemical behaviour of platinum in hydrochloric acid solution. G. Grube and H. Reinhardt (Z. Elektrochem., 1931, **37**, 307—320; cf. A., 1929, 1403).—From experiments on the dissolution of Pt in HCl solutions of H_2PtCl_6 the position of the equilibrium $2H_2PtCl_4 \quad H_2PtCl_6+Pt+2HCl$ has been approx. determined at 60°. The following values of ${}_0E_h$ at 60° have been obtained: $PtCl_4''|PtCl_6''$, $+0{\cdot}745\pm0{\cdot}01$; $Pt|PtCl_6''$, $+0{\cdot}765\pm0{\cdot}01$; $Pt|PtCl_4''$, $+0{\cdot}785\pm0{\cdot}01$ volt. Compact and fine-grained grey deposits of Pt are obtained by electrolysis at 60° of a 0·1*M* solution of H_2PtCl_6 in 5*N*-HCl with a current density of 0·01—0·02 amp. per sq. cm.; the current yield of Pt is 60—70%. R. Cuthill.

Electrolytic reduction of chloroplatinic acid in hydrochloric acid solution. I. O. Stelling (Z. Elektrochem., 1931, **37**, 321—328).—The potential of a Pt electrode in a HCl solution of H_2PtCl_6 which has been partly reduced by electrolysis is, for a given HCl concentration, represented by the equation $E=E'+RT/2F\,.\log$ (platinic)/(platinous) $(Cl)^2$, where (platinic) and (platinous) are calculated from the initial composition of the solution and the amount of

current passed. At 50° the value of ${}_0E_h$ is +0·74 volt. The cathodic current density–potential curves of a 0·1M solution of H_2PtCl_6 in HCl show discontinuities, corresponding with the processes $Pt^{\cdot\cdot\cdot\cdot}+2\Theta=Pt^{\cdot\cdot}$, $Pt^{\cdot\cdot}+2\Theta=Pt$, $Pt^{\cdot\cdot\cdot\cdot}+4\Theta=Pt$, and $2H^{\cdot}+2\Theta=H_2$, but these are apparently complicated by the presence of a film on the electrode. R. CUTHILL.

Electrochemical and chemical behaviour of polonium in tartaric acid solution. M. HAISSINSKY (Compt rend., 1931, **192**, 1448—1451).—Using Joliot's method (cf. A., 1927, 633) and a solution of Po of concentration $2\times10^{-9}N$ in N-tartaric acid the velocity of deposition is only about one fourth that in AcOH under similar conditions. There are two crit. potentials, 0·38 and 0·03 volt (cf. A., 1930, 713). A similar solution, but with a Po concentration of $7{\cdot}6\times10^{-9}N$, lost no Po when centrifuged; after the addition of aq. NH_3 to raise p_H to 7—8 the solution was found, however, to lose 42% Po in an hour. It is inferred that Po forms a sol. complex with tartaric acid similar to Bi (cf. A., 1914, ii, 148), the Po being present in two forms of different valencies. C. A. SILBERRAD.

Measurement of the electricity liberated during the downgrade reactions of organic compounds. J. H. WOLFENDEN (Nature, 1931, **128**, 69).—No systematic effect due to the fermentation of sucrose by yeast could be observed in the cell C|15% sucrose|15% sucrose+yeast|C. No evidence of a continuous supply of electrical energy from a chemical reaction proceeding irreversibly has been obtained (cf. this vol., 703). L. S. THEOBALD.

Passivity of chromium. W. J. MÜLLER (Z. Elektrochem., 1931, **37**, 328—330).—The observations and theory of E. Müller and Essin (this vol., 173) are essentially in agreement with the author's theory. The influence of the acid anion on the temp. at which passive Cr becomes active in an acid solution is, however, ascribed to variation in the solubility of the protective film, the solubility being maximal in HCl. Activation by cathodic liberation of H_2 is attributed to mechanical loosening of the oxide film. R. CUTHILL.

Becquerel effect of the second order. G. E. MUCHIN and M. I. SILBERFARB (Ukrain. Chem. J., 1930, **5**, [Sci.], 323—347).—The Becquerel effect of the second order is measured by $B=(E_1-E_0)100/E_0t$, where E_1 is the max. p. d. observed during illumination with a C arc of a Pt electrode in H_2SO_4 solution, as measured against a Hg_2Cl_2 electrode, E_0 is the p. d. in the dark, and t is the time of illumination in min. The difference in potential is partly due to heating of the solution, and this part is given by $W=(E_W-E_0)100/E_0 30$, where E_W is the p. d. found by illuminating vessels covered with black paper during 30 min. W is in all cases negative. The value of $B-W$ increases from −0·121 in 0·05M-H_2SO_4 to +0·453 in 0·49M-acid, and at higher concentrations of acid it falls to −0·033 in 1·24M-H_2SO_4. R. TRUSZKOWSKI.

Velocity and affinity of chemical processes. J. V. MEDVEDEV (Bull. Acad. Sci. U.S.S.R., 1931, 393—400).—A theoretical discussion, based principally on Nernst's work. T. H. POPE.

Thermal decomposition of chlorine monoxide. J. J. BEAVER and G. STIEGER (Z. physikal. Chem., 1931, **B**, **12**, 93—108).—The thermal decomp. of Cl_2O at 100—140° in a quartz vessel appears to be a complex chain reaction, normally ending in explosion, and not, as Hinshelwood supposed (A., 1924, ii, 749), a simple bimol. reaction. After the period of induction, the velocity at 100—130° may be represented by $-d[Cl_2O]/dt=k[Cl_2O]$, and that at 140° by $-d[Cl_2O]/dt=k[Cl_2O]^{0\cdot75}$; in both equations the velocity coeff., k, is approx. proportional to the initial pressure of Cl_2O. Judged by the effect of variations in the ratio of surface area to vol. of the containing vessel the reaction as a whole is homogeneous in either a quartz or a glass vessel. Some intermediate product, comparatively stable at 0°, is formed during the period of induction and sets up reaction chains with the monoxide, and then when the concentration of the latter has become small reacts with itself explosively. Probably after the period of induction the concentration of this intermediate product remains appreciably const. until very near the end of the reaction, its reaction with the monoxide thus becoming kinetically unimol. The intermediate product may be the oxide ClO, and it is very probable that ClO_2 also plays an important part. The reaction is not affected by Cl_2, O_2, N_2, air, or CO. R. CUTHILL.

Thermal decomposition of nitryl chloride. A homogeneous gas reaction of the first order. H. J. SCHUMACHER and G. SPRENGER (Z. physikal. Chem., 1931, **B**, **12**, 115—131).—The thermal decomp. of nitryl chloride (cf. A., 1929, 1395) at 100—150° is a homogeneous unimol. reaction, the heat of activation calc. from the temp. coeff. being about 20·5 kg.-cal. The collision number is, however, exceptionally small under moderate pressures, and, probably in consequence of this, the velocity coeff. increases with increasing pressure, and has not reached a steady value even at 10 atm. H_2, O_2, Cl_2, CO_2, N_2, and CO all accelerate the reaction to approx. the same extent; NO_2 has an accelerating effect which is about 20% greater, and a mixture of NO_2 and Cl_2 in the stoicheiometric ratio has the same effect as undecomp. nitryl chloride. R. CUTHILL.

Possibility of bimolecular association reactions. L. S. KASSEL (J. Amer. Chem. Soc., 1931, **53**, 2143—2147).—The bimol. association reaction is regarded as the reverse of the unimol. decomp., and is shown, theoretically, to be possible in the case of complex mols. at a considerable fraction of all collisions. The polymerisation of C_2H_4 (this vol., 436) is probably of this type. J. G. A. GRIFFITHS.

Thermal decomposition of methane. II. Homogeneous reaction. G. C. HOLLIDAY and W. J. GOODERHAM (J.C.S., 1931, 1594—1604; cf. A., 1929, 773).—The decomp. of CH_4 in SiO_2 bulbs is mainly a homogeneous reaction. Above 900° the reaction proceeds in two stages: in the first, 2 mols. of CH_4 react to form C_2H_2, which, in the second stage decomp. to H and C. F. J. WILKINS.

Thermal decomposition of carbon tetrabromide. H. A. TAYLOR (J. Physical Chem., 1931, **35**, 1795—1799).—The thermal decomp. of CBr_4,

investigated colorimetrically, is a heterogeneous reaction apparently of the first order between 300° and 330°. The average energy of activation, calc. by means of Arrhenius' equation, is 57,200 g.-cal.

L. S. THEOBALD.

Thermal decomposition of diazomethane. E. W. R. STEACIE (J. Physical Chem., 1931, **35**, 1493—1495).—The slow decomp. of diazomethane in quartz between 140° and 220° (products N_2 and C_2H_4) is apparently bimol.; calc. heat of activation 36×10^3 g.-cal. per mol. Traces of org. matter cause serious explosions. L. S. THEOBALD.

Thermal decomposition of dimethyltriazene. Homogeneous unimolecular reaction. H. C. RAMSPERGER and J. A. LEERMAKERS (J. Amer. Chem. Soc., 1931, **53**, 2061—2071).—The rate of decomp. at 200—230° of 0·019—8 cm. of dimethyltriazene has been measured by the increase of pressure (factor, 2·175). The reaction is homogeneous and of the first order; the velocity coeff., $4{\cdot}05\times10^{11}e^{-33,800/RT}$, falls with initial pressures less than 1 cm. The data are in agreement with the theories of Rice and Ramsperger (A., 1927, 833). J. G. A. GRIFFITHS.

Influence of hydrogen on chemical changes in silica vessels. M. W. TRAVERS, L. E. HOCKIN, and T. J. P. PEARCE (Nature, 1931, **128**, 66).—In the condensation of C_2H_6 at 600° reproducible results can be obtained only in thick-walled SiO_2 vessels or in thin-walled vessels surrounded by an atm. of H_2. This suggests that in SiO_2 there exists a complex equilibrium which consists of solid phase : glass–gas interface: gas–glass interface : gas phase. The H_2 in the solid phase may be more highly dissociated than in the gaseous phase and the life of the H atoms passing from glass–gas to gas–glass interface may be long enough to bring about processes commonly attributed to at. H in the adsorbed layer on the SiO_2.

L. S. THEOBALD.

Explosive reactions. W. P. JORISSEN (Natuurwetensch. Tijds., 1931, **13**, 189—202).—Previous work on the explosion limits of various three-component gaseous mixtures is summarised. Three principal types of mixture are recognised, according to the type of diagram obtained, but there are at least eight less common types, which are described and discussed. The diagrams obtained with solid explosive mixtures are described and the similarity with those obtained with gases is indicated.

H. F. GILLBE.

Photographic flame studies in the petrol engine. L. WITHROW and T. A. BOYD.—See B., 1931, 618.

Reaction between arsenious acid and iodine. H. A. LIEBHAFSKY (J. Physical Chem., 1931, **35**, 1648—1654).—The kinetics of the reaction $H_3AsO_3+I_3^-+H_2O=H_3AsO_4+2H^++3I^-$ are discussed (cf. A., 1906, ii, 76). L. S. THEOBALD.

Carbon dioxide absorption by solutions of sodium and potassium hydroxide. K. MASAKI (J. Biochem. Japan, 1931, **13**, 211—217).—Aq. *N*-NaOH absorbs CO_2 more rapidly (1 : 0·93) than *N*-KOH at 11°, whilst at 18° and 25° the KOH solution more rapidly absorbs the gas, the ratios being 1 : 1·17 and 1 : 1·29 respectively. F. O. HOWITT.

Reactions involving hydrogen peroxide, iodine, and iodate ion. IV. Oxidation of iodine to iodate ion by hydrogen peroxide. H. A. LIEBHAFSKY (J. Amer. Chem. Soc., 1931, **53**, 2074—2090; cf. this vol., 324, 573).—The velocity of the reaction $I_2+5H_2O_2=2IO_3'+2H^{\cdot}+5H_2O$ has been investigated at 0° over a wide range of initial concentration of IO_3', H_2O_2, $HClO_4$, and I_2. The oxidation of I to IO_3' does not proceed appreciably by the direct oxidation of I, I', or HIO by H_2O_2. The induction period, which occurs at certain concentration, is prolonged by low $[IO_3']$ and $[H^{\cdot}]$ and high $[H_2O_2]$, and is attributed to the building up of the intermediate HIO_2. The following mechanism is in accord with the observations: (*a*) I_2+H_2O — $H^{\cdot}+I'+HIO$ (rate determining step), (*b*) $IO_3'+I'+2H^{\cdot}=H_2I_2O_3$, (*c*) $H_2I_2O_3+H_2O_2=2HIO_2+H_2O$, (*d*) $HIO_2+HIO=H_2I_2O_3$ (cf. A., 1930, 1378), (*e*) $HIO_2+H_2O_2=IO_3'+H^{\cdot}+H_2O$. I is reduced to I' by H_2O_2 when $[H^{\cdot}]$ is less than $4\times10^{-3}N$, since the I' formed by the reaction $HIO+H_2O_2=H^{\cdot}+I'+H_2O+O_2$ cannot be as effectively removed as at higher $[H^{\cdot}]$ at which reaction (*b*) is favoured, and hence the H_2O_2 is decomp. catalytically by the I_2–I' couple. The results do not establish the sp. rate of the hydrolysis of I_2 (reaction *a*), but indicate that the coeff. is probably greater than 0·06 at 0° and 0·6 at 25°.

J. G. A. GRIFFITHS.

Interaction between nitrogen trichloride and nitric oxide at −150°. III. Interaction of nitric oxide and chlorine at −80° and −150°. W. A. NOYES (J. Amer. Chem. Soc., 1931, **53**, 2137—2143).—In the presence of CCl_4, NO and Cl_2 combine much more slowly at − 150° than at −80°. The reaction is very slow at − 180°. Further support is obtained for the mechanisms proposed for the reactions between NO and NCl_3 (this vol., 52). The structure of N_2O is discussed. J. G. A. GRIFFITHS.

Velocity and heat of saponification of amides. E. CALVET (Compt. rend., 1931, **192**, 1569—1572).—The velocity of saponification by NaOH of aliphatic amides at 17° has been measured by determining the NH_3 evolved. The reaction is bimol. and decreases rapidly as shown by the values of *k*: formamide, 4·45; acetamide, 0·0692; propionamide, 0·0669; butyramide, 0·0237; valeramide, 0·0239; and hexamide, 0·0237. The corresponding heats of saponification in g.-cal. are respectively: 6·73, 6·55, 6·6, 5·8, 5·65, 5·6 (all $\times10^{-3}$). F. R. SHAW.

Kinetic theory of the velocity of biochemical processes. I. J. V. MEDVEDEV (Bull. Acad. Sci. U.S.S.R., 1931, 277—313).—Mainly a theoretical paper, with a few data concerning the inversion of sucrose by invertase. The interaction of a particle of an enzyme with a mol. of the substrate undergoing chemical change, resulting in an enormous increase in the velocity of this change, is regarded as consisting in the transference to the mol. of substrate of a quantum of energy, which is the true agent of the acceleration of the reaction. The association of the enzyme particle with the mol. of substrate accompanying the transference of the energy quantum differs from that of chemical compounds and is regarded as an impact of the second type. On this basis it is possible to calculate the order of the abs. magnitude of

the chemical reaction with the help of the equations of static mechanics. The results obtained in this way for the inversion of sucrose by invertase agree with the experimental data within the limits of accuracy of these. T. H. POPE.

Kinetics of transitions in polymorphic solids. A. F. BENTON and R. D. COOL (J. Physical Chem., 1931, **35**, 1762—1769).—The rates of transition of HgI_2 and of TlI have been measured by means of a dilatometer in which vol. changes are transmitted by an inert gas instead of a liquid. Both transitions are autocatalytic in each direction. The rate of reaction increases with increasing temp. intervals above and below the transition temp.; in the latter case this rate increases to a max. with a fall in temp. and then decreases to values which are very small at liquid air temp. The rate is sensitive to the thermal history of the sample. With TlI the rate of conversion is the same in air, CO_2, or N_2. The transition temp. for TlI lies between 150° and 174° and probably between the narrower limits 160° and 170°, and for HgI_2 at 1 atm. it is between 123° and 129·5°. The vol. changes are 0·0028 and 0 003 c.c. per g., respectively, the red variety being denser in each case. L. S. THEOBALD.

Thermal decomposition of potassium chlorate. J. B. M. COPPOCK, J. COLVIN, and J. HUME (Trans. Faraday Soc., 1931, **27**, 283—284).—The decomp. of $KClO_3$ at 223° is interfacial and proceeds from nuclei on the surface. Crystals of $KClO_3$ in light contact with particles of MnO_2 or rubbed with MnO_2 failed to show any increase in the rate of decomp. J. W. SMITH.

Rate of calcination of limestone. C. C. FURNAS. —See B., 1931, 629.

Kinetics of reactions between colloids. I. Formation of uranium–vanadium complexes. V. A. KARGIN (Z. anorg. Chem., 1931, **198**, 79—87).—The reaction between UO_3 and V_2O_5 sols has been studied spectrophotometrically and by potentiometric titration. The change of the extinction coeff. E with time indicates the formation of the colloidal compounds $UO_3,2V_2O_5$,aq., and UO_3,V_2O_5,aq. The reaction is of zero order and exhibits a marked induction period; it takes place between the particles which are in true solution, and not between the colloidal particles. The addition of an abnormally high quantity of uranyl salts is necessary to cause coagulation of sols containing the complexes, owing to the production of a compound $3UO_3(UO_3,2V_2O_5)$,aq., of which the naturally occurring uranovanadates are probably derivatives. The induction period, and the total period of the reaction, diminish on dilution of the mixed sols, the former being determined by the time required for the production of nuclei of the complex acids; addition of a sol in which the final reaction product is present reduces the induction period less than does addition of a sol in which the induction period has just terminated, owing to the protective action of the double layer and hydrate envelope which are subsequently formed. H. F. GILLBE.

Reaction between magnesium and salt solutions. II. I. IITAKA (J. Iron Steel Inst. Japan, 1930, **16**, 1056—1063).—The velocity of reaction of Mg with dil. HCl ([Cl′] kept at $10^{-2}N$; [H$^{\cdot}$] 0—10^{-13}) diminishes with decrease in [H$^{\cdot}$], but does not vanish when [H$^{\cdot}$]=0; it is const. for [H$^{\cdot}$] 10^{-4} to 10^{-11}. The stirring effect is attributed to autocatalysis, a compound of Mg, H_2O, and Cl′ being formed.

CHEMICAL ABSTRACTS.

Influence of stress on corrosion. D. J. McADAM, jun. (Amer. Inst. Min. Met. Eng., Tech. Pub., 1931, No. 417, 39 pp.).—The behaviour of various metals under similar conditions of corrosion is illustrated. The rate of net damage (lowering of the fatigue limit) varies as the 3rd to the 5th power of the corrosion stress. The conditions favouring intercryst. corrosion are discussed. CHEMICAL ABSTRACTS.

Initial corrosion rates of metals. R. H. BROWN, B. E. ROETHELI, and H. O. FORREST.—See B., 1931, 681.

Method of testing the local-element theory of corrosion. W. GUERTLER and B. BLUMENTHAL.—See B., 1931, 681.

Catalysis by heavy metal ions in aqueous solution, and autoxidation of sulphite solutions. J. FRANCK and F. HABER (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1931, **13**, 250—256).—Homogeneous catalysis in aq. solution by heavy metal ions is attributed to their reacting with constituents of the solution to give radicals or atoms, which in turn react with other constituents of the solution, *e.g.*, with dissolved O_2 in autoxidation, the heat of activation in this instance being small or even zero. If a new atom or radical is produced in the second reaction, a reaction chain is established, and ends only when the atoms or radicals combine to form saturated mols. In absence of O_2, $H_2S_2O_6$ is formed in alkali sulphite solutions containing the $Cu^{\cdot\cdot}$ ion, the intermediate product being the anion of monothionic acid, SO_3', which acts as a free radical: $2SO_3''+2Cu^{\cdot\cdot}=2SO_3'+2Cu^{\cdot}$, $2SO_3'=S_2O_6''$. If, however, O_2 is present, the SO_4'' ion and free OH result: $SO_3H+O_2+SO_3''+H_2O=2SO_4''+OH+2H^{\cdot}$, or possibly $HSO_3+O_2=HSO_5$, $HSO_5+SO_3''+H_2O=2SO_4''+OH+2H$. The chain is propagated by the reactions $SO_3''+OH=SO_3'+OH'$, and $SO_3'+H^{\cdot}=SO_3H$, which explains why autoxidation does not occur in strongly alkaline solutions. In the photo-reaction, the primary process is probably $SO_3'',H_2O+h\nu=SO_3'+H+OH'$. R. CUTHILL.

Action of ferrous iron in induced reactions. D. RICHTER (Ber., 1931, **64**, [*B*], 1240—1243).—The possibility that the induced oxidation of H_3PO_2 by O in presence of $Fe^{\cdot\cdot}$ is a chain reaction is strengthened by the observation that it is restricted by typical negative catalysts, *e.g.*, quinol, I, and $NHPh_2$. Similar observations are recorded for the effect of benzyl and *iso*propyl alcohol on the induced oxidation of Na_2SO_3. H. WREN.

Reduction of silver halides by sodium sulphite and nitrite in the presence of inductors and a cheap developer in photography. R. B. L. VERMA and N. R. DHAR (J. Physical Chem., 1931, **35**, 1770—1776).—AgCl, AgBr, AgI, and AgCNS are reduced by developers in the following, decreasing order: metol, pyrogallol, quinol, hydrazine sulphate, NH_2OH,HCl, and $FeSO_4$. Na_2SO_3 or $NaNO_2$ alone does not reduce

Ag salts but increases reduction by the developers, the order remaining unchanged. Reduction in the Ag salts is in the order $AgCl > AgBr > AgCNS > AgI$. The efficiency of ordinary developers can be maintained by increasing the Na_2SO_3 and diminishing the metol or quinol present. L. S. THEOBALD.

Comparative catalytic dehydration [of alcohols] by sulphuric acid and alkali hydrogen sulphates. J. B. SENDERENS (Compt. rend., 1931, **192**, 1422—1425).—To test the hypothesis that the differences in catalytic activity as regards dehydration of alcohols (cf. A., 1929, 695; 1930, 889) of H_2SO_4, $NaHSO_4$, and $KHSO_4$ are due to their differing avidity for water, the amounts of water absorbed from saturated air in equal times are shown to be in the order of this activity; the amounts absorbed in 110 days by $H_2SO_4+2H_2O$, $NaHSO_4$, and $KHSO_4$ are in the ratios 33·2, 21·6, and 16·0. C. A. SILBERRAD.

Catalytic effect of solvents. Decomposition of malonic acids. R. E. BURK and W. DAUS (J. Physical Chem., 1931, **35**, 1461—1473).—The rate of decomp. of malonic acids, especially the benzyl derivative, has been determined in different solvents. Oleic and palmitic acids, *o*-, *m*-, and *p*-chloronitrobenzene show no catalytic effect, but dimethylaniline has a marked effect, accompanied by a lowering of the temp. coeff., which, however, is not due to salt formation. Mechanisms for activation by the catalyst are discussed. L. S. THEOBALD.

Catalytic action of manganese on oxidation of quinol. E. A. SYM (Annalen, 1931, **487**, 174—196).—In buffered solutions the catalytic effect of Mn on the oxidation of quinol to benzoquinone is most marked at p_H about 7·0, and, unlike the autoxidation, is depressed by addition of quinone. It decreases with time, and increases with increasing concentrations of quinol, Mn, and O_2. In non-buffered solutions dissolved $Mn(OH)_2$ exerts a greater effect less dependent on quinol concentration. Evidence for the formation of a catalytically active Mn–quinol complex is obtained both by a kinetic study of the reaction and by determinations of the solubility of $Mn(OH)_2$ in aq. quinol, but very different results are obtained for the dissociation coeff. of the supposed complex by the two methods. During the air-oxidation of quinol in presence of an excess of an aq. suspension of $Mn(OH)_2$ the quinhydrone formed carries down with it much of the Mn, and it is to this behaviour that the suppression of catalysis by quinone is attributed. H_2O_2 is formed during the autoxidation of quinol, but the method employed to detect it [oxidation of $Ce(OH)_3$] could not be used in presence of Mn. Neither $Fe^{\cdot\cdot}$ nor $Fe^{\cdot\cdot\cdot}$ salts catalyse the air-oxidation of quinol under the conditions employed with Mn, and the activity of Mn is unaffected by glycine, Na K tartrate, or $Na_4P_2O_7$. H. A. PIGGOTT.

Effect of neutral salts on the rate of hydrolysis of cellulose acetate in acetic acid solutions. J. F. FUESS and C. J. STAUD (J. Amer. Chem. Soc., 1931, **53**, 1934—1941).—The rate of hydrolysis of cellulose acetate dispersed in AcOH containing small amounts of H_2O. H_2SO_4, H_3PO_4, and $NaHSO_4$ is retarded by the addition of $NaNO_3$, KNO_3, Na_2SO_4, K_2SO_4, or NaCl; NaCl has the least effect. Addition of the salts after partial hydrolysis also causes a retardation. All hydrolyses were carried out at 53±1°. H. BURTON.

Velocity of crystallisation of chrome alums. S. I. ORLOVA and N. N. PETIN (J. Gen. Chem. Russ., 1931, **1**, 65—69).—The velocity of crystallisation of chrome alums is unaffected by light, and is greater for K than for Na salts. The accelerating action of various substances is in the order: $H_2SO_4 > HNO_3 > Na_2SO_3 > K_2SO_4 > NaNO_3 > KNO_3 > Na_2SO_4$. R. TRUSZKOWSKI.

Absolute rates of heterogeneous gas reactions. B. TOPLEY (Nature, 1931, **128**, 115—116).—An expression for a decomp. reaction catalysed by a surface in which the catalysis depends on adsorption, thermal activation, and break-up into new mol. species is applied to various gas reactions on heated wire catalysts. L. S. THEOBALD.

Quantum mechanics of adsorption catalysis. M. BORN and V. WEISSKOPF (Z. physikal. Chem., 1931, **B**, **12**, 478).—A correction (cf. this vol., 576). F. L. USHER.

Intermediate compound theory of heterogeneous catalysis. An attempt at a quantitative investigation of the range of validity of this theory for the reaction $2H_2+O_2 \longrightarrow 2H_2O$ on a copper catalyst. F. J. WILKINS and S. H. BASTOW (J.C.S., 1931, 1525—1532).—A quant. method has been devised to test the validity of the intermediate compound theory of heterogeneous catalysis for the reaction $2H_2+O_2 \longrightarrow 2H_2O$ on an activated Cu catalyst. When Cu is heated in an atm. of H_2 and O_2 at 10^{-2} mm. more reaction takes place than that calc. on the assumption that only the oxidation of Cu and the reduction of the oxide are occurring in the system. This excess reaction is attributed to the formation of H_2O in an activation catalysis at the Cu_2O surface. At 142°, the activation catalysis preponderates, but as the temp. is raised it becomes of decreasing importance, and at 250° the intermediate compound catalysis appears to account for practically the entire reaction. F. J. WILKINS.

Temperature coefficient of the thermal decomposition of ammonia on platinum. J. K. DIXON (J. Amer. Chem. Soc., 1931, **53**, 2071—2074; cf. this vol., 803).—The rate of decomp. at 1 atm. of NH_3 on a Pt gauze catalyst has been determined dynamically, with and without the addition of N_2 and H_2, at 772°, 826°, and 858°. The rate is proportional to the pressure of NH_3 and inversely proportional to that of H_2; as the pressure of H_2 is increased, the inhibiting effect approaches a const. value. The heat of activation is 40,000 g.-cal. per mol. (cf. A., 1929, 890). J. G. A. GRIFFITHS.

Limitations in capacity of a platinum catalyst for ammonia oxidation. H. W. WEBB.—See B., 1931, 674.

Decomposition of nitrous oxide at low pressures on a platinum catalyst. G. VAN PRAAGH and B. TOPLEY (Trans. Faraday Soc., 1931, **27**, 312—322).—The activity of the Pt wire used as catalyst increases during use, and ultimately reaches a max. When the

catalyst in this state is brought in contact with N_2O no reaction occurs until the temp. lies within the range 490—720°. Reaction starts slowly and either dies away when only partial decomp. has been effected, or, if the temp. is high enough, rapidly increases in speed and then abruptly slows down before reaction is complete. It is suggested that the primary reaction is $N_2O+Pt=N_2+Pt(O)_{adsorbed}$, followed by $Pt(O)_{adsorbed}+N_2O=Pt+N_2+O_2$. The peculiar behaviour of the catalyst in the state of max. activity is ascribed to the existence at the active centres of energy chains, during the existence of which the mean kinetic energy associated with each group of active Pt atoms corresponds with a temp. much higher than that of the system as a whole. R. CUTHILL.

Topochemistry of contact catalysis. V. Hydrogenating activity, magnitude, and structure of nickel surfaces. G. M. SCHWAB and L. RUDOLPH (Z. physikal. Chem., 1931, **B**, **12**, 427—448; cf. A., 1929, 1150).—The hydrogenating activity and the surface area of Ni decrease with a rise in temp., or with the duration of reduction; for a given sample activity increases more rapidly than surface. The surface area was calc. from the initial rate of dissolution of the powder in acid as compared with that of polished sheet. Hydrogenation of Et cinnamate, the reaction chosen for reference, proceeds linearly with time, and the velocity is proportional to the quantity of Ni after allowing for a fraction of the metal which is poisoned by a substance of undetermined nature. From the relation between the activity and the surface area it is inferred that active centres occur chiefly in the edges and angles of the micro-crystals of the metal. F. L. USHER.

Preparation and testing of nickel catalysts for hydrogenation. H. ADKINS and L. W. COVERT (J. Physical Chem., 1931, **35**, 1684—1691).—Improved methods for the prep. of Ni catalysts are described and the relative merits of Na_2CO_3, $NaHCO_3$, and KOH as precipitants for depositing Ni on kieselguhr have been measured for the hydrogenation of PhMe, $COMe_2$, $CH_2Ph{\cdot}OH$, and resorcinol. Comparisons of 8 different Ni catalysts are made from (i) the time required for the middle 60% hydrogenation, (ii) the temp. at which max. pressure of H_2 is reached, (iii) the time required for absorption of all the H_2, and (iv) the ratios of *cyclo*hexylcarbinol/toluene and *cyclo*hexane-1 : 3-diol/*cyclo*hexanol in the case of $CH_2Ph{\cdot}OH$ and resorcinol, respectively. The question of a basis of comparison for Ni catalysts is discussed. So many variables are involved, however, that a satisfactory basis is practically impossible. With Ni catalysts there is no necessary relationship between rate of hydrogenation and the relative rates of competitive reactions. L. S. THEOBALD.

Relation between the activity of catalysts for the synthesis of methyl alcohol and their chemical and crystalline structure. II. Absorption measurements of the gaseous reactants. G. NATTA and E. CASAZZA (Giorn. Chim. Ind. Appl., 1931, **13**, 205—212; cf. A., 1930, 552).—The coeffs. of absorption of CO_2, CO, and H_2, respectively, by various metallic oxide catalysts used in the synthesis of MeOH have been measured. Catalysts which show a strong absorption for H_2 are not suitable, since they bring about further hydrogenation and formation of CH_4. The most active catalysts are those which show a high absorption for CO and for CO_2; *e.g.*, those prepared by decomp. of the precipitated basic carbonates are more active than those obtained from the hydroxides, and the catalysts obtained from certain varieties of neutral $ZnCO_3$ have an even greater activity and absorbing power for CO_2. O. J. WALKER.

Competitive hydrogenations. II. F. F. DIWOKY and H. ADKINS (J. Amer. Chem. Soc., 1931, **53**, 1868—1875).—The rate of hydrogenation of the following substances over a nickel catalyst at 125—175°/125—200 atm. decreases in the order quoted: quinoline, C_6H_6, PhMe, PhOH, benzyl alcohol, pyridine, $NHPh_2$, acetanilide, NH_2Ph. Hydrogenation of mixtures of any two of the above compounds with H_2 sufficient to reduce completely one of the components, and determination of the products formed, show that preferential reduction occurs in the following order: quinoline, pyridine, NH_2Ph, benzyl alcohol, PhOH, $NHPh_2$, C_6H_6, acetanilide, PhMe. NH_2Ph has practically no effect on the hydrogenation of quinoline or pyridine, but all these bases inhibit the reduction of C_6H_6 or PhMe. The hydrogenation of $NHPh_2$ is accelerated by C_6H_6 or PhMe. There is no relationship between the relative rates of hydrogenation of the above compounds singly and in mixtures. H. BURTON.

Explosion during catalytic reduction of nitroanisole in the liquid phase. T. S. CARSWELL (J. Amer. Chem. Soc., 1931, **53**, 2417—2418).—400 g. of nitroanisole in an autoclave at 250° containing a Ni catalyst rapidly absorbed hydrogen at 500 lb. per sq. in., but exploded violently after 20 min. (cf. A., 1928, 600). J. G. A. GRIFFITHS.

Protection of iron in aerated saline solutions: an Evans pile. E. HERZOG and G. CHAUDRON.—See B., 1931, 682.

Electrodeposition of chromium from ammonium chromioxalate. A. MAZZUCCHELLI.—See B., 1931, 682.

Chemical action in the glow discharge. VI. Oxidation of carbon monoxide. VII. Dissociation and oxidation of methane. A. K. BREWER and P. D. KUECK (J. Physical Chem., 1931, **35**, 1281—1292, 1293—1302; cf. A., 1930, 1533).—VI. In a $2CO:O_2$ mixture at liquid air temp. an electric discharge gives CO_2, but with an excess of CO or neutral gases carbon suboxide is deposited with the CO_2 on the tube walls. CO alone dissociates into CO_2 and the suboxide. In the negative glow the rate of oxidation of CO is practically independent of pressure, but it is proportional to the current. It is accelerated by excess of CO when the total CO $\ngtr$ 80% and retarded by that of O_2 almost in proportion to the amounts added. In the positive column the rate is proportional to current and independent of pressure below 10 mm. Above this pressure it is slightly less than proportional to the current, whilst at higher pressures the rate increases rapidly to the ignition point. Ignition is apparently confined to the positive column. The CO_2 formed in the negative glow reaches the walls as

positive ions, but in the positive column is deposited mainly as neutral mols. In the spectrum of the negative glow bands of the first negative group for CO appear with approx. equal intensity from 0·5 to 10 mm. pressure. The data indicate a simple ion cluster mechanism in the negative glow and an ion chain mechanism in the positive column. The $CO^{\cdot}$ ions appear to be more effective than $O_2^{\cdot}$ ions in initiating the reaction. In the negative glow the ratio M/N, *i.e.*, the no. of mols. synthesised per positive ion, is 2.

VII. CH_4 is quantitatively converted into C_2H_4 and H_2 in the glow discharge at the temp. of liquid air, one mol. of C_2H_4 being formed per $CH_4^{\cdot}$ ion. (At room temp. a large amount of a greyish-yellow deposit is formed on the walls of the tube.) In a CH_4–$2O_2$ mixture CO_2 and H_2O are the sole products of reaction; no H_2O_2 is formed as is the case with $2H_2$–O_2 mixtures. The rate of oxidation is accelerated to a max. at the 1 : 1 mixture by excess of CH_4. O_2 retards the reaction even more than does A, whilst He at first has an accelerating effect even in relatively large amounts and then retards reaction. The reaction between CH_4 and O_2 is initiated primarily by $CH_4^{\cdot}$ ions; it is most pronounced in the negative glow, is negligible in the dark spaces, and is approx. const. in the positive column. $M/N_{obs.}$ is approx. 7, but a val. of 6 is more probably correct. The efficiency of the positive column in terms of electron volts per mol. rapidly increases with pressure above 5·5 mm., indicating the presence of ionic chain reactions.

L. S. THEOBALD.

Reactions of ionised gases : synthesis of nitric acid. M. LAPORTE (Compt. rend., 1931, **192**, 1555—1558).—To effect more completely the union of ionised O and N a current of air and N_2, in controllable proportions together with steam, is passed between the armatures (of Hg at 140°) of a condenser similar to Berthelot's ozoniser; the products are cooled and the gases passed into aq. NaOH. The frequency of the oscillating discharge used is about 500,000. The presence of steam in the ozoniser greatly facilitates the reaction. Only O_3 is produced if the temp. of the electrodes is below 100°, but none at 140°. The best proportion of air to N_2 is such that O_2 forms 3% of the whole. The efficiency of the process is about 2%.

C. A. SILBERRAD.

Decomposition of sodium azide by controlled electron bombardment. R. H. MÜLLER and G. C. BROUS (J. Amer. Chem. Soc., 1931, **53**, 2428).—With potentials at or less than 11·5 volts, no effect was observed, but with higher potentials N_2 was evolved. Thermal decomp. was absent. J. G. A. GRIFFITHS.

Applicability of Einstein's law of photochemical equivalence. B. K. MUKERJI and N. R. DHAR (J. Physical Chem., 1931, **35**, 1790—1794).—Determinations of the quantum efficiency at different temps. and with different wave-lengths show that this law fails in most of the following reactions: $(CO_2K)_2$ and I, $H\cdot CO_2Na$ and $HgCl_2$, quinine sulphate and H_2CrO_4, $H\cdot CO_2Na$ and I, $KMnO_4$ and $(CO_2H)_2$, $FeSO_4$ and I, $NaNO_2$ and I, H_2CrO_4 and $(CO_2H)_2$, sodium potassium tartrate and Br, sodium citrate and I, sodium malate and iodine, $(CO_2NH_4)_2$ and $HgCl_2$ in the presence of eosin, the photo-oxidation of CHI_3 in amyl alcohol or C_6H_6, and the bleaching of dicyanine. Quantum efficiency increases with a rise in temp. and with an increase in frequency. The reactions which show the most marked deviations are strongly exothermal. L. S. THEOBALD.

Correlation of certain photochemical reactions and wave-length of light. II. F. C. HYMAS (J.S.C.I., 1931, **50**, 193—195T).—When exposed to light from a vac. Hg vapour arc, the $COMe_2$–methylene-blue reaction responds almost exclusively to radiation between 250 and 400 mμ, whilst the KNO_3–KNO_2 reduction covers the region 220—400 (max. 255) mμ. The KI–starch reaction is suitable for the range 220—320 (max. 255) mμ, and the oxalic acid–uranyl sulphate reaction for the range 220—500 mμ (max. 325 and 260, min. 280 mμ). In general, when corrected on the basis of equal energy distribution, the photochemical effects increase with decrease of wave-length, the exception being the $COMe_2$–methylene-blue reaction.

Quantum yield in photolysis of silver chloride. P. FELDMANN (Z. physikal. Chem., 1931, **B**, **12**, 449—466; cf. A., 1928, 815).—AgCl was exposed to radiation of wave-length 365 mμ under $NaNO_2$ solution, and the liberated Cl, which was present exclusively as chloride, was determined potentiometrically. The quantum yield approached 1 for short exposures, but decreased on prolonged illumination owing to recombination of Ag and Cl. Irregularities exceeding the experimental error were encountered.

F. L. USHER.

Photolysis of silver chloride. P. FELDMANN and A. STERN (Z. physikal. Chem., 1931, **B**, **12**, 467—477).—Irregularities in the results obtained in determining the quantum yield (cf. preceding abstract) were traced to a delay of several min. in the attainment of a const. potential after interrupting the illumination. When this error is eliminated the mean quantum yield is 0·99 if the chloride is under $NaNO_2$ solution. Under water, the quantum yield is only 0·5, the discrepancy probably being due to recombination rather than to formation of HOCl, which could not be detected. F. L. USHER.

Action of low-speed electrons on photographic emulsions. R. E. BURROUGHS (Rev. Sci. Instr., 1931, [ii], **2**, 321—328).—The image produced is due to radiations excited by the electrons in the residual gas covering the emulsion, and not appreciably by direct energy transfer. The lowest energy electron recorded is not primarily characteristic of the emulsion, but is related to the crit. potential of the residual gas. The sensitivity of emulsions to electrons is proportional to their sensitivity to blue and ultraviolet light. J. LEWKOWITSCH.

Photosynthesis in tropical sunlight. I. II. Photosynthesis of formaldehyde and carbohydrates from alkali hydrogen carbonates in the presence of coloured insoluble substances. G. G. RAO and N. R. DHAR (J. Physical Chem., 1931. **35**, 1418—1423, 1424—1432).—I. CH_2O is formed when CO_2 and H_2O are exposed to sunlight in the presence of chlorophyll, methylene-blue, malachite-green, methyl-orange, colloidal $Fe(OH)_3$, uranyl nitrate,

$Cr_2(SO_4)_3$, and $CuSO_4$ (cf. A., 1925, ii, 884). CO_2 issuing from a suspension of chlorophyll exposed to the light of a W-filament lamp contained traces of CO. Burk's experiments (A., 1927, 1040) are criticised.

II. Exposure to sunlight of a 2% solution of $NaHCO_3$ containing $CoCO_3$ gives small amounts of CH_2O, whilst solutions containing $NiCO_3$ give larger amounts and carbohydrate in addition. Small quantities of reducing sugar were also obtained by exposing to sunlight aq. solutions of CH_2O containing ZnO, $FeCl_3$, or methyl-orange. A suggested mechanism is discussed.

L. S. THEOBALD.

Action of sunlight on allylthiocarbimide. D. GANASSINI (Arch. Ist. Biochim. Ital., 1931, **3**, 1—10).—Allylthiocarbimide kept in sunlight in bottles (*a*) dry, containing air, and (*b*) containing water and air, turned yellow and deposited a ppt., showing, respectively, 15% and 5% decomp. after one month. The products detected indicate that the following photochemical reactions occur: $3C_3H_5{\cdot}NCS+3H_2O=C_3H_5{\cdot}NH_2+(C_3H_5)_2O+2HCNS+H_2S+CO_2$ and $9HCNS=2(CNS)_3+3HCN+3H_2S$, and that H_2SO_4 and NH_3 are formed by secondary reactions A slight yellow colour developed in a completely filled bottle, and control samples remained unchanged.

R. K. CALLOW.

Reaction of potassium pyrosulphate with ammonia and amines and of pyrosulphuric acid and monohydrate with pyridine. P. BAUMGARTEN (Ber., 1931, **64**, [*B*], 1502—1506).—In cold aq. solution $K_2S_2O_7$ reacts with NH_3 and its derivatives or *tert.* amines thus: $K_2[SO_4(SO_3)]+2NH_3=K_2SO_4=NH_2{\cdot}SO_3NH_4$ and $K_2[SO_4(SO_3)]+R_3N=K_2SO_4+R_3N{\cdot}SO_2{\cdot}O$. Examples cited are NH_3, NH_2Ph, NMe_3, pyridine. For $K_2S_2O_7$ the constitution $K_2\left[{}^{O}_{O}\!>\!S\!\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}\!\rightarrow SO_3\right]$ is suggested. An analogous structure is assigned to $H_2S_2O_7$ mainly on account of the immediate production from it and pyridine of *N*-pyridiniumsulphonic acid. Since anhyd. H_2SO_4 and pyridine also yield *N*-pyridiniumsulphonic acid it probably contains the compound $\overset{+}{H_2O}{\cdot}SO_2{\cdot}\overset{-}{O}$ in equilibrium with the dihydroxyl form or its association products.

H. WREN.

Preparation of chemically pure potassium and sodium nitrites. D. S. SLAVINA (Trans. Inst. Pure Chem. Reag., 1931, **10**, 21—35).—Commercial $NaNO_2$ can be freed from NaCl and $NaNO_3$ by recrystallisation. Commercial KNO_2 cannot be freed from KCl and KNO_3 by recrystallisation and the method of decomp. with $AgNO_2$ is recommended.

E. S. HEDGES.

Action of anhydrides on metals. M. LEMARCHANDS and H. L. ROMAN (Compt. rend., 1931, **192**, 1381—1383).—CO_2 passed over K mixed with sand gives a max. yield (17%) of $K_2C_2O_4$ at 230—240°; Na one of 1·5% at 350°, the predominant reaction in this case being $CO_2+4Na=C+2Na_2O$. These results are in conformity with thermochemical data.

C. A. SILBERRAD.

Stability constants of complexes in aqueous solution. W. KNOBLOCH (Lotos, 1930, **78**, 110—111; Chem. Zentr., 1931, i, 1869).—Addition of excess of NH_3, NH_2Me, $NHMe_2$, pyridine, Na aminoacetate, K Na tartrate, and Na citrate, but not of formamide, glycerol, acetonitrile, thiocarbamide, carbamide, hexamethylenetetramine, NH_2Ph, or *o*-toluidine, gave stable complexes with $Cu^{\cdot\cdot}$; with $Cd^{\cdot\cdot}$, KI, KBr, KCl, and K tartrate gave positive, whilst urethane, thiocarbamide, pyrocatechol, resorcinol, quinol, nitroguanidine, and alkali thiocyanate gave negative results. Substitution of H in NH_3 by alkyl diminishes the stability; complex formation increases in the order Cl, Br, I, CN.

A. A. ELDRIDGE.

Cæsium tetrabromide. N. RAE (J.C.S., 1931, 1578—1581).—The only solid polybromides of Cs are the tri- and tetra-bromides. The "pentabromide" described by Wells is a tetrabromide.

F. J. WILKINS.

Cæsium tetraiodide. N. RAE (J. Physical Chem., 1931, **35**, 1800—1802).—The volatilisation curve for a fused mass of Cs+I (excess) shows a break corresponding with CsI_4, the v. p. of which is much lower than that of I (cf. A., 1930, 1374).

L. S. THEOBALD.

Preparation and characterisation of di- and tri-calcium silicate and calcium aluminate. I. WEYER (Zement, 1931, **20**, 48—51; Chem. Zentr., 1931, i, 1423).—2CaO and $1SiO_2$ were heated 5 times for $\frac{3}{4}$ hr. at 1400°; at first only the γ-form of $2CaO,SiO_2$ was obtained, the amount of β-form then increasing to 85%. Crystallographic and *X*-ray measurements are recorded for both forms. The compounds $3CaO,SiO_2$ and $3CaO,Al_2O_3$ were also obtained and similarly examined.

A. A. ELDRIDGE.

Hydrosol of silicic acid. III. Stability and influence of electrolytes. K. INABA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, **15**, 277—287).—When NaOH is added to silicic acid sols containing 0·0001*N*-NaOH, the charge on the particles and the viscosity are increased and the stability is decreased. In solutions containing more than 0·01*N*-NaOH, however, the viscosity decreases and the stability increases, a mol. solution of Na_2SiO_3 being formed. No coagulation is observed when KCl or $BaCl_2$ is added to sols containing less than 0·01*N*-NaOH, but above this concentration $BaCl_2$ gives a ppt., due to the formation of insol. $BaSiO_3$.

E. S. HEDGES.

Preparation and properties of refractory carbides, nitrides, and borides. C. AGTE and K. MOERS [with HEYNE and K. BECKER] (Z. anorg. Chem., 1931, **198**, 233—275).—Pure TiC, ZrC, HfC, NbC, and TaC have been prepared by heating the metals or their oxides with C at 1700—2100° in a graphite tube and sintering the product in A at a high temp., whereby impurities are volatilised. TiC has m. p. 3410°±90°. TiN, ZrN, and TaN, prepared by heating the metals in N_2 at 1100—1200° in a Mo tube and purified by sintering in N_2, have m. p. (±50°) 3220°, 3255°, and 3360°, respectively. The solidus curves for the mixtures TaN–TaC and TiN–TiC have been determined; the mixed crystals produced in the former system at high temp. are not stable at room temp., whereas those formed in the latter system are stable. The carbides, nitrides, and borides of Ti, Zr, Hf, V, and Ta have been prepared by passing the vapour of a halide of the metal, mixed with H_2 and

a hydrocarbon vapour. N_2, or BBr_3 vapour, over a heated W filament. ZrB and HfB have m. p. 3265° and 3335°, respectively. SiC has been prepared by the same reaction on a W or ZrC filament; it forms yellow transparent crystals which have no measurable conductivity either at room temp. or at very high temp. The prep. of single crystals of these compounds is described. The sp. resistances have been determined over a wide range of temp. The borides have the highest conductivity, which is greater than that of the respective metal, and the carbides the lowest; TiC alone has a negative temp. coeff. At very high temp. (3500—4000°) the sp. resistances all tend to the same limiting value, viz., $2—2{\cdot}5\times10^{-4}$.

H. F. GILLBE.

Anhydrous lower bromides of zirconium. R. C. YOUNG (J. Amer. Chem. Soc., 1931, **53**, 2148—2153).—$ZrBr_3$ is prepared by reducing $ZrBr_4$ with Al in an atm. of H_2 at 450° in the hot–cold tube. $ZrBr_3$ is a bluish-black powder which turns brown on partial hydrolysis and affords H_2 and a rapidly fading yellow acid solution with H_2O. $Zr^{\cdot\cdot\cdot}$ reduces CrO_4'' to $Cr^{\cdot\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$ to $Fe^{\cdot\cdot}$, $Bi^{\cdot\cdot\cdot}$ to Bi, $Cu^{\cdot\cdot}$ to $Cu^{\cdot}$, $TiO^{\cdot\cdot}$ to $Ti^{\cdot\cdot}$; $SnCl_2$ and $ZnSO_4$ are not reduced.

$ZrBr_2$ is prepared at 350° by the reaction $2ZrBr_3 \longrightarrow ZrBr_4+ZrBr_2$; it is a black powder which ignites spontaneously in air, and reacts violently with H_2O, H_2 being liberated. The reaction $2ZrBr_2 \longrightarrow ZrBr_4+Zr$ is fairly rapid above 400°. J. G. A. GRIFFITHS.

Interaction between nitric oxide and hydrogen sulphide in the presence of water. H. B. DUNNICLIFF, S. MOHAMMAD, and J. KISHEN (J. Physical Chem., 1931, **35**, 1721—1734).—NO reacts with H_2S in aq. solution to form $(NH_4)_2S_2O_3$, NH_4NO_2, S, N_2O, and N_2. H_2SO_4 accelerates the reaction in its early stages, apparently increases the proportion of N_2O formed, and practically prevents the formation of NH_3 in the solution. NO in an atm. of H_2 has no action on aq. solutions of NH_4NO_2 or of NH_3 (dil.). It forms NH_4 polysulphides and small quantities of $(NH_4)_2S_2O_3$ when passed into NH_4 sulphide solution; N_2O and N_2 are evolved. Excess of NO increases the yield of N_2O, but with an excess of NH_4 sulphide pure N_2 is formed. A saturated solution of H_2S reduces N_2O completely to N_2 and NH_3, with the formation of S. Dil. solutions of $(NH_4)_2S_2O_3$ are converted into sulphate by NO. Small quantities of N_2 are evolved when solutions of NH_4NO_2 are kept in contact with H_2S for several days (cf. A., 1928, 1342). Possible reactions accounting for the observed products are outlined. L. S. THEOBALD.

Reactions and properties of nitric oxide and its compounds. I. Action of nitric oxide on sodium hyposulphite. H. GEHLEN (Ber., 1931, **64**, [*B*], 1267—1276).—The action between NO and alkaline $Na_2S_2O_4$ proceeds mainly thus: $Na_2S_2O_4+6NO+2NaOH=Na_2SO_3,N_2O_2+Na_2SO_4+2N_2O+H_2O$, and to a minor extent: $Na_2S_2O_4+6NO+2NaOH=2Na_2SO_3,N_2O_2+N_2O+H_2O$. A simplified method for the prep. of 98·5% $Na_2S_2O_4$ free from NaCl is given. The analogous isolation of $K_2SO_3.N_2O_2$ is recorded.

H. WREN.

Reduction of nitric oxide. M. L. NICHOLS and C. W. MORSE (J. Physical Chem., 1931, **35**, 1239—1252).—The effect of temp., acidity, and concentration of the reducing agent ($SnCl_2$ and $TiCl_3$) on th reduction products of NO has been determined. Wit $SnCl_2$ the amount of NO reduced in 30 min. decreases almost linearly with a rise in temp., but with TiCl a max. occurs at 25°. Above 0° the rate of reductio of NO by $SnCl_2$ depends on the rate of formation of nitrohydroxylaminic acid ($H_2N_2O_3$). Below 25° th rate of reduction by $TiCl_3$ depends on the speed of th reduction reaction, but above 25° the formation of $H_2N_2O_3$ is the limiting factor. Reduction is decreased with an increase in acidity, slightly with $SnCl_2$, and markedly with $TiCl_3$; an increase in concentration of the reducing agent also decreases reduction. The reduction of $H_2N_2O_3$ can be represented by $H_2N_2O_3 \longrightarrow H_2N_2O_2 \longrightarrow H_4N_2O_2 \longrightarrow NH_2OH \longrightarrow NH_3$. The relative proportion of N_2O and N_2 in the final product depends on the relation of the speed of the decomp. reaction to the speed of the reduction reaction. NH_2OH is the apparent end-product with $SnCl_2$ because of its very slow rate of reduction to NH_3 by this reagent. The addition of platinised Pt to the $SnCl_2$ and of $FeCl_2$ to the $TiCl_3$ increases reduction by increasing the rate of dissolution of NO.

L. S. THEOBALD.

Heavy metal phosphides. I. Action of hypophosphite on nickel and cobalt salts. R. SCHOLDER and H. HECKEL (Z. anorg. Chem., 1931, **198**, 329—351).—With alkaline solutions of Ni and Co salts hypophosphites yield a mixture of metal and phosphides, and with acid solutions a mixture of various phosphides, which on drying at room temp. retain much H_2O and O. By treatment with aq. HCl and with AcOH fairly pure Ni_2P and Ni_5P_2 respectivel have been isolated, but the O content is increased owing to decomp. of the H_2O present. By using alcoholic HCl or anhyd. AcOH, O-free phosphides ma be prepared. On dissolution in HCl both yield H_2, H_3PO_3, and $NiCl_2$, PH_3 probably being formed as an intermediate product. The phosphides are regarded not as salts of PH_3, but as compounds of an intermetallic type. Phosphides are not produced by the action of H_3PO_2 on Ni and Co complex cyanides.

H. F. GILLBE.

Phosphoric acid. IV. Oxonium salts of orthophosphoric acid with certain organic compounds. G. B. KING and J. H. WALTON (J. Physical Chem., 1931, **35**, 1745—1755).—F.-p. data for H_3PO_4 with different org. substances show the existence of the following: $AcOH,H_3PO_4$, m. p. 33·8°; $AcCO_2H,H_3PO_4$, m. p. 36·4°; $PhCHO,H_3PO_4$, m. p. 43·0°; $MeO{\cdot}C_6H_4{\cdot}CHO.H_3PO_4$, m. p. 83·6°; $PhCOMe,H_3PO_4$, m. p. 87·9°; $COPh_2,H_3PO_4$, m. p. 71·3°; (coumarin) $C_9H_6O_2,H_3PO_4$, m. p. 113·4°. Propionic, *n*-butyric, *n*-hexoic, and phenylacetic acids, $CH_2Cl{\cdot}CO_2H$, and BzOH form no compounds. Oxalic, succinic, cinnamic, and malic acids decompose when heated with H_3PO_4. The additive compounds are probably true oxonium salts. Kendall's acidity rule holds, and H_3PO_4 forms additive compounds with org. compounds less readily than does H_2SO_4.

L. S. THEOBALD.

Co-ordination compounds of phosphorus and antimony pentachlorides. J. C. HUTTON and H. W. WEBB (J.C.S., 1931, 1518—1525).—By the action o

PCl_5 on dry pyridine a *compound*, $H,PCl_6,2C_5H_5N$, is obtained in which the covalency of P is at least six. In $CHCl_3$ solution $SbCl_5$ and pyridine give two *products*, $SbCl_5,C_5H_5N$ and $2SbCl_5,3C_5H_5N$, the former when $SbCl_5$ is in excess and the latter when pyridine is in excess. With no diluent and at higher temp. a third *derivative*, $H,SbCl_6,C_5H_5N$, is obtainable. Its structure is probably similar to that of the above P compound. By the action of EtOH on $2SbCl_5,3C_5H_5N$ the *compound* $2SbCl_5,2HCl,3C_5H_5N$ is formed. The possible existence of singlet linkings in these pentachlorides is discussed. It is further suggested that the hypothesis that chemical reaction is preceded by the formation of co-ordination compounds may be extended to chlorination.

F. J. WILKINS.

Reactions of the dioxides of selenium and tellurium with the halogen acids. T. W. PARKER and P. L. ROBINSON (J.C.S., 1931, 1314—1324).—Direct union of SeO_2 and HCl to $SeO_2,2HCl$ takes place at 107°. HBr and SeO_2 give the corresponding compound at 30° : at higher temp. liquids are formed which deposit H_2SeO_3 on cooling, whilst below 30° solids are produced. Temp.–composition curves indicate a region of stability between 2° and 8° corresponding with $SeO_2,4{\cdot}5HBr$. The solubilities of TeO_2 in aq. HCl and HBr have been determined.

F. J. WILKINS.

Constitution of the sulphates of molybdenum. F. H. NICHOLLS, H. SAENGER, and W. WARDLAW (J.C.S., 1931, 1443—1446).—Mo^{V} and Mo^{III} sulphates have been investigated. The following complex *oxysulphates* of Mo have been isolated :

$(NH_4)_2SO_4,(MoO_2)_2SO_4,2H_2O$ and
$4R_2SO_4,5(MoO_2)_2SO_4$,aq. ($R{=}C_5H_6N$) ;
$R_2SO_4,2Mo_2O(SO_4)_2,6H_2O$ ($R{=}NH_4$, K, Rb). The constitution of these compounds is discussed. The existence of the substance $Mo_2O_3(SO_4)_2$ was not confirmed.

F. J. WILKINS.

Oxy-salts of molybdenum and ammonium. V. CAGLIOTI (Gazzetta, 1931, **61**, 257—264).—The interaction of solutions of H_2O_2 and of ordinary $(NH_4)_2MoO_4$ gives only the two oxy-salts $5(NH_4)_2O,12MoO_4,18H_2O$ and $5(NH_4)_2O,9MoO_3,3MoO_4,10H_2O$. Ammonium trimolybdate gives no oxy-salts with H_2O_2, but the latter reacts with solutions of $(NH_4)_2MoO_4$ to give the compound $5(NH_4)_2O,6MoO_3,6MoO_4,13H_2O$ with evolution of NH_3. *X*-Ray examination shows that the introduction of up to 2·26% of active O into the $(NH_4)_2MoO_4$ mol. does not materially alter its structure.

O. J. WALKER.

Compounds of sexavalent molybdenum with hydroxylamine. W. F. JAKÓB and B. JEZOWSKA (Rocz. Chem., 1931, **11**, 229—253).—NH_2OH first forms double so-called polyhydroxylamine compounds with molybdic acid, and these compounds decompose spontaneously, to yield N_2 and N oxides as products of oxidation of NH_2OH, Mo being transiently reduced to the Mo^{IV} form. This, however, is almost immediately oxidised back to Mo^{IV} by NH_2OH, part of which is thereby reduced to NH_3, whilst the remainder combines with Mo^{VI} to yield salts of Heide and Hofmann's series of hydroxylaminomolybdic acids (A., 1896, ii, 605). These have the general formula $[(Mo_2NOH)(MoO_4)_9]M_4H_4$ and contain exclusively Mo^{VI}; their reducing properties are due to NH_2OH. On dissolution in $KHCO_3$ solution these salts are converted into $[(Mo_2NOH)(CO_3)_3O_6]K_5H_3$, precipitated by EtOH from aq. solution. The polyhydroxylamine compound $[Mo(NOH)_2(MoO_4)_2](NH_4)_2H_2$, is prepared and described, whilst the composition of compounds containing more NH_2OH, such as those described by Canneri (A., 1928, 260), must be regarded as doubtful, owing to the instability of the compounds and to the impossibility of obtaining reproducible results in their synthesis. The above results are discussed from the viewpoint of polar theories of at. structure.

R. TRUSZKOWSKI.

Complex acid tungstates. R. H. VALLANCE (J.C.S., 1931, 1421—1428).—Formic acid and aq. Na tungstate in slightly acid solution give Na paratungstate, $5Na_2O,12WO_3,28H_2O$. The corresponding K and Ba salts, obtained by precipitation, crystallise with 11 and 27 mols. H_2O, respectively. No evidence of the existence of $4Na_2O,10WO_3,23H_2O$ has been obtained. The solubility of Na paratungstate in H_2O has been determined over the temp. range 0—102°.

F. J. WILKINS.

Preparation of standard uranium oxide and determination of its saturation current. A. N. PILKOV (J. Gen. Chem. Russ., 1931, **1**, 133—142).—Fergansk urano-vanadate ore is dissolved in HCl, and $BaCl_2$ and H_2SO_4 are added to the filtrate, thereby removing Ra, meso- and radio-Th, U, and Io. $Bi(NO_3)_3$ and $Pb(NO_2)_2$ are added to the filtrate from $BaSO_4$, and H_2S is passed, Ra-*D*, Ra-*F*, and Ra-*G* being adsorbed on the ppt. of sulphides. The filtrate is freed of excess of H_2S, excess of Br is added, and the solution is kept 10 days, with occasional shaking. Heavy metals are then precipitated as hydroxides by CO_2-free aq. NH_3, and $Ca(OH)_2$ and $Mg(OH)_2$ are removed from the ppt. by CO_2-free H_2O. The ppt. is then treated with $(NH_4)_2CO_3$, yielding a solution of $UO_2CO_3,2(NH_4)_2CO_3$ and NH_4VO_3, which on boiling with HNO_3 deposits $(NH_4)_2U_2O_7$ and V_2O_5 ; these are converted into nitrates and the dry mixture is extracted with Et_2O, from which uranyl nitrate is separated by shaking with H_2O. $UO_2(NO_3)_2$ thus prepared is again purified by fractional adsorption as above, and the final product on ignition yields chemically and radiologically pure U_3O_8.

R. TRUSZKOWSKI.

Gaseous compound of polonium. (MME.) I. CURIE and M. LECOIN (Compt. rend., 1931, **192**, 1453—1454).—On heating to a red heat Ni on which Po has been deposited (cf. A., 1928, 810), in a current of N_2 in a quartz tube dipping into an acid solution, practically all the Po condenses on a cool part of the tube. If, however, the gas used is $CO+CO_2$, only a portion can be so recovered, and that distributed all along the tube ; the rest, which may amount to half, is found in the acid, indicating the formation of a gaseous compound of Po, possibly a carbonyl.

C. A. SILBERRAD.

Preparation of sources of polonium of high activity. (MME.) I. CURIE and F. JOLIOT (J. Chim. phys., 1931, **28**, 201—205).—Deposits of Po of high activity can be obtained by rotating polished Ni or Ag

in a solution of a salt of Po containing $0\cdot2N$-HNO_3 and $0\cdot1N$-HCl. Deposits may be formed on other metals by volatilisation in a current of gas. E. S. HEDGES.

Liesegang rings. O. F. TOWER and E. E. CHAPMAN (J. Physical Chem., 1931, **35**, 1474—1476; cf. A., 1929, 643).—The method of Hedges and Henley (A., 1928, 1323) does not apply to rings of CdS and ZnS. Liesegang's rings of MnS are formed from $0\cdot1$—$2N$-$MnCl_2$ placed on gelatin containing NH_4 sulphide or on agar containing NH_4 or Na sulphide. Rings of NiS or CoS are formed from $0\cdot7$—$2N$-$NiCl_2$ or $CoCl_2$ on $0\cdot4$—$0\cdot6N$-Na_2S in agar. L. S. THEOBALD.

Sulphides and selenides of rhenium. H. V. A. BRISCOE, P. L. ROBINSON, and E. M. STODDART (J.C.S., 1931, 1439—1443).—Either H_2S or $Na_2S_2O_3$ precipitates *rhenium heptasulphide* from K per-rhenate solutions: in the second case the precipitation is quant. When heated, the heptasulphide gives the disulphide. The corresponding *selenides* have been prepared. F. J. WILKINS.

Sulphur [thio-]derivatives of per-rhenic acid. W. FEIT (Z. angew. Chem., 1931, **44**, 65—66).—By passing excess of H_2S through saturated aq. K perrhenate, a yellow solution was obtained which became dark brown (A) after 2—3 days and was not precipitated by salts of Fe, Ni, Co, or Zn; dark ppts. were formed with Ag, Pb, Cu, $Hg^{\cdot\cdot}$ and $Tl^{\cdot}$ salts. On concentrating the solution A brown crystals of K perrhenate, containing a small amount of an isomorphous thio-derivative, were formed; on complete evaporation a H_2O-soluble dark brown mass (14—15% S), probably a mixture of partly substituted thio-rhenates, was obtained. On treating solution A with Tl_2SO_4 a dark brown ppt., probably consisting of $TlReS_4$, was obtained; further addition of Tl_2SO_4 to the yellow filtrate yielded *thallous monothioper-rhenate*, $TlReO_3S$, golden needles. The solution of the salt gradually deposited sulphide after acidification. E. LEWKOWITSCH.

Change in properties of oxides of iron, aluminium, and chromium in relation to the ignition temperature. P. P. BUDNIKOV and K. E. KRAUSE (Kolloid-Z., 1931, **55**, 330—333).—Fe_2O_3 is completely dehydrated by ignition at 650°, Al_2O_3 at 750°, and Cr_2O_3 at 850°. With rising temp. of ignition the solubility of all these oxides in HCl falls. The solubility is in the order $Fe_2O_3 > Al_2O_3 > Cr_2O_3$. Cr_2O_3 has an optimum solubility when ignited at 300°. The density of all these oxides increases with rising temp. of ignition. The particle size of the ignited oxides varies between $0\cdot003$ and $0\cdot0005$ mm. E. S. HEDGES.

Nickelous oxide. M. PRASAD and M. G. TENDULKAR (J.C.S., 1931, 1403—1407).—The density and electrical resistance of NiO increase, whilst its solubility in H_2SO_4 and its catalytic activity decrease, as its temp. of prep. is raised. This effect is particularly marked at temp. about 800°. NiO probably exists in two forms, a black variety prepared at 400° and another, which is greenish-yellow, obtained at 1000°. F. J. WILKINS.

Action of sulphuric acid on nickel-copper matte. M. PRASAD and M. G. TENDULKAR (J.C.S., 1931, 1407—1411).—The slight solubility of Ni from a Ni–Cu matte in H_2SO_4 is due probably to the formation of a little Ni_2O_3. The incomplete removal of Cu is attributed to the formation of CuO,4NiO. F. J. WILKINS.

Optically active tetrammines of bivalent platinum and palladium. H. REIHLEN and W. HUHN (Naturwiss., 1931, **19**, 442).—Many $\alpha\beta$-diamines have been prepared by the catalytic hydrogenation of N-acetyl-α-amino-acid nitriles. These form di- and tetra-ammine complex salts with bivalent Pt and Pd. Since these mols. are optically active, there is no plane of symmetry. A. J. MEE.

Examples of titration in Wood's light. A. G. NASINI and P. DE CORI (Atti III Cong. Naz. Chim., 1929, 668—678; Chem. Zentr., 1931, i, 2088).—A discussion. A. A. ELDRIDGE.

Increase of accuracy in quantitative emission spectral analysis. G. SCHEIBE, C. F. LINSTROM, and O. SCHOETTLER (Z. angew. Chem., 1931, **44**, 145—151).—By means of a method based on studies of the relation between the density of a photographic image and wave-length and the quant. relations between the intensity of spectral lines and their term analyses, impurities in a given compound may be determined with an accuracy of $\pm3\%$. For the evaluation of such results a graphical method utilises only three measurements of the galvanometer displacements in a thermo-electric photometer. F. G. TRYHORN.

Spectrum analysis of alloys. G. GUZZONI (Atti III Cong. Naz. Chim., 1929, 636—637; Chem. Zentr., 1931, i, 2087—2088).—The comparison method affords the most accurate results, but a complete series must be prepared for each binary alloy. Schweitzer's method, although less accurate, is convenient. The relation between the concentration of an element and the intensity of its lines is hyperbolic; hence only a portion is suitable for quant. work. The intensity change caused by the presence of a third substance introduces difficulties, but the method can be applied to ternary alloys. A. A. ELDRIDGE.

Qualitative micro-electrolysis with small electrodes. H. J. BRENNEIS (Mikrochem., 1931, **9**, 385—394).—The electrodes consist of two fine Pt wires sealed through a glass tube; the upper ends of the wires are connected to fixed terminals in a small base-board which themselves are connected to the terminals of the accumulator, and a drop of the solution to be tested is placed between the lower ends of the wires, which are then placed in a closed chamber in which the air is kept saturated with moisture to avoid evaporation of the drop. Any deposit on the cathode is tested by microchemical methods for the identification of the metal; an anode deposit is tested for MnO_2 and PbO_2. A. R. POWELL.

"Isopyknoscopic" volumetric determination of the concentration of solutions of pure compounds. A. DEL CAMPO, C. NOGAREDA, and M. G. DE CELIS (Anal. Fís. Quím., 1931, **29**, 386—391).—The end of a burette is drawn out to a capillary and bent at 90°. The solution of unknown concentration, containing a dye, is allowed to flow through the

capillary into a solution of known concentration of the same substance, at a point below the surface. The unknown concentration is determined by adjusting that of the second solution until the thread of coloured liquid neither rises nor falls.

H. F. GILLBE.

Colorimetric determination of p_H in sea-water. O. G. IBÀÑEZ (J. Marine Biol. Assoc., 1931, **17**, 483—488).—The p_H of sea-water is unaffected by the preservation of samples in glass tubes if a minimal air space is left and if a little $HgCl_2$ is added.

C. W. GIBBY.

Hydrogen electrode. V. CUPR and O. VIKTORIN (Z. anorg. Chem., 1931, **198**, 363—374; cf. this vol., 910).—The anomalies encountered in determinations of hydrolysis in solutions of Zn, Mg, and Cd sulphate are due to the use of the H electrode. Denham's results are ascribed to the use of Pt-black; an exchange of H ions with other cations probably occurs on the surface of the electrode, and this causes irregularities in measurements with feebly acid or feebly buffered solutions.

H. F. GILLBE.

Microchemical detection of hydrogen peroxide and vanillin. C. GRIEBEL (Mikrochem., 1931, **9**, 313—315).—A 1% solution of vanillin in 25% HCl containing 10% of EtOH yields bluish- to violet-black aggregates of hair-like needles with H_2O_2. Perborates give a similar result with vanillin, but ClO′, ClO_2′, NO_2′, and NH_4Cl are without action.

A. R. POWELL.

Use of bromate in volumetric analysis. V. Internal indicators suitable for use in direct titrations. G. F. SMITH and H. H. BLISS (J. Amer. Chem. Soc., 1931, **53**, 2091—2096; cf. A., 1924, ii, 614).—16 org. dyes of different colours have been selected as suitable internal indicators in volumetric bromate reactions. In many cases, back titration of excess of bromate is rendered unnecessary, and titrations are possible in the cold and at lower acidities than permissible heretofore. All of the indicators are applicable in the determination of As^{III}.

J. G. A. GRIFFITHS.

Volumetric determination of iodides. P. FLEURY and J. COURTOIS.—See B., 1931, 630.

Volumetric determination of fluorine by means of cerous nitrate. G. BATCHELDER and V. W. MELOCHE (J. Amer. Chem. Soc., 1931, **53**, 2131—2136).—Excess of $Ce(NO_3)_3$ is added to the neutral fluoride solution, and the excess is determined at 80° by titration with $KMnO_4$ in the presence of ZnO. The ppt. is filtered just before the end-point. A better, and direct titration of 0·15 g. of NaF in 10 c.c. with $Ce(NO_3)_3$ is effected at room temp. in the presence of 0·02 g. per litre of ampho-magenta (diazotised *p*-aminoethylacetanilide coupled with 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid; colour change deep blue to purple). SO_4″, PO_4‴, and C_2O_4″ interfere. The anomalies observed in the method involving methyl-orange were not confirmed (A., 1930, 1542).

J. G. A. GRIFFITHS.

Reaction of fluorides. C. PERTUSI (Atti III Cong. Naz. Chim., 1929, 573—575; Chem. Zentr., 1931, i, 2089—2090).—Addition of a solution of benzidine acetate to one of a fluoride in presence of $Hg(OAc)_2$ affords in the cold and in absence of much H˙ or OH′ a yellow ppt., stable at 105—110°, $[(\cdot C_6H_4\cdot NH_2,HF)_2]_2,HgF_2$.

A. A. ELDRIDGE.

Determination of potassium and sodium fluorides. A. V. FROST (Trans. Inst. Pure Chem. Reag., 1931, **10**, 53—61).—An investigation of the accuracy of different methods of determining F shows that the CaF_2, PbClF, and gravimetric ThO_2 methods give accurate results; the $NaHF_2$ and volumetric CaF_2 methods give an error of 0·2—0·4%. The determination of SO_4″ after precipitation of F as CaF_2 is inaccurate.

E. S. HEDGES.

Determination of bound sulphuric acid in presence of chromium salts. E. A. NIKITINA and A. V. BABAJEVA (Trans. Inst. Pure Chem. Reag., 1931, **10**, 20).—The determination of SO_4 in mixtures of $CrCl_3$ and alkali sulphates is satisfactory, using a cold 1% solution of $BaCl_2$. In the presence of chromates or dichromates a preliminary reduction is essential; precipitation with 1% $BaCl_2$ in the cold or with 1% $Ba(OAc)_2$ and warming is recommended.

E. S. HEDGES.

Colorimetric determination of ammonia. K. G. MAKRIS (Z. anal. Chem., 1931, **84**, 241—242).—The test for NH_3 previously described (A., 1930, 1263) is made the basis of the colorimetric determination.

R. CUTHILL.

Oxidation and determination of hydrazine and of semicarbazide by means of potassium iodate. V. HOVORKA (Coll. Czech. Chem. Comm., 1931, **3**, 285—301).—The liberation of I from the excess of the reagent and the KI produced during the oxidation of N_2H_4 by KIO_3 may be suppressed by adding $Hg(ClO_4)_2$, since non-ionised HgI_2 is formed; any I which is produced is converted into HgI_2 and $Hg(IO_4)_2$. In presence of H_2SO_4 the oxidation is slow, and in presence of HCl rapid, but the quantity of HCl added must be insufficient to convert all the Hg present into $HgCl_2$. Under the conditions described the reaction is complete within 30—35 min., and an excess of KI may then be added and the liberated I titrated with $Na_2S_2O_3$ solution. Semicarbazide may be determined in acid solution by the same method. Oxidation of the N_2H_4 by hypobromite in alkaline solution yields low results, owing to the occurrence of secondary reactions resulting in the formation of NH_3.

H. F. GILLBE.

Titration of phosphoric acid. P. VILLARD (Compt. rend., 1931, **192**, 1332—1334).—A criticism of Sanfourche's results (cf. this vol., 812), based on those of the author (cf. Compt. rend., 1930, **191**, 1101).

C. A. SILBERRAD.

Detection of acids. S. I. DIJATSCHKOVSKI and T. I. ISAENKO (J. Gen. Chem. Russ., 1931, **1**, 81—84).—The powder examined is placed near a cathode on a sheet of wet filter-paper, a crystal of $AgNO_3$ is placed near an anode, and a current is passed, when AsO_4‴ produces a reddish-brown stain around the crystal, and PO_4‴ a yellow stain. CNS′ is detected similarly by the appearance of a red stain around a crystal of $Fe(NO_3)_3$, which becomes surrounded by a blue ring in the presence of $Fe(CN)_6$‴ and $Fe(CN)_6$⁗. A starch paper placed beneath the anode turns blue in the presence of I′, whilst a paper dipped in Schiff's

reagent and fixed above the anode becomes coloured in the presence of Br′. Cl′ is detected by the coloration given by a starch–iodide paper at the anode, and CN′ by suspending a paper soaked in NH_4 polysulphide over the anode, and then washing it with a few drops of HCl, and adding $FeCl_3$, when a red colour due to CNS′ appears. R. TRUSZKOWSKI.

Titanous chloride in the determination of arsenic, antimony, and bismuth. A. OLIVERIO (Annali Chim. Appl., 1931, **21**, 211—216).—The necessary apparatus for the potentiometric titration of As, Sb, and Bi (cf. Zintl and Wattenberg, B., 1923, 295; Zintl and Rauch, B., 1925, 430, 787) is not everywhere available, but the reaction $As^{\cdot\cdot\cdot}+3Ti^{\cdot\cdot\cdot}\rightarrow As+3Ti^{\cdot\cdot\cdot\cdot}$ proceeds practically to completion and may be used for the determination of As and Sb; details of the procedure are given. This method is not applicable to Bi, for which, however, an indirect method is described. T. H. POPE.

Nitro-perchloric acid for determination of silica in vegetable substances. L. LEMATTE, G. BOINOT, E. KAHANE, and (MME.) M. KAHANE (Compt. rend., 1931, **192**, 1459—1462).—The org. matter is totally removed and the SiO_2 left pure and insol. by heating the material with about 10 times its vol. of a mixture (40 : 60) of fuming HNO_3 and $HClO_4$ (*d* 1·61). Accurate results are obtained with as much as 12 g. of material (*e.g.*, bran). C. A. SILBERRAD.

Determination of carbon monoxide by means of silver oxide. W. MANCHOT and G. LEHMANN (Ber., 1931, **64**, [*B*], 1261—1266; cf. A., 1927, 331).—The important factors in the reaction are intense agitation and the use of about 3 times the necessary amount of Ag reagent. Lower temp. can be compensated by increased time of agitation. Alternatively, a measured volume of Ag solution is treated with a slight excess of Cl-free NaOH and shaken with the gas; the mixture is acidified with AcOH and the unconsumed Ag in the filtrate is titrated with NaCNS. The presence of H_2, CH_4, or C_2H_4 is without influence. Accurate results are obtained for CO in coal gas, possibly without the necessity of pre-treatment with fuming H_2SO_4. With the usual apparatus a CO content of about 2% can be determined and with a larger absorption vessel the concentration of the gas may be as low as 1—0·25%. In the ordinary ammoniacal Ag reagent, the essential component is AgOH, the function of NH_3 being to discriminate between Ag and AgOH (also achieved by AcOH). Excess of NH_3 diminishes the sensitiveness of the reagent. AgOH held in solution by pyridine is more sensitive towards CO than that dissolved by NH_3 and apparently more sensitive than AgOH precipitated by NaOH. H. WREN.

Determination of carbon monoxide by burning with oxygen, using a new double catalyst. A. SCHMIDT (Z. angew. Chem., 1931, **44**, 152—155).—CO, in presence of air, is not quantitatively converted into CO_2 when passed over heated CuO (wire); the conversion becomes quant., and much higher streaming velocities are permissible, when a double catalyst consisting of fine quartz particles (1—2 mm.) and a trace of CuO (0·008—60 g. of quartz) is used. F. G. TRYHORN.

Determination of sodium plus potassium as benzidine sulphate. H. B. BROWN and A. T. SHOHL (J. Biol. Chem., 1931, **91**, 745—749).—Na+K in small quantities of fæces, milk, or urine are rapidly determined (±2%) by the benzidine method (Stadie and Ross, A., 1926, 100) if Ca and Mg are first removed (in one precipitation) as CaC_2O_4 and $MgNH_4PO_4$, and phosphate and Fe are then precipitated together as $FePO_4$ and $Fe(OH)_3$. J. W. BAKER.

Microchemical detection of sodium with uranyl acetate. A. MARTINI (Mikrochem., 1931, **9**, 422—423).—The reagent is prepared by dissolving 1 part of $UO_2(NO_3)_2,6H_2O$ in 4 parts of glacial AcOH, allowing the solution to cool, and pouring the supernatant liquor from the crystals. One drop of this solution is added to 1 drop of the solution to be tested for Na, to which a little powdered $(NH_4)_2CO_3$ has been added. When effervescence ceases a drop of pyridine is added; in the presence of Na tetrahedral crystals of Na UO_2 acetate separate round the edges of the liquid. Ba, Mg, Cd, Cu, Co, Ni, K, NH_4, Rb, and Cs salts do not interfere. A. R. POWELL.

Colorimetric determination of sodium. R. A. MCCANCE and H. L. SHIPP (Biochem. J., 1931, **25**, 449—456).—The Na is precipitated as $NaZn(UO_2)_3(OAc)_8$ and the U is determined colorimetrically with $K_3Fe(CN)_6$. The method is applicable to neutral or acid solutions. Ca, Mg, and Fe do not interfere; phosphates, which can be removed with $Zn(OAc)_2$, do so. Na may be determined directly in the presence of 30 times its wt. of K. The limits of the method are 0·02—0·8 mg. Na; in the absence of phosphates the range is 0·01—0·4 g. Na. S. S. ZILVA.

Determination of small quantities of alkalis in acids insoluble in water [*e.g.*, tungstic acid]. G. HEYNE (Z. angew. Chem., 1931, **44**, 328—329).—The alkalis are removed by electrodialysis in an apparatus comprising a central horizontal drum closed at each end with membrane filter discs communicating with vertical tubes containing distilled H_2O in which the electrodes are immersed against the outer sides of the filters. On passing a current at 220—440 volts through the drum the H_2O from the anode compartment passes to the cathode compartment, thereby washing out the adsorbed salts in the H_2WO_4 suspension contained in the drum. The solution in the cathode compartment is evaporated to dryness and the alkalis are determined as usual. A. R. POWELL.

Use of volumetric methods for determining the basic constituents in quicklime and slaked lime. F. MACH and R. HERRMANN.—See B., 1931, 675.

Separation of lead from barium, calcium, and strontium with ammonium acetate. F. FEIGL and L. WEIDENFELD (Z. anal. Chem., 1931, **84**, 220—224).—Comments on Majdel's paper (this vol., 453). It is probable that when $PbSO_4$ and $BaSO_4$ are precipitated together an adsorption complex is formed. R. CUTHILL.

Mechanism of precipitation processes. V. Some types of precipitation reaction. Z. KARAO-

GLANOV and B. SAGORTSCHEV (Z. anorg. Chem., 1931, **198**, 352—362).—The amount of Cl contained in $BaSO_4$ precipitated by adding H_2SO_4 to $BaCl_2$ solutions is independent of the period of contact between the ppt. and the solution. In presence of HCl the Cl content of the ppt. is not markedly altered, but it diminishes as the rate of precipitation is reduced. CaC_2O_4, precipitated from a solution of $CaCl_2$, is free from Cl. The Cl content of $PbSO_4$ precipitated rapidly by adding a $PbCl_2$ solution to aq. H_2SO_4 diminishes with the period of contact, whereas if the precipitation is slow the Cl content increases with the period of contact; reverse precipitation yields a product containing much less Cl. Analogous experiments have been carried out on the precipitation of $PbCrO_4$; the results when $PbCl_2$ and $PbBr_2$ are used resemble those obtained for the precipitation of $PbSO_4$ from the corresponding halide. Three types of precipitation processes are recognised: (1) those in which no secondary reactions occur; (2) those in which a secondary reaction, independent of time, takes place; and (3) those in which the quantity of secondary product varies with time. The secondary reaction becomes increasingly pronounced as the solubility of the halide used decreases. H. F. GILLBE.

Gravimetric microanalysis of beryllium silicate rocks. Separation and determination of phosphoric acid and aluminium. H. THURNWALD and A. A. BENEDETTI-PICHLER (Mikrochem., 1931, **9**, 324—332; cf. A., 1930, 1544).—The rock is decomposed with HF and H_2SO_4, the P_2O_5 precipitated as phosphomolybdate, and finally determined as $MgNH_4PO_4$, and the Al_2O_3 in the filtrate is determined with 8-hydroxyquinoline after removal of excess of Mo with H_2S. A. R. POWELL.

Micro-determination of copper with salicylaldoxime. W. REIF (Mikrochem., 1931, **9**, 424—429).—The Cu solution is treated with dil. aq. NH_3 until blue, then with feebly acid $AcONH_4$ until the blue colour disappears, and finally with a 5% solution of salicylaldoxime in EtOH. The ppt. is collected in a Pregl filter tube, washed alternately with cold H_2O and EtOH, dried at 105°, and weighed; it contains 18·95% Cu. If Ni and $Fe^{\cdots}$ are present the former is precipitated with dimethylglyoxime in neutral tartrate solution and the Cu precipitated in the filtrate with the aldoxime, the $Fe^{\cdots}$ being retained in solution by the tartrate. A. R. POWELL.

Microchemical reaction of salts of copper and other heavy metals. I. M. KORENMAN (J. Chem. Ind. Russ., 1931, **8**, 276).—Characteristic cryst. salts are obtained by the addition of a solution of 2 parts of saturated aq. picric acid and 1 part of 10% aq. NH_3 to solutions containing the following min. quantities of heavy metal: Cu 0·00005 mg., Ag 0·02 mg., Co 0·0003 mg., Ni 0·0001 mg., Cd 0·001 mg., Hg 0·00015 mg., Au 0·0002 mg. R. TRUSZKOWSKI.

Drop method for [detecting] copper. K. M. FILIMONOVITSCH (Ukrain. Chem. J., 1930, **5**, [Sci.], 383—386).—Cu (0·0635 mg.) may be detected by adding $MnCl_2$, NaOH, and NaOBr solutions to the solution under examination and to 0·001*M*-$CuSO_4$, and heating to boiling, when a red coloration appears simultaneously in both tubes. Cr gives a yellow colour under these conditions, whilst other ions do not interfere. R. TRUSZKOWSKI.

Separation and determination of gallium. III. Separation of gallium from bivalent elements and those of the rare earths, and determination of all these elements. S. ATO (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1931, **15**, 289—301).—Ga can be separated quantitatively from Zn, Cd, Pb, Mn, Ni, Co, Mg, Ca, Sr, and Ba and from rare-earth elements, such as La, Ce, Pr, and Nd, in AcOH solution by precipitation with camphoric acid or Na camphorate solution, and can be determined by igniting the ppt. and weighing as Ga_2O_3. The elements remaining in the filtrates from the ppt. of Ga can be determined as usual. Bivalent elements of the H_2S group (Pb, Cd, etc.) can be separated quantitatively from Ga by precipitation with H_2S in HCl solutions. The adhesion of the Ga ppt. with camphoric acid to the wall of the vessel can be avoided by adding about 2% of NH_4NO_3 before the camphoric acid. E. S. HEDGES.

Precipitation of manganese by water-soluble carbonates. A. JILEK and J. LUKAS (Chem. Listy, 1931, **25**, 225—230, 249—254).—Mn is precipitated quantitatively by $(NH_4)_2CO_3$ only under special conditions. Na_2CO_3 and K_2CO_3 ppt. about 99·8% of the Mn present, guanidine carbonate 98—100%, Li_2CO_3 and Tl_2CO_3 give high values (101%), owing to adsorption of Li or Tl on the precipitate of mixed hydroxide and carbonate, and Rb_2CO_3 and Cs_2CO_3 give practically quant. precipitation. R. TRUSZKOWSKI.

Permanganometric investigations. I. J. H. VAN DER MEULEN (Chem. Weekblad, 1931, **28**, 377—381).—Mn salts are oxidised to $KMnO_4$ at 55—60° by $K_2S_2O_8$ in presence of $AgNO_3$ or Ag_2SO_4 as catalyst and HF or H_3PO_4, or, preferably, a mixture of both acids. The excess of $K_2S_2O_8$ is decomp. by heating the liquid to the b. p., and, after cooling, the $KMnO_4$ is determined by addition of KI and titration of the liberated I with $Na_2S_2O_3$. Fe^{III} salts do not interfere, as they are converted into inactive complexes. H. F. GILLBE.

Molybdenum-blue in analysis. S. L. MALOWAN (Z. anal. Chem., 1931, **84**, 209—217).—A review of the literature. R. CUTHILL.

Stable colorimetric comparison substance for cœruleo-molybdimetry. G. DENIGÈS (Bull. Soc. Pharm., Bordeaux, 1930, **68**, 1—3; Chem. Zentr., 1931, i, 2088).—A solution containing either $Cu(OAc)_2$ (3 g.), $CuSO_4$ (1·80 g.), and AcOH (2 c.c. in 50 c.c.) or $Co(NO_3)_2$ (5%, 36 c.c.), AcOH (2 c.c.), and $Cu(OAc)_2$ (3 g.) is equiv. in colour to that obtained by treating 5 c.c. of a solution containing 12 mg. P_2O_5 per litre with the Mo reagent. The test and comparison solutions must be compared in equal layer depths. A. A. ELDRIDGE.

Electrometric titration of uranium with ceric sulphate. D. T. EWING and (MRS.) M. WILSON (J. Amer. Chem. Soc., 1931, **53**, 2105—2110).—A hot solution of U sulphate in 2% H_2SO_4 is reduced in a Zn reductor and titrated electrometrically with $Ce(SO_4)_2$ in an atm. of CO_2 or N_2. The reagent added between the two end-points is a measure of the U present.

The two end-points obtained when U acetate in 2—4*M*-HCl is treated similarly are less sharp. When $Fe^{\cdot\cdot}$ is also present, the first end-point occurs when all tervalent U is oxidised to quadrivalent U, the second, when all quadrivalent U is oxidised to sexavalent U, and the third when all $Fe^{\cdot\cdot}$ is oxidised to $Fe^{\cdot\cdot\cdot}$.

J. G. A. GRIFFITHS.

Iodometric determination of small quantities of tin. R. HOLTJE (Z. anorg. Chem., 1931, **198**, 287—296).—The correct end-point of $Na_2S_2O_3$–I titrations, using starch as indicator, is obtained when the solution contains 0·2—1% HCl and 0·1—0·5% KI. I, KIO_3, and $KBrO_3$, but not $K_2Cr_2O_7$, are suitable for standardisation of $Na_2S_2O_3$ solutions for use in micro-analysis. Sn^{II}, in quantities of less than 1 mg., may be determined by addition of a slight excess of I solution and titration of the excess with $Na_2S_2O_3$ in absence of air; the mean error is 5 microg. KIO_3, but not $KBrO_3$, may be used in place of I. Sn^{IV} may be reduced with Fe or Al; Fe (powder) is the more satisfactory and its action is accelerated and rendered complete by addition of a small quantity of KI. Reduction by Zn yields low results, and with Mg the reduction is incomplete and $Sn(OH)_4$ separates. Details are given of the determination, to within 5 microg., of 1 mg. or less of Sn.

H. F. GILLBE.

Specific detection of zirconium. F. FEIGL, P. KRUMHOLZ, and E. RAJMANN (Mikrochem., 1931, **9**, 395—400).—$ZrOCl_2$ in HCl solution gives a characteristic brown ppt. with a solution of *p*-dimethylaminoazophenylarsinic acid in 5% alcoholic HCl. Ti, Mo, and W give similar ppts., but addition of H_2O_2 inhibits the reaction in these cases. Sn gives a brown ppt. in dil. HCl solution, but not in 2*N*-HCl. To detect traces of Zr a drop of the solution is placed on a filter-paper which has been impregnated with a solution of 0·1 g. of the reagent in a mixture of 5 c.c. of conc. HCl and 100 c.c. of EtOH. The paper is then immersed for a short time in 2*N*-HCl at 50—60° to dissolve the excess of reagent from the paper; a brown spot insol. in the acid indicates Zr (sensitivity 1 : 500,000).

A. R. POWELL.

Micro-determination of m. p. H. LINSER (Mikrochem., 1931, **9**, 253—268).—The apparatus described by Klein (A., 1929, 1261) is useful for the identification of org. compounds by determining their m. p. if certain precautions are taken and the apparatus is standardised on a series of known substances.

A. R. POWELL.

Application of resistance thermometers to ebullioscopy and tonometry. I. Comparison of resistance with standard mercury thermometers. A. ZMACZYNSKI (Rocz. Chem., 1931, **11**, 327—353).—Swientosławski's ebullioscope is adapted to the standardisation of thermometers. Pt resistance thermometers are more sensitive and permit more accurate reading than do Hg thermometers. The temp. of 0·007° obtained using Michels' apparatus is reproducible with an accuracy of 0·0005°. R. TRUSZKOWSKI.

High-temperature electric furnace and a micro-adaptation. R. C. EMMONS (Science, 1931, **73**, 499—500).—Furnaces electrically heated by nichrome or Pt wire, and a small C resistance furnace are described. L. S. THEOBALD.

Ebullioscope for testing purity of liquids. W. SWIENTOSŁAWSKI (Compt. rend., 1931, **192**, 1457—1459; cf. A., 1927, 642).—A more elaborate apparatus, with two separate condensing columns, for determining with greater accuracy the difference between boiling and condensing temp. is described.

C. A. SILBERRAD.

Vacuum sublimation under the microscope. L. KOFLER and W. DERNBACH (Mikrochem., 1931, **9**, 345—349).—The apparatus comprises a square glass plate covered with a vac. bell, the upper, circular glass cover of which is a plane parallel to the glass plate. The tube for attachment to the pump is fused into one side of the bell. By means of the apparatus the actual formation of the sublimate on the underside of the cover can be observed under the microscope at magnifications up to 135 diameters.

A. R. POWELL.

Fluorescence microscope. M. HAITINGER (Mikrochem., 1931, **9**, 430—440).—The illuminating system comprises an arc lamp with cored Fe electrodes provided with brass cooling channels, quartz lenses, and Cr-plated Fe mirrors. The object under examination is illuminated by means of a quartz dark field condenser and the light is filtered through $CuSO_4$ solution. The iron arc provides a powerful source of light of wave-length 3000—4000 Å.

A. R. POWELL.

Quantitative determination of the colour and intensity of fluorescence phenomena. M. HAITINGER (Mikrochem., 1931, **9**, 441—450).—The intensity of the fluorescence of a substance is measured by comparing the light passing through red, green, and blue filters photometrically with that reflected from a standard substance under the same conditions; the results are then plotted in the triangular diagram of König as percentages of the total light emitted and the position of the point is calc. on a rectangular pair of axes, one of which coincides with the base of the triangle. The rectangular co-ordinates of this point are a measure of the colour tone of the fluorescence.

A. R. POWELL.

Refractometer for reactive liquids. W. C. DAVIES and W. J. JONES (J. Physical Chem., 1931, **35**, 1490—1492).—An instrument based on the principle of the spectrometer with a prism filled with liquid is described. AcCl has n_F^{20} 1·39335, n_D^{20} 1·38708, and n_C^{20} 1·38548. L. S. THEOBALD.

***X*-Ray fibre photography.** S. ZEIDENFELD (Nature, 1931, **128**, 70).—The arrangement used for obtaining an *X*-ray photograph of wool, artificial silk, and ramie fibre is described. L. S. THEOBALD.

Improved null instrument for glass electrode or other high-resistance circuits. S. E. HILL (Science, 1931, **73**, 529—530).—The incorporation of a special vac. tube in the circuit permits the use of thick glass membranes of small area or of thick-walled glass bulbs. L. S. THEOBALD.

Micro-hydrogen electrode. F. SAUNDERS (J. Amer. Chem. Soc., 1931, **53**, 2180).—The electrode is made by modifying a Pt hypodermic needle, insulating the outside with bakelite paint, and platinising the inside. J. G. A. GRIFFITHS.

Use of quinhydrone electrode. G. M. Moir (Analyst, 1931, **56**, 445—448).—The use of the quinhydrone electrode is described. Test-tubes with U-tubes filled with 5% agar in 3·5*N*-KCl, as bridges, are preferred to the usual type of electrode vessel.
T. McLachlan.

Simple, inexpensive quinhydrone cell for rapid work. J. G. Davis (Analyst, 1931, **56**, 449—450; cf. preceding abstract).—In a modification of Moir's vessel the test-tube is drawn out at the bottom to form a U-tube, omitting the agar bridge. The [H˙] of solids may be determined by making a cell containing a mixture of finely-powdered quinhydrone and the substance to be tested. T. McLachlan.

Reduced circular bridge with additional resistances. J. Biczyk (Rocz. Chem., 1931, **11**, 376—378).—A new type of Wheatstone bridge is described. R. Truszkowski.

Lampbank rheostat. C. C. Coffin (J. Amer. Chem. Soc., 1931, **53**, 2180—2181).—To one terminal of each lamp is soldered a hook perpendicular to the axis. By this means, the lamps are pivoted about a brass rod below which is a brass strip against which the other terminals of the lamps, when lowered, press.
J. G. A. Griffiths.

New cell for electrodialysis. H. N. Holmes and A. L. Elder (J. Physical Chem., 1931, **35**, 1351—1354).—With the cell described Na˙ and Cl′ were removed from 0·01*N*-NaCl after 10 hr. dialysis at 155 volts at 165—170°. Satisfactory removal of salts from gelatin and of HCl from silica gel was also obtained. L. S. Theobald.

Extraction-dialyser. H. Raab (Chem.-Ztg., 1931, **55**, 395).—The extraction-dialyser is suitable for use at atm. or reduced pressure. W. J. Boyd.

Leakage of helium through pyrex glass at room temperature. II. G. P. Baxter and H. W. Starkweather (Science, 1931, **73**, 618).—A continuous regular loss of He corresponding with that previously observed (A., 1929, 903) has been maintained. In 3·5 years the total loss of He amounts to approx. 3·5% (35 c.c.). L. S. Theobald.

Simple device for humidity regulation. G. E. R. Hervey and J. G. Horsfall (Science, 1931, **73**, 617—618).—An apparatus for controlling R.H. to ±2% is described. L. S. Theobald.

Modification of Krogh's differential manometer. D. E. Fink (Science, 1931, **73**, 592—593).
L. S. Theobald.

Apparatus to circulate liquid under constant pressure in a closed system. Anon. (Science, 1931, **73**, 566). L. S. Theobald.

Tilting stopcock. P. L. du Nouy (Science, 1931, **73**, 530).—Hg in a small glass vessel is utilised for cutting off low-pressure supplies of gas.
L. S. Theobald.

Levelling vessel for producing a constant receiving pressure in gas analysis. W. Herbert and W. Wahlig (Chem.-Ztg., 1931, **55**, 474).—The liquid displaced from the burette by the gas evolution passes through a side limb into a reservoir of special design so that the liquid in the burette is not in direct contact with that in the reservoir. The pressure of the gas, being governed by the difference in levels of the burette and the side limb, remains const. while the reservoir is stationary. H. J. Dowden.

Transference of small quantities of liquids. G. Owen (J.S.C.I., 1931, **50**, 189—190T).—The manipulation of small quantities of liquids is facilitated by the use of a bent narrow glass tube of capillary bore. Transfer of the liquid is effected by siphoning, which commences automatically.

Automatically controlled slow cooling or heating. G. Owen (J.S.C.I., 1931, **50**, 190T).—Details are given of a device for inserting a hydrostatic resistance into the flow of gas used for heating; the value of this resistance increases or decreases at any desired rate.

Modified form of Kundt's tube. R. C. Colwell (Science, 1931, **73**, 480).—An apparatus suitable for lecture demonstration is described.
L. S. Theobald.

Recrystallisation apparatus. H. Ulich (Chem. Fabr., 1931, 278—279).—Two flasks (one inverted) with side tubes are connected by a wide glass tube containing a Schott filter plate and surrounded by an electrical heating spiral. By inverting the apparatus and employing the side connexions a salt can be dissolved, the solution filtered and crystallised, and the crystals washed with absence of air, under pressure, in vac. etc. C. Irwin.

Alchemical apparatus. J. R. Partington (Nature, 1931, **128**, 118).—The alchemical "water-bath" (bain-marie) may actually represent a small charcoal brazier. L. S. Theobald.

Arabic source of Zadith's "Tabula Chemica." H. E. Stapleton and M. H. Husain (Nature, 1931, **127**, 926).—Historical. L. S. Theobald.

Democritus. H. Kopp (Riv. Chim. scient. ind., 1930, **1**, 211—213; Chem. Zentr., 1931, i, 2014).

Geochemistry.

Origin of subterranean water. F. Dienert (Compt. rend., 1931, **192**, 1402—1404).—An experiment is described demonstrating that rain-water passes down through surface soils to the underground water level. The view that subterranean water supplies largely depend on condensation of water vapour from the air in the soil, which in the author's opinion is possible only from air actually circulating in the soil, is opposed. C. A. Silberrad.

Relative radioactivity of deep-well waters in Manila and vicinity. R. H. Aguilar (Philippine J. Sci., 1931, **45**, 183—197).—Measurements show no wide variations and the average results compare very

favourably with those obtained in other parts of the world. The Ra emanation content is far below the min. necessary to produce any therapeutic effect, and there is thus no support for the belief that the radioactivity confers a special medicinal value.

N. H. HARTSHORNE.

Variation due to rain in salinity of tidal pools. R. LAMI (Compt. rend., 1931, **192**, 1579—1580).—The surface water of three tidal pools 3 hr. after isolation from the sea, about 1 mm. rain having fallen, had fallen to 30·81, 31·78, and 24·40, and that of the last at 4 cm. depth to 31·46. At 10 cm. in all cases the salinity was practically that of the sea, about 34.

C. A. SILBERRAD.

Dissolved phosphorus and inorganic nitrogen in the water of the Mississippi River. A. H. WIEBE (Science, 1931, **73**, 652).—Analytical data for sol. P, nitrate-N, and NH_3-N for 1929—1930 are recorded. Inorg. N is apparently not a limiting factor in plankton production, but sol. P may become one at certain periods. L. S. THEOBALD.

Possible role of micro-organisms in the precipitation of calcium carbonate in tropical seas. W. BAVENDAMM (Science, 1931, **73**, 597—598).—Carbamide bacteria, which occur in many sea muds, can ppt. $CaCO_3$ under certain conditions. Other observations support the view that the formation of $CaCO_3$ sediments is primarily a microbiological process.

L. S. THEOBALD.

Soils of the bed of Lake Albert, S. Australia. J. K. TAYLOR and H. G. POOLE (J. Counc. Sci. Ind. Res. Austral., 1931, **4**, 83—95).—Chemical and physical examination of the soils is described. The lack of uniformity and high salinity of the soils are unfavourable to reclamation. A. G. POLLARD.

Muds of the Clyde sea area. III. Chemical and physical conditions; rate and nature of sedimentation; and fauna. H. B. MOORE (J. Marine Biol. Assoc., 1931, **17**, 325—358; cf. A., 1930, 448).—The PO_4''' content, O_2 adsorption, p_H, H_2O content, *d*, and rate of sedimentation have been determined.

C. W. GIBBY.

Russian eruptive and metamorphic rocks. Z. NEMOVA and F. LOEWINSON-LESSING (Mem. Com. Geol., Moscow, 1930, [ii], No. 186, 361).—Analyses (1676) are recorded. CHEMICAL ABSTRACTS.

Minerals in nephelinic syenite of Kassa Is. (Los Archipelago, French Guinea). Pneumatolytic phases of these syenites. A. LACROIX (Compt. rend., 1931, **192**, 1322—1326).—The nephelinic syenite contains, besides greyish soda-orthoclase and nepheline, acmite and arfvedsonite, with a little pyrochlore, lavenite, and fluorite. In a pegmatitic facies occur astrophyllite, eucolite with inclusions of catapleiite and accompanied by cancrinite, intensely fluorescent blue sodalite, and wine-red villiaumite. Other geodes yield serandite (cf. this vol., 332), natrolite, rhodochrosite, and pyrophanite. Elsewhere occur nodules of natrolite containing fine crystals of analcite, *d* 2·243—2·248, coloured rose by Mn, and accompanied by scales of stilpomelane. The bulk of the above minerals are ascribed to the author's "constructive" phase of pneumatolysis, secondary zeolites and pyrite following in the "destructive" phase. Apophyllite does not occur (cf. A., 1890, 1077). C. A. SILBERRAD.

Action of heat on braunite. S. PAVLOVITCH (Compt. rend., 1931, **192**, 1400—1402).—Braunite crystals, *d* 4·81, containing 8·92% SiO_2 and perfectly homogeneous, when heated in N_2, were transformed at 1190° into many minute crystals of the same; at 1400° in 4 hr. 3·8 wt.-% of O_2 was evolved, with formation of tephroite, $MnSiO_4$, and a partly fused eutectoid of tephroite and hausmannite, Mn_3O_4. Analysis showed 30% tephroite and 70% hausmannite. Braunite is therefore $(MnSi)_2O_3$. When heated in air at 1400° only 2·78% O_2 was evolved (cf. A., 1894, 99).

C. A. SILBERRAD.

Clays as minerals and as colloids. C. E. MARSHALL (Trans. Ceram. Soc., 1931, **30**, 81—96).—A table is given in which clays are classified as minerals on the basis of existing knowledge. The problem of base exchange is discussed from the colloidal and the mineralogical points of view. Recent *X*-ray work on the structure of clays is reviewed. Clays are considered as polydisperse colloidal systems, and a centrifugal method of carrying out mechanical analysis down to 0·2 μ is described. The distribution of particle size in 4 types of clay is tabulated. A brief account is given of the different types of coagulation. F. SALT.

Melilite. F. MACHATSCHKI (Zentr. Min. Geol., 1931, **A**, 28—30; Chem. Zentr., 1931, i, 1895).—A discussion of the formula. A. A. ELDRIDGE.

Composition and age of thucholite. A. FAESSLER (Zentr. Min. Geol., 1931, **A**, 10—18; Chem. Zentr., 1931, i, 1895).—The following elements were detected spectroscopically: U, Th, Pb, Lu, Yb, Er, Ho, Dy, Tb, Gd, Sm, Nd, Pr, Ce, La, Ru (?), Zr, Y, Sr, As, Zn, Fe, V, Ca; spectroscopic determinations indicated: ThO_2 14 3, U_3O_8 1·65, Y 8, Sr, 1·3, Zr 0·6—0·7, Fe and Ca 2—3%. Other proportions are estimated. The age is estimated at 250×10^6 years.

A. A. ELDRIDGE.

Composition of eucrite. R. BRAUNS (Zentr. Min. Geol., 1931, **A**, 18—23; Chem. Zentr., 1931, i, 1895).—The felspar is closely related to anorthite (80—87%). The CaO content of the pyroxenes is insufficient for the ratio CaO : (Fe,Mg)O = 1 : 1. Hence in the diopside pyroxenes a solid solution of $(Mg,Fe)SiO_3$ is postulated. A. A. ELDRIDGE.

Radium in rocks. III. Radium content of Hawaiian lavas. C. S. PIGGOT (Amer. J. Sci., 1931, [v], **22**, 1—8; cf. this vol., 332).—The average Ra content of 16 samples of Hawaiian lavas is $0·96\times10^{-12}$ g. per g. All samples from the Kilauea crater, of whatever age, had the same content (cf. A., 1909, ii, 848). C. W. GIBBY.

The system of monticellite. D. BELIANKIN and B. IVANOV (Amer. J. Sci., 1931, [v], **22**, 72—80).—Ural monticellite contained: SiO_2 32·88, TiO_2 0·25, Al_2O_3 3·76, FeO 8·20, MnO 10·45, MgO 13·03, CaO 28·62, Na_2O 1·57, K_2O 0·54, P_2O_5 0·18, CaS 0·23, total 99·71%. C. W. GIBBY.

Alkaline rocks of the Highwood type in S.E. Idaho. A. L. ANDERSON and V. R. D. KIRKHAM (Amer. J. Sci., 1931, [v], **22**, 51—68).—A petrographic description is given. C. W. GIBBY.

Age of flint. M. Burton (Nature, 1931, **128**, 32—33).—A discussion. A criterion for the age of flint is suggested. L. S. Theobald.

Unique iron meteorite from Mexico. H. H. Nininger (Amer. J. Sci., 1931, [v], **22**, 69—71).—An analysis and description are given. C. W. Gibby.

Origin of the salt domes of the gulf coastal plain of the United States. E. de Golyer (J. Inst. Petroleum Tech., 1931, **17**, 331—333).—A discussion. N. H. Hartshorne.

Moot points in salt dome theory. L. Owen (J. Inst. Petroleum Tech., 1931, **17**, 334—337).—The areal distribution of salt domes, the derivation of the "cap rock," and the shape of the salt mass are discussed. The calcite in the cap rock may have been originally incorporated with the anhydrite, collected by the anhydrite in its upward movement, or introduced by surface waters. The shape of the salt mass is probably an inverted cone, and if this is so the search for oil in the flank wells of the dome should not end with the striking of salt. N. H. Hartshorne.

Salt dome geochemistry. M. Stuart (J. Inst. Petroleum Tech., 1931, **17**, 338—345).—A genetic relation between salt domes and the oil sometimes associated with them can, if it exists, be due only to the occurrence of animal and vegetable life in the original salt lake from the dried deposit of which the dome was extruded. The existence of $CaSO_4$ in the cap rock is due to the action of calcareous waters either on sulphate layers in the deposit corresponding with the kieserite and polyhalite zones in the Stassfurt beds, or Fe sulphide as found in the Indian deposits. The presence of anhydrite as well as gypsum in the cap is a possible result of pressure and the dehydrating action of dissolved salts. The occasional association of dolomite with the gypsum is attributed to an abundance of $MgSO_4$ in the upper layers of the salt deposit forming the dome. The absence of cap rock in the Roumanian domes is thought to be due to their having been extruded to such an extent that only the "anhydrite zone" remains to form a cap; this contains practically no soluble sulphates. The effect of pressure on the "flow" of different zones of a salt deposit becomes less marked with increasing depth, and may possibly be connected with the accompanying decrease in the combined H_2O. N. H. Hartshorne.

Base exchange and the formation of coal. W. H. A. Penseler (N.Z. J. Sci. Tech., 1931, **12**, 284—295).—Claystone samples from the Waikato coal seams were generally of an acid character, and the predominant exchangeable bases were Ca and Mg. Contrary to Taylor's views, the formation of the bituminous coal examined does not appear to have been controlled by base exchange and hydrolysis in the roofing clay. A. G. Pollard.

Origin of coal. E. Berl, A. Schmidt, and H. Koch (Z. angew. Chem., 1931, **44**, 329—330). W. Fuchs and O. Horn (*ibid.*, 330).—Polemical (cf. B., 1931, 456). A. R. Powell.

Lignin theory [of the origin of coal]. R. Lieske and K. Winzer (Brennstoff-Chem., 1931, **12**, 205—211; cf. A., 1930, 570, 571, 1017).—The occurrence of whole leaves which have been converted into coal is not inconsistent with the lignin theory of coal formation; contrary to general belief, not only the veins, but the whole of the leaf contains relatively large amounts of lignin. The lower *d* of some fossil woods compared with fresh wood corresponds with the determined loss in cellulose content; the higher *d* of other fossil woods is due to deposition therein of material from the surrounding medium. The decomp. of cellulose in the lower layers of the peat bog is attributed mainly to hydrolysis by the peat acids, the sugars thereby formed being further decomposed by micro-organisms. The question as to whether sp. cellulose-decomp. bacteria or fungi are present or not is therefore immaterial. A. B. Manning.

Classification and development of carbonaceous minerals. H. Briggs.—See B., 1931, 659.

Microscopic structure and origin of coking and bituminous coals. A. Duparque (Compt. rend., 1931, **192**, 1472—1474).—The great majority of coking coals are produced from deposits rich in lignin and free from spores, cuticle, and resinous material; a small number from such as contained much cutin, or from mixed deposits of ligneous tissue, spores, and cuticle. The three classes of bituminous coal—forge, gas, and long-flame—are due to different processes acting on deposits rich in cutin, and consisting largely of spores and cuticle. The anthracites formed by metamorphosis of such coals (cf. this vol., 818) differ greatly from other anthracites. This duality of origin explains the difference between two coals showing the same content of volatile matter. C. A. Silberrad.

Composition of the mother substance of the coals of the Kuzneck basin. M. D. Zaleski and E. F. Tschirkova (Bull. Acad. Sci. U.S.S.R., 1931, 269—275).—Many coal strata of the Koltschuginski region of the Kuzneck basin contain mineralised $CaCO_3$, which includes well-preserved vegetable residues. T. H. Pope.

Palæobotany of coal from Wemyss Colliery, East Wemyss, Fife. D. J. W. Kreulen (Fuel, 1931, **10**, 270—273).—The durain of this coal is rich in spores. Photomicrographs are reproduced. A. B. Manning.

Organic Chemistry.

Configurational relationship of hydrocarbons. II. Optical rotations of hydrocarbons of the normal series. P. A. Levene and R. E. Marker (J. Biol. Chem., 1931, **91**, 761—772).—l-β-*Methyl*-n-*butan*-α-*ol*, b. p. 127°/760 mm., $[\alpha]_D^{25}$ −2·41° (*brucine phthalate*, $[\alpha]_D$ +1·15° in EtOH), is converted by PBr_3 into *d*-α-bromo-β-methyl-*n*-butane, b. p. 119°/760 mm., $[\alpha]_D$ +2·16°, converted through its Grignard compound by CO_2 into d-β-*methyl*-n-*valeric acid*, b. p. 110°/30 mm., $[\alpha]_D^{25}$ +3·66°, and by MeCHO into d-γ-*methyl*-n-

hexan-ε-ol, b. p. 146—147°/760 mm., $[\alpha]_D^{22}$ +4·24°. Reduction of the corresponding iodide with Zn+HCl affords d-*γ-methyl*-n-*hexane*, b. p. 91—92°/760 mm., $[\alpha]_D^{22}$ +3·67° (+9·87°). Similarly using higher homologues of the aldehyde are obtained d-*γ-methyl*-n-*heptan-ε-ol*, b. p. 72°/22 mm., $[\alpha]_D^{23}$ +2·98°, the *bromide*, b. p. 63°/16 mm., $[\alpha]^{23}$ +4·82°, of which is converted by hydrolysis of its Grignard compound into d-*γ-methyl*-n-*heptane*, b. p. 116—118°/760 mm., $[\alpha]^{22}$ +4·45° (+11·97°); d-*γ-methyl*-n-*octan-ε-ol*, b. p. 89°/15 mm., $[\alpha]_D$ +3·67° (*bromide*, b. p. 94°/20 mm., $[\alpha]^{23}$ +5·63°); d-*γ-methyl*-n-*octane*, b. p. 143—144°/760 mm., $[\alpha]_D^{23}$ +5·27° (+14·18°). In the *l*-series are similarly prepared: l-*ε-methyl*-n-*octan-β-ol*, b. p. 92°/15 mm., $[\alpha]_D$ −0·32°; l-*ε-methyl*-n-*octane*, b. p. 53°/25 mm., $[\alpha]_D$ −0·46°; l-*ζ-methyl*-n-*nonan-γ-ol*, b. p. 105°/15 mm., $[\alpha]^{24}$ −0·65°; l-*ζ-methyl*-n-*nonane*, b. p. 72°/25 mm., $[\alpha]^{22}$ −0·59°; l-*ζ-methyl*-n-*decan-γ-ol*, b. p. 117°/22 mm., $[\alpha]^{24}$ −0·33°; and l-*ζ-methyl*-n-*decane*, b. p. 94°/30 mm., $[\alpha]_D^{24}$ −0·39°. Levene and Marker's rule (this vol., 598) concerning the direction of rotation of secondary carbinols is also applicable to the active hydrocarbons. The max. rotation values calc. indirectly are included in parentheses.

J. W. BAKER.

Preparation of hydrocarbons and alcohols by reduction of fats under high pressure. W. SCHRAUTH, O. SCHENCK, and K. STICKDORN (Ber., 1931, 64, [*B*], 1314—1318).—Hydrocarbons are produced by the hydrogenation of fats at temp. exceeding 350° and pressures up to 200 atm. in presence of Ni, whereas alcohols corresponding with the fatty acids are formed in presence of Cu at temps. not greatly exceeding 320°/200 atm. Mixed catalysts can be employed under conditions which vary according to the catalyst and the nature of the fat. Reaction is applicable to any fatty acid or ester and to fatty-aromatic carboxylic acids. The following examples are cited: dodecane from Me laurate; hydrocarbons from coconut oil and hydrogenated sperm oil; dodecane and octadecane from lauric and stearic acids respectively; dodecyl alcohol from Me laurate; decyl alcohol from Me decoate; fatty alcohols from coconut oil; octyl and octadecyl alcohols from octoic and stearic acids respectively.

H. WREN.

Catalytic oxidation of non-benzenoid hydrocarbons and mineral oils in their vapour phase. R. SHIMOSE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, 15, 251—276).—Maleic acid, with CO_2 and CH_2O, is the main product of the catalytic oxidation of the following vapours with air: *n*-pentane, *n*-heptane, *n*-octane, β-amylene, β-*iso*amylene, di*iso*amyl, and *cyclo*hexane. Decahydronaphthalene gives phthalic acid in addition to the products mentioned. Maleic acid is obtained as a main product from gasoline, and both maleic and phthalic acids from kerosene, kerosene treated with 98% H_2SO_4, spindle oil treated with 98% H_2SO_4, liquid and solid paraffin; CO_2 and CH_2O are also among the products in each case. The catalysts used were oxides or salts of V, Mo, U, Cr, and Mn. Mineral oils are considered to contain polynaphthenes.

E. S. HEDGES.

Hydrogenation of unsaturated hydrocarbons under the electric discharge. Y. VOLMAR and G. HIRTZ (Bull. Soc. chim., 1931, [iv], 49, 684—702).—When a slow stream of H_2 and C_2H_4 is submitted to the silent electric discharge at 20 mm., the % hydrogenation, reaction velocity, and yield of saturated hydrocarbons increase with the proportion of H_2 in the mixture. The C deposited similarly decreases from 19% with excess of C_2H_4 to 2·6—5·5%. CH_4 and C_3H_8 as well as C_2H_6 are among the reaction products. Since under similar conditions a mixture of C_2H_6 and H_2 yields polymerisation but not scission products, the saturated mol. is stable, and it is suggested that the primary reaction is scission of the C_2H_4 mol. at the double linking. The free CH_2 radical thus formed reacts with excess of H_2 giving CH_4, or with a second mol. of C_2H_4 to yield, after hydrogenation, C_3H_8, or decomposes yielding C and H. Since the yield of saturated hydrocarbons and of CH_4 from a mixture of 1 mol. of C_2H_4 and 1 mol. of H_2 increases as the pressure decreases, the proportion of higher homologues decreasing, either active H or a compound activated by the H is considered the hydrogenating agent. In hydrogenation of C_2H_4 at low pressures in the silent discharge CH_4 and not C_2H_6 is the stable and chief product.

Under similar conditions C_2H_2 yields a mixture containing (initial ratio, C_2H_2, 1 part; H_2 4 parts) acetylenic hydrocarbons up to C_{10} and saturated hydrocarbons up to C_8. It is impossible to assert that the olefines also formed represent an intermediate stage, and the presence of CH_4 in the reaction products indicates the possibility of scission at the triple linking as a primary reaction. The percentage of polymerised products increases with the duration of the exposure to the electric discharge and with the pressure. At very low pressures polymerisation products practically disappear, and with a rapid flow hydrogenation to CH_4 should be practically quant. Active H is probably the hydrogenating agent. The proportion of olefinic and saturated hydrocarbons increases as the percentage of H in the initial mixture decreases. It is possible that the C_2H_4 and C_2H_2 may themselves be activated under these conditions.

R. BRIGHTMAN.

Dichloroacetylene (II) and the influence of rate of reaction on the stereochemical course of halogen addition at the acetylenic linking. E. OTT and K. PACKENDORFF (Ber., 1931, 64, [*B*], 1324—1329; cf. A., 1930, 1402).—The preparation of dichloroacetylene from trichloroethylene by means of pure KOH is effected without danger only when a rapid current of gas is used. Addition of a small amount of water-glass to KOH before granulation ensures a non-dangerous catalyst which becomes inactive if excess of water-glass is used. Reaction proceeds safely with pure KOH if 5% of Et_2O is admixed with the trichloroethylene. Distillation of a solution of dichloroacetylene in Et_2O gives a product, b. p. 32·5°/743 mm., apparently an unstable mol. *compound* insensitive to O. It can be preserved unchanged in the dark, but when exposed to light is converted into a number of *compounds*, one of which, Et_2O,C_2Cl_2, has b. p. 47·5°/18 mm., d_4^{20} 1·1753, and does not contain an unsaturated linking; a second *substance* (?)$[Et_2O,C_2Cl_2]_2$, b. p. 110°/18 mm., is described. Rapid addition of I to dichloroacetylene in CCl_4 yields

10% of liquid dichlorodi-iodoethylene, b. p. 72°/0·06 mm., m. p. 5—7°, d_4^{20} 2·9437, and 90% of the solid isomeride, m. p. 70°, whereas the slower addition in Et_2O leads to only traces of the liquid isomeride. Similarly, the slow addition of Br to acetylenedicarboxylic acid in the dark yields exclusively dibromofumaric acid, whereas the more rapid addition in sunlight leads to a product containing up to about 25% of dibromomaleic acid.

Slow autoxidation of dichloroacetylene yields in addition to $COCl_2$, CO, and CO_2 an oil with an odour resembling that of an acid chloride and transformed by NH_2Ph into an anilide, m. p. 186°. H. WREN.

Catalytic dehydration of aliphatic alcohols in the gaseous phase in presence of pumice moistened with sulphuric or phosphoric acid. J. B. SENDERENS (Compt. rend., 1931, **192**, 1335—1337).—Passage of the vapours of $Pr^{\alpha}OH$, $Pr^{\beta}OH$, and $Bu^{\beta}OH$ over pumice moistened with $H_2SO_4,3H_2O$ gives the same results as with $NaHSO_4$ (cf. A., 1930, 889). With EtOH at 135° pure Et_2O is formed in quant. yield, and there is no evidence of deterioration of the catalyst; at 140° a little C_2H_4 is also formed. MeOH is dehydrated above 140°, best at 145—155°, to Me_2O. Use of syrupy H_3PO_4 in place of H_2SO_4 gives with EtOH no Et_2O, and only a comparatively feeble generation of C_2H_4 at 180—185°. H. A. PIGGOTT.

Conversion of polyhydric alcohols into mono- and poly-chlorohydrins with thionyl chloride. P. CARRÉ and P. MAUCLERE (Compt. rend., 1931, **192**, 1567—1569).—Glycerol is converted by $SOCl_2$ in presence of piperidine successively into mono-, di-, and tri-chlorohydrins. Mannitol gives a complex mixture, but mannide forms a mono-, b. p. 128—130°/17 mm. (*phenylurethane*, m. p. 163°), and a di-chlorohydrin, m. p. 67°. Hydrobenzoin affords a mixture with 1 mol. of $SOCl_2$ but with 2 mols. dichlorostilbene, m. p. 190°, is obtained. Excess of $SOCl_2$ with cotton cellulose causes only 1 atom of Cl to combine for each $C_6H_{10}O_5$ unit, and with reprecipitated cellulose decomp. takes place. F. R. SHAW.

Ethylene chlorohydrin. II. G. BOZZA and G. GALLARATI (Giorn. Chim. Ind. Appl., 1931, **13**, 163—173; cf. A., 1930, 1269).—The value of n_D^{2} is 1·4421 and the values for aq. solutions are virtually linear in relation to the composition by wt. Aq. solutions show the min. b. p. 97·8°/760 mm., or 80·55°/400 mm.; at 400 mm. the azeotropic mixture contains 45% (0·132 mol.) of the chlorohydrin, this proportion changing little with the pressure. Solutions in saturated NaCl have the min. b. p. 101·4°/760 mm. or 85·4°/400 mm. (57·8% or 0·234 mol. of chlorohydrin). Chlorohydrin solutions must be distilled rapidly at low temp., as the hydrolysis velocity coeff. is about 0·006 at 100°, so that 10% decomposes during about 8 hr. boiling. The vapours generally differ greatly from the liquids in equilibrium with them, so that separation of mixtures into pure components and azeotrope is easy. The displacement of the azeotrope by NaCl renders possible concentration by alternate distillations of aq. and NaCl solutions. Diagrams are given showing the course of the distillation of any aq. solution of the chlorohydrin. T. H. POPE.

Action of organic bases on dichloro-tertiary alcohols, CRR(OH)·CHCl₂. A. AVY (Bull. Soc. chim., 1931, [iv], **49**, 514—522).—The products obtained by the action of org. bases on dichloro-*tert.* alcohols in anhyd. media differ widely according to the nature of the base. With 5*N*-alcoholic NH_3, dimethyldichloromethylcarbinol yields 2 : 2 : 5 : 5-tetramethyldihydropyrazine, m. p. 83—84° (*chloroplatinate*, m. p. 194—195°); with 7*N*-alcoholic NH_2Me at 100° for 4 hr. it furnishes a complex *substance*, $H·[NMe·C(CMe_2)]_3·NHMe$(?), sublimes and melts at 85—90°/3 mm., and with 7*N*-$NHMe_2$ in C_6H_6 at 100° for 4 hr. the ethylene oxide, $\begin{matrix}CMe_2\\O\end{matrix}\!\!>\!CH·NMe_2$, b. p. 28—30°/13 mm. [*methiodide*, m. p. 245° (decomp.)]. Dichloromethyldiethylcarbinol similarly yields *tetraethyldihydropyrazine*, b. p. 89°/3 mm. (*chloroplatinate*), a complex *compound*, $C_{22}H_{44}N_4$, b. p. 101—102°/2·5 mm., and with a 33% solution of $NHMe_2$ in C_6H_6 at 130° for 5 hr., an *ethylene oxide*, b. p. 65°/12 mm. NMe_3 does not react with these dichloro-*tert.*-alcohols at 130° and NHPhMe and $NHPh_2$ do not react at 140°. R. BRIGHTMAN.

Derivatives of pentane-αδε-triol. R. PAUL (Compt. rend., 1931, **192**, 1574—1576).—Et allylacetate is reduced by Na and EtOH to Δ^{δ}-pentenol [*phenylurethane*, b. p. 184—185°/16 mm.; *allophanate*, m. p. 147—148° (decomp.)], which adds Br to give *δε-dibromopentanol* (I), b. p. 132—133°/16 mm., which, when distilled, loses HBr to form *1-bromomethyltetrahydrofuran*, b. p. 66—67°/20 mm., and αβε-tribromopentane. KOAc and Ac_2O transform I into *αβε-triacetylpentane*, b. p. 170°/16 mm., converted by $ZnCl_2$ into *δ-bromo-Δ^{δ}-pentenyl acetate*, b. p. 103—105°/18 mm., hydrolysed by $Ba(OH)_2$ to *pentane-αδε-triol*, b. p. 190—191°/13 mm. (*triphenylurethane*, m. p. 92°). F. R. SHAW.

Preparation of acetals. F. PAUER (Monatsh., 1931, **58**, 1—11).—Improved methods for the prep. of acetals by Claisen's method (A., 1896, i, 463) using formimido-ethers (A., 1883, 731) obtained from alcohols and anhyd. HCN (preparation in 95% yield described) are detailed. From PhCHO and glycerol is obtained benzylideneglycerol, b. p. 152—154°/12 mm. (94% yield), together with *hydroxymethyleneglycerol*, $OH·CH_2·CH\!<\!\begin{matrix}O—CH·OH\\CH_2·O\end{matrix}$, decomp. by H_2O into CO_2, H_2O, and allyl alcohol. From equimol. proportions of glycerol, HCN, and HCl is obtained *glyceryl orthoformate*, $C_3H_5O_3\!:\!CH$, b. p. 126°/12 mm., together with a little of the *diglyceryl* ester $C_3H_6O_2\!:\!CH·O·C_3H_5$, b. p. 150—160°/12 mm. J. W. BAKER.

Hexosemonophosphate (Robison), natural and synthetic. P. A. LEVENE and A. L. RAYMOND (J. Biol. Chem., 1931, **91**, 751—760).—The structure of the dextrose-6-phosphate (this vol., 63) synthesised from *iso*propylideneglucose and its identity with Robison's ester (A., 1923, i, 86; osazone, m. p. 154—154·5°, and not 139° as previously recorded) are established by the following data. Dextrose-6-phosphate is converted through its *brucine* salt, $[\alpha]^{25}$ −16·6° in H_2O, into its *barium* salt, $[\alpha]_D^{25}$ +16·6° in H_2O, oxidised by $Ba(IO)_2$ to the aldonic acid (*tribrucine*, $[\alpha]^{25}$ −29·9° in H_2O, and *trisodium*, $[\alpha]^{25}$ +1·9° in H_2O,

salts), the lactone formation of which was followed polarimetrically at 25°. The rotation–time curve is identical with that of the aldonic acid similarly prepared from the Robison ester. Dextrose-3-phosphate (*loc. cit.*; brucine salt, $[\alpha]^{25}$ −14·5° in aq. pyridine) is similarly oxidised to the aldonic acid (*dibrucine*, $[\alpha]_D^{23}$ −24·5° in H_2O, and *trisodium*, $[\alpha]^{25}$ +1·3°, salts). Thus both hexosemonophosphates have free OH groups in the 4- and 5-positions.

J. W. BAKER.

Reduction of carbon disulphide. J. A. MITCHELL, E. OTT, and E. E. REID (Ind. Eng. Chem., 1931, **23**, 694—696).—Dithiolmethane distils over with CS_2 when the latter is reduced with Zn dust and boiling AcOH, practically no H_2S being produced. Addition of $Pb(OAc)_2$ in 50% EtOH solution to the distillate gives a yellow ppt. of the methylenebistrithiocarbonate, $CH_2(S\cdot CS_2)_2Pb$, formed by interaction of the CS_2 with the Pb dimercaptide. Corresponding Ag, Cu, Ni, Hg'', Fe''', Co, and Na salts are described. The free methylenebistrithiocarbonic acid, precipitated as a heavy brown oil on adding conc. HCl to an aq. solution of the Na salt, readily loses CS_2 and the residue gives a Pb salt which may be $CH_2<\begin{matrix}S\cdot CS_2\\ S\cdot Pb\end{matrix}$ or a mixture of dimercaptide and bistrithiocarbonate.

C. HOLLINS.

Xanthates and nitrosoxanthates. L. CAMBI and L. SZEGÖ [with A. CAGNOSSO] (Atti R. Accad. Lincei, 1931, [vi], **13**, 93—99).—The compound, $Fe(NO)_2(S\cdot CS\cdot OEt)_2$, regarded by Manchot and Davidson (A., 1929, 526) as a Fe'' compound, may be obtained readily by the action of NO on Fe''' xanthate in EtOH and appears to be Fe''' nitrosoxanthate, one of the NO groups exerting the functions of a halogen. This interpretation is in agreement with the magnetic susceptibility and reactions of the compound.

T. H. POPE.

Ethyl chlorosulphinate and mixed alkyl sulphites. P. CARRÉ and P. MAUCLÈRE (Compt. rend., 1931, **192**, 1738—1740).—Et_2SO_3 and PCl_5 yield $POCl_3$, SO_2, $SOCl_2$, and EtCl. EtOH (1 mol.), pyridine (1 mol.), and $SOCl_2$ (1 mol.) at 0° give *Et chlorosulphinate*, $Cl\cdot SO_2Et$, decomp. about 18°, the presence of which is shown by its reaction with alcohols to yield mixed alkyl sulphites. The following were prepared: Me Et sulphite, b. p. 52—53°/14 mm., 140—142° (decomp.)/760 mm.; *Me Bu sulphite*, b. p. 86—88°/14 mm.; *Et Bu sulphite*, b. p. 94—96°/14 mm.; *Pr$^{\alpha}$ Bu sulphite*, b. p. 102—104°/14 mm. The constitution of these products is proved by their ready hydrolysis to Na_2SO_3 and the respective alcohols.

R. S. CAHN.

Esterification with mixed anhydrides and mixtures of anhydrides. I. A. ROLLETT [with F. PAVLOVITSCH and F. SCHOLZ] (Monatsh., 1931, **58**, 47—58).—The relative proportions of BzOEt and AcOEt formed by interaction of EtOH with an equimol. mixture of BzCl and NaOAc at 190° can be determined by titration of the total acids formed, distillation of the AcOEt, and quant. ester hydrolysis. When the ratio mixed anhydride/EtOH=1/1, only 30 mol.-% of the total esters formed is BzOEt. Addition of an extra mol. of NaOAc has only a slight effect, decreasing the BzOEt to 27·7 mol.-%, whilst similar addition of 1 mol. of NaOBz increases the amount of BzOEt to 45 mol.-%. When the ratio is 1/2, 40 mol.-% of BzOEt is formed, this value being largely diminished (to 20·8 mol.-%) by addition of another mol. of NaOAc, but only slightly increased (to 49 mol.-%) by similar addition of 1 mol. of NaOBz. Sources of error in the measurements are investigated and in anhyd. medium no appreciable esterification of the acids formed in the reaction $R\cdot CO\cdot O\cdot COR'+R''OH \longrightarrow R\cdot CO_2R''+R'\cdot CO_2H$ or $\longrightarrow R'\cdot CO_2R''+R\cdot CO_2H$, could be detected.

J. W. BAKER.

Three-carbon system. XXVI. Some substituted acrylic acids. G. A. R. KON, E. LETON, R. P. LINSTEAD, and L. G. B. PARSONS (J.C.S., 1931, 1411—1418; cf. A., 1930, 1582).—The introduction of a Me group into the α-position retards the mobility and shifts the equilibrium towards the αβ-form in the system β-ethyl-Δ^{α}-pentenoic acid $\longleftrightarrow$ β-ethyl-Δ^{β}-pentenoic acid, and an Et group has a similar effect in the system β-methyl-Δ^{α}-hexenoic acid $\longleftrightarrow$ β-methyl-Δ^{β}-hexenoic acid. The αβ- and βγ-acids are prepared from the β-OH-esters by known methods, and are purified by partial esterification. The following are recorded: *Et β-hydroxy-β-methylhexoate*, b. p. 98°/13 mm. (*Ag* salt); *Et β-hydroxy-α-methyl-β-ethylvalerate*, b. p. 105—108°/17 mm.; β-ethyl-Δ^{α}-pentenoic acid (21%, 0·64); α-methyl-β-ethyl-Δ^{α}-pentenoic acid (50%, 0·0058), b. p. 122°/12 mm. (*Ag* salt); α-methyl-β-ethyl-Δ^{β}-pentenoic acid, b. p. 116—117°/14 mm.; β-methyl-Δ^{α}-hexenoic acid (33%, 0·39) (exists in a stereoisomeric *form*, m. p. 40°); *β-methyl-Δ^{β}-hexenoic acid*, b. p. 113°/10 mm.; *β-methyl-α-ethyl-Δ^{α}-hexenoic acid* (57%, 0·0030), b. p. 127°/12 mm. (*Ag* salt); and β-methyl-α-ethyl-Δ^{β}-hexenoic acid, b. p. 130°/13 mm. The percentages and figures given above refer respectively to the proportions of αβ-acids at equilibrium and to the mobility.

D. A. FAIRWEATHER.

Differentiation of *cis*- and *trans*-ethylenic compounds by catalytic hydrogenation. III. β-Chlorocrotonic acid and β-chloro*iso*crotonic acid. C. PAAL, H. SCHIEDEWITZ, and K. RAUSCHER (Ber., 1931, **64**, [*B*], 1521—1530; cf. A., 1930, 740).—Catalytic hydrogenation of the two β-chlorocrotonic acids and their Na salts proceeds unusually rapidly with quant. production of butyric acid and HCl or NaCl. Since β-chlorobutyric acid and its Ca salt are not attacked by H in presence of small amounts of Pd, it follows that the Cl atom must be first removed with intermediate production of crotonic and *iso*crotonic acid, which suffer further reduction. β-Chloro*iso*crotonic acid is hydrogenated more rapidly than β-chlorocrotonic acid. Semi-hydrogenation of the β-chlorocrotonic acids proceeds essentially but not quantitatively according to the scheme:

$$CMeCl{:}CH\cdot CO_2H+H_2=CHMe{:}CH_2\cdot CO_2H+HCl.$$

With β-chloro*iso*crotonic acid or its Na salt semi-hydrogenation proceeds approx. twice as rapidly as with β-chlorocrotonic acid and its Na salt. The ready replaceability of Cl in the chlorocrotonic acids in contrast with its stability in β-chlorobutyric acid under like conditions is attributed to the negativing influence of the ethylenic linking. Hydrogenation of the β-chlorocrotonic acids proceeds more rapidly than that of the crotonic acids, although requiring twice the

quantity of H. The evidence thus obtained confirms the conclusion that β-chloro*iso*crotonic acid and β-chlorocrotonic acid are *cis*- and *trans*-forms respectively. H. WREN.

Rapid determination of solid saturated fatty acids. T. P. HILDITCH and J. PRIESTMAN (Analyst, 1931, 56, 354—367).—Bertram's method is modified by oxidising either the soap with alkaline $KMnO_4$ at 35—50°, or the free fats in $COMe_2$ with anhyd. $KMnO_4$. For rapid work it is advisable to carry out a parallel determination by an improved form of the Twitchell process, which, by itself, however, may give misleading results. T. MCLACHLAN.

Determination of solid unsaturated fatty acids. L. V. COCKS, B. C. CHRISTIAN, and G. HARDING (Analyst, 1931, 56, 368—380).—The Pb salts of the mixed acids are prepared in 92—93% (by wt.) EtOH, left over-night at 15—20°, washed with light petroleum, b. p. 40—60°, and then crystallised from 92—93 wt.-% EtOH at 15—20° for 3 hr., after which the free solid acids are liberated and weighed. The I val. of these acids is determined and, after allowing a mean of 90 for the unsaturated acids unless interfering acids such as erucic acid are present, the proportion of saturated and unsaturated acids may be found. T. MCLACHLAN.

Distribution of saturated and unsaturated higher fatty acids in mixed synthetic glycol esters. R. BHATTACHARYA and T. P. HILDITCH (J.C.S., 1931, 901—907).—By oxidising the products of interaction of glycol, a saturated acid (lauric, palmitic, or stearic acid), and a mixture of oleic and linoleic acids, the proportion of fully saturated ester is determined, the proportions of saturated and unsaturated esters being estimated from the I absorption. It is found that the molar percentage of disaturated or diunsaturated esters obtained is proportional to the square of the molar percentage of saturated or unsaturated acids in the total acids present, compared with the cube of the molar percentage when glycerol is the alcohol present (this vol., 63), *i.e.*, the fatty acids are combined indiscriminately, two or three at a time, with the alcohol according to their relative concentrations. The significance of some regular variations from the y–x^2 curve is discussed. G. DISCOMBE.

Ether-soluble lead salt of lumbang oil. D. M. BIROSEL (Philippine J. Sci., 1931, 45, 251—261).—3·79% of heptadecoic (probably identical with daturic) acid, m. p. 57·5°, has been isolated from lumbang oil. Cryst. salts of Pb, Li, Sr, and U are described; Rb, Na, and K give cryst. hydrogen salts, as well as normal salts, the alcoholic solutions of which gelatinise on cooling. E. LEWKOWITSCH.

Micro-analytical determination of certain hydroxy-acids by means of the photo-electric cell. A. S. WILLIAMS, R. H. MULLER, and J. B. NIEDERL (Mikrochem., 1931, 9, 269—287).—The method is based on the colour produced by the reaction of the acids with a feebly acid solution of $FeCl_3$, the light intensity of the resulting coloured solution being measured by means of the photo-electric colorimeter. Good results are obtained with solutions containing more than 0 1—0·3 mg. of lactic, citric, tartaric, or salicylic acid. A. R. POWELL.

Reagent concentration in the Walden inversion. W. D. BANCROFT and H. L. DAVIS (J. Physical Chem., 1931, 35, 1253—1269).—Mainly a discussion. The rate of conversion of *l*-chlorosuccinic acid into malic acid is proportional to the [OH′], the final products being mixtures of *d*- and *l*-malic acids; alkaline solutions favour the preponderance of *d*-acid to an extent approx. proportional to the alkalinity. Good yields of this acid can be prepared by keeping a warm solution of chlorosuccinic acid alkaline to phenolphthalein. In the hydrolysis of *l*-bromosuccinic acid less than 2·7 equivs. of Ag_2O per mol. of acid give a product containing excess of *l*-malic acid, whilst larger proportions give more than 50% of *d*-acid. A mechanism is outlined whereby acid hydrolysis of the lactone gives a malic acid of the same rotation and configuration as the original chlorosuccinic acid and alkaline hydrolysis results in a Walden inversion. L. S. THEOBALD.

Determination of mixtures of isomeric unsaturated compounds. III. Review of the iodometric method and a new bromometric method. R. P. LINSTEAD and J. T. W. MANN (J.C.S., 1931, 723—725).—The iodometric method (A., 1927, 1167) is inapplicable to itaconic and mesaconic acids owing to slowness of addition. The Br addition of these acids, obtained by using a 0·05*N*-Br solution in 40% aq. KBr, proceeds at a measurable rate, the Br remaining after 10 min. being determined by treatment with KI and titration with $Na_2S_2O_3$. G. DISCOMBE.

Olefinic acids. IV. Two types of tautomerism of itaconic acids. Connexion between configurational and tautomeric changes in alkali. R. P. LINSTEAD and J. T. W. MANN (J.C.S., 1931, 726—740).—Citraconic, mesaconic, and itaconic acids on heating with alkali at 105° yield the equilibrium mixture containing 15% of citraconic (*cis*-αβ-), 69% of mesaconic (*trans*-αβ-), and 16% of itaconic (βγ-) acid, the configurational change proceeding through the βγ-isomeride. The γ-methyl-γ-ethyl-itaconic and -aticonic acids can be interconverted slowly by boiling with 25—33% alkali, the equilibrium mixture containing 28·4% of itaconic acid. The slow equilibration of the itaconic–aticonic system is attributed to steric hindrance. G. DISCOMBE.

Olefinic acids. V. Influence of bases on the condensation of aldehydes and malonic acid; Knoevenagel reaction. S. E. BOXER and R. P. LINSTEAD (J.C.S., 1931, 740—751).—The reaction product from *n*-butaldehyde and malonic acid in presence of organic bases at room temp. and then at 100° depends on the base used (cf. A., 1926, 1245; 1928, 1214; 1929, 1271, 1275). Δ^{α}-*n*-Hexenoic acid is obtained when pyridine is used in mol. proportion, whilst triethanolamine in small quantity gives nearly pure Δ^{β}-acid, m. p. 12°, b. p. 109°/15 mm., d^{17} 0·9600, n_D^{17} 1·4402, other bases giving a mixture of the two, the Δ^{β}-acid also being obtained by the hydrolysis of *Et butylidenemalonate*, b. p. 144°/25 mm., $d_4^{19.3}$ 1·0029, from Et malonate, *n*-butaldehyde, and Ac_2O. From

propaldehyde impure Δ^{β}-*n*-pentenoic acid, and from *iso*valeraldehyde Δ^{β}-*iso*heptenoic acid, is obtained by the use of triethanolamine. The condensation of *cyclo*pentanone with Et cyanoacetate in presence of triethanolamine proceeds less rapidly than when piperidine is used. G. DISCOMBE.

Chloride and other derivatives of dichloromaleic acid. "Kauder's tetrachloride." L. LEDER (J. pr. Chem., 1931, [ii], **130**, 255—288).—Chlorination of succinyl chloride in presence of Fe powder at 145° gives a little dichloromaleic anhydride and 81% of dichloromaleyl chloride (I). Refractometric data indicate that preps. of I exist mainly in (*a*) *sym.*- or (*b*) *asym.*-forms, which with NH_2Ph in C_6H_6 give colourless, m. p. 193°, and yellow, m. p. 170°, *dianilides*, respectively; *b* is converted into *a* by treatment with $AlCl_3$. The yellow dianilide is hydrolysed more readily by dil. alkali than the colourless form. Both forms of I react almost quantitatively with NH_2Ph, but only one (probably *a*) with MeOH, in C_6H_6. Dichloromaleic anhydride and NH_2Ph in $CHCl_3$ afford *dichloromale*-N-*phenylimide* (or the corresponding *anil*), m. p. 148° (decomp.), whilst an *isomeride*, m. p. 202°, is obtained from I and the yellow dianilide (not from the colourless form) at 140°. MgMeBr and I give mainly a *substance* (probably the lactone of $\alpha\beta$-dichloro-γ-hydroxy-γ-methyl-Δ^{α}-pentenoic acid), m. p. 81° (not affected by O_3), and a small amount of a liquid *isomeride*. *Dyes* are prepared from I and 1-amino-, 1-amino-4-methyl-, and 1-amino-4-methoxy-anthraquinones; the shades on cotton are recorded.

Treatment of I with PCl_5 at 230° gives unchanged material and hexachloroethane. No tetrachloride of dichloromaleic acid is formed, nor could any be obtained by Kauder's procedure (A., 1885, 651). The m. p. (41·5°) of Kauder's tetrachloride may be the transition point (45°) of rhombic hexachloroethane.

Succinic anhydride is obtained in 92% yield when $COCl_2$ is passed through the acid at 210°.

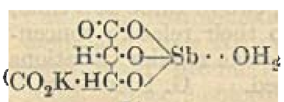
H. BURTON.

Decarboxylation of dihydroxymaleic acid. W. FRANKE and G. BRATHUHN (Annalen, 1931, **487**, 1—52).—The spontaneous decomp. of dihydroxymaleic acid, $[CO_2H\cdot C(OH)\colon]_2 \longrightarrow OH\cdot CH_2\cdot CHO + 2CO_2$, is more rapid in buffered than in non-buffered aq. solution, but its velocity bears the same relation to p_H in both cases, being greatest at p_H 2·7, corresponding with the mono-H salt This suggestion that the univalent ion $(C_4H_3O_6)'$ is the actively decomp. constituent is confirmed by measurements of the relation between the velocity coeff. of decarboxylation and the degree of dissociation of the free acid, its Li H salt, and Li salt solutions of varying p_H; these show a proportionality between the velocity coeff. of decarboxylation and concentration of the primary ion, and also indicate decomp. of the free acid itself at 1/40 the velocity for the ion. The ratio of the two ionisation coeffs. of the acid is that of a *trans*-acid of this series.

H_3BO_3 exerts a stabilising action proportional both to its own concentration and that of the dihydroxy-acid. A kinetic investigation similar to the above indicates the formation of an equimol. complex for which a structure is suggested. Minute traces of Fe are without appreciable influence on decarboxylation, but larger amounts catalyse the decomp. The effect is a max. at p_H 4—5, and is not directly proportional to the Fe concentration. The autocatalytic stage is suppressed, due, it is suggested, to the effect of Fe on the keto-enol equilibrium. The catalytic effect is also shown by other metals of the Fe group, Cu, Zn, and Al, but only slightly by noble metals in colloidal form; in the case of Cu the activity increases continuously with p_H.

The velocity of decomp. is generally less in org. solvents due to depression of formation of the active ion, and the inverse proportionality of $-\log k$ (for decarboxylation) to the dissociation const. of the solvent is established for H_2O, MeCN, MeOH, EtOH, and $COMe_2$. The catalytic action of weak bases in aq. solution does not appear to be related to the strength of the base. There is a marked decrease in activity in the series $NH_2Ph > NHMePh > NMe_2Ph$. In all cases an ill-defined max. occurs at the mono-H salt, further additions of base leading to a suppression of the decomp. The effect is more marked in non-aq. solvents in which the active salt might be expected to be more stable. H. A. PIGGOTT.

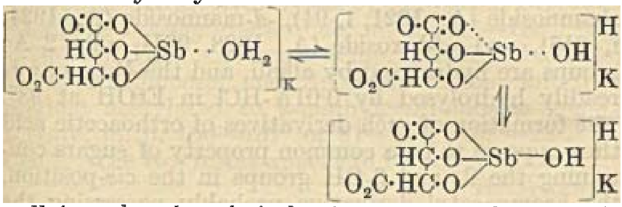
Constitution of tartar emetic. H. REIHLEN and E. HEZEL (Annalen, 1931, **487**, 213—224).—F.-p. determinations show that Na antimonyl tartrate, and, by analogy, tartar emetic (too insoluble for measurement), are not associated in H_2O. α-*Phenylethylammonium* and p-*nitro*-α-*phenylethylammonium antimonyl tartrate* prepared from the Ba salt ($+2H_2O$) (both non-resolvable) crystallise without H_2O of crystallisation. The H_2O in other salts is, therefore, not constitutive. Tartar emetic contains one CO_2H group, but not the other, bound to Sb, because it is only weakly acidic, but is very easily esterified. The formula $CO_2K\cdot CH(OH)\cdot CH(OH)\cdot CO_2SbO$ is incorrect (because the OH groups must be involved in the complex), as also is $CO_2K\cdot CH(OH)\cdot CH\cdot CO_2Sb\cdot OH$ (because neither malic nor mesotartaric acid forms a similar compound).



(I.)

Formula I, shown to be unstrained by models, is supported by the replacement of the H_2O by pyridine in Ba antimonyl tartrate, which probably exists as acidic $[C_5H_5N\cdot\cdot SbC_4H_2O_6]H$ in the solid state, and as the salt $[H_2O\cdot\cdot SbC_4H_2O_6]H,C_5H_5N$ in solution (because the rotation increases rapidly with dilution to that of tartar emetic). The existence of the auxiliary valency in I is supported by the loss of H_2O from the Na salt in vac. at room temp., but from the K salt only at 120°, owing to the larger ionic vol. of the cation, and the free acid exists only in the anhyd. form. I is further supported by the fact that $0{\cdot}1M$-K mesotartrate can dissolve only 0·7 atom of Sb at room temp., that no antimonyl compound can be isolated from this solution, and that $M[\alpha]_D$ for $0{\cdot}1N$-tartar emetic solution is 7·5—8·7 times that of $0{\cdot}2N$-Na K tartrate solution. Unlike the corresponding B and As compounds, tartar emetic is only slightly hydrolysed to $HK[C_4O_6H_4] + Sb(OH)_3$, but its acid reaction (a

0·2N solution has p_H 4·2 at 16°) is due to intramolecular hydrolysis":



dl-Acetyl-α-phenylethylamine, m. p. 75° (not 57°, A., 1894, i, 579), b. p. 176°/15 mm., gives the p-*nitro*-derivative, m. p. 122° (oxidised by $KMnO_4$ to p-NO_2·C_6H_4·CO_2H), which is slowly hydrolysed to dl-p-*nitro-α-phenylethylamine*, m. p. 27°, b. p. 162°/14 mm. [*hydrochloride*; *sulphate* (+2H_2O cryst.)], non-resolvable as hydrogen tartrate or malate.

R. S. CAHN.

Methylose series. I. E. VOTOČEK and S. MALACHTA (Coll. Czech. Chem. Comm., 1931, **3**, 265—275).—The product of the action of aq. HCN solution on Ba δ-ketorhamnonate consists of two salts differing in solubility in H_2O. The less sol. one (56%) affords the *dilactone* of *α-methyltetrahydroxyadipic acid* (I), m. p. 196° (decomp.), $[\alpha]_D$ −182° to −107·6°, (*diphenylhydrazide*, m. p. 187—188°). The more sol. salt (21·6%) gives a *dilactone* isomeric with I, +½H_2O, m. p. 166—167°, $[\alpha]_D$ −154°·1 to −75·7°; anhyd. *form*, m. p. 172°, $[\alpha]_D$ −162·8° to −75·6° (*bisphenylhydrazone*, m. p. 236—237°). Crystallographic measurements of the forms of the dilactones and of δ-ketorhamnonolactone have been made.

F. R. SHAW.

Use of 2 : 4-dinitrophenylhydrazine as reagent for carbonyl compounds. O. L. BRADY (J.C.S., 1931, 756—759; cf. A., 1926, 394).—The alcoholic solution of the carbonyl compound is added to the mixture of 1 g. of reagent in 2 c.c. of conc. H_2SO_4, and 15 c.c. of EtOH are added. The dinitrophenylhydrazones of cyclo*heptanone*, m. p. 148°, cyclo-*octanone*, m. p. 163°, cyclo*pentadecanone*, m. p. 105°, *crotonaldehyde*, m. p. 190°, *glyoxylic acid*, m. p. 190° (decomp.), *anisaldehyde*, m. p. 250°, m-*hydroxybenzaldehyde*, m. p. 241°, *cuminaldehyde*, m. p. 241°, *piperonal*, m. p. 265° (decomp.), p-*nitrobenzaldehyde*, m. p. 320°, *phenylacetaldehyde*, m. p. 110°, *cinnamaldehyde*, m. p. 248°, *camphor*, m. p. 175°, *fenchone*, m. p. 140° after sintering at 125°, *pulegone*, m. p. 142°, *ionone*, m. p. 125—128°, and 1-(2′ : 4′-*dinitrophenyl*)-3 : 5-*dimethylpyrazole*, m. p. 122°, from acetylacetone, and 1-(2′ : 4′-*dinitrophenyl*)-3(or 5)-*phenyl*-5(or 3)-*methylpyrazole*, m. p. 151°, from benzoylacetone are described.

G. DISCOMBE.

Formaldehyde condensation by J. Blanc's method. Intermediate stage of formation of bakelite from phenol and formaldehyde. N. N. VOROSCHCOV and E. N. IURUIGINA (J. Gen. Chem. Russ., 1931, **1**, 49—64).—The action of H·CHO on HCl at low temp. gives an optimum yield of dichlorodimethyl ether. Addition of $ZnCl_2$ and C_6H_6 and heating to 60° under various conditions gives CH_2PhCl, p-xylylene dichloride, phenylchlorotolylmethane, and dichloroditolylmethane. Pyridine and 1-nitronaphthalene in place of C_6H_6 do not react. Formation of pp'-dihydroxydiphenylmethane is the intermediate stage in "bakelite" formation using PhOH in place of C_6H_6. Other acids may also be used, H ions having a catalytic action.

E. B. UVAROV.

Course of organic chemical reactions. II. Intermolecular and intramolecular reactivity of hydrazonium compounds. A. WOHL [with A. PRANSCHKE] (Ber., 1931, **64**, [*B*], 1381—1389).—β-Chloropropaldehyde diethylacetal, N_2H_4,H_2O, NaI, and EtOH at 100° yield β-*hydrazinopropaldehyde diethylacetal*, b. p. 73°/0·4 mm. (*H oxalate*, m. p. 122°), and NN-*di-γγ-diethoxy*-n-*propylhydrazine*, b. p. 125°/0·7 mm. (*H oxalate*). Treatment of the hydrazino-acetal with Me_2SO_4 and aq. KOH affords β-N^{α}-*methylhydrazinopropaldehyde diethylacetal*, NH_2·NMe·CH_2·CH_2·CH(OEt)$_2$, b. p. 55—56°/0·1 mm. (*H oxalate*), transformed by MeI and KOH into the corresponding *methiodide*, m. p. 91°, which yields NH_3 when reduced with Na and EtOH. Methylation is preferably effected with MeI in Et_2O. Treatment of the methiodide with AgCl yields the corresponding, very hygroscopic *methochloride*, analysed as the *chloroplatinate* $C_9H_{24}O_2N_2Cl_6Pt$. The methochloride is hydrolysed by HCl in H_2O to the very hygroscopic β-*methylhydrazinopropaldehyde methochloride*, identified as the corresponding *chloroplatinate*, m. p. 197—198°, which passes in acid solution into the *chloroplatinate*, $C_{10}H_{24}N_4Cl_6Pt$, m. p. 191—195° (decomp.). β-*Dimethylhydrazinopropaldehyde diethylacetal hydrogen oxalate*, m. p. 102°, from the iodide, Ag oxalate, and oxalic acid, passes in oxalic acid solution into (?) the *H oxalate* of the *semiacetal*, m. p. 82—86°. If the acidity of the solution is diminished by gradual addition of $CaCO_3$, *dimethylpyrazoline H oxalate*, m. p. 146°, is formed. Pyrazoline is methylated with MeI and the dimethylpyrazoline is identified as the H oxalate, m. p. 146—147° (*v.s.*), *picrate*, m. p. 154—155°, *chloroplatinate*, m. p. 76—78°, and *chloroaurate*, m. p. 152—153°. The H oxalate of the quaternary acetalised base, in presence of $CaCO_3$, does not give a hydrazone with PhCHO or p-nitrobenzaldehyde. The trimethylhydrazino-oxalate behaves similarly.

H. WREN.

Preparation of keten. E. OTT, R. SCHROTER, and K. PACKENDORFF (J. pr. Chem., 1931, [ii], **130**, 177—179).—An apparatus for the prep. of keten in yields of about 50% is described; $COMe_2$ vapour is passed over a hot W filament.

H. BURTON.

Action of chloroacetone on dimagnesium dibromoacetylene. S. A. ZABOEV (J. Gen. Chem. Russ., 1931, **1**, 143—149).—The product of the reaction is an *oil*, d_4^0 1·277, having the structure [:C·CMe(OH)·CH_2Cl]$_2$. Prolonged action of aq. Ag_2O gives the corresponding *hydroxy*-derivative, m. p. 115—118°.

E. B. UVAROV.

Oximes. J. V. DUBSKÝ, F. BRYCHTA, and M. KURAS (Publ. Fac. Sci. Univ. Masaryk, 1930, No. 129, 3—26).—The Cu salts of acetonedicarboxylic acid, oximinoacetone, dioximinoacetone, trinitrosopropane, and aminoacetoxime are green, that of diaminoacetoxime is black, and of phenylmethylpyrazolone brown. Dioximinoacetone gives a blue colour with the smallest traces of Fe$^{\cdot\cdot}$; its Ni salt is brownish-black. Trinitrosopropane has a black Fe$^{\cdot\cdot\cdot}$ salt, and brown Ni and Co salts. The oxime of

acetonedicarboxylic acid gives a green Co salt and an orange Pb salt. Phenylmethylnitrosopyrazolone forms a greenish-blue Fe'' salt. R. TRUSZKOWSKI.

Reasons for the difference in the behaviour of analogous compounds of bivalent cobalt, nickel, and copper containing diacetyldioxime. E. THILO and H. HEILBORN (Ber., 1931, 64, [B], 1441—1455).—The action of dimethylglyoxime on ignited $CoCl_2$ in anhyd. $COMe_2$ yields a red salt which gradually, particularly in presence of a little H_2O, passes into Feigl's green salt. Since the red compound vigorously evolves HCl with conc. H_2SO_4, whereas the green compound does not, the constitutions $[DH_2CoH_2D]Cl_2$ and $[(DH_2)_2CoCl_2]$ are respectively ascribed to them [DH_2=OH·N:CMe·CMe:N·OH]. In $COMe_2$ the equilibria exist $CoCl_2+2DH_2 \rightleftharpoons$ red salt$\longrightarrow$green salt. The precipitation of unchanged green halide from solution by conc. H_2SO_4 and the displacement of the Br atoms of Feigl's bromide into the outer sphere by ethylenediamine are regarded as criteria of the *trans*-structure of the salt. Attempts to prepare the base corresponding with Feigl's salts were only partly successful.

The tendency of the addition of acids to $Ni(DH)_2$ [DH=OH·N:CMe·CMe:N·O⁻] according to the scheme $Ni(DH)_2+2HX \longrightarrow [Ni(DH_2)_2]X_2$ diminishes with decreasing strength of acid. Similar addition occurs only when the dissociation const. of the acid is equal to or greater than 5×10^{-2}. The differing behaviour of Ni and Co appears to lie in the ability of the former to give a stable $Ni(DH)_2$, since it is co-ordinatively quadrivalent even in the salt-like derivatives of this compound, whereas Co is co-ordinatively sexavalent in all stable compounds with DH_2, and hence does not yield a stable cobalt diacetyldioxime in which it must be co-ordinatively quadrivalent. In $COMe_2$, $Cu(DH)_2$ yields only the two green *salts* DH_2CuSO_4 and $DH_2Cu(PO_4H_2)_2,0{\cdot}5H_2O$; other acids do not react or yield the corresponding salts free from DH_2. Only those salt-like DH_2 compounds of Cu are stable which contain 1 mol. of org. component; the tenacity of DH_2 is less towards Cu than towards Ni. Gaseous HCl converts Ni chloromethylglyoxime into $C_3H_5O_2N_2ClNiCl_2$ and chloromethylglyoxime. The following *salts* are described: $C_8H_{18}O_4N_4Ni(SO_4)_2$; $C_4H_8O_2N_2NiSO_4,2H_2O$ and the anhyd. compound; $C_4H_8O_2N_2NiC_2O_4$ and the dihydrate; $C_4H_{12}O_2N_2Ni(PO_4)_2$. All the Ni compounds are very sensitive to H_2O, moist air, EtOH, NH_2Ph, etc., giving red Ni dimethylglyoxime. They react immediately with gaseous NH_3 giving NH_4 salts and $Ni(DH)_2$ or $DNi(NH_3)_2$. H. WREN.

Historical resume of the chemistry of oses particularly since the time of Emil Fischer. G. BERTRAND (Bull. Soc. chim., 1931, [iv], 49, 627—650).

Acetyl monoses. VII. Isomeric triacetyl-methyl-*d*-ribosides. P. A. LEVENE and R. S. TIPSON (J. Biol. Chem., 1931, 92, 109—115).—Ribose is converted by Ac_2O and pyridine at 0° into *tetra-acetylribose*, m. p. 110°, $[\alpha]^{24}$ −52·0° in $CHCl_3$, converted by HBr in AcOH into *triacetylribosidyl bromide*, m. p. 96°, $[\alpha]^{25}$ −209·3° in $CHCl_3$. This is converted by MeOH in the presence of Ag_2CO_3 into *γ-triacetylmethyl-*d*-riboside*, m. p. 77—78°, $[\alpha]^{24}$ +2·4° in $CHCl_3$, in which, as in the corresponding γ-triacetylmethyl-*l*-rhamnoside (A., 1921, i, 94), -*d*-mannoside (A., 1924, i, 615), and -*d*-lyxoside (A., 1928, 991), only 2 Ac groups are hydrolysed by alkali, and the Me group is readily hydrolysed by 0·01*N*-HCl in EtOH at 98°. The formation of such derivatives of orthoacetic acid thus appears to be a common property of sugars containing the 2- and 3-OH groups in the *cis*-position, the bromoacetyl derivative probably possessing the α-configuration. Methylriboside with Ac_2O and pyridine affords the normal Ac_3 derivative, b. p. 120°/0·05 mm., $[\alpha]_D^{26}$ −17·4° in $CHCl_3$, stable under the above conditions of HCl hydrolysis. J. W. BAKER.

Rotatory powers of some sugar-hydrazones in relation to the stereochemical structure of the α-carbon atom. E. VOTOČEK, F. VALENTIN, and O. LEMINGER (Coll. Czech. Chem. Comm., 1931, 3, 250—264).—The rotations of the following phenylbenzylhydrazones in MeOH are in agreement with the Hudson rule: d-*arabinose*, m. p. 173°, *l*-arabinose, *d*-xylose, *d*-lyxose, *l*-rhamnose, rhodeose, fucose, *d*-mannose, 1-*α-rhamnohexose*, m. p. 183—184°, and *d*-α-glucoheptose. On the other hand, ethyl-, butyl-, and di-phenylhydrazones of different sugars show no regularity in the rotations. *Phenyl*-p-*chlorobenzylhydrazine*, m. p. 44° (*hydrochloride*), affords the following *hydrazones* (the figures in parentheses are the final values of $[\alpha]_D$ in MeOH and are in agreement with the Hudson rule): *p*-chlorobenzaldehyde, m. p. 109°; $COMe_2$, m. p. 68°; furfuraldehyde, m. p. 101—102°; PhCHO, m. p. 99°; *l*-arabinose, m. p. 172° (−6·4°); *d*-arabinose (+2·8°); *d*-xylose, $0{\cdot}5H_2O$, m. p. about 80° (−21·1°); *d*-lyxose, m. p. 134—135° (+29·2°); *d*-ribose, m. p. 144—145° (−17·2°); *l*-rhamnose, m. p. 118—119°; *d*-fucose, m. p. 153° (+11·8°); *d*-glucose, m. p. 155—156° (−13·2°); *d*-mannose, m. p. 167—168° (+12·9°); *d*-galactose, $0{\cdot}5H_2O$, m. p. 161° (−9·8°); *l*-α-rhamnohexose, m. p. 172° (+10·0°); and *d*-α-glucoheptose, m. p. 158—159° (−13·5°). The rotations of the following *dibenzylhydrazones* in MeOH also agree with the rule: *l*-arabinose, m. p. 135° (−1·3°); *d*-arabinose, m. p. 133—135° (+1·0°); *d*-ribose, m. p. 101—103° (−15·2°); *d*-xylose, m. p. 130° (−8·6°); *d*-lyxose, m. p. 115—118° (+27·7°); *l*-rhamnose, m. p. 121—123° (−10·3°); rhodeose, m. p. 162·5° (0°); fucose, m. p. 162·5° (0°); *d*-glucose, m. p. 99—101° (−1·0°); *d*-mannose, m. p. 156—157° (+12·9°); *d*-galactose, m. p. 151—152° (−4·3°); *l*-α-rhamnohexose, m. p. 164° (+2·4°); and *d*-α-glucoheptose, m. p. 140—141° (−15·6°). The conclusion is reached that the benzyl group enhances the rotation so that the configuration of the rest of the sugar chain has no influence on the sign of the rotation of the hydrazone.

F. R. SHAW.

Solubility of carbohydrates in dioxan and applicability of the solutions. B. HELFERICH and H. MASAMUNE (Ber., 1931, 64, [B], 1257—1260).—The solubilities of α- and β-glucose, lævulose, galactose, α- and β-methylglucoside, mannitol, sucrose, and β-phenylglucoside in dioxan at b. p., 20°, and 12—16° are recorded. Acetobromoglucose, β-methylglucoside, and Ag_2O in dioxan at 100° followed by treatment of

the product with Ac_2O in pyridine yield *ethylidene-β-methyl-d-glucoside diacetate*, m. p. 175—177°, $[\alpha]_D^{19}$ −65·8° in $CHCl_3$, hydrolysed by MeONa in $CHCl_3$ to *ethylidene-β-methyl-d-glucoside*, m. p. 182—183°, $[\alpha]_D^{19}$ −79·3° in H_2O. At room temp. β-methylglucoside, acetobromoglucose, and Ag_2O in dioxan afford a product acetylated to β-methylgentiobioside hepta-acetate, m. p. 150—151° or 81—83°, $[\alpha]_D^{18}$ −23·7° in $CHCl_3$; the two forms appear to be polymorphic.
H. WREN.

Dextrose. H. HIBBERT (Science, 1931, **73**, 500—501).—The structures which follow from the assumption that the normal C·O·C valency angle is 32° are worked out.
L. S. THEOBALD.

Microchemical determination of dextrose in sugar solutions and in urine. C. CIMERMAN and P. WENGER (Mikrochem., 1931, **9**, 295—299).—The sugar solution is added to a known amount of a boiling alkaline solution of Cu tartrate which is then centrifuged and a drop of the clear solution tested for the presence of Cu with filter-paper impregnated with guaiacum and a drop of 0·5% KCN solution. More of the sugar solution is added and boiling and centrifuging are repeated until no Cu test is obtained on the paper.
A. R. POWELL.

Action of alkali molybdates on dextrose. E. DARMOIS and J. MARTIN (J. Chim. phys., 1931, **28**, 149—162).—Dextrose combines with molybdates of the type $NaHMoO_4$, giving compounds of the type $(2C_6H_{12}O_6,MoO_3)Na$. Polarimetric investigations of the kinetics of the reaction indicate that it is unimol. with respect to dextrose. Both $H^{\cdot}$ and MoO_4'' catalyse the mutarotation of dextrose. Mutarotation experiments at 0° suggest the presence of a small proportion of a labile form of dextrose in equilibrium with the stable forms. The labile form probably combines with molybdates.
E. S. HEDGES.

Derivatives of 6-methoxy-*d*-glucose. B. HELFERICH and E. GÜNTHER (Ber., 1931, **64**, [*B*], 1276—1280).—Fresh investigations result in the isolation of 6-methoxy-*d*-glucosazone, m. p. 184—187° (corr., decomp.), $[\alpha]_D^{18}$ −69° in EtOH, which is certainly not identical with 3-methoxyglucosazone (cf. A., 1929, 1044). 6-Methoxy-*d*-glucose is transformed by NaOAc and Ac_2O into β-6-*methoxy*-d-*glucose tetra-acetate*, m. p. 91—98° (corr.), $[\alpha]_D^{21}$ +20·9° in $CHCl_3$ (depresses the f. p. of the corresponding 3-OMe-compound), and α-6-*methoxy*-d-*glucose tetra-acetate*, m. p. 119—120° (corr.), $[\alpha]_D^{21}$ +111·8° in $CHCl_3$. The β-compound is transformed through the acetobromo-derivative into 6-methoxy-β-methylglucoside triacetate, m. p. 107—108°, $[\alpha]_D^{18}$ −12·4° in $CHCl_3$, and thence into 6-methoxy-β-methylglucoside, $[\alpha]_D^{19}$ −26·4° in H_2O.
H. WREN.

Unsaturated reduction products of sugars. XVI. Products of the dismutation of sugars. M. BERGMANN and L. ZERVAS (Ber., 1931, **64**, [*B*], 1434—1438).—Hydroxyglucal tetra-acetate and phenylhydrazine in 50% AcOH give an *acetylated phenylosazone*, $C_{20}H_{22}O_3N_4$, decomp. 205° (corr.), $[\alpha]_D^{17}$ −98·6° in pyridine, also obtained from hydroxygalactal tetra-acetate and hydrolysed by NaOMe in $CHCl_3$ to the *phenylosazone* $C_{18}H_{22}O_2N_4$, decomp. 183° (corr.), $[\alpha]_D^{17}$ −159·8° in pyridine. Hydroxyglucal tetra-acetate is converted by NH_3 in MeOH and subsequently by phenylhydrazine into a *phenylosazone*, $C_{18}H_{22}O_3N_4$ or $C_{18}H_{20}O_3N_4$, decomp. 187° (corr.) (also derived after hydrolysis with NaOH), which differs from the osazone derived similarly from hydroxygalactal tetra-acetate. Hydroxycellobial acetate affords an *osazone*, decomp. 173°. Hydrolactal acetate yields a similar product. Other osazones are obtained if hydrolysis precedes treatment with phenylhydrazine.
H. WREN.

Thiosugars and their derivatives. XVI. Walden inversion during fission of α-alkylglucothiosides by mercuric chloride. W. SCHNEIDER and W. SPECHT (Ber., 1931, **64**, [*B*], 1319—1320; cf. this vol., 73).—Observation of the sp. rotation of α-methyl-, α-ethyl-, and α-propyl-glucothioside during fission under the influence of $HgCl_2$ shows that a min. value is passed through, after which a gradual rise to approx. the value of the equilibrium dextrose mixture is noted. Fission is therefore accompanied by a Walden inversion at the 1-C atom of the sugar with formation of β-glucose.
H. WREN.

Thiosugars and their derivatives. XVII. Properties of β-glucothiose tetra-acetate. W. SCHNEIDER and A. BANSA (Ber., 1931, **64**, [*B*], 1321—1324; cf. this vol., 73).—Octa-acetyl-ββ-diglucosyl disulphide, m. p. 144°, $[\alpha]_D^{20}$ −185° in $PhNO_2$, when treated with Al–Hg by a modification of Wrede's method gives glucothiose tetra-acetate, $C_6H_7O_5Ac_4$·SH, m. p. 113—114° (lit. 75°), $[\alpha]_D^{20}$ −2·14° in *s*-tetrachloroethane; mutarotation is observed in 90% EtOH, pyridine, and dioxan. Oxidation with I transforms it smoothly into octa-acetyl-ββ-diglucosyl disulphide, whilst Ac_2O in pyridine and diazomethane afford β-glucothiose penta-acetate, m. p. 121°, and β-methylglucothioside tetra-acetate, m. p. 94—95°. The *compound*, $C_6H_7O_5Ac_4$·S·HgCl, m. p. 155°, $[\alpha]_D^{20}$ −64·81° in *s*-tetrachloroethane, and β-2 : 3 : 4 : 6-*tetra-acetyl*-1-*benzoylglucothiose*, m. p. 126°, $[\alpha]_D^{20}$ −12·44° in *s*-tetrachloroethane, are described.
H. WREN.

Structure of carbohydrates and their optical rotatory power. VI. 4-Glucosidomannose and its methylated derivatives. W. N. HAWORTH, E. L. HIRST, and H. R. L. STREIGHT (J.C.S., 1931, 1349—1354).—Structural rigidity of derivatives of 4-glucosidomannose on methylation is demonstrated. Complete methylation of 4-β-glucosidomannonic acid yields *methyl octamethyl*-4-β-*glucosidomannonate*, m. p. 118°, $[\alpha]_D^{21}$ −19·5° in $CHCl_3$, −3° in C_6H_6, which on hydrolysis yields 2 : 3 : 5 : 6-tetramethyl-γ-mannonolactone and 2 : 3 : 4 : 6-tetramethylglucopyranose. Similarly methylation of 4-β-glucosido-α-methylmannoside gives *heptamethyl*-4-β-*glucosido*-α-*methylmannoside*, b. p. 177—180°/0·01 mm. (bath temp.), $[\alpha]_D^{21}$ +28° in H_2O, +74° in $COMe_2$, hydrolysed to 2 : 3 : 4 : 6-tetramethylglucopyranose and 2 : 3 : 6-trimethylmannose (*anilide*, m. p. 127—128°). The results provide further evidence of absence of isomeric change during the methylation of α-methylmannoside.
D. A. FAIRWEATHER.

Structure of carbohydrates and their optical rotatory power. VII. 4-Galactosidomannose and its methylated derivatives. W. N. HAWORTH,

E. L. Hirst, and M. M. T. Plant (J.C.S., 1931, 1354—1358).—Evidence complementary to that in the preceding abstract is furnished on the behaviour of 4-galactosidomannose. Methylation of 4-β-galactosido-α-methylmannoside gives *heptamethyl-4-β-galactosido-α-methylmannoside*, b. p. about 170°/0·02 mm., $[\alpha]_D^{20}$ +41° in C_6H_6, +63° in Et_2O, hydrolysed to 2 : 3 : 4 : 6-tetramethylgalactopyranose and 2 : 3 : 6-trimethylmannose. *Methyl octamethylgalactosidomannonate*, prepared from 4-β-*galactosidomannonic acid* (Ca salt), gives on hydrolysis 2 : 3 : 4 : 6-tetramethylgalactose and tetramethyl-γ-mannonolactone. The behaviour of 4-galactosidomannose is therefore exactly analogous with that of its epimeride lactose.

D. A. Fairweather.

Sugars of human milk : gynolactose and allolactose. M. Polonovski and A. Lespagnol (Compt. rend., 1931, 192, 1319—1320).—*Gynolactose*, m. p. 205°, $[\alpha]_D$ 27° in water, and *allolactose*, m. p. 165° (*phenylosazone*, m. p. 172°), are present in human milk-serum, and are separated by repeated fractional crystallisation from H_2O. The former is feebly reducing, does not show mutarotation, and does not form an osazone in absence of free acid. The latter is similar to lactose in reducing properties, and shows rapid mutarotation. Both are hydrolysed by dil. acids, the former more readily, to dextrose and galactose.

H. A. Piggott.

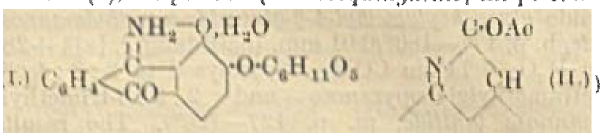
Phloridzin. R. Weidenhagen (Z. Ver. deut. Zucker-Ind., 1931, 81, 125—129).—The sugar component of phloridzin is β-dextrose. Phloridzin and phlorin are hydrolysed by the β-glucosidase of emulsin, but not by the β-*h*-fructosidase of yeast (cf. A., 1930, 1316). Cryst. dextrose was obtained after hydrolysis of phloridzin with HCl.

J. H. Lane.

Preparation of the cyanidin from quercetin. Y. Asahina and M. Inubuse (Ber., 1931, 64, [B], 1256—1257).—When treated with Na-Hg in alkaline solution, quercetin affords only a trace of the carbinol base of the cyanidin. Its rhamnoglucoside, rutin (from *Sophora japonica*), is transformed by reduction and treatment of the product with HCl into the *cyanidin chloride*, $C_{15}H_{11}O_6Cl,H_2O$ (*compound* $C_{15}H_{11}O_6Cl,FeCl_3$).

H. Wren.

Structure of nitrogenous derivatives of hydroxyanthraquinone glucosides. A. Müller (Ber., 1931, 64, [B], 1410—1431).—Alizarin or its diacetate is converted by NH_3 in MeOH into the *salt* $C_{14}H_7O_4(NH_4)$, decomp. by org. acids. Alizarin-glucoside tetra-acetate is transformed into the *imonium* salt of 1-hydroxy-2-glucosoxyanthraquinone-9-imine (I), m. p. 199° (also *sesquihydrate*, m. p. 198—



199°, and *dihydrate*, m. p. 197—198°), sol. without change in AcOH. It is converted by Ac_2O and NaOAc at 100° into (?)O-*acetyl-2-acetoglucosoxyanthrapyridone* (II), m. p. 292° (decomp.), transformed by H_2SO_4–AcOH into 1 : 9 : 9-*triacetoxy-2-acetoglucosoxyanthrone*, m. p. 153—154° after softening at 150°, whereas treatment with Ac_2O in anhyd. pyridine affords the *imonium* salt of 1-*acetoxy-2-acetoglucosoxyanthraquinone-9-imine*, m. p. 218°, stable to cold formic acid, but converted by the boiling acid into acetylacetoglucosylalizarin, m. p. 195—196°, and by NaOH in EtOH into alizaringlucoside. With Ac_2O and NaOAc at 100° or with Ac_2O and pyridine, the imonium salt yields the corresponding N-*acetyl* derivative $C_{32}H_{31}O_{14}N$, m. p. 218°, hydrolysed by boiling formic acid or NaOH to acetylacetoglucosylalizarin or the free glucoside respectively.

Acetoglucosylalizarin and NH_2Me in EtOH afford the *methylammonium* salt $C_{21}H_{23}O_9N$, m. p. 220° (indef.) after becoming discoloured above 207°, immediately decomp. by AcOH to the alizarin-glucoside and converted by Ac_2O and AcONa at 100° or Ac_2O and pyridine at room temp. into the completely acetylated alizaringlucoside. The *dimethylammonium* salt, m. p. 235° after becoming discoloured, behaves similarly. The *imonium* salt of 1-*hydroxy-2-cellobioxyanthraquinone-9-imine*, m. p. 230°, and its *sesquihydrate*, m. p. 230° after softening at 218°, are described. Hydroxy-2-acetoglucosylanthrarufin, MeOH, and NH_3 yield the *imonium* salt $C_{20}H_{19}O_9N,0·5H_2O$, m. p. 237° after softening at 170°. The behaviour of 1-hydroxy-2 : 7-diacetoglucosoxyanthraquinone with NH_3 is described. 2 : 6-Diacetoglucosylrufiopin affords the *imonium* salt $C_{26}H_{27}O_{15}N$, m. p. 213° (also *monohydrate*), whilst acetoglucosylquinalizarin gives the *compound* $C_{20}H_{19}O_{10}N$, acetylated to $C_{34}H_{32}O_{17}N$, m. p. 223° (decomp.); acetocellobiosylquinalizarin yields the *substance* $C_{26}H_{29}O_{15}N,H_2O,1·5H_2O$, m. p. 224°. Acetoglucosylchrysazin affords the *imonium* salt $C_{20}H_{19}O_8N,0·5H_2O$, decomp. about 200° (also +0·5H_2O and 3·5H_2O), converted by dil. HCl into chrysazinglucoside. 1-Hydroxy-8-glucosoxyanthraquinone-9-imonium is converted by Ac_2O in cold pyridine into 1-*hydroxy-8-acetoglucosoxyanthraquinone-9-imonium*, $C_{28}H_{27}O_{12}N$, m. p. 165—166°, transformed by HCl in EtOH into acetoglucosylchrysazin and by Ac_2O and NaOAc at 100° into *compounds* $C_{32}H_{29}O_{13}N$, decomp. about 270°, and $C_{32}H_{30}O_{15}$ or $C_{34}H_{32}O_{16}$, m. p. 212°. The *imonium* salt of 1 : 4(or 1 : 5)-*dihydroxy-8-glucosoxyanthraquinone-9-imine*, $C_{20}H_{19}O_9N,H_2O$, decomp. 200°, is described. The hydrolysis of the following completely glucosylated hydroxyanthraquinones by NH_3 in MeOH is described: acetoglucosylerythro-oxyanthraquinone to 1-*glucosoxyanthraquinone*, m. p. 225—230° after softening at 220°; anthrarufin acetoglucoside to 1 : 5-*diglucosoxyanthraquinone* (+0·5H_2O), m. p. 226—227°; diacetoglucosylhystazarin to 2 : 3-*diglucosoxyanthraquinone* (+H_2O), m. p. 232·5—233° after softening at 228°. 1-*Amino-2-acetoglucosoxyanthraquinone*, m. p. 153°, is obtained from acetoglucosyl bromide, 1-amino-2-hydroxyanthraquinone and Ag_2O in quinoline.

H. Wren.

Synthetic nucleosides. III. Theophylline-*d*-glucodesoside. P. A. Levene and F. Cortese (J. Biol. Chem., 1931, 92, 53—57).—Condensation of 1-bromo-3 : 4 : 6-tribenzoyl-*d*-glucodesose (A., 1923, i, 653) with the Ag salt of theophylline affords the *tribenzoate*, m. p. (indef.) 150—193°, $[\alpha]_D^{20}$ +14·2° in $CHCl_2·CHCl_2$, hydrolysed by $Ba(OH)_2$ in MeOH to

theophylline-d-*glucodesoside*, m. p. 258°, $[\alpha]_D^{18}$ $-26{\cdot}9°$ in H_2O. J. W. BAKER.

Polysaccharides. VIII. Evidence of continuous chains of α-glucopyranose units in starch and glycogen. W. N. HAWORTH and E. G. V. PERCIVAL (J.C.S., 1931, 1342—1349).—Trimethylamylose and trimethylglycogen have been degraded to tetramethylglucopyranose and 2 : 3 : 5 : 6-tetramethyl-γ-gluconolactone. The results are interpreted as evidence of the presence of α-glucopyranose units in each of these polysaccharides.
D. A. FAIRWEATHER.

Plant colloids. XXVII. Differentiation of amylo- and erthyro-substances in starch. M. SAMEC [with E. PEHANI and J. STOJKOVIC] (Kolloidchem. Beih., 1931, **33**, 103—130).—The amylo- and erythro-substances in sols of potato-starch, made by boiling with H_2O under pressure, may be differentiated by adsorption on cotton, the amylo-substance being more strongly adsorbed. The viscosity of aq. amylo-sols increases rapidly with rise of temp., but that of erythro-sols remains unaltered. In $EtOH-H_2O$ mixtures the amylo-sols have a higher relative viscosity than in H_2O, whilst EtOH has little effect on the viscosity of erythro-sols. Whilst the sp. viscosity of amylo-sols is markedly influenced by the addition of neutral salts, that of the erythro-sols is scarcely affected. These observations lead to the conclusion that the amylo-substance is relatively more highly associated, hydrated, and electrically charged than the erythro-substance. The erythro-compounds are more rapidly hydrolysed by acids and by H_2O_2 than the amylo-compounds. The amylopectin fractions obtained by fractional dissolution of starch contain fatty acids. E. S. HEDGES.

Plant colloids. XXVI. Relations between phosphorus and nitrogen in potato- and wheat-starch. M. SAMEC [with W. BENDGER] (Kolloidchem. Beih., 1931, **33**, 95—102).—Determinations of the P and N in potato- and wheat-starch after treatment with dil. acids and alkalis support the view that a substance (phytovitellin), containing both P and N, is combined with the polysaccharide by means of a radical containing P. The linking is looser in wheat- than in potato-starch, and the main portion of both P and N can be extracted. By careful treatment of wheat-starch with alkalis the N-containing substance can be removed preferentially and the P left in the starch becomes electrochemically active, the wheat-starch then becoming similar in properties to potato-starch. Treatment of the residue with hot H_2O causes a substance containing P to be split off, and the starch reverts to the wheat type. Heating the starch with H_2O under pressure at 120° removes substances containing P, the ratio N/P falling to 0·7, whilst the electrical conductivity and active $[H^{\cdot}]$ decrease. The N content is not altered by this treatment. E. S. HEDGES.

Inulin. XI. H. PRINGSHEIM and W. G. HENSEL (Ber., 1931, **64**, [*B*], 1431—1434).—Sufficiently active inulinase could not be obtained from dahlia, but is derived from *Aspergillus niger*; this converts inulin into a new *difructose anhydride acetate*, m. p. 121·5—122°, $[\alpha]_D^{20}$ $+25{\cdot}0°$ in $CHCl_3$. H. WREN.

[Inulin. II. Supposed depolymerisation of inulin.] E. BERNER (Ber., 1931, **64**, [*B*], 1531; cf. this vol., 716).—The values 3700 and 4900 are recorded for the mol. wt. of inulin in freezing formamide. H. WREN.

Polysaccharides. VI. Trimethylcellulose. VII. Isolation of octamethylcellobiose, hendecamethylcellotriose, and a methylated cellodextrin (cellotetrose ?) as crystalline products of the acetolysis of cellulose derivatives. W. N. HAWORTH, E. L. HIRST, and H. A. THOMAS (J.C.S., 1931, 821—824, 824—829).—$COMe_2$-sol. cellulose acetate can be completely methylated by treatment with Me_2SO_4 and 30% aq. NaOH in $COMe_2$ at 55°. Cellulose pulp and finely-ground cellulose on similar methylation in two stages yielded trimethylcellulose, m. p. 215—216°, $[\alpha]_D$ $-10{\cdot}0°$ in $CHCl_3$, mol. wt. 2500 in camphor, different samples varying only in the viscosity of their solutions. Acetolysis of trimethylcellulose at 15°, followed by simultaneous deacetylation and methylation, yields tetramethylmethylglucoside (15%), heptamethyl-β-methylcellobioside (18%), and *decamethyl-β-methylcellotrioside*, b. p. 208—220°/0·02 mm., m. p. 117—118°, $[\alpha]_D$ $-14{\cdot}5°$ in MeOH, mol. wt. 620 in camphor, hydrolysed to a mixture of tetramethylglucopyranose and 2 : 3 : 6-trimethylglucopyranose. From the residue is obtained a methylated cellodextrin, m. p. 151—152°, $[\alpha]_D$ $-10°$ in H_2O, mol. wt. 855 in camphor, not methylated by Ag_2O and MeI, yielding on acetolysis and methylation tetramethylmethylglucopyranoside (30%) and heptamethyl-β-methylcellobioside (25%). G. DISCOMBE.

Formation of alkali-celluloses. G. CHAMPETIER (Compt. rend., 1931, **192**, 1593—1595).—The absorption curve of NaOH from aq. solutions by cellulose shows, by the titration method, the formation of the compounds $(C_6H_{10}O_5)_2,NaOH$, $(C_6H_{10}O_5)_3,2NaOH$, $(C_6H_{10}O_5)_4,3NaOH$, and $C_6H_{10}O_5,NaOH$, in solutions containing from 10 to 60% of NaOH. C. N. VASS.

Isolation of *n*-propylguaiacol as a degradation product of lignin. M. PHILLIPS (Science, 1931, **73**, 568—570).—The phenolic portion of the oil obtained by distilling lignin with Zn dust yields, in addition to guaiacol, *n*-propylguaiacol (confirmed through the 3 : 5-dinitrobenzoyl derivative). These two substances thus appear to be the fundamental units in the structure of lignin. L. S. THEOBALD.

Lignin. II. E. WEDEKIND, O. ENGEL, K. STORCH, and L. TAUBER (Cellulosechem., 1931, **12**, 163—173).—Contrary to Hillmer (B., 1926, 46) there appears to be a free OH group in phenol-lignin, since it gives readily an alkali-insol. *Ac* derivative, m. p. 175—180° after colouring at 150° and sintering (*Me* derivative, decomp. 175°). Phenol-lignin, for which the formula $[(C_8H_7O_2)(OMe)(OH)(C_6H_4{\cdot}OH)]_x$ is proposed, and acetylphenol-lignin yield colloidal solutions in $COMe_2$ and $CHCl_3$. In transport experiments in EtOH phenol-lignin wanders to the cathode. The possibility of a CO group condensation between phenol and lignin is discussed. Phenol-lignin and lignin behave in the same way towards oxidising agents. *Resorcinol-lignin* (*Ac* derivative, m. p. 160—170° after darkening at 145—150° and sintering), *guaiacol-lignin* [the phenol-lignin acids of the oak and pine (A., 1923,

i, 1183), and phenol-metalignin (A., 1927, 597)], all of which give *Ac* derivatives, resemble phenol-lignin in their properties. A. RENFREW.

Lignin. III. R. O. HERZOG and A. HILLMAR (Ber., 1931, 64, [*B*], 1288—1306; cf. A., 1929, 915).—The ultra-violet absorption spectrum of lignin preps. and of various benzenoid derivatives has been examined according to Henri's method, using the H line as source of light. A standard alkali lignin is prepared by treating rye straw with 2% methyl-alcoholic NaOH at room temp. in absence of O_2 and light of short wave-length and purification of the product by electrodialysis. Therewith are compared ligninsulphonic acid from pine, rye, and larch, alkali lignin from rye, jute, and larch, alkali methyl-lignin from rye, primary ethyl-lignin from beech, glycol-lignin from pine, and pectin lignin from flax. The connexion between botanical origin of the lignin and position of the chief max. in the region of long wave-length and between the chemical nature of the prep. and the intensity of absorption is very marked. Among benzenoid derivatives, substitution in the C_6H_6 nucleus leads to increased absorption and extension of the region of absorption towards longer wave-lengths. Only when a single, saturated substituent is introduced is the character of the C_6H_6 spectrum preserved and merely a displacement is observed (cf. PhMe, PhEt, PhPr, allylbenzene, β-phenylethyl alcohol). A double linking or a OH group in a side-chain is without effect if two or more C atoms are interspersed between it and the C_6H_6 nucleus. If the double linking is in conjugation with the ring or the OH group is proximate to the nucleus, three bands are observed (as with PhCHO) in contrast to the two bands of C_6H_6. The presence of OH attached to the nucleus does not essentially alter the C_6H_6 character, but the intensity of the C_6H_6 bands of longer wave-length is increased about 10-fold, and displacement towards the red increases in the sequence pyrogallol, phenol, pyrocatechol. The picture is reproduced by derivatives of the phenols. Coniferaldehyde gives a spectrum differing greatly from that of coniferyl alcohol. The continued conjugation of the C:C double linking and of the C:O group in the side-chain with the nucleus causes a very marked increase of the absorption coeffs. and a simultaneous displacement of the whole region of absorption towards greater wave-lengths.

It is considered that the well-defined band at $\lambda=276$ mμ in lignin is characteristic of a C_6H_6 derivative, since the presence of a series of double linkings, carbonyl or optically similar groups in conjugated position in lignin is excluded by the chemical evidence. This conception is in harmony with the presence of a second stronger band in the extreme ultra-violet which is very prominent in ligninsulphonic acid at λ 233 mμ. Spectroscopic and chemical evidence indicates in lignin the presence of a substance composed fundamentally of di- or tri-hydric phenols which are partly methylated. Double linkings in conjugation with the C_6H_6 nucleus or similar ketonic or aldehydic groups in free form do not appear to be present. Glycols, oxides, or ether-like linkings are not excluded. H. WREN.

Thermal decomposition of αζ-diamino-*n*-hexane hydrochloride. A. MULLER and E. FELD (Monatsh., 1931, 58, 12—21).—K phthalimide converts αζ-dibromo-*n*-hexane into *αζ-phthalimido-n-hexane*, dimorphous, m. p. 181° and 170° on remelting, hydrolysed by HCl (*d* 1·19) at 180—190° to αζ-diamino-*n*-hexane dihydrochloride. The hexamethyleneimine obtained (A., 1922, i, 761) by thermal decomp. of this is proved by direct comparison to be 2-ethylpyrrolidine (*p-toluenesulphonyl* derivative, m. p. 76·5—77°; *phenylthiourethane*, m. p. 88°), the *Bz* derivative, b. p. 185°/11 mm., of which is oxidised by $KMnO_4$ to γ-benzamido-*n*-hexoic acid identical with a synthetic specimen (cf. this vol., 943). J. W. BAKER.

Reactions of primary amines with sulphur chloride and with sulphur and lead oxide at ordinary temperatures. T. G. LEVI (Gazzetta, 1931, 61, 294—300).—NH_2Et (3 mols.) and S_2Cl_2 (1 mol.) in Et_2O yield *1 : 4-diethyl-2 : 3 : 5 : 6-tetrathiodiazine*, $NEt<\substack{S\cdot S\\ S\cdot S}>NEt$, m. p. 35°. Benzylamine and S_2Cl_2 in C_6H_6 in presence of PbO give *bisthiobenzothioamide*, m. p. 100°. The following compounds prepared from secondary amines are also described: *bisdipropylamino-disulphide*, which does not solidify at −75°; *bisdi*iso*butylamino-disulphide*, m. p. 31°; *bisdibenzylamino-disulphide*, m. p. 79°. E. E. J. MARLER.

Polythioamines higher than the dithio-compounds. T. G. LEVI (Gazzetta, 1931, 61, 286—293; cf. this vol., 474).—By the action of S in presence of PbO on the corresponding secondary bases the following trisulphides have been prepared: *bisdimethylamino-*, m. p. −28° to −31°; *bisdiethylamino-*, which does not solidify at −80°; *bispiperidino-*, m. p. 74°; also *bispiperidino-tetrasulphide*, m. p. 78°. E. E. J. MARLER.

Separation and isolation of organic bases by electrodialysis. E. GEBAUER-FULNEGG and A. I. KENDALL (Ber., 1931, 64, [*B*], 1067—1072).—The process has been applied to the separation of histidine from histamine or choline, of an artificial mixture of protein or gelatin from histamine or choline, and of the base from histamine dipicrate or chloroplatinate. It is suitable for the separation of relatively strong, crystalloidal bases from mixtures with amphoteric or more weakly basic substances or from colloids. It can be advantageously employed in purification of bases by separation from their picrates, chloroplatinates, or compounds with the salts of heavy metals. H. WREN.

Higher amino-alcohols. I. Action of the Grignard reagent on ethyl γ-dimethylaminobutyrate. C. PRELOG and V. HANOUSEK (Coll. Czech. Chem. Comm., 1931, 3, 276—280).—Ethyl γ-dimethylaminobutyrate reacts with MgEtBr to give a mixture of *ζ-dimethylaminohexan-γ-one*, b. p. 70—75°/13 mm. (*picrate*, m. p. 111·5°; *picrolonate*, m. p. 135·5°; *semicarbazone hydrochloride*, m. p. 190—191°), and *ζ-dimethylamino-γ-ethylhexan-γ-ol*, b. p. 100—105°/13 mm. [*hydrochloride*, m. p. 173—174°; *picrate*, m. p. 104—105°; *methiodide*, m. p. 133—134° (*chloroaurate*, m. p. 88°; *chloroplatinate*, m. p. 220° (decomp.); *picrate*, m. p. 104°)]. The same mixture is obtained

independently of the proportions of the reacting substances. F. R. SHAW.

Co-ordination compounds of the chloroplatinates of choline and its esters. H. W. DUDLEY (J.C.S., 1931, 763—769).—The stability of choline-acylcholine chloroplatinates is determined by the acyl group (A., 1929, 1479), decreasing with increasing size of acyl group. *Propionylcholine* [*chloroaurate*, m. p. 131—133°; *chloroplatinate*, m. p. 244° (decomp.)], *cholinepropionylcholine chloroplatinate*, m. p. 262° (decomp.), n-*butyrylcholine chloroplatinate*, m. p. 244° (decomp.), *choline*-n-*butyrylcholine chloroplatinate*, m. p. 254° (decomp.), n-*valerylcholine chloroplatinate*, m. p. 237° (decomp.), n-*hexoylcholine chloroplatinate*, m. p. 236—238° (decomp.), *dibutylacetyl(decoyl)choline chloroplatinate*, m. p. 236° (decomp.), *cholinepyruvylcholine chloroplatinate*, m. p. 248° (decomp.), *cholineglycollylcholine chloroplatinate*, m. p. 244° (decomp.), *acetylglycollylcholine chloraurate*, m. p. 158—160°, and *chloroplatinate*, m. p. 232° (decomp.), are described. The m. p. of mixtures of choline and choline ester chloroplatinates which form co-ordination compounds are above those of either of the components.
G. DISCOMBE.

Synthetic preparation and isolation of some of the simpler amino-acids. W. COCKER and A. LAPWORTH (J.C.S., 1931, 1391—1403).—Improved general methods of isolation are given for a number of the more soluble amino-carboxylic acids. In the preparation of α-amino-nitriles from open-chain aldehydes and ketones by means of NH_3 and HCN, heating is not necessary and the nitriles are readily hydrolysed by 40% H_2SO_4 at atm. pressure. *dl*-α-Amino*iso*butyric acid gives a *phenylcarbamido*-derivative of m. p. 187—188° (decomp.); *dl*-methylaspartic acid gives with phenylcarbimide the *hydantoin*
$\begin{matrix} CO—NH \\ NPh·CO \end{matrix}$ >CMe·CH_2·CO_2H, p. 146° (decomp.).
D. A. FAIRWEATHER.

Nitrate formation from amino-acids. B. SJOLLEMA (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 468—470).—When aq. solutions of aliphatic amino-acids are treated with $KMnO_4$ at room temp. a rise in temp. occurs and a brown ppt. is formed. If after 1 hr. the excess of $KMnO_4$ is reduced with H_2O_2 a colourless liquid remains which contains appreciable quantities of nitrate. Possible mechanisms are discussed. J. W. SMITH.

Method of assigning optically active α-amino-acids to the *d*- or *l*-series. II. O. LUTZ and B. JIRGENSONS (Ber., 1931, 64, [B], 1221—1232).—Application of the method already described (A., 1930, 460) to lysine, arginine, α-amino-β-3 : 4-dihydroxyphenylpropionic acid, ornithine, histidine, tryptophan, proline, and oxyproline shows that these natural amino-acids, like natural aspartic acid, belong to the *l*-series. The varying optical activity of the amino-acids in neutral, acid, or alkaline solution is attributed to their existence mainly as internal salts in aq. solution. In the presence of increasing amounts of HCl the dissociation of the basic portion greatly increases, whereas increase of NaOH facilitates dissociation of the CO_2H. H. WREN.

Compounds of dextrose with ethyl amino-acetate and glycylglycine ester. H. VON EULER and K. ZEILE (Annalen, 1931, 487, 163—174).—The isolation of cryst. Et α-cyanoethylaminoacetate hydrochloride, m. p. 100° (corr.), is described (cf. A., 1926 942). By interaction of the $NaHSO_3$ derivative of Et pyruvate with Et aminoacetate and aq. KCN, *Et α-cyano-α-carbethoxymethylaminopropionate*, liquid, is obtained; it is converted by NaOEt (1 mol.) and NaOH (2 mols.) in EtOH into the yellow, hygroscopic *salt* CO_2Na·CMe:N·CH_2·CO_2Na, reduction of which with Na–Hg is accompanied by hydrolysis to glycine. The interaction of dextrose with Et aminoacetate in presence of Al–Hg to remove the H_2O produced gives a cryst. *glucoside*, m. p. 112° (corr.), converted by dry NH_3–EtOH into the corresponding *amide*, m. p. 140° (corr.), and hydrolysed, slowly in aq. solution, and rapidly in presence of acids, into its constituents. It is fermentable at a velocity approx. the same as that of dextrose. Diketopiperazine and indefinite products were obtained from dextrose and glycylglycine ester, but the latter combines when melted with acetobromoglucose or tetra-acetylglucose with formation of the *tetra-acetylglucoside*, m. p. 140° (corr.), convertible as before into the *amide* (?), m. p. 90°.
H. A. PIGGOTT.

Synthesis of γ-amino-*n*-hexoic acid and of 5-keto-2-ethylpyrrolidine. A. MÜLLER and E. FELD (Monatsh., 1931, 58, 22—28).—The Et ester of succinic acid monochloride (obtained from the acid and di-ester by Fourneau and Sabetay's method, A., 1928, 1115) reacts with ZnEtI to give, after hydrolysis, γ-keto-*n*-hexoic acid, the *phenylhydrazone*, m. p. 73°, of which is reduced by Al amalgam to *γ-amino*-n-*hexoic acid*, m. p. 180—181° [*hydrochloride*, m. p. 120—121°; *chloroplatinate*, m. p. 190—191° (decomp.)], benzoylated to *γ-benzamido*-n-*hexoic acid*, m. p. 146·5—147° (*Me* ester, m. p. 87·5°). Distillation of the γ-amino-acid affords *5-keto-2-ethylpyrrolidine*, b. p. 130°/8 mm., m. p. 22° [*hydrochloride*; *chloroplatinate*, m. p. 125—127° (decomp.)]. All m. p. are corr. J. W. BAKER.

Formation of sodium derivatives of compounds containing a reactive methylene group. K. G. NAIK and L. D. SHAH (J. Indian Chem. Soc., 1931, 8, 45—49).—*N*-Alkyl and *N*-aryl substituted cyanoacetamides react with Na in C_6H_6 or Et_2O at the b. p. of the solvent, the Na derivatives formed being insol. in C_6H_6. The reactivity of the arylated amides is much less than that of the alkyl compounds. The prep. of *sodiocyanoacet-methylamide*, m. p. 225° (decomp.), *-butylamide*, m. p. 200° (decomp.), *-heptylamide*, m. p. 195° (decomp.), -o-*toluidide* (decomp. above 220°), -m-*toluidide* (decomp. above 230°), -p-*toluidide* (decomp. above 245°), *-benzylamide* (decomp. 205°); *-α-naphthylamide* (discolours above 170°), and *-β-naphthylamide* (darkens above 205°) is described. G. DISCOMBE.

Mercury acetamide as mercurating agent. K. G. NAIK and L. D. SHAH (J. Indian Chem. Soc., 1931, 8, 29—35).—In place of HgO and $Hg(OAc)_2$ (A., 1899, i, 54, 428; 1902, i, 656, 849; 1898, i, 635; 1909, i, 218), mercury acetamide is used as a mercurating agent (A., 1909, i, 464). The OH·Hg group

replaces H in the CH_2 group of various *N*-alkylated cyanoacetamides, yielding hydroxymercuricyanoacetamides, decomp. by H_2S, $(NH_4)_2S$, and Na_2S, KI, phenylhydrazine, and N_2H_4,H_2O, and by hot 0·25*N*-HCl.

Hydroxymercuricyanoacet-methylamide, m. p. 300° (discolours at 287°), *-ethylamide*, m. p. 300° (discolours at 285°), -n-*propylamide*, m. p. 280° (decomp. after darkening at 265°), -n-*butylamide*, m. p. above 300°, -iso*butylamide*, m. p. 300° (darkens above 280°), -n-*amylamide*, m. p. 285° (decomp.); -iso*hexylamide*, m. p. 273° (decomp.), and -n-*heptylamide*, m. p. 284° after darkening at 270°, are described. *Cyanoacet*-n-*butylamide*, m. p. 73°, -iso*butylamide*, m. p. 45°, -n-*amylamide*, m. p. 47°, -iso*hexylamide*, m. p. 42°, and -n-*heptylamide*, m. p. 67°, are also described. The *hydroxymercuri*-derivatives of ethyl cyanoacetate, cyanoacetamide, cyanoacet-anilide, -*m*-toluidide, -*o*-toluidide, -*p*-toluidide, -1 : 3 : 4-xylidide, and -1 : 4 : 5-xylidide all have m. p. above 300°; those of cyanoacetbenzylamide, m. p. 293°, -α-naphthylamide, m. p. 272° (after darkening at 253°), and -β-naphthylamide, m. p. 283° (decomp.), are also described.

G. DISCOMBE.

Arylamides of lævulic acid. Conversion of 5-keto-2-hydroxy-1-phenyl-2-methyltetrahydropyrrole into lævulanilide. R. LUKES and V. PRELOG (Chem. Listy, 1931, **25**, 76—79).—Lævulanilide condenses with *p*-toluidine to yield γ-p-*tolyliminovaleranilide*, m. p. 153°, giving lævulanilide and acet-*p*-toluidide on hydrolysis, and γ-p-*tolylaminovaleric acid*, m. p. 82·5°, on hydrogenation. γ-*Phenyliminovaleri*-p-*toluidide*, m. p. 142—143°, is prepared as above, and yields on hydrolysis lævul-*p*-toluidide and acetanilide. The product of hydrogenation of γ-phenyliminovaleranilide is γ-anilinovaleric acid, which on dehydration yields 1-phenyl-2-methylpyrrolid-5-one. The above reactions indicate that lævulanilide has the structure $COMe\cdot CH_2\cdot CH_2\cdot CO\cdot NHPh$.

R. TRUSZKOWSKI.

Structure of carbamide in aqueous solution. G. DEVOTO (Ber., 1931, **64**, [*B*], 1329—1332).—In reply to Ebert (this vol., 609), reasons are adduced in favour of the view that the polar formula for carbamide in aq. solution is the most probable. H. WREN.

Cyanogen, thiocyanogen, and methylamine. H. EMDE and T. HORNEMANN (Arch. Pharm., 1931, **269**, 336—340).—The possibility that HCN in plants may arise from the oxidation of NH_2Me, or other amines, is discussed. NH_2Me in excess gives 10% yield of HCN with CrO_3 in H_2SO_4. Aq. NH_2Me when saturated with H_2S and heated at 200° with S or $Na_2S_2O_3$ gives some thiocyanic acid. A. A. LEVI.

Hexacyanocobaltic acid and methyl alcohol. F. HÖLZL [with A. SALLMANN] (Monatsh., 1931, **58**, 29—46).—Hexacyanocobaltic acid dissolves in abs. MeOH between −10° and +65° to form the *oxonium* salt $H[CO(CN)_6](H\cdot OHMe)_2$. Tensimetric measurements show that with diminishing pressure this is converted first into $H_2[CO(CN)_6](H\cdot OHMe)$ and finally into the free complex acid. Under no conditions could a *tert.*-oxonium salt be obtained. Within the above temp. limits the solubility in MeOH (data given) increases rapidly with rise of temp. The alkali titre of a solution of $H_3[Co(CN)_6]$ in MeOH decreases on keeping (at 65° or 98°), due to esterification of the co-ordinated HCN, which is accelerated by the presence of small amounts of H_2O or by rise of temp. Methylcarbimide is formed and a reddish-violet ppt., which consists of a mixture of the *compounds* $[(CN)_3(H_2O)_2\cdot Co\cdot CN\cdot Co(CN)_3(CNMe)(H_2O)_2]$ (I) and $[(CN)_3(H_2O)_2\cdot Co\{\cdot(CN)\cdot Co(CN)_2(H_2O)_2\}_2CN\cdot Co(CN)_2(CNMe)(H_2O)_2]$ (II), containing hexacovalent Co and a μ-cyano-bridge, I (rose) being converted into II (violet) by H_2O. When I is heated to 100°/vac. only some of the CN linkings are split ($-2H_2O$) giving the *compound* $[(MeNC)(CN)(H_2O)Co{:}(CN)_3{:}Co(CN)_2(H_2O)]$, whilst II ($-6H_2O$) similarly affords the compound $[(CN)_2(H_2O)Co{:}(CN)_3{:}\{Co{:}(CN)_3{:}\}_2Co(CN)(CNMe)(OH_2)]$. These cyano-aquo-complexes possess acidic character and their formation under such mild conditions suggests that the CN linkings in hexacyanocobaltic acid are derived from the *iso*-form, HNC, the C atom being bound to the central Co atom. J. W. BAKER.

Properties of the β-chlorovinylarsines and their interaction with benzene in presence of aluminium chloride. Production of 9 : 10-dimethylanthracene. C. S. GIBSON and J. D. A. JOHNSON (J.C.S., 1931, 753—756).—β-Chlorovinyldichloroarsine, ββ'-dichlorodivinylarsine, and ββ'β''-trichlorotrivinylarsine all yield with C_6H_6 in presence of $AlCl_3$ 9 : 10-dimethylanthracene, produced also from ββ'-dichlorodivinylchloroarsine in the same way (A., 1926, 1030 : 1929, 1434), thus confirming the view that 9 : 10-dimethyl-9 : 10-dihydroanthracene (A., 1887, 753; 1914, i, 156) is actually 9 : 10-dimethylanthracene. G. DISCOMBE.

Silico-organic compounds. II. Hydrogenation and rearrangement of silicomethane derivatives. B. DOLGOV and I. VOLNOV (J. Gen. Chem. Russ., 1931, **1**, 91—104).—Hydrogenation of org. Si compounds containing a C_6H_6 nucleus does not take place due to the anticatalytic action of the Si. There is no resemblance between the behaviour of *tert.*-alcohols and the corresponding Si compounds, which do not undergo hydrogenation in the substituent C_6H_6 rings, do not condense with PhOH, or react with phenylcarbimide. Compounds of the type $RSiR'_3$ when heated with H_2 under pressure undergo the rearrangement $2RH+Si_2R'_6 \xleftarrow{+H_2} 2RSiR'_3 \longrightarrow R_2SiR'_2+SiR_4$, where R, R' are Et, Me, Pr, Ph. In the case of *iso*butyl- and *iso*amyl-triethylsilicomethane a more complex rearrangement and condensation takes place. E. B. UVAROV.

Hydrogenation and decomposition of organic silicon compounds at high temperatures and pressures. I. V. N. IPATIEV and B. N. DOLGOV (J. Gen. Chem. Russ., 1931, **1**, 5—12).—$SiEt_4$ at 350—360°/30—80 atm. is transformed by H into disilicon hexaethyl and C_2H_6. Under the same conditions $SiPhEt_3$ eliminates C_6H_6, forming Si_2Et_6, and by an interchange of radicals gives $SiPh_2Et_2$ and $SiEt_4$, and a condensation product. $SiPh_4$ is transformed above 490° into an inert condensation product. Unsymmetrical silico-org. compounds tend to assume a symmetrical structure under these conditions.

E. B. UVAROV.

1-Methyl-2-ethyl*cyclo*propane. LESPIEAU and R. L. WAKEMAN (Compt. rend., 1931, **192**, 1395—1397).—Hexane-βδ-diol, d_4^{21} 0·9516, is converted by PBr_3 and a little pyridine into *βδ-dibromo-n-hexane*, b. p. 81·5—83°/10 mm., d_4^{22} 1·5756, which with Zn and 95% EtOH at the b. p. gives 1-*methyl*-2-*ethyl*cyclo*propane*, b. p. 63·9—64·9°, d_4^{21} 0·6961. The Raman spectrum points to the absence of the isomeric ethylenic hydrocarbon; nevertheless the substance decolorises aq. $KMnO_4$, and shows an optical exaltation which is considered to be due to the *cyclo*propane ring.

H. A. PIGGOTT.

Preparation of trimethylene hydrocarbons; 1-methyl-2-propyl*cyclo*propane. LESPIEAU and R. L. WAKEMAN (Compt. rend., 1931, **192**, 1572—1573).—The action of Mg in Et_2O on β-bromopropaldehyde (prepared from crotonaldehyde and HBr at low temp.) affords *β-bromoheptan-γ-ol*, b. p. 99—101°/10 mm., which reacts with PBr_3 to give *βδ-dibromoheptane*, b. p. 99—100°/12 mm., debrominated with Zn to 1-*methyl*-2-*propyl*cyclo*propane*, b. p. 92—93°/ 747 mm.

F. R. SHAW.

Oxidation of *cyclo*hexadiene with permanganate, perbenzoic acid, and free oxygen. N. D. ZELINSKI and A. N. TITOVA (Ber., 1931, **64**, [*B*], 1399—1406).—Distillation of *cis-cyclo*hexane-1 : 4-diol with 2 mols. of $KHSO_4$ gives a mixture of *cyclo*hexadiene (40% yield) and Δ^3-*cyclo*hexenol, b. p. 164—164·5°/763 mm., d_4^{20} 0·9845; a similar mixture is obtained when anhyd. $MgSO_4$ is employed, except that the more volatile $\Delta^{1:3}$-*cyclo*hexadiene predominates in the hydrocarbon mixture. If half the above quantities of $KHSO_4$ or $MgSO_4$ are used, the main product is Δ^3-*cyclo*hexenol. Oxidation of $\Delta^{1:4}$-*cyclo*hexadiene with $KMnO_4$ yields *tetrahydroxy*cyclo*hexane*, m. p. 241—242° after darkening at 216° (dihydrate), possibly the racemic form of the erythritol obtained from sugar beet. The non-cryst. residue from the above experiment is transformed by Ac_2O into 1 : 2 : 4 : 5-*tetraacetoxy*cyclo*hexane*, m. p. 52—54° and 168°, and a *tetra-acetyl* derivative, m. p. 101°. Oxidation of Δ^3-*cyclo*hexenol by $KMnO_4$ or perbenzoic acid yields cyclo*hexanetriol*, m. p. 122° after softening at 104°. $\Delta^{1:4}$-*cyclo*Hexadiene in $CHCl_3$ is oxidised by perbenzoic acid to the corresponding 1 : 2 : 4 : 5-*dioxide*, m. p. 110° (converted by H_2O at 100° into cyclo*hexane*-1 : 2 : 4 : 5-*tetraol monohydrate*, m. p. 195° (slight decomp.), and a fraction, b. p. 85—86°/25 mm., with the approx. composition of the dioxide. The autooxidation of $\Delta^{1:3}$-*cyclo*hexadiene is fully discussed.

H. WREN.

Determination of bromine in highly brominated hydrocarbons. F. SCHULZ (Coll. Czech. Chem. Comm., 1931, **3**, 281—284).—The Stepanoff method (A., 1907, ii, 50) for determination of halogen in hexabromobenzene, m. p. 327°, pentabromotoluene, m. p. 288°, and hexabromonaphthalene, m. p. 317° (m. p. determined in a special apparatus), is successful if EtOH be replaced by BuOH.

F. R. SHAW.

Aromatic compounds of fluorine. VIII. Reactions with *p*-bromofluorobenzene. G. SCHIEMANN and R. PILLARSKY (Ber., 1931, **64**, [*B*], 1340—1345).—Since F is much more firmly attached than Br to the C_6H_6 nucleus it is possible so to treat *p*-bromofluorobenzene that only the Br atom is removed and the fluorophenyl residue is introduced. *p*-Bromofluorobenzene, b. p. 155°/767 mm., m. p. −8° to −7·5°, d_4^{20} 1·7267, is prepared in 80% yield by addition of Br to fluorobenzene in presence of Fe filings [2 : 4(or 3 : 4)-*dibromofluorobenzene*, m. p. 69°, is obtained as by-product] or from *p*-bromoaniline through the corresponding *diazonium fluoborate*, decomp. 133°. 4-Fluorodiphenyl is monobrominated to 4′-*bromo*-4-*fluorodiphenyl*, m. p. 98° (corr.), oxidised by CrO_3 in AcOH to *p*-bromobenzoic acid. The main product of the action of Na and EtBr on *p*-fluorobromobenzene in Et_2O is 4 : 4′-difluorodiphenyl, m. p. 88—89°, *p*-fluoroethylbenzene, b. p. 142—143°/755 mm., being obtained in smaller amount. With PrBr the yield of p-*fluoropropylbenzene*, b. p. 164—165°/759 mm., obtained is only 5%, whilst with *iso*amyl bromide no trace of *p*-fluoro*iso*amylbenzene is produced. Mg *p*-fluorophenyl bromide, readily obtained in Et_2O solution, is transformed by PhCHO into *p*-fluorobenzhydrol, m. p. 48°, in 47% yield and by acetonitrile into p-*fluoroacetophenone*, b. p. 77—78°/10 mm., m. p. −4·5°, in 7% yield.

H. WREN.

Position of the nitroso-group among substituents capable of activating suitably placed halogens etc. in aromatic nuclei. R. J. W. LE FEVRE (J.C.S., 1931, 810—813).—Nitrosobenzene can be mono-*p*-brominated in C_6H_6 at 6—8°. The Br atom is removed, very slowly, by the action of an AcOH solution of $AgNO_3$ at room temp., whilst picryl bromide reacts less rapidly. *p*-Nitrosodimethylaniline and 2 : 4 : 6-trinitrodimethylaniline are readily hydrolysed by *N*-NaOH, whilst 2 : 4-dinitrodimethylaniline is scarcely attacked. These observations are explained by Robinson's formulation of nitrosobenzene as a crotonoid or crotenoid system (A., 1918, i, 548; 1925, i, 800; 1930, 1566).

G. DISCOMBE.

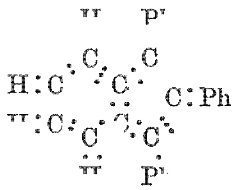
Polymerisation processes. II. Two dimerides of α-methylstyrene. E. BERGMANN, H. TAUBADEL, and H. WEISS (Ber., 1931, **64**, [*B*], 1493—1501; cf. A., 1930, 901).—The similarity of the unsaturated dimeride of α-methylstyrene and of the corresponding derivative of *as*-diphenylethylene suggests that the former substance is *βδ-diphenyl-δ-methyl-Δ^β-pentene*; the hypothesis is confirmed as follows. Addition of Na to α-methylstyrene or the unsaturated dimeride and alcoholysis of the product affords a mixture of isomeric *βε-diphenyl-γδ-diphenyl*-iso*propylhexanes*, b. p. 290—310°/22 mm. The Na derivative and CO_2 afford the dicarboxylic *acid* $C_{38}H_{42}O_4$, m. p. 268—269° (decomp.). Ozonisation of the dimeride followed by reductive fission gives acetophenone and phenyl*iso*butaldehyde in small amount. Mesityl oxide, $AlCl_3$, and C_6H_6 give β-phenyl-β-methylpentan-δ-one, b. p. 121°/12 mm., transformed by MgPhBr and subsequent distillation into βδ-diphenyl-δ-methyl-Δ^β-pentene, b. p. 170—171°/17 mm., identical with the unsaturated dimeride. The analogous suggestion that the saturated dimeride is 3-*phenyl*-1 : 1 : 3-*trimethylhydrindene* is verified as follows. Whilst most simply obtained from α-methylstyrene and $SnCl_4$, it is also prepared from βδ-diphenyl-δ-methyl-Δ^β-pentene and $SnCl_4$ or $AlCl_3$ and C_6H_6. Dimethylacrylic acid is transformed by $AlCl_3$ and C_6H_6

into β-*phenyl*isovaleric acid, b. p. 165—166°/20 mm., and β-*phenyl*-βδδ-*trimethylpentane*-3 : 5-*dicarboxylic acid*, m. p. 200°. β-*Phenyl*isovaleryl *chloride*, b. p. 125—126°/16 mm., and $AlCl_3$ in boiling CS_2 afford 1 : 1-*diphenylhydrind-3-one*, b. p. 119°/13 mm., converted by MgPhBr into 3-*phenyl*-1 : 1-*dimethylhydrinden-3-ol*, m. p. 88—89°, which could not be etherified; treatment of it with K and MeI in boiling xylene gave 3-*phenyl*-1 : 1-*dimethylindene*, m. p. 50—51°. β-Methylcinnamic acid is transformed by $AlCl_3$ and C_6H_6 into ββ-*diphenylbutyric acid*, m. p. 102—103°. *Me* ββ-*diphenylbutyrate*, b. p. 182—183°/13 mm., is converted by MgMeI into δδ-*diphenyl*-β-*methylpentan*-β-*ol*, b. p. 185—187°/13 mm., transformed by HCl and $SnCl_4$ in C_6H_6 into 3-phenyl-1 : 1 : 3-trimethylhydrindene, m. p. 53°, identical with the saturated dimeride. H. WREN.

o- and m-Divinyl- and -diacetylenyl-benzenes. M. DELUCHAT (Compt. rend., 1931, **192**, 1387—1389; cf. A., 1930, 588).—*o*-Di-(α-hydroxyethyl)benzene (A., 1930, 471) is converted by PBr_3 in $CHCl_3$ into its *dibromohydrin*, m. p. 91°, which crystallises in optically active hemihedral forms, and when distilled with excess of quinoline at 3 mm. gives o-*divinylbenzene*, b. p. 78·5°/11 mm., d^{21} 0·934. This differs from its position isomerides in that it does not polymerise at room temp.; its *tetrabromide*, m. p. 71—74°, gives $C_{10}H_8$ and other products with excess of KOH in EtOH, but on careful treatment with NaOEt gives αα-*dibromo*-o-*divinylbenzene*, b. p. 125—126°/2 mm., d^{13} 1·714, o-(α-*bromovinyl*)*acetylenylbenzene*, b. p. 127°/11 mm., $d^{21.5}$ 1·4105 (*Ag* salt), and o-*diacetylenylbenzene*, b. p. 82°/14 mm., m. p. −20°, $d^{17.5}$ 0·9788 (*Ag* salt). The *dibromohydrin* of *m*-di(hydroxyethyl)benzene, an unstable liquid, is decomposed by distillation at 2 mm. into m-*divinylbenzene*, b. p. 52°/3 mm., d^{20} 0·926, and m-α-*bromoethylvinylbenzene*, b. p. 88·5°/3 mm., d^{20} 1·319, when distilled with quinoline; the former is the main product. The *tetrabromide*, m. p. 64°, of *m*-divinylbenzene is converted by KOH in EtOH into m-*diacetylenylbenzene*, b. p. 78°/15 mm., m. p. −2·5°, d^{18} 0·9669 (*Ag* salt, sinters 280°). All three acetylenic derivatives give yellow ppts. with ammoniacal CuCl. H. A. PIGGOTT.

Electron affinity of free radicals. II. Diphenyl-α-naphthylmethyl, diphenyldiphenylyl- and phenyldiphenylyl-α-naphthyl-methyl. H. E. BENT (J. Amer. Chem. Soc., 1931, **53**, 1786—1794; cf. A., 1930, 699).—The free energy changes, ΔF, of the reaction $Na(s)+R$ (in Et_2O)$=Na^++R^-$ are −17·9, −18·6, −19·1, and −19·5 kg.-cal., where $R=Ph_3C$, $Ph_2C(\alpha\text{-}C_{10}H_7)$, $Ph_2C\cdot C_6H_4Ph$, and $PhC(\alpha\text{-}C_{10}H_7)\cdot C_6H_4Ph$, respectively. The electron affinities of the four radicals in the gaseous state are computed to be approx. 60 kg.-cal. Since the larger radicals, as compared with the smaller, have slightly greater electron affinities and smaller tendencies to form ethane derivatives, it is suggested that owing to steric hindrance the C atoms cannot approach so closely, and hence the energy liberated is smaller. The solvent has essentially equal effects on the four equilibria. J. G. A. GRIFFITHS.

Polycentricity as cause of resistance to association of free radicals. A. LOWENBEIN (Annalen, 1931, **487**, 97—104).—Mainly theoretical. On the electronic theory "polycentric" free radicals, *e.g.*, pentaphenylethyl, pentaphenyl*cyclo*pentadienyl, etc., have symmetrical structures with an intra-at. linking of the free valency electrons as the cause of their slight tendency to association. In the case of triphenylindenyl (annexed formula), among others, this implies that monosubstitution in a Ph nucleus cannot lead to isomerism. It is reported that the action of HBr on 1 : 2-diphenyl-3-*p*-tolyl- and 2 : 3-diphenyl-1-*p*-tolyl-1-indenols gives the same *bromide*, m. p. 112°. H. A. PIGGOTT.



Effect of nitrates on dinuclear benzene derivatives. G. BACHARACH and J. E. BROLLES, jun. (Rec. trav. chim., 1931, **50**, 732—735).—Diphenyl and dibenzyl are not nitrated by $LiNO_3$ according to Menke's method (A., 1925, i, 386, 655), but with $Cu(NO_3)_2$ the former yields *p*-nitrodiphenyl and *pp'*-dinitrodiphenyl, and the latter *pp'*-dinitrodibenzyl. Whereas benzoin is oxidised to benzil by this method, benzil and stilbene are unaffected by both nitrates. J. D. A. JOHNSON.

Orientation effects in the diphenyl series. IX. Nitration of 4-chloro-4'-fluoro- and 4-bromo-4'-fluoro-diphenyl. (MISS) E. E. J. MARLER and E. E. TURNER (J.C.S., 1931, 1359—1363).—4-Nitro-4'-aminodiphenyl is converted into 4-*fluoro*-4'-*nitrodiphenyl*, m. p. 120—121°, which is reduced to 4-*fluoro*-4'-*aminodiphenyl*, m. p. 121°, and this gives 4-*chloro*-4'-*fluorodiphenyl*, m. p. 87—88°. This is dinitrated, and the proportions of 4-*chloro*-4'-*fluoro*-2-*nitrodiphenyl* (72%) and of 4-*chloro*-4'-*fluoro*-2'-*nitrodiphenyl* (28%) present as intermediates are determined by analysis of the dinitrated mixture. Similarly 4-bromo-4'-nitrodiphenyl is reduced and converted into 4-*bromo*-4'-*fluorodiphenyl*, m. p. 99—100°, which passes during dinitration through 4-*bromo*-4'-*fluoro*-2-*nitrodiphenyl* (86%) and 4-*bromo*-4'-*fluoro*-2'-*nitrodiphenyl* (14%). The mononitro-derivatives cannot be isolated. D. A. FAIRWEATHER.

Diphenyl and its derivatives. VII. New 3 : 3'-disubstituted diphenyls. L. MASCARELLI and D. GATTI (Gazzetta, 1931, **61**, 320—325; cf. A., 1930, 205, 464).—Diazotisation of 3-nitro-3'-aminodiphenyl followed by the Sandmeyer reaction gives 3-*bromo*-3'-*nitro*-, m. p. 92°, 3-*iodo*-3'-*nitro*-, m. p. 96—97°, 3-*chloro*-3'-*nitro*-, m. p. 101°, and 3-*hydroxy*-3'-*nitro-diphenyl*, m. p. 114—116°. E. E. J. MARLER.

Aromatic compounds of fluorine. VII. 4 : 4'-Difluoro-2-nitrodiphenyl and reactions of fluoro-compounds of diphenyl. G. SCHIEMANN and W. ROSELIUS (Ber., 1931, **64**, [*B*], 1332—1340).—4 : 4'-Difluoro-2-nitrodiphenyl, m. p. 94—94·5°, obtained from 2-nitrobenzidine is identical with the product of the nitration of 4 : 4'-difluorodiphenyl, previously regarded as the 3-nitro-compound. The derivatives must therefore be considered to be 4 : 4-difluoro-2-aminodiphenyl, 2 : 4 : 4'-trifluoro-, 2 : 4 : 4'-trifluoro-5-nitro-, 2 : 4 : 4'-trifluoro-5-amino-, and 2 : 4 : 4' : 5-tetrafluoro-diphenyl. 4 : 4'-Difluoro-2-

nitrodiphenyl is converted by 2 mols. of KOH in boiling MeOH into 4-*fluoro-2-nitro-4-methoxydiphenyl*, m. p. 79—80°, and by a large excess of the reagent into *dinitro-4 : 4′-dimethoxybenzerythrene*, $[\cdot C_6H_4\cdot C_6H_3(OMe)\cdot NO_2]_2$, m. p. 202—203° (corr.). 2 : 4 : 4′-Trifluoro-5-nitrodiphenyl and 2 mols. of KOH in MeOH afford 5 : 5′-*dinitro-2 : 2′ : 4 : 4′-tetramethoxydiphenyl*, m. p. 182—183°. 4′-*Fluoro-2-nitro-4-piperidinodiphenyl*, m. p. 74—74·5°, is derived from 4 : 4′-difluoro-2-nitrodiphenyl and piperidine at 165—172°. Drastic nitration of 4 : 4′-difluorodiphenyl or 4 : 4′-difluoro-2-nitrodiphenyl yields a non-homogeneous product from which 4 : 4′-*difluoro-2 : 3′-diaminodiphenyl*, m. p. 86·6°, is prepared.

o-Tolidine is transformed along the usual lines into 4 : 4′-*difluoro-3 : 3′-ditolyl*, m. p. 59°, b. p. 137—138°/21 mm., converted by HNO_3 (*d* 1·5) in AcOH into 4 : 4′-*difluoro-6-nitro-3′ : 3′-ditolyl*, m. p. 89·5°, obtained also from 6-nitro-*o*-tolidine through the corresponding *bisdiazonium borofluoride*, decomp. 97·5—98·5°. H. WREN.

Modes of reaction of phosphorus pentachloride. II. E. BERGMANN and A. BONDI (Ber., 1931, 64, [*B*], 1455—1480; cf. A., 1930, 1050).—Unlike *as*-diphenylethylene, αα-diphenyl-Δ^{α}-propene, αα-diphenyl-Δ^{α}-butene, ααγ-triphenyl-Δ^{α}-propene, αα-diphenyl-β-methyl-Δ^{α}-propene, αγ-diphenyl-Δ^{α}-propene, and γ-phenyl-Δ^{γ}-pentene do not react with PCl_5 or Na, although they readily add halogen. Allylbenzene is inactive, whereas triphenylethylene affords chlorotriphenylethylene, m. p. 117°, and stilbene in $CHCl_3$ reacts with 4 mols. of PCl_5 giving a product transformed by ice into stilbene dichloride, m. p. 193°, obtained also from *iso*stilbene. Addition is not restricted by halogen in the *p*-position. Thus, p-*chlorodiphenylethylene*, $ClC_6H_4\cdot CPh\colon CH_2$, b. p. 164°/16 mm., from *p*-chlorobenzophenone and MgMeI followed by distillation with steam, yields p-*chlorodiphenylvinylphosphinic acid*, $ClC_6H_4\cdot CPh\colon CH\cdot PO_3H_2$, m. p. 181° (*Pb, Hg*¨, *Cu, Fe*‴, *Al, Zn, Ba, Ca* salts), oxidised by CrO_3 to *p*-chlorobenzophenone. Similarly, as-*di*-p-*chlorodiphenylethylene*, m. p. 91°, obtained from *pp′*-dichlorobenzophenone and MgMeI (αα-*di*-p-*chlorophenylethyl alcohol*, m. p. 167—168°) affords pp′-*dichlorodiphenylvinylphosphinic acid*, m. p. 158—159° (*Ag, Pb, Hg*¨, *Cu, Sn*¨, *Co, Mn, Fe*¨, *Al, Zn, Ba, Ca* salts), oxidised to *pp′*-dichlorobenzophenone. The *p*-OMe group is more restrictive. Thus, *as*-di-*p*-methoxydiphenylethylene does not react, whereas *p*-methoxydiphenylethylene, m. p. 75°, yields p-*methoxydiphenylvinylphosphinic acid*, m. p. 145° (*Ag, Pb, Zn, Al, Hg*¨, *Cu, Co, Fe*¨, *Ba*, and *Ca* salts), converted in boiling PrOH or AcOH into *p*-methoxydiphenylethylene and H_3PO_3 and hydrogenated in presence of Pd–$BaSO_4$ to β-phenyl-β-*p*-methoxyphenylethane-α-phosphinic acid, m. p. 102—103°. *p*-Chlorobenzoyl chloride and anisole in presence of CS_2 and $AlCl_3$ give p-*chloro*-p-*methoxybenzophenone*, m. p. 127°, transformed by MgMeI and subsequent acid treatment into as-p-*chlorophenyl*-p′-*methoxyphenylethylene*, m. p. 77°, which yields p-*chloro*-p′-*methoxydiphenylvinylphosphinic acid*, m. p. 132—133° (*Ag, Pb, Cu, Ba, Hg*¨, *Sn*¨, *Co, Fe, Al, Zn*, and *Ca* salts), decomposed by boiling AcOH, oxidised to *p*-chloro-*p′*-methoxybenzophenone, and hydrogenated to β-p-*chlorophenyl*-β-p-*methoxyphenylethane-α-phosphinic acid*, m. p. 126—127°. AcOEt is grignarded with Mg and *o*-bromoanisole to αα-*di*-o-*anisylethyl alcohol*, m. p. 125°, converted by acid into as-*di*-o-*methoxydiphenylethylene*, m. p. 90°, unaffected by PCl_5. as-*Phenyl*-o-*bromophenylethylene*, b. p. 155—156°/12 mm., and as-*phenyl*-o-*chlorophenylethylene*, b. p. 162—163°/18 mm., do not add PCl_5; the effect appears attributable to the size of the halogen atom, since as-*phenyl*-o-*fluorophenylethylene*, b. p. 137°/11 mm., affords o-*fluorodiphenylvinylphosphinic acid*, m. p. 180° (*Ag, Pb, Cu, Hg*¨, *Co, Fe*‴, *Zn, Ba*, and *Ca* salts), oxidised to *o*-fluorobenzophenone. [Methyl anthranilate is transformed into the *diazonium fluoroborate*, $C_8H_7O_2N_2F_4B$, decomp. 102°, whence successively *Me* o-*fluorobenzoate*, b. p. 89—90°/14 mm., *o*-fluorobenzoic acid, o-*fluorobenzoyl chloride*, b. p. 85°/14 mm., and o-*fluorobenzophenone*, b. p. 150°/16 mm. (dimorphous *oxime*, m. p. 126°), are obtained; the ketone is converted by MgMeI into *as*-phenyl-*o*-fluorophenylethylene or α-*phenyl*-α-*fluorophenylethyl alcohol*, m. p. 45°.] Whereas *p*-phenyldiphenylethylene gives p-*phenyldiphenylvinylphosphinic acid*, m. p. 201°, oxidised to *p*-phenylbenzophenone and hydrogenated to p-*phenyl*-ββ-*diphenylethane-α-phosphinic acid*, m. p. 236° (decomp.), and as-p-*tolyl*-p-*diphenylylethane*, m. p. 102—103°, yields a non-cryst. phosphinic acid, o-*phenyldiphenylethylene*, m. p. 55—56°, appears to yield an isomeric *hydrocarbon*, m. p. 86°, in place of the phosphinic acid; the substance is not identical with 9-*phenyl*-9-*methylfluorene*, m. p. 84—85°, prepared by treating 9-methoxy-9-phenylfluorene with Na and subsequently with MeI. as-*Phenyl*-m-*methoxyphenylethylene*, b. p. 168°/14 mm., does not afford a phosphinic acid probably by reason of the formation of an insol., yellow compound of the hydrocarbon and PCl_5. as-*Phenyl*-m-*chlorophenylethylene*, b. p. 152—153°/14 mm., from m-*chlorobenzophenone*, m. p. 82°, is transformed into m-*chlorodiphenylvinylphosphinic acid*, m. p. 168° (*Ag, Pb, Cu, Sn, Al, Zn, Co, Hg*¨, *Ba*, and *Ca* salts), oxidised to *m*-chlorobenzophenone. *iso*Safrole and *iso*eugenol methyl ether yield compounds with PCl_5, hydrolysed to their components. p-*Di*-α-*phenylvinylbenzene*, m. p. 138—139°, from *p*-dibenzoylbenzene and MgMeI followed by " acid treatment " yields the *phosphinic acid* $C_6H_4(CPh\colon CH\cdot PO_3H_2)_2$, m. p. 210°. α-Phenyl-$\Delta^{\alpha\gamma}$-butadiene gives a product considered to be δ-*phenyl*-$\Delta^{\alpha\gamma}$-*butadienephosphinic acid*, m. p. 192° (decomp.) [*Ag, Pb, Fe*‴, *Sn*¨, *Hg*¨, *Cu, Al, Zn, Ba*, and *Ca* salts], since it is hydrogenated to δ-*phenylbutanephosphinic acid*, m. p. 95°, not resolvable by brucine or quinine (*brucine* salt, m. p. 95°, [α] −69·89° in $CHCl_3$; *quinine* salt, m. p. 99—100°, [α] −100° in $CHCl_3$). α-Phenyl-$\Delta^{\alpha\gamma}$-pentadiene and αδ-diphenylbutadiene do not add PCl_5.

1-Benzylidene- and 1-piperonylidene-indenyl-2-phosphinic acid are converted by Zn dust and aq. NaOH into indenyl-2-phosphinic acid, m. p. 184°. Indene and PBr_5 in C_6H_6 afford 1 : 2-dibromohydrindene, b. p. 140°/12 mm.

The close analogy in the behaviour of Na and PCl_5 justifies the belief that addition of the latter is a reaction of at. residues differing from that of halogen mols. In the P pentahalides, one halogen atom is

united differently from the remaining four. The structure of the PCl_5 mol. is considered in detail.

H. WREN.

Action of lithium on tolane. E. BERGMANN and O. ZWECKER (Annalen, 1931, **487**, 155—163).—The constitution of 1 : 2 : 3-triphenylnaphthalene (cf. A., 1928, 1034) is confirmed by its oxidation by CrO_3 in AcOH to *o*-benzoylbenzoic acid, its reduction by Na and amyl alcohol to a *tetrahydro*-derivative, m. p. 136—137°, and its conversion by addition of Na followed by hydrolysis into the 1 : 4(?)-*dihydro*-derivative, m. p. 165°. The last-named is dehydrogenated in contact with Pd–$BaSO_4$. The crude Li derivative of 1 : 2 : 3-triphenylnaphthalene gives on alcoholysis 9-phenyl-1 : 2 : 3 : 4-dibenz-9 : 10-dihydroanthracene (*loc. cit.*), with CO_2 gives 2 : 3 : 4-triphenyl-α-naphthoic acid, and with I or Hg gives triphenylnaphthalene and 9-*phenyl*-1 : 2 : 3 : 4-*dibenzanthracene*, m. p. 227° [the constitution of which follows from the hydrolysis of its Na additive product to the 9 : 10-dihydro-derivative (above)], by disproportionation of the primarily formed 1 : 2 : 3-triphenylnaphthyl. The constitution of 9-phenyl-1 : 2 : 3 : 4-dibenz-9 : 10-dihydroanthracene is confirmed by its oxidation with CrO_3 to *o*-benzoylbenzoic acid and phenanthraquinone. In contrast to its behaviour with Hg, the product of interaction of Li and tolane in Et_2O is converted by I into 4-*iodo*-1 : 2 : 3-*triphenylnaphthalene*, m. p. 225°, reduced by Zn and KOH in MeOH to 1 : 2 : 3-triphenylnaphthalene, and by Na and amyl alcohol to an *isomeride* (geometrical ?), m. p. 151°, of 1 : 2 : 3-triphenyltetrahydronaphthalene; it reacts with Li with formation of 4-lithio-1 : 2 : 3-triphenylnaphthalene.

H. A. PIGGOTT.

Allylisomerism in hydrocarbons. E. BERGMANN and H. WEISS (Ber., 1931, **64**, [*B*], 1485—1493).—*Phenyl benzhydryl ketone*, m. p. 135—136°, prepared by the action of boiling aq. H_2SO_4 on phenylhydrobenzoin or, together with *phenyldibenzhydrylcarbinol*, m. p. 229—231°, from Na diphenylmethyl and BzCl, is converted by $MgCH_2PhCl$ into *ααβγ-tetraphenylpropan-β-ol*, m. p. 136—137°, dehydrated by H_2SO_4 and AcOH at 100° to *ααβγ-tetraphenyl-Δ^{α}-propene*, m. p. 142°, *ααβγ-tetraphenyl-Δ^{β}-propene*, m. p. 131°, and a *hydrocarbon* $C_{27}H_{22}$, m. p. 109—110°; under somewhat different conditions, *ααβγ-tetraphenyl-β-propyl acetate*, m. p. 151—153°, is also produced. The structure of ααβγ-tetraphenyl-Δ^{α}-propene is established by its production (with *ααβεζζ-hexaphenyl-$\Delta^{\alpha\epsilon}$-hexadiene*, m. p. 222°) from ααβ-triphenyl-β-bromomethylethylene and MgPhBr. It adds Br with great difficulty, ultimately giving the nuclear-substituted *compound* $C_{27}H_{20}Br_2$, m. p. 114°, whereas the isomeride, m. p. 131°, readily adds Br and loses HBr to give (?) *γ-bromo-ααβγ-tetraphenyl-Δ^{β}-propene*, m. p. 151°. The hydrocarbon, m. p. 131°, is readily oxidised by CrO_3 in AcOH to BzOH and *o*-dibenzoylbenzene, presumably with intermediate formation of 1 : 2 : 3-triphenylhydrindene; ααβγ-tetraphenyl-Δ^{α}-propene is much more slowly converted into *o*-dibenzoylbenzene, isomerisation to the Δ^{β}-propene regulating the rate of the change. ααβγ-Tetraphenyl-Δ^{α}-propene and Na give a red *Na* compound, hydrolysed to ααβγ-tetraphenylpropane, m. p. 87—89°, and converted by Hg into the original substance. The Δ^{β}-propene is slowly transformed by Na into a brown product sparingly sol. in Et_2O and yielding when treated with Hg a resin from which ααβγ-tetraphenyl-Δ^{α}-propene and *ααβγδεζζ-octaphenyl-$\Delta^{\alpha\epsilon}$-hexadiene*, m. p. 255°, are extracted; the only definite product of hydrolysis is ααβγ-tetraphenylpropane in minimal amount.

Et β-phenylpropionate and Mg α-naphthyl bromide afford *α-naphthyl β-phenylethyl ketone*, m. p. 53—54°. *Et methylbenzylacetoacetate*, b. p. 117—118°/12 mm., and MgPhBr give *αα-diphenyl-β-benzyl-Δ^{α}-propene*, m. p. 70—71°.

H. WREN.

Synthesis of alkyl naphthalenes. III. 2 : 3 : 5-Trimethylnaphthalene. D. G. WILKINSON (J.C.S., 1931, 1333—1336).—*o*-Xylyl bromide condenses with ethyl sodiomethylacetoacetate to give *Et* o-*xylylmethylacetoacetate*, b. p. 177—179°/20 mm., which on hydrolysis with 10% NaOH affords β-o-*tolyl*iso*propyl methyl ketone*, b. p. 132—133°/20 mm. (*semicarbazone*, m. p. 152—153°). This is reduced by Na and EtOH to *δ-o-tolyl-γ-methyl*-sec.-*butyl alcohol*, b. p. 152—153°/20 mm., which is converted by way of its bromide and cyanide into γ-*o*-tolyl-αβ-dimethylbutyric acid (amide, m. p. 73°), the *acid chloride* of which (b. p. 140—145°/15 mm.) with $AlCl_3$ gives 1-*keto*-2 : 3 : 5-*trimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m. p. 87°. Reduction of the ketone by Clemmensen's method furnishes 2 : 3 : 5-*trimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, dehydrogenated with Se to 2 : 3 : 5-*trimethylnaphthalene* (*picrate*, m. p. 122°; *styphnate*, m. p. 148—149°).

D. A. FAIRWEATHER.

Fluorine derivatives of naphthalene. G. SCHIEMANN, W. GUEFFROY, and W. WINKELMULLER (Annalen, 1931, **487**, 270—287; cf. A., 1930, 201).—The hydrofluoroboric acid method gives usually good yields of fluoronaphthalene compounds. 1-Fluoro- but not 2-fluoro-naphthalene gives homogeneous substitution products. 1-Fluoronaphthalene (I) (*picrate*, m. p. 113°) has m. p. −9° to −8°, b. p. 212°/760 mm. (slight decomp.), 89°/17 mm. 2-Fluoronaphthalene (II) (*picrate*, m. p. 101°) has m. p. 61°, b. p. 211·5°/737 mm., 90°/16 mm. I and $ClSO_3H$ at 0—5° give 1-fluoronaphthalene-4-sulphonyl chloride (also obtained from diazotised naphthionic acid and HF), which when heated with H_2O at 130—150° for 15 hr. yields 1-*fluoronaphthalene*-4-*sulphonic acid* ($2+H_2O$), m. p. 100° (*Na*, *Pb*, and *Ag* salts; *amide*, m. p. 206°; *anilide*, m. p. 144°), also obtained from I and oleum (15% SO_3). II and $ClSO_3H$ in CCl_4 give 2-*fluoronaphthalene*-6(?)-*sulphonyl chloride*, m. p. 97°, b. p. 144°/0·05 mm., hydrolysed to the corresponding *acid* ($+1H_2O$), hygroscopic, m. p. 105° (*Na* and *Pb* salts; *amide*, m. p. 133°; *anilide*, m. p. 129°), which was also obtained in poor yield from II and oleum (15% SO_3). Diazotised β-naphthylamine-1-sulphonic acid and HF gave 2-*fluoronaphthalene*-1-*sulphonyl chloride*, m. p. 59·5° [*anilide*, m. p. 142·5° (decomp.)]. Nitration of I gives 1-*fluoro*-4-*nitronaphthalene* (III), m. p. 80° (transformed by KOH in EtOH into 4-nitro-1-ethoxynaphthalene, and thereafter by conc. HCl nto 4-nitro-α-naphthol). Nitration of II gives a mixture of mono- and di-nitro-compounds (from which by hydrolysis 1-nitro-2-methoxy- and 1-nitro-2-ethoxy-naphthalene were obtained), a mixture of

dinitro-compounds, or 2-*fluoro-?-trinitronaphthalene*, m. p. 192—193°, according to the experimental conditions. III with Zn and HCl yields 4-*fluoro-α-naphthylamine*, m. p. 48°, b. p. 162°/16 mm. [*hydrochloride*, m. p. 280° (decomp., sealed tube); *sulphate*, m. p. 230°; *Bz* derivative, m. p. 197°], which by the hydrofluoroboric acid method gives 4-*fluoronaphthyl-1-diazonium fluoroborate*, decomp. 163°, and I: 4-*difluoronaphthalene*, m. p. 31·5°, b. p. 97—98°/21 mm. 1:5-Diaminonaphthalene affords *naphthalene*-1:5-*bisdiazonium fluoroborate*, decomp. 180° (commencing at 150°), and 1:5-*difluoronaphthalene*, m. p. 70·5°. 4-*Bromo*-1-*fluoronaphthalene*, m. p. 37°, was obtained (*a*) from I by bromination in CCl_4, and (*b*) from 4-bromo-α-naphthylamine by the hydrofluoroboric acid method, and was oxidised by CrO_3 in AcOH in the presence of V_2O_5 to *o*-phthalic acid and 3-*bromo-6-fluorophthalic acid* (?), m. p. 155° after sintering at 150°. 4-*Bromonaphthalene*-1-*diazonium fluoroborate* decomposes at 151·5°. R. S. Cahn.

Monosulphonic acids of 1-methylnaphthalene. V. Vesely and F. Štursa (Coll. Czech. Chem. Comm., 1931, 3, 328—332).—The isomeride obtained in the prep. of the 4-sulphonic acid by cold sulphonation of 1-methylnaphthalene (A., 1930, 593) is the 5-*sulphonic acid*, m. p. 115° (*amide*, m. p. 176—178°), converted by KOH into 5-methyl-α-naphthol. Sulphonation at 110—120° with H_2SO_4 (*d* 1·84) gives the 3-*sulphonic acid* (*chloride*, m. p. 124—125°; *amide*, m. p. 143—144°), isolated as *Ba* salt, an isomeride being also formed. Fusion of the Na salt of the 3-sulphonic acid with KOH gives 4-methyl-β-naphthol. A. A. Levi.

2-Ethylnaphthalene and its hydrogenation products. G. Levy (Compt. rend., 1931, 192, 1397—1399).—2-Ethylnaphthalene (A., 1908, i, 411), purified by means of its picrate, m. p. 76—77°, has m. p. −7·5°, b. p. 252°/760 mm., d_4^{15} 0·9958. Reduction with Na and EtOH gives a *dihydro*-derivative, b. p. 241°/760 mm., d_0^0 0·9772. With Ni (reduced at 280°) and H_2 at 200°, a *tetrahydro*-derivative, probably 2-ethyl-1:2:3:4-tetrahydronaphthalene, b. p. 114—115°/16 mm., 237°/760 mm. (corr.), d_4^{15} 0·9447, is formed; on further hydrogenation at 160° over Ni (reduced at 250°) it is converted into the *decahydro*-derivative, b. p. 221°/760 mm. (corr.), 92°/13 mm., $d_4^{13\cdot2}$ 0·8763. H. A. Piggott.

[**Action of halogens on fulvenes.**] E. Bergmann (Ber., 1931, 64, [*B*], 1481—1485).—The constitution of 2:3:6-tribromoindone is established synthetically (cf. A., 1930, 1569). The action of Mg and *p*-dibromobenzene in Et_2O on Et orthoformate leads to p-*bromobenzaldehyde diethylacetal*, b. p. 140°/16 mm., hydrolysed to *p*-bromobenzaldehyde, converted by malonic acid and NH_3 into *p*-bromocinnamic acid. Addition of Br to Me *p*-bromocinnamate affords *Me αβ-dibromo-β-*p*-bromophenylpropionate*, m. p. 111°, converted by KOH in aq. EtOH into p-*bromophenylpropiolic acid*, m. p. 201° (decomp.), which by successive treatment with Br and P_2O_5 gives 2:3:6-tribromoindone, m. p. 145—146°. 2:6-*Dibromo-3-phenylindoneoxime*, m. p. 160°, is described. The red substance $C_{22}H_{14}O_2$ obtained by oxidation of monobromodiphenylbenzofulvene (*loc. cit.*) is an *o*-diketone, since it affords a *monoxime*, $C_{22}H_{15}O_2N$, m. p. 245° (decomp.) after darkening at 220°, and a *quinoxaline*, $C_{28}H_{18}N_2$, m. p. 215°. H. Wren.

Stability of organic molecular compounds. T. S. Moore, F. Shepherd, and E. Goodall (J.C.S., 1931, 1447—1456).—The partition curves of picric acid and NH_2Ph between H_2O and $CHCl_3$ were determined. The following are equilibrium consts., determined by the partition method, for the reaction: picric acid+hydrocarbon (or derivative) in $CHCl_3$ additive compound: C_6H_6 0·08 (0·09); PhMe 0·09 (0·12); *o*-, *m*-, and *p*-xylenes 0·12 (0·16), 0·10 (0·14), 0·12 (0·16); mesitylene 0·12 (0·18); $C_{10}H_8$ 2·17; 1- and 2-$C_{10}H_7Me$ 2·76, 3·44; tetrahydronaphthalene 0·20 (0·26); $PhNO_2$ 0·56; *m*-dinitrobenzene 1·03; *o*- and *p*-nitrotoluenes 0·41, 0·57; 2:4-dinitrotoluene 0·67; 2:4:6-trinitrotoluene 1·02; 1-$C_{10}H_7\cdot NO_2$ 1·02; PhBr 0·06 (0·09); *o*- and *p*-dichlorobenzenes 0·07 (0·10), 0·00 (0·03); 1-$C_{10}H_7Br$ 0·17 (0·23). The following are equilibrium consts. for the reaction NH_2Ph+ NO_2-compound additive compound: 2:4:6-trinitrotoluene 0·56; 1:5-$C_{10}H_6(NO_2)_2$ 0·57; *p*- and *m*-dinitrobenzenes 0·18, 0·17; 2:4-dinitrotoluene 0·10 (0·15); *m*-bromonitrobenzene 0·02 (0·06); *p*-chloronitrobenzene 0·01 (0·03); 1-$C_{10}H_7\cdot NO_2$ (0·02); $PhNO_2$ (0·01). Figures in parentheses are corrected for the mol.-vol. effect. The assumptions that (*a*) the compounds are formed from 1 mol. of each constituent, (*b*) that association of picric acid and NH_2Ph in $CHCl_3$ is negligible, and (*c*) that combination of picric acid or $NHPh_2$ with $CHCl_3$ does not alter the relative order of consts. are justified. The effect (apart from compound formation) of a number of substances on the partition curves obscures only the lower consts. The results are discussed and it is concluded (*a*) that introduction of a NO_2-group into a hydrocarbon changes the mode of its reaction with picric acid, and (*b*) that the reaction of $NHPh_2$ with mononitro-compounds may be purely physical, becoming chemical with di- and tri-nitro-compounds. The compound $C_{10}H_7\cdot NO_2(1),C_6H_2(NO_2)_3\cdot OH$ has m. p. 71°. R. S. Cahn.

Interaction of anilides and hypochlorous acid. D. R. Pryde and F. G. Soper (J.C.S., 1931, 1510—1514).—Velocity coeffs. are recorded for the formation of *N*-Cl derivatives in buffered solutions from pure HOCl and acetanilide, *o*-, *m*-, and *p*-acetamidobenzoic acids, *o*-, *m*-, and *p*-chloroacetanilides. These are proportional to the [OH′] over the range p_H 5·7—6·2 examined. The implications of this relation and the possibility of the reaction proceeding between the *aci*-form of the anilide and OCl′ are discussed. R. S. Cahn.

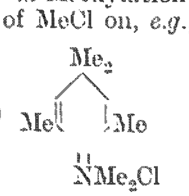
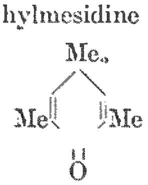
Direct interchange of chlorine in the interaction of *p*-toluenesulphonamide and *N*-chloroacetanilide. D. R. Pryde and F. G. Soper (J.C.S., 1931, 1514—1518).—The times for 50% hydrolysis of *N*-chloroacetanilide (I) and *p*-toluenesulphonchloroamide (II) in neutral solution at 25° are 7 days and 7 min., respectively. The former estimate is confirmed by the stability of aq. solutions of I in the presence of phenols. A neutral aq. solution of I reacts with *p*-toluenesulphonamide to form II and acetanilide, the bimol. velocity coeff. being 0·47 at

25°. This reaction must proceed by direct interchange of Cl, because it is several hundred times as fast as the production of HOCl from I. The velocity is approx. the same in 0·1N-HCl, and since II is more unstable than I towards HCl, the rate of production of Cl_2 from I in this medium is increased by the addition of p-toluenesulphonamide. R. S. CAHN.

Use of polychlorobenzenes in the synthesis of dyes. II. Preparation of chloronitroanilines from *o*- and *p*-dichlorobenzenes. A. I. KIPRIANOV and M. M. DASCHEVSKI (Ukrain. Chem. J., 1930, 5, [Tech.], 241—248).—Heating a dichloronitrobenzene with conc. aq. NH_3 in an autoclave gives the corresponding chloronitroaniline. The effects of concentration and quantity of NH_3 are discussed. The use of bronze autoclaves is not recommended owing to the injurious effect of Cu on the reaction. E. B. UVAROV.

Action of nitrous acid on 3-nitro- and 4-nitrodimethylaniline and the so-called β-3 : 4-dinitrodimethylaniline. H. H. HODGSON and E. W. SMITH (J.C.S., 1931, 1508—1510).—The α-form of 3 : 4-dinitrodimethylaniline (I) (J.C.S., 1920, **117**, 1) has the structure assigned to it, but the β-form is a mixture of I and 2 : 4 : 5-trinitrodimethylaniline (II). When the prep. is carried out at 30°, 2 : 4 : 5-trinitromonomethylaniline replaces II. I is also prepared from 3-nitrodimethylaniline and HNO_3. HNO_2 with 3-nitro- and 4-nitroso-dimethylaniline yields N-nitroso-3-nitro- and N-nitroso-4-nitro-monomethylaniline, respectively, hydrolysed by boiling conc. HCl to 3-nitro- and 4-nitro-methylaniline, respectively. R. S. CAHN.

Nuclear alkylation of aromatic bases. I. Action of methyl alcohol on the hydrochlorides of *o*- and *p*-toluidine, mesidine, and dimethylmesidine. D. H. HEY (J.C.S., 1931, 1581—1594).—Contrary to the usual view, methylation may occur in the m-position in the Hofmann–Martius reaction after the p- and o-positions have been substituted. Phenols, hydrocarbons, and acridine derivatives are by-products. m-Methylation is considered to occur by action of MeCl on, *e.g.*, N-dimethylmesidine to yield

(I)   (II.)

I, which either by loss of HCl and migration of a Me group yields N-dimethyl*iso*duridine, or is hydrolysed to II, which by rearrangement yields *iso*durenol. Alkylation was carried out in electrically-heated steel autoclaves, temp. being the most important factor in determining the extent of the reaction. Fe had no effect on the yield of phenols obtained. MeOH and o-toluidine hydrochloride, heated at 260—280° for 10 hr., yielded mesitol (III), *iso*durenol (*bromo*-derivative, m. p. 135°; *phenylurethane*, m. p. 178—179°; *benzoate*, m. p. 71—72°; *bromoisodurenyl acetate*, m. p. 98°), mesidine (>50%) (IV) (p-*toluenesulphonyl* derivative, m. p. 167°; *picrate*, m. p. 189—191°), *iso*duridine (V), m. p. 217·5°, b. p. 258—260° (*picrate*, m. p. 199—200°), 1 : 3 : 7 : 9-tetramethylacridine (VI), and another acridine derivative, m. p. 73—74° (possibly 1 : 3-dimethylacridine). MeOH and p-toluidine hydrochloride, heated at 250—275° for 12 hr., gave III, IV, V, and VI. Mesidine hydrochloride and MeOH, heated at 240—270° for 12 hr., gave III, hexamethylbenzene, IV, V, and an acridine derivative. Methylation of mesidine (cf. A., 1907, i, 122) yielded N-methylmesidine, b. p. 220—221° (*picrate*, m. p. 179°; p-*toluenesulphonyl* derivative, m. p. 145—146°), or N-dimethylmesidine [*picrate*, m. p. 182° (decomp.)], according to the conditions. Dimethylmesidine, MeOH, and conc. HCl, heated at 230—250° for 12 hr., gave III, pentamethylphenol (*phenylurethane*, m. p. 215°; *Bz* derivative, m. p. 127°), methylamines, IV, and V. R. S. CAHN.

Catalytic hydrogenation of nitriles under reduced pressure: a correction. V. GRIGNARD, R. ESCOURROU, and A. FARGIER (Bull. Soc. chim., 1931, [iv], 49, 522—527).—Hydrogenation of phenylacetonitrile in presence of PtO_2 on pumice at 150°/80 mm. yields, not the imine, but a mixture (mol. compound) in approx. equimol. proportions of phenylacetonitrile and β-phenylethylamine which distils at 215°, together with a little β-phenylethylamine carbonate, m. p. 83—84°. Similarly, PhCN in presence of Ni at 175°/13 mm. yields an equimol. mixture, b. p. 80—82°/15 mm., of PhCN and benzylamine, together with dibenzylamine and a little benzylamine carbonate, m. p. 89—90°. Hydrogenation of phenylacetonitrile in presence of an equal wt. of Ac_2O at 175—180°/18—20 mm. (Pt-black catalyst) affords β-phenylethylacetamide, indicating that the imine formed in the first stage of the hydrogenation is acetylated more rapidly than it condenses, but that the acetylated imine is too readily hydrogenated to be isolated. R. BRIGHTMAN.

Nitration of derivatives of α- and β-naphthylamines. I. Nitration of methyl and ethyl α-naphthylcarbamates and of *N*-α-naphthyl-*N'*-ethylcarbamide. C. GROENEVELD (Rec. trav. chim., 1931, 50, 681—707).—An investigation of the protection afforded in nitration, by conversion of an NH_2 group into the corresponding ethylcarbamide or Me (Et) carbamates. Me (I) and Et (II) α-naphthylcarbamates give with HNO_3 (d 1·45), *Me* (III), m. p. 205—207° (decomp.), and *Et* (IV), m. p. 183—185°, 2 : 4-*dinitro-α-naphthylcarbamates*, hydrolysed to 2 : 4-dinitro-α-naphthylamine. The latter is also formed by nitration of N-α-naphthyl-N'-ethylcarbamide. I and II with 100% HNO_3 give 2 : 4 : 5-trinitro-α-naphthylamine (V), formed also by nitrating III and IV, and a little *Me* (VI), m. p. 230°, and *Et*, m. p. 196—198°, 2 : 4 : 5-*trinitro-α-naphthylcarbamates* (?) (VII). N-α-Naphthyl-N'-ethylcarbamide with 100% HNO_3 gives V and N-(2 : 4 : 5-trinitro-α-naphthyl)-N'-nitro-N'-ethylcarbamide, the presence of the latter being inferred from the formation of VI and VII when the nitration product is treated with the appropriate alcohol. The nitration of α-naphthylamine derivatives is discussed. J. D. A. JOHNSON.

Preparation of benzidinesulphone. C. COURTOT and R. EVAIN (Bull. Soc. chim., 1931, [iv], 49, 527—530).—Benzidinesulphone, m. p. 327—328° (Ac_2, m. p. 382—383°; Bz_2 derivative, m. p. 384—385°), is

obtained (yield 70%) by sulphonation of benzidine (finely-powdered) with 1600 parts per mol. of 21% oleum at 70—80° for 5 hr. The sulphate of the sulphone is precipitated on dilution with ice and decomposed with 20% NaOH. More dil. or small amounts of oleum give lower yields and more conc. oleum affords no proportionate increase. Benzidine sulphate as starting material is unnecessary (cf. A., 1890, 57). Although benzidinesulphone is not readily tetrazotised in presence of HCl, the finely-divided sulphate obtained by pouring a H_2SO_4 solution on to ice is readily tetrazotised. R. BRIGHTMAN.

Action of *p*-nitrobenzeneazo-β-naphthol on sodium hydrogen sulphite. IV. Hydrogen sulphite compounds of azo-dyes. N. N. VOROSCHCOV and P. A. BELOV (J. Gen. Chem. Russ., 1931, **1**, 39—47).—*p*-Nitrobenzeneazo-β-naphthol forms a hydrogen sulphite compound in EtOH or $CHCl_3$ solution, which is decomposed by alkali, giving unchanged para-red, showing that the NO_2 group is not affected. The hydrogen sulphite compound forms Ca, Ba, Ni, Cu, Pb, Ag *salts*. Dissociation of the Na salt increases with dilution in aq. solution and with addition of OH ions. Increase of H ions slightly increases the stability up to a limit. E. B. UVAROV.

Constitution of *o*-hydroxyazo-compounds. K. VON AUWERS and E. WOLTER (Annalen, 1931, **487**, 79—97).—Refractometric data are determined for a number of derivatives of *o*-hydroxyazo-compounds and quinonephenylhydrazones, but cannot be used to distinguish between the azo- and hydrazone formulæ for benzeneazo-α- and -β-naphthols; the similarity of their behaviour, however, indicates that they have similar structures, and both are therefore azo-compounds (cf. A., 1930, 214).

Interaction of benzeneazo-*p*-cresol with $Cl\cdot CO_2Et$ gives the O-*carbethoxyl ether*, m. p. 46—47°, b. p. 236°/14 mm., the constitution of which is determined by reduction to the *hydrazo*-derivative (I), m. p. 69° [*Bz derivative* $C_7H_6(O\cdot CO_2Et)\cdot NH\cdot NBzPh$ (II), m. p. 143°], with Zn and AcOH in cold EtOH; further reduction in boiling EtOH proceeds in the two directions: $C_7H_6(OH)\cdot NH\cdot CO_2Et + NH_2Ph \longleftarrow C_7H_6(O\cdot CO_2Et)\cdot NH\cdot NHPh$ (I) $\longrightarrow C_7H_6(OH)\cdot NH_2 + NHPh\cdot CO_2Et$. Reduction of II gives 3-hydroxy-*p*-tolylurethane and benzanilide; the absence of rearrangement of an *N*- into an *O*-acyl derivative under these conditions is confirmed by the reductive fission of benzoquinone- and benzaldehyde-acetyl- and -benzoyl-phenylhydrazones and 3-phenylhydrazino-*p*-cresol. The O-*carbethoxyl* derivatives, m. p. 86—87° and 67—68°, respectively, of β-benzeneazo-α- and α-benzeneazo-β-naphthols were not successfully reduced to stable hydrazo-derivatives; in both cases NH_2Ph was formed, but no other product was isolated in a pure condition. A quant. study of the reductive fission of the Bz derivatives of the benzeneazonaphthols gave similar results in the two cases, favouring the *O*-Bz structure. A similar study of the Bz derivative of 5-chloro-2 : 6-dihydroxy-1-benzeneazonaphthalene indicates that fission occurs (about 90%) to the aminonaphthol and benzanilide, and (10%) to the benzamidonaphthol and NH_2Ph. H. A. PIGGOTT.

Addition of phenylthiocarbimide to alkylhydrazines. M. BUSCH and R. SCHMIDT (J. pr. Chem., 1931, [ii], **130**, 342—346).—Fischer's phenylethylthiosemicarbazide from ethylhydrazine and phenylthiocarbimide combines with PhCHO to give *benzylidene-4-phenyl-2-ethylthiosemicarbazone*, m. p. 104°, and reacts with HNO_2 to form phenylethylthiocarbamide; it must therefore be the 4-phenyl-2-ethylthiosemicarbazide, $NH_2\cdot NEt\cdot CS\cdot NHPh$. Ethylhydrazine hydrochloride, however, reacts with phenylthiocarbimide (2 mols.) in EtOH to give the *hydrochloride* (decomp. 291°) of 3-*anilino-1-ethylthiodiazolone-ω-anil*, m. p. 147°. Benzylhydrazine hydrochloride similarly affords with phenylthiocarbimide the *hydrochloride*, decomp. 295°, of *anilinobenzylthiodiazoloneanil*, m. p. 128°, but phenylhydrazine gives 1 : 4-diphenylthiosemicarbazide. F. R. SHAW.

Diazo-compounds. A. QUILICO (Gazzetta, 1931, **61**, 326—332).—The oxidising properties of normal diazo-hydrates are discussed, and evidence is adduced in favour of the formula R·NO:NH suggested by Angeli (A., 1926, 947; 1929, 1290). E. E. J. MARLER.

1-Diazo-β-naphthol-4-sulphonic acid. M. BATTEGAY, H. SILBERMANN, and P. KIENZLE (Bull. Soc. chim., 1931, [iv], **49**, 716—723).—Nitration of 1-diazo-β-naphthol-4-sulphonic acid yields an extremely stable nitrodiazo-compound, decomp. 203°, converted by elimination of the N_2 group, reduction, and elimination of the SO_3H group with Na–Hg into 2 : 6-aminonaphthol (Ac_2, m. p. 220°, and Bz_2 derivative, m. p. 234°). Further evidence that the NO_2 group enters the 6-position is obtained by conversion of the aminonaphthol into 2 : 6-dihydroxynaphthalene (diacetate, m. p. 175°) (cf. A., 1930, 205), also obtained from 6-amino-β-naphthol-4-sulphonic acid. The 6-chloro-β-naphthol-4-sulphonic acid obtained from the aminonaphtholsulphonic acid by the Sandmeyer reaction is converted by excess of PCl_5 at 170—180° into 2 : 6 : 8(or 1 : 3 : 7)-trichloronaphthalene, m. p. 113°, phosphoric esters of chloronaphthol being also formed, and some 1 : 4 : 6-*trichloro-β-naphthol*, m. p. 136—137° (*benzoate*, m. p. 175—176°). Chlorination of 1-diazo-β-naphthol-4-sulphonic acid in H_2SO_4 (100%) at 65—70° yields 6-*chloro-1-diazo-β-naphthol-4-sulphonic acid*, decomp. 180—182°, converted by successive elimination of the N_2 and SO_3H groups into 6-chloro-β-naphthol, m. p. 115° (benzoate, m. p. 124—125°). 6-*Bromo-1-diazo-β-naphthol-4-sulphonic acid* and 6-*bromo-β-naphthol-4-sulphonic acid* are similarly obtained, but with Na–Hg the latter affords β-naphthol. Elimination of the SO_3H group with HCl (20% and 37%) at 130° and at 180° yielded tars, but oxidation with $KMnO_4$ yields 4-bromophthalic acid, m. p. 170—171°. Sulphonation of 1-diazo-β-naphthol-4-sulphonic acid with 20% and 30% oleum at 50° and 70—75° for 30 hr. yielded no definite product, but a product containing Cl was obtained with $ClSO_3H$ at 70—75°. R. BRIGHTMAN.

Transformation of diazoaminobenzene into aminoazobenzene. E. ROSENHAUER (Ber., 1931, **64**, [*B*], 1438—1439).—Contrary to Earl, benzenediazoaminoazobenzene is not an intermediate product of the transformation but a secondary product of the

aminoazobenzene. Its isolation establishes the intermediate formation of diazonium salt. H. WREN.

Action of $\alpha\gamma$-dichloropropylene on sodium derivatives of phenols. L. BERT (Compt. rend., 1931, **192**, 1565—1567).—The α-Cl atom in $\alpha\gamma$-dichloropropylene is the more reactive and the compound reacts with the Na derivatives of phenols to form β-*chloroallyl ethers* of the following (all b. p. at 20 mm.): phenol, b. p. 120—121°; *o*-cresol, b. p. 132—133°; *m*-cresol, b. p. 137—138°; *p*-cresol, b. p. 137—138°; cumenol, b. p. 156°; carvacrol, b. p. 156—157°; thymol, b. p. 157·5°; guaiacol, b. p. 153—154°; eugenol, b. p. 185°; *iso*eugenol, b. p. 189°; salicylaldehyde, b. p. 179°; Me salicylate, b. p. 188°; β-naphthol, b. p. 195°, m. p. 60°; quinol, b. p. 213—214°, m. p. 69°. The products from α-naphthol, pyrocatechol, and resorcinol decompose when distilled at 20 mm. F. R. SHAW.

Nitrosation of phenols. XI. Constitution of 3-chloro-4-nitrosophenol. H. H. HODGSON (J.C.S., 1931, 1494—1499; cf. A., 1930, 1281).—As previously suggested (A., 1929, 1062), direct nitrosation of *m*-chlorophenol yields 3-chloro-4-nitrosophenol (I), m. p. 135°, and not 3-chlorobenzoquinone-4-oxime (II), since the product (*a*) is reduced by sodium hyposulphite and Na_2CO_3 to 3-chloro-4-aminophenol, (*b*) reacts more readily than II with NH_2OH, and (*c*) forms a picrate. I in MeOH gives a deep green colour with a drop of conc. H_2SO_4 or oleum, and a deep red with more oleum. I with HCl in Et_2O yields II, and with CH_2N_2 the Me ether of II. I with $AgNO_3$ and (but not without) NH_3, and I and II with AgOAc and NaOAc give the *Ag* salt, brick-red, of II, which with MeI gives the Me ether of II. I and II give the p-*nitrophenylhydrazone* of II, m. p. indef. (blue in aq. or alcoholic NaOH or NH_3, owing to isomerisation to a double indamine structure). With NH_2OH,HCl in MeOH or EtOH I gives *m*-chlorophenol, whereas II gives only a trace. Addition of β-naphthylamine to I and NH_2OH,HCl in MeOH gives 3-*chloro*-1-*hydroxybenzene*-4-*azo*-β-*naphthylamine*, m. p. 210—212°. Addition of β-naphthol and NaOAc gives similarly an azo-compound with I, but not with II. The *picrate* of I has m. p. 151° (decomp.), and 3-*chloro*-4-*nitroanisole picrate*, m. p. 174·5° (decomp.). I in dry Et_2O or C_6H_6 with $AlCl_3$ yields II. R. S. CAHN.

Indicators. II. 2 : 6-Dinitrophenol. I. V. KULIKOV and S. V. PANOVA (Trans. Inst. Pure Chem. Reag., 1931, **10**, 36—45).—The greatest yield of 2 : 6-dinitrophenol in the nitration of *o*-nitrophenol is obtained in the presence of definite proportions of AcOH and H_2SO_4. It is possible to isolate 30—35% of 2 : 6- and 40% of 2 : 4-dinitrophenol in the pure state. E. S. HEDGES.

Explosion during catalytic reduction of nitroanisole in the liquid phase. T. S. CARSWELL.—See this vol., 919.

Use of polychlorobenzenes in the synthesis of dyes. I. Preparation of chloronitrophenols, chloroaminophenols, and chloroaminophenolsulphonic acids from *o*- and *p*-dichlorobenzene. A. I. KIPRIANOV and P. P. MICHAILENKO (Ukrain. Chem. J., 1930, **5**, [Tech.], 225—239).—Hydrolysis of 2 : 5- and 3 : 4-dichloronitrobenzenes gives 4 : 2 : 1- and 2 : 4 : 1-chloronitrophenols, giving rise to green dyes with Na polysulphide. Reduction of 4-chloro-2-nitrophenol with Na_2SO_3 gives the corresponding *chloroaminophenol*, m. p. 138°. Methods for the prep. of two chloroaminophenolsulphonic acids are described. Analogous attempts to prepare corresponding derivatives of 2 : 3-dichloronitrobenzene were unsuccessful. An explanation of the failure is put forward. E. B. UVAROV.

Phenacetin hydrochloride. I. H. SANBORN (J. Physical Chem., 1931, **35**, 1345—1350).—Phenacetin combines with HCl mol. for mol. to form the hydrochloride, m. p. 154°/741 mm., stable in an atm. of HCl, but decomposing under room conditions, and in H_2O, into its components. L. S. THEOBALD.

β-Phenylethylamines. II. Synthesis of tyramine. K. H. SLOTTA and W. ALTNER (Ber., 1931, **64**, [*B*], 1510—1520; cf. this vol., 213).—β-Phenylethyl alcohol is converted into β-phenylethyl bromide by distillation with 48% aq. HBr or, preferably, by repeated saturation with gaseous HBr and heating of the mixture at 100°. Treatment of the bromide with HNO_3 (*d* 1·51) at 0—10° affords in 48% yield β-*p*-nitrophenylethyl bromide, m. p. 69°, which yields with hexamethylenetetramine in $CHCl_3$ the additive *compound*, $C_{14}H_{20}O_2N_5Br$, m. p. 181—182° according to the rate of heating (best isolated by keeping the mixture at room temp. and periodic removal of the precipitated adduct). Treatment of the additive compound with 95% EtOH and conc. HCl affords β-*p*-nitrophenylethylamine hydrochloride, m. p. 214°, in 85% yield, reduced by $SnCl_2$ and conc. HCl to the *Sn* compound, $C_{16}H_{28}N_4Cl_{12}Sn_2$, converted by successive diazotisation, heating in aq. solution, treatment with Na_2CO_3, and extraction with anisole into β-*p*-hydroxyphenylethylamine (tyramine), m. p. 165—166° after softening at 155°, in 64% yield. β-*p*-Nitrophenylethyl bromide, phthalimide, and anhyd. K_2CO_3 at 150° afford β-p-*nitrophenylethylphthalimide*, m. p. (indef.) 223—224° after softening at 190°, reduced by $SnCl_2$ and HCl through a $Sn^{....}$ double salt to β-p-*aminophenylethylphthalimide hydrochloride*, m. p. 231—232°. β-*p*-Aminophenylethylamine is obtained by fission of the $Sn^{....}$ salt described above with K_2CO_3 and NaOH, reduction of β-*p*-nitrophenylethylamine hydrochloride with Zn–Hg, or reductive fission of β-*p*-nitrophenylethylphthalimide with Na_2S.

β-Phenylethyl bromide and hexamethylenetetramine yield the *product* $C_{14}H_{21}N_4Br$, m. p. 177—178°, converted by 96% EtOH and conc. HCl into β-phenylethylamine hydrochloride in 82·5% yield. H. WREN.

2-Nitro-*m*-cresol. A. CORBELLINI and C. RAVAZZONI (Atti R. Accad. Lincei, 1931, [vi], **13**, 132—137; cf. this vol., 956).—Repetition of the series of reactions employed by Gibson (J.C.S., 1923, **123**, 1270) to establish the constitution of the nitro-*m*-cresol, m. p. 41°, shows that this compound is 6-(not 2-)nitro-*m*-cresol. The values of the m. p. given by Jacobsen (A., 1883, 1124) for 3-methoxyphthalic acid and its anhydride are actually those for 4-methoxyphthalic acid and anhydride, and if Gibson obtained this acid from the nitro-*m*-cresol, transference of the

substituent from the 2- to the 6-position must be assumed. The methoxytoluic acid obtained according to Gibson's scheme has m. p. 138—139° (not 114°) and is identical with the 3-methoxy-*o*-toluic acid formed on oxidation of β-*m*-homosalicylaldehyde methyl ether (Chuit and Bolsing, A., 1906, i, 283). Oxidation of 3-methoxy-*o*-toluic acid by means of alkaline $KMnO_4$ gives 3-methoxyphthalic acid, m. p. 173—174° (anhydride, m. p. 159—160°); a mixture of this anhydride with that prepared from 3-nitrophthalic acid (Corbellini and Rossi, *loc. cit.*) has the same m. p. T. H. Pope.

Phosphoric esters of 2 : 4-diphenyl-α-naphthol. A new case of dimorphism. A. Franssen (Bull. Soc. chim., 1931, [iv], **49**, 550—556).—When 2 : 4-diphenyl-α-naphthol (I) is heated for 7—8 hr. with PCl_5 in CCl_4, *tri*-2 : 4-*diphenyl-α-naphthyl phosphate* is obtained, m. p. 198—199° (from CCl_4) and m. p. 130° (from C_6H_6), together with a residue sol. in EtOH containing acid phosphoric esters, and, probably, unchanged I, but only traces of 1-chloro-2 : 4-diphenylnaphthalene and di-2 : 4-diphenyl-α-naphthyl ether. The form m. p. 130° is converted into the form m. p. 198—199° by suspension in boiling EtOH; the reverse transformation is effected at about 200°. On hydrolysis tri-2 : 4-diphenyl-α-naphthyl phosphate affords I and a little di-2 : 4-diphenyl-α-naphthyl phosphate, m. p. 220—221°. R. Brightman.

Synthesis of 4-ethylguaiacol (4-hydroxy-3-methoxyethylbenzene). K. Brand and G. Westerburg (Arch. Pharm., 1931, **269**, 326—335).—Condensation of vanillin and malonic acid in pyridine with a little piperidine at 100° gives ferulic acid (4-hydroxy-3-methoxycinnamic acid). A higher temp. gives an oil [(?) 4-hydroxy-3-methoxystyrene] which easily resinifies. Hydroferulic acid (from the reduction of ferulic acid with Pd–$CaCO_3$ catalyst) when distilled with soda-lime gives a small yield of 4-ethylguaiacol. Apocynin benzoate (from apocynol benzoate, the prep. of which is improved; cf. J.C.S., 1908, **93**, 1520) is reduced by Clemmensen's method to 4-ethylguaiacol benzoate. This substance, and its NO_2 derivative, are identical with similar products obtained from beech-wood creosote. Hydrolysis gives 4-ethylguaiacol. A. A. Levi.

Bases derived from substituted propenylbenzenes. Preparation of pure methylamine. T. M. Sharp and W. Solomon (J.C.S., 1931, 1468—1478).—α-Acetoxy-β-bromopropylbenzenes, containing an AcO group in the *p*-position to the side-chain, yield αβ-di(methylamino)-compounds on treatment with NH_2Me; when, however, the substituent is in the *m*-position or when the *p*-OH group is methylated, methylamino-alcohols are formed. *iso*Myristicin acetoxybromide gives the α-NHMe-β-OH-derivative. Acetyl*iso*chavibetol acetoxybromide gives two bases; one of these probably has the NHMe group in the α-position, but the structure of the other is uncertain, as both yield an α-OH-β-NHMe-compound on methylation. The position of the substituents is determined by comparison with bases derived from the corresponding methoxybromides. Migration of the NHMe group is assumed to take place through compounds of the type $R\cdot CH<\begin{smallmatrix}CHMe\\NMe\end{smallmatrix}$ (cf. A., 1914, i, 667, 828).

Acetyl*iso*eugenol dibromide in AcOH with AgOAc gives the *acetoxybromide*, crystals, which with NH_2Me in EtOH at 110° yields αβ-*di(methylamino)-α-4-hydroxy-3-methoxyphenylpropane* (*sulphate*, m. p. 254°). *iso*Myristicin dibromide similarly yields the *acetoxybromide*, m. p. 62—64°, and *α-methylamino-β-hydroxy-α-3-methoxy-4 : 5-methylenedioxyphenylpropane*, an oil [*hydrochloride*, m. p. 233—235° (decomp.) after sintering at 231°; *hydrobromide*, m. p. 239° (decomp.); *oxalate*, m. p. 251° (decomp.); *picrate*, m. p. 179—182°]. This, when boiled with Ac_2O and AcCl and subsequently hydrolysed by alcoholic KOH, is partly transformed into its diastereoisomeride (*hydrochloride*, m. p. 212—216°). *Acetyl*iso*chavibetol dibromide*, m. p. 109—111° (prep. from *acetyl*iso*chavibetol*, m. p. 101°, in Et_2O), similarly gives the *acetoxybromide*, a syrup; *base* A, $C_{11}H_{17}O_3N$, m. p. 143—146° [*oxalate* $+1\cdot5H_2O$, m. p. 222·5° (decomp.)], and *base* B, $C_{11}H_{17}O_3N$, m. p. 166—167° [*oxalate*, m. p. 222·5° (decomp.)]. Base *A* with CH_2N_2 yields α-methylamino-β-hydroxy-α-3 : 4-dimethoxyphenylpropane, m. p. 60—62° [hydrochloride, m. p. 206—207°; *oxalate*, m. p. 147° (decomp.)] (cf. A., 1910, i, 411). Base *B* similarly yields a *Me ether*, m. p. 95—97° [*hydrochloride*, m. p. 204—205°; *oxalate*, m. p. 147° (decomp.)]. *iso*Myristicin dibromide and NaOMe gives *β-bromo-α-methoxy-α-3-methoxy-4 : 5-methylenedioxyphenylpropane*, a varnish, which with $NHMe_2$ in EtOH at 130° gives 3-methoxy-4 : 5-methylenedioxyphenyl ethyl ketone (A., 1912, i, 196), and *β-methylamino-α-methoxy-α-3-methoxy-4 : 5-methylenedioxyphenylpropane*, an oil [*hydrochloride*, m. p. 252° (decomp.)], which with cold HCl yields *β-methylamino-α-hydroxy-α-3-methoxy-4 : 5-methylenedioxyphenylpropane*, m. p. 122—124° (*hydrochloride*, m. p. 194—198°). Methyl*iso*eugenol dibromide similarly yields the *methoxybromide*, a syrup, *β-methylamino-α-methoxy-α-3 : 4-dimethoxyphenylpropane*, an oil (*hydrochloride*, m. p. 167° to a cloudy liquid clear at 190°), and *β-methylamino-α-hydroxy-α-3 : 4-dimethoxyphenylpropane*, m. p. 130—131° [*oxalate*, m. p. 217—218° (decomp.)]. This last base, together with neutral material, was also obtained when the Me ether of base *A* or *B* was treated with PCl_5 in $CHCl_3$, followed by boiling with alcoholic KOH. *p*-Hydroxyphenylethylcarbinol (A., 1908, i, 260) on acetylation followed by treatment with Br yields *p-acetoxypropenylbenzene dibromide*, m. p. 125—129°, which with AgOAc and AcOH gives *β-bromo-α-p-diacetoxy-α-phenylpropane*, oil. This with NH_2Me in EtOH at 110° gives neutral material and *αβ-di(methylamino)-α-p-hydroxyphenylpropane* (*sulphate*, $+1\cdot5H_2O$, m. p. 211—213°). All m. p. are corrected.

A method is given for preparing NH_2Me,HCl containing less than 0·5% of NH_4Cl from material containing 5% of the latter. R. S. Cahn.

Decomposition products of safrole with methyl alcohol and alkali. T. Hiraidzumi (J. Soc. Chem. Ind. Japan, 1931, **34**, 208—212B).—Benzoylation of the mixture of methoxymethyl-4-propenylpyrocatechols obtained by the action of MeOH and KOH on safrole gives benzoylmethoxy*iso*eugenol and *benz-*

*oylmethoxyiso*chavibetol, m. p. 55°, also obtained as follows: the mixed methoxymethyl-4-propenylpyrocatechols give diacetyl-4-propenylpyrocatechol, hydrolysed by NH_3 in Et_2O to 4-propenylpyrocatechol, new m. p. 105·5°, and b. p. 152°/7 mm. (cf. A., 1908, i, 260) (*Et_2 ether*, m. p. 54·5°; *Bz_2* derivative, m. p. 100°). The 2-Ac derivative of this when condensed with Na and chlorodimethyl ether gives acetylmethoxy*iso*chavibetol, hydrolysed and benzoylated to benzoylmethoxy*iso*chavibetol. Physical properties are recorded for pure methoxy*iso*eugenol, b. p. 144°/10 mm., and methoxy*iso*chavibetol, b. p. 154°/10 mm. (decomp. when kept), recovered from the Bz derivatives.

A. A. Levi.

Separation of methoxy*iso*chavibetol from methoxy*iso*eugenol. T. Kuwata (J. Soc. Chem. Ind. Japan, 1931, **34**, 212—214B).—Separation is effected by fractionation of the Ac derivatives.

A. A. Levi.

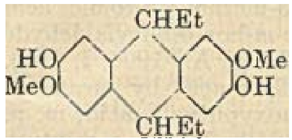
Primary additive products in indirect substitution in the benzene nucleus. III. Additive products of 4 : 4′-dialkoxydiphenyls with nitric acid. J. van Alphen (Rec. trav. chim., 1931, **50**, 657—668; cf. this vol., 723).—The stability of additive compounds of dialkoxydiphenyls and HNO_3 is shown to be related to the basicity of the former. 4 : 4′-*Dimethoxy*-3 : 3′-*dimethyldiphenyl* (I), m. p. 154·5°, gives with 2 mols. of HNO_3 in CCl_4 a blue additive compound which rapidly decomposes and when crystallised gives 5(?)-*nitro*-4 : 4′-*dimethoxy*-3 : 3′-*dimethyldiphenyl*, m. p. 137°. Methylation of *pp*′-diphenol gives 4′-*hydroxy*-4-*methoxydiphenyl* (II), m. p. 183·5°, which behaves like I, giving 3′-*nitro*-4′-*hydroxy*-4-*methoxydiphenyl* (III), m. p. 117°. The *Ac* derivative (m. p. 101°) of II similarly gives 3-*nitro*-4′-*acetoxy*-4-*methoxydiphenyl*, m. p. 152·5°, hydrolysed to 3-*nitro*-4′-*hydroxy*-4-*methoxydiphenyl*, m. p. 127°. Methylation of the last gives 3-*nitro*-4 : 4′-*dimethoxydiphenyl*, m. p. 121° (also prepared from III), nitrated to 3 : 3′-dinitro-4 : 4′-dimethoxydiphenyl. From II, 3 : 3′ : 5′(?)-*trinitro*-4′-*hydroxy*-4-*methoxydiphenyl*, m. p. 219° (*Ac* derivative, m. p. 218°), has also been prepared. 4-*Methoxy*-, m. p. 158°, and 4-*ethoxy*-4′-*benzoyloxydiphenyl*, m. p. 175·5°, form no additive compound with HNO_3. 4-*Methoxy*-4′-*ethoxydiphenyl*, m. p. 152°, from II by ethylation or by methylation of 4-*ethoxy*-4′-*hydroxydiphenyl*, m. p. 168°, gives a relatively stable additive *compound* with 2 mols. of HNO_3.

J. D. A. Johnson.

Dissociable organic oxides: a dimethoxyrubrene. C. Dufraisse and R. Buret (Compt. rend., 1931, **192**, 1389—1391).—The prep. from *p*-methoxyphenylacetylene of the *carbinol* $OMe·C_6H_4·C⋮C·CPh_2·OH$, m. p. 67—68° (*Me ether*, m. p. 119—210°; *Et ether*, m. p. 104—105°), its *chloride*, m. p. 137—138°, a *dimethoxyrubrene*, m. p. 244—245° ($+0·5C_6H_6$, m. p. 238—239°), and α-*anisoyl*-ββ-*diphenylethylene*, m. p. 104—105°, is reported. The dimethoxyrubrene has the characteristic properties and absorption spectrum of the rubrenes, and when insolated in solution in presence of O_2 forms an *oxide*, which, however, yields only 52% of its oxidic O in the gaseous form on dissociation.

H. A. Piggott.

Structure of di*iso*eugenol. R. D. Haworth and C. R. Mavin (J.C.S., 1931, 1363—1366).—Di*iso*eugenol has the annexed structure, since its Me_2 ether is oxidised



2 : 3 : 6 : 7-*tetramethoxyanthraquinone* (I), which has been synthesised. Dimethyl*iso*eugenol is stable to $KMnO_4$ in $COMe_2$, but with CrO_3 in AcOH gives 2 : 3 : 6 : 7-*tetramethoxy*-9-*ethylanthranol* (?), red, m. p. 193°, or using more CrO_3 I, yellow, m. p. 344°. *m*-Hemipinic acid, veratrole, and $AlCl_3$ in CS_2 give 4 : 5 : 3′ : 4′-*tetramethoxy*-2-*benzoylbenzoic acid*, m. p. 222—223°, which when heated with 80% H_2SO_4 gives I.

R. S. Cahn.

Dehydration of *cis*- and *trans*-secondary cyclanols. G. Vavon and M. Barbier (Bull. Soc. chim., 1931, [iv], **49**, 567—582).—The rate of dehydration of secondary alcohols of the *cyclo*pentane, *cyclo*hexane, terpene, and aliphatic series by 3% of H_2SO_4 in Bu_2O at 120°, 140°, and 160° has been determined. The dehydration is normally autocatalytic, the rate finally decreasing progressively, whether H_3PO_4, I, or H_2SO_4 is used as catalyst. H_3PO_4 only dissolves slowly in Bu_2O and is less satisfactory than H_2SO_4. The gradual disappearance of I during the reaction leads to erratic results. Comparing the time required for 25% dehydration, *cyclo*pentanol and its homologues are dehydrated more readily than the corresponding *cyclo*hexanols; *e.g.*, at 140° in 45 min. with *cyclo*pentanol, and in 155 min. with *cyclo*hexanol. For the *trans*-*cyclo*pentanols at 120° the following are the comparative times: 1-propyl-, 72; 1-*iso*propyl-, 64; dipropyl-*cis*-*cis*-, 35; for *cis*-isomeride of dipropyl-*cis*-*cis*-*cyclo*pentanol, 25% dehydration is attained only in 75 min. at 120°. In all other cases examined the *cis*-isomeride is dehydrated much more rapidly than the *trans*. The 2-substituted *cyclo*hexanols are dehydrated more rapidly than the corresponding 4-derivatives: with the *trans*-1 : 2-*cyclo*hexanols the rate of dehydration increases with the substituent group in the order: Me, Et, Pr^α, Pr^β, Bu. With the *cis*-isomerides the rate of dehydration varies irregularly with the substituent alkyl group. Similarly, for the 1 : 4-*cyclo*hexanols the rate of dehydration increases in the order: Pr^β, Bu, *tert*.-Bu, for the *cis*- and *trans*-isomerides. These results are in contradiction with the assumption that the isomeride which dehydrates most readily is that in which the *tert.* OH group and the H atom eliminated are spatially closest together (*trans*-isomeride). Since the structures established from steric hindrance principles are based on various reactions yielding consistent results, and other evidence is available to show that the *cis*-structure favours the elimination of halogen or hydracid to give olefines, the assumption of *trans*-dehydration is rejected. The order of 25% dehydration at 160° of dibutylcarbinol (36 min.), *n*-butyl-*sec*.-butylcarbinol (12 min.), and di-*tert*.-butylcarbinol (3 min.) supports the same view, the last, which is the most readily dehydrated, alone containing no H atom in close relation to the OH group. The times of 25% dehydration of neomenthol (10 min. at 140°), menthol (30 min. at 160°), *iso*borneol (5 min. at 77°),

and borneol (37 min. at 160°) are in agreement with results of other workers. R. BRIGHTMAN.

Heteropolarity. XIV. Constitution and colour. W. DILTHEY (Ber., 1931, 64, [B], 1280—1285).—The blue colour produced when triphenylmethyl chloride reacts with *p*-dianilinobenzene in CS_2 is due to the *salt* $C_6H_4(NHPh)_2,C_6H_4(:NPh)_2,HCl$, m. p. 182—183°, which yields the *base* $C_{36}H_{30}N_4$, m. p. 132—135°. Presumably the colour obtained with the perchlorates of anisylcarbinols etc. depends on a similar cause (cf. A., 1928, 627; this vol., 487). H. WREN.

[Supposed *meri*quinonoid compounds from diphenyl-*p*-phenylenediamine and triarylcarbonium salts.] I. LIFSCHITZ (Ber., 1931, 64, [B], 1439—1440).—A reply to Schwechten (this vol., 835). H. WREN.

Intermediate products in the synthesis of greater di- and tri-arylmethane dyes. I. TOMIOKA (J. Soc. Chem. Ind., Japan, 1931, 34, 176—178B).—Dimethylaminobenzhydrol is formed as an intermediate product during the condensation of PhCHO and $NPhMe_2$ to give the leuco-base of malachite-green. Of the general methods for the formation of diarylmethane derivatives, the initial condensation occurs most easily in the reaction in which CH_2O is used, to give the diphenylmethane; the use of PhCHO giving the benzhydrol form and of BzCl to give the benzophenone derivative are reactions having a slower initial condensation. $NPhMe_2$ condenses with $PhCCl_3$ to give dichloro-*p*-dimethylaminodiphenylmethane much more easily than it condenses with BzCl, but not as easily as it does with PhCHO to give the benzhydrol. E. H. SHARPLES.

Monomethyl and monoethyl ethers of *p*-xylylene glycol. R. QUELET (Compt. rend., 1931, 192, 1391—1393).—Treatment of a *p*-xylylene glycol dialkyl ether (1·5 mols.) with AcCl (1 mol.) and a trace of $ZnCl_2$ replaces a single alkoxyl group by Cl, giving the corresponding *p*-alkoxymethylbenzyl chloride in almost quant. yield; this is either hydrolysed directly with dil. aq. NaOH at 150°, or converted into the acetate by heating with NaOAc and this hydrolysed with aq.-alcoholic NaOH. The following are described: p-*xylylene glycol monomethyl ether*, b. p. 152°/16 mm., d_4 1·076 (*phenylcarbamido*-derivative, m. p. 62°; *acetate*, b. p. 150°/16 mm., d_4^{20} 1·08; *chloride*, b. p. 125°/17 mm., d_4^{20} 1·095), and p-*xylylene glycol monoethyl ether*, b. p. 154°/16 mm., d_4^{17} 1·047. Small amounts of the monoalkyl ethers are also formed by action of KOH in 95% EtOH on ωω'-dichloro-*p*-xylene (the yield is not increased by use of more dil. EtOH), and during etherification, *e.g.*, by action of EtBr on the Na derivative of the glycol. H. A. PIGGOTT.

Dehydration by heat of *d*-α-phenyl-ββ-dibenzylethylene glycol (αγ-diphenyl-β-benzylpropane-αβ-diol). A. MCKENZIE and E. R. L. GOW (Bull. Soc. chim., 1931, [iv], 49, 709—715).—When dehydrated by slow distillation at 350—400 mm., *d*-α-phenyl-ββ-dibenzylethylene glycol yields *r*-αγ-diphenyl-α-benzylacetone; in presence of pumice 1-phenyl-2-benzylindene is also formed, and in presence of porous brick some dibenzyl ketone. In the latter case an oil, α_D $+0·33°$, not racemised by alcoholic KOH, and probably the *d*-glycol are also obtained. Since, however, *d*-αγ-diphenyl-α-benzylacetone is partly racemised by distillation, the semipinacolic dehydration of the glycol is not excluded. It is suggested that the *d*-ketone is formed first by semipinacolin dehydration: *d*-$C(CH_2Ph)_2(OH)·CHPh·OH \longrightarrow C(CH_2Ph)_2(\dot{O})·CHPh \longrightarrow$ *d*-$CH_2Ph·CO·CHPh·CH_2Ph$, and subsequently racemised, the PhCHO formed in the distillation resulting from decomp. of the dibenzyl ketone. R. BRIGHTMAN.

Phenylsulphopropionic acids. I. C. H. K. MULDER and (MME.) M. A. VAN DAM-VEENHOVEN (Rec. trav. chim., 1931, 50, 719—724).—The action of K_2SO_3 on atropic acid, and treatment of the product with AcOH, gives *K H β-sulpho-α-phenylpropionate* ($+H_2O$), [*Ba* salt ($+0·5H_2O$)], converted into the *strychnine* ($+3H_2O$) and *brucine* ($+6H_2O$) salts. The strychnine salt ($+2H_2O$) of the pure *d*-acid is obtained after 10 crystallisations, the corresponding Ba salt having $[M]^{20}+185°$. The brucine salt after eight crystallisations leads to the Ba salt of the *l*-acid (not quite pure), $[M]^{20}$ $-178°$. The *d*-acid (not isolated) has $[M]_D$ $+194°$, not changed by conversion into the Na or Na H salt. Addition of K_2SO_3 to cinnamic acid leads to K H β-sulpho-β-phenylpropionate, from which the *quinine* ($A,2B+5\frac{1}{2}H_2O$), *strychnine* ($A,2B+3\frac{1}{2}H_2O$), and *brucine* ($A,2B+6H_2O$) salts are prepared. Fractional crystallisation of the quinine salt leads to the *l*-Ba salt, $[M]_D$ $-14·8°$ (acid, not isolated, has $[M]_D$ $+3·2°$). Neutralisation of the latter with NaOH causes the rotation to rise slightly for the first mol. of NaOH and then to fall to $-14°$ for the second mol. J. D. A. JOHNSON.

Preparation in a pure state and reactions of crystalline enolates. W. SCHLENK, H. HILLEMANN, and I. RODLOFF (Annalen, 1931, 487, 135—154).—Colourless, cryst. *Na enolates* of Me diphenylacetate ($+0·5Et_2O$), diphenylacetaldehyde ($+Et_2O$), and Me fluorene-9-carboxylate (A., 1928, 1037; not analysed) are obtained by interaction of the carbonyl compounds with CPh_3Na in Et_2O. They react with acyl chlorides etc. to form *C*-acyl derivatives, *e.g.*, $CPh_2:CH·ONa+R·COCl \longrightarrow CPh_2(COR)·CHO+NaCl$, of which the following are described: (from diphenylacetaldehyde) *benzoyl*-, m. p. 98—99°; *acetyl*-, m. p. 59°; *benzyl*-, m. p. 85—87° (converted by MgPhBr into αββγ-tetraphenylpropyl alcohol), and *benzhydryl-diphenylacetaldehyde*, m. p. 159—160° ($CHPh_2Br$); *ethyl diphenylmalonaldehydate*, m. p. 65—66° ($Cl·CO_2Et$); *ββδδ-tetraphenylpentan-γ-one-αε-dial*, m. p. 118—119° ($COCl_2$); *ααββ-pentaphenylpropaldehyde* (CPh_3Cl), m. p. 115—120° (with dissociation; also dissociated, yielding CPh_3-, in $Ph·CO_2Et$); (from Me diphenylacetate) *Me benzoyl*-, m. p. 118° (also obtained in pyridine; gives with N_2H_4,H_2O a *substance*, m. p. 210°); *acetyl*-, m. p. 57° (N_2H_4,H_2O derivative, m. p. 90°); *benzyl*-, m. p. 125—127°; *carboxymethyl*-, m. p. 96°, and *benzhydryl*-, m. p. 110° (sinters 105°), *-diphenylacetates*; *Me ααβββ-pentaphenylpropionate*, (CPh_3Cl), m. p. 163° (from Me fluorene-9-carboxylate): *Me 9-benzoylfluorene-9-carboxylate*, m. p. 121°, and *Me fluorene-9:9-dicarboxylate* ($Cl·CO_2Me$), m. p. 167°, hydrolysed by KOH in MeOH to fluorene-9-carboxylic acid. Benzoyldiphenyl-

acetaldehyde and PhOH result from interaction of the enolate with $Ph\cdot CO_2Ph$, but no reaction occurs with PhCHO or $Et_2C_2O_4$; the Bz derivative gives with N_2H_4,H_2O 3 : 4 : 4-*triphenyl*iso*pyrazole* (?), m. p. 168—170° (decomp.; sinters 157°). The enolate of diphenylacetaldehyde gives with I an unstable *iodine* derivative which decomposes spontaneously into *tetraphenylsuccindialdehyde*, m. p. 127—128° (cyclic *azine*, $C_{28}H_{22}N_2$, m. p. 173—174°). The dialdehyde is reversibly dissociated into yellow radicals in $Ph\cdot CO_2Et$ or $C_{10}H_8$. The unstable I derivative of Me diphenylacetate decomposes into a *peroxide*, $C_{30}H_{26}O_6$, m. p. 151—153° (decomp.), of Me tetraphenylsuccinate, also obtained by action of Cu-bronze on Me diphenylchloroacetate in C_6H_6.

The action of Ph·NCO or Ph·NCS is analogous to that of acyl chlorides, *C*-phenyl-carbamido- or -thiocarbamido-derivatives being obtained, *e.g.*, *formyldiphenylacetanilide*, m. p. 115—117°, and *Me phenylthiocarbamidodiphenylacetate*, m. p. 113—114°; the last-named is hydrolysed by MeOH–KOH to diphenylthioacetanilide. An impure specimen of *Me H diphenylmalonate*, m. p. 123° (decomp.), was obtained by action of CO_2 on the enolate of diphenylacetic acid; CS_2 gives carbomethoxydithioacetic acid [isolated as *Ag* salt $CPh_2(CO_2Me)\cdot CS\cdot SAg$; *Bz* derivative, blue, m. p. 138°; *disulphide*, m. p. 173°].

ββββ'β'-*Pentaphenyl*iso*propyl alcohol*, m. p. 208—209° (*Ac* derivative, m. p. 211—213°), is obtained as a by-product in the reaction between $CHPh_2\cdot CHO$ and CPh_3Na; $CHPh_2\cdot CO_2Me$ and $CHPh_2Na$ similarly give $CHPh_2\cdot CO\cdot CHPh_2$. The *acetate* of benzpinacolin alcohol has m. p. 165°. The interaction of *Me* βββ-*triphenylpropionate*, m. p. 125°, with MgPhBr gives *Me* αβββ-*tetraphenylpropionate*, m. p. 240°; the *Et* ester, m. p. 219—220°, is similarly prepared.

H. A. PIGGOTT.

Physical properties of optical antipodes. G. KORTÜM (Ber., 1931, 64, [*B*], 1506—1510).—Contrary to Campbell and Garrow (A., 1930, 1289), measurable differences in the sp. rotation and solubility in H_2O are not observed with *d*- and *l*-mandelic acids if the preps. are sufficiently purified. H. WREN.

3-Methoxyphthalic acid. A. CORBELLINI and E. ROSSI (Gazzetta, 1931, 61, 281—285).—3-Nitrophthalic acid (A., 1925, 1066) on replacement of the NO_2-group by OH and treatment with CH_2N_2 gives 3-methoxyphthalic acid, m. p. 173—174° (anhydride, m. p. 160°). This confirms the work of Bentley and co-workers (J.C.S., 1907, 91, 107), who describe 3-methoxyphthalic acid, m. p. 173—174° (anhydride, m. p. 160—161°), prepared by oxidation of 5-methoxy-α-naphthol, but disagrees with that of Jacobsen (A., 1883, 1124). E. E. J. MARLER.

Unsaturated acids of the succinic series. P. CORDIER (Ann. Chim., 1931, [x], 15, 228—308; cf. this vol., 483).—Prolonged action of Ac_2O on αβ-di(aralkyl) derivatives of succinic acid containing one double linking gives derivatives of α-hydroxysuccinic anhydride by addition of AcOH and subsequent hydrolysis. The OH group so formed has acidic properties. Diphenylmaleic anhydride is unchanged by prolonged boiling with Ac_2O. α-Methoxybenzylidene-β-phenylethylsuccinic acid (A., 1929, 1273) is reduced to α-*methoxybenzyl*-β-*phenylethylsuccinic acid*, m. p. 98°, also obtained by reduction and hydrolysis of α-hydroxy-α-methoxybenzyl-β-phenylethylsuccinic anhydride (*loc. cit.*), the Me ether of which, when hydrolysed with KOH in EtOH, gives the same hydroxy-anhydride and α-methoxybenzylidene-β-phenylethylsuccinic acid. Hydrolysis of α-methoxy-αβ-dibenzylsuccinic anhydride (A., 1930, 915) with KOH in EtOH gives the corresponding hydroxy-anhydride (corr. m. p. 65°; cf. *loc. cit.*), and, by prolonged action, *dibenzylmaleic acid*, m. p. 80° (decomp.) (*anhydride*, m. p. 92°), reduced to *i*-dibenzylsuccinic acid. Dibenzylmaleic anhydride by prolonged action of Ac_2O gives α-hydroxy-αβ-dibenzylsuccinic anhydride. Condensation of anisaldehyde with benzylsuccinic acid gives α-*anisylidene*-β-*benzylsuccinic acid*, m. p. 154° (rapid heating) (*anhydride*, m. p. 124°), reduced to α-methoxybenzyl-β-benzylsuccinic acid, m. p. 160—161°. Prolonged treatment of the above anhydride with Ac_2O gives α-*hydroxy*-α-p-*methoxybenzyl*-β-*benzylsuccinic anhydride* (*Me ether*, m. p. 57°). A. A. LEVI.

Colour changes of sulphonephthaleins, benzeins, and phthaleins. I. M. KOLTHOFF (J. Physical Chem., 1931, 35, 1433—1447).—Mainly a discussion. The concentration of the lactone form in an aq. solution of phenolphthalein is approx. 10^4 times that of the carboxylic acid configuration. The colour change of the sulphonephthaleins in their alkaline range is quant. controlled by the equilibrium between the quinone and the quinone phenolate forms. α-Naphtholphthalein in aq. solution is present mainly as the quinonoid form. The colour change of the sulphonephthaleins, benzeins, and phthaleins in acid solution is attributed to the weak basic character of the quinone group. Moderately sol. benzeins can replace the corresponding sulphonephthaleins with advantage as indicators. L. S. THEOBALD.

Constitution of bile acids. XVI. Halogenated dehydrocholic acids and dehydrodeoxycholic acids. W. BORSCHE and K. DIACONT (Z. physiol. Chem., 1931, 198, 115—126; cf. this vol., 841).—ICl in AcOH with dehydrocholic acid (I) yields *di-iododehydrocholic acid*, m. p. 187—188 (decomp.) (*Me* ester, m. p. 220° (decomp.)], and (in small amount) *iododehydrocholic acid*, m. p. 158° (decomp.). Bromination in AcOH gives 2-bromodehydrocholic acid (II) [*Me* ester, m. p. 204° (decomp.), obtained by means of CH_2N_2 or by bromination of the ester of I]. Bromination of I in $CHCl_3$ yields a *product*, $C_{50}H_{67}O_{10}Br_3$, m. p. 175° (decomp.). II is oxidised by $KMnO_4$ to bilianic acid. Bromination of I in AcOH furnishes *tetrabromodehydrocholic acid*, m. p. 168—170°. Bromination of dehydrodeoxycholic acid (III) in AcOH gives a *product*, $C_{50}H_{69}O_7Br_3$, m. p. 125—126°. Bromination of the Me ester of III with 1 mol. of Br gives *Me dibromodehydrodeoxycholate*, m. p. 186°, and with 4 mols. of Br, *Me tribromodehydrodeoxycholate*, m. p. 168—169°.

J. H. BIRKINSHAW.

Constitution of bile acids. XVII. Action of phosphorus pentachloride on some keto-acids of the bile acid group. A new way into the lithocholic acid series. W. BORSCHE and A. L.

MORRISON (Z. physiol. Chem., 1931, **198**, 165—180; cf. preceding abstract).—Lassar-Cohn's "*iso*dehydrocholal" (A., 1892, i, 741) proves to be 3-*chloro*-7 : 13-*diketocholenic acid*, m. p. 252° (*Me* ester, m. p. 193°; *dioxime* of Me ester, m. p. 257°). Decomp. of the reduction product from dehydrocholic acid and PCl_5 with MeOH instead of alkali gave a mixture of Me chlorodiketocholanate and *Me dichlorodiketocholanate*, m. p. 148° (*dioxime*, m. p. 264—265°). The latter separated on keeping the mixture. The acid mixture obtained by hydrolysis when heated above its m. p. until no more HCl was evolved gave chlorodiketocholenic acid. The latter with H_2SO_4 gave dehydrocholic acid, and by Clemmensen reduction, *chloro*-3-*cholenic acid*, m. p. 174—175° (*Me* ester, m. p. 120°; *disemicarbazone*, unchanged at 300°). Chlorocholenic acid with H_2SO_4 yielded *dehydrolithocholic acid*, m. p. 140—141° (*Me* ester, m. p. 116—117°; *oxime* of Me ester, m. p. 148°), which with HNO_3 gave lithobilianic acid, m. p. 276°.

From dehydrodeoxycholic acid by the method outlined, *chloro*-3-*keto*-7-*cholenic acid*, m. p. 195—199° (*Me* ester, m. p. 131—135°), was obtained. Diketo-7 : 13-cholanic, bilianic, *iso*bilianic, and deoxybilianic acids by similar treatment gave corresponding acid chlorides, which were converted by MeOH into the esters. J. H. BIRKINSHAW.

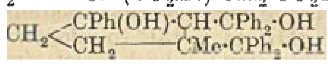
Constitution of bile acids. XXXVI. *apo*-Cholic acid. H. WIELAND and V. DEULOFEU (Z. physiol. Chem., 1931, **198**, 127—134; cf. this vol., 841).—Thermal decomp. of *apo*cholic acid (I) at about 340° yields a β-*cholatrienic acid*, m. p. 131—133°, in which only two double linkings are saturated by hydrogenation, giving β-*cholenic acid*, m. p. 142—143°, but a small amount of cholanic acid is also formed as by-product. Oxidation of I with perbenzoic acid gives dihydroxycholadienic acid, which on reduction forms β-*apo*cholic acid (cf. A., 1922, i, 1027).

J. H. BIRKINSHAW.

Ursodeoxycholic acid. IV. K. KAZIRO (Z. physiol. Chem., 1931, **197**, 206—212; cf. A., 1930, 89).—Thermal decomp. of ursodeoxybilianic acid (I) yields a *pyro-acid* (II), m. p., 182° (*Me* ester, m. p. 129—131°), a cyclic ketone, by loss of CO_2 and H_2O. The acid ester of I (m. p. 150—152°) gives the same pyro-acid (II). The Me_3 ester of I, m. p. 94°, on distillation furnishes an *isomeride*, m. p. 69—70°. The open ring of I is a six-C ring. J. H. BIRKINSHAW.

Synthesis of substances analogous to bile acid degradation products. I. Methods of attachment of carboxylated side-chains to the *cyclo*pentane nucleus. J. W. BAKER (J.C.S., 1931, 1546—1556).—Attempts to synthesise substances possessing the structures considered probable for the acids $C_{13}H_{20}O_6$ and $C_{16}H_{24}O_8$ (A., 1928, 1007; 1930, 1435) obtained from cholesterol etc. were unsuccessful, but several substances similar to, or possibly derivable from, them were prepared. Modified directions are given for the prep. of Et β-methylbutane-αβδ-tricarboxylate, which with "mol." Na in C_6H_6 gave *Et* 3-*methyl*cyclo*pentanone*-2 : 3-*dicarboxylate* (I), b. p. 130—134°/2—2·5 mm. (gives no semicarbazone) (cf. A., 1918, i, 22). The structure of I is proved by oxidation with alkaline $KMnO_4$ to α-methylglutaric acid, α-hydroxy-α-methylglutaric acid (*Ag* salt), and a little succinic acid. I is only partly ethylated by alcoholic NaOEt and EtI or Et_2SO_4, but with $NaNH_2$ and EtI yields *Et* 3-*methyl*-2-*ethyl*cyclo*pentanone*-2 : 3-*dicarboxylate* (II), b. p. 135°/3 mm. (*hydrazone dihydrazide*, m. p. 163°), the constitution of which is proved by hydrolysis to γ-*methyl*-n-*hexane*-αγδ-*tricarboxylic acid*, m. p. 155° (*Ag* salt). II does not condense with Zn and Et α-bromopropionate in C_6H_6. Et dimethylacetoacetate, Et α-bromopropionate, and Zn in C_6H_6 yield *Et* β-*hydroxy*-ααα′β-*tetramethylglutarate*, b. p. 125—127°/6 mm., which on reduction by Clemmensen's method or on treatment with PCl_5 followed by alcoholic KOH affords ααα′β-*tetramethylglutaconic acid*, m. p. 128° (*Ag* salt). This on reduction in AcOH with H_2 and Pt-black gives ααα′β-*tetramethylglutaric acid*, m. p. 121°. The sodio-derivative of II with Et fumarate in EtOH gives a *substance*, b. p. 124—126°/8 mm. (hydrolysed to adipic acid), but with Et bromosuccinate gives *Et* 2-*carbethoxy*-1-*keto*cyclo*pentyl*-2-*succinate* (III), b. p. 211—215°/10 mm., which with boiling conc. HCl gives 1-*keto*cyclo*pentyl*-2-*succinic acid*, m. p. 138—139° (*anhydride*, m. p. 116°).


(III.)


(IV.)

II with excess of MgPhBr gave a substance, m. p. 231°, possibly IV. Et γ-bromo-*n*-valerate does not condense with the 5-sodio-derivative of Et 2-methyl*cyclo*pentanone-2-carboxylate. R. S. CAHN.

Properties of benzaldehyde. J. R. POUND (J. Physical Chem., 1931, **35**, 1496—1497).—Values of d^{30}, n^{20}, and η^{30} for PhCHO containing up to 14·01 wt.-% BzOH are given; probable values for pure PhCHO are d_4^{30} 1·0365, d_4^{14} 1·0567, η^{30} 0·01296, and n_D^{20} 1·5460. L. S. THEOBALD.

Basic properties of hydrazones. R. CIUSA and G. OTTOLINO (Gazzetta, 1931, **61**, 189—190; cf. A., 1922, i, 474).—On passing gaseous HCl into hot solutions of aromatic arylhydrazones or by boiling these compounds with conc. HCl, green, resinous substances separate. By treating an equimol. mixture of benzaldehydephenylhydrazone and PhCHO or PhCHO (2 mols.) and phenylhydrazine (1 mol.) with $ZnCl_2$ (Giacalone's method) a green product with a golden lustre is obtained. The substance obtained by crystallisation from glacial AcOH is a *zincichloride* of the *compound* $C_{33}H_{26}N_4$, which is regarded as the base of a triphenylmethane dye,

$CHPh{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}CPh{:}C_6H_4{:}N{\cdot}N{:}CHPh$.

O. F. LUBATTI.

Condensation of aldehydes with hydrazones. IV. Condensation of benzaldehyde with salicylaldehydephenylhydrazone. A. GIACALONE (Gazzetta, 1931, **61**, 301—305; cf. A., 1930, 213; this vol., 222).—In presence of $ZnCl_2$, PhCHO (1 mol.) condenses with salicylaldehydephenylhydrazone (2 mols.), giving the *bisphenylhydrazone* (I), m. p. 210° (Bz_4 derivative, m. p. 125—126°), of 4 : 4′-*dihydroxytriphenylmethane*-3 : 3′-*dialdehyde*, $CHPh[C_6H_3(OH){\cdot}CHO]_2$, m. p. 55°, obtained by condensing PhCHO with salicylaldehyde in presence of H_2SO_4. Condensation of salicylaldehyde with

dihydrazinotriphenylmethane in AcOH gives 4 : 4'-bis-*o*-hydroxybenzylidenedihydrazinotriphenylmethane, $CHPh(C_6H_4\cdot NH\cdot N\colon CH\cdot C_6H_4\cdot OH)_2$, m. p. 115—116° ($Bz_4$ derivative, m. p. 205—206°), isomeric with I.
E. E. J. MARLER.

Nitration of brominated 3-hydroxybenzaldehydes and bromination of nitrated 3-hydroxybenzaldehydes, with cases of group migration. H. H. HODGSON and E. W. SMITH (J.C.S., 1931, 1500—1508).—The following nitrations are by HNO_3 (*d* 1·42), unless otherwise stated. Colours given in parentheses are produced (1) by KOH on the solution in EtOH, and (2) by conc. H_2SO_4 on the solid. Mercuriacetato-3-hydroxybenzaldehyde with Br in Ac_2O gives 2-bromo-3-hydroxybenzaldehyde, m. p. 148° (not 141—142°, A., 1925, i, 674) (I), which yields 2-*bromo*-4-*nitro*-3-*hydroxybenzaldehyde*, yellow, m. p. 176° [p-*nitrophenylhydrazone*, m. p. 265° (bluish-violet) (orange)], and 2-*bromo*-6-*nitro*-3-*hydroxybenzaldehyde*, buff, m. p. 174° [p-*nitrophenylhydrazone*, m. p. 230° (pale red) (no colour)], both of which with Br in EtOH give 2 : 4-*dibromo*-6-*nitro*-3-*hydroxybenzaldehyde* (II), m. p. 148° and m. p. 152·5° after long boiling in xylene [p-*nitrophenylhydrazone*, m. p. 249° (decomp.) (red) (amber); *Me ether*, m. p. 119°]. I with HNO_3 (*d* 1·5) gives 2-*bromo*-4 : 6-*dinitro*-3-*hydroxybenzaldehyde* (III), m. p. 131° [p-*nitrophenylhydrazone*, m. p. 242° (decomp.) (bluish-violet) (pale yellow)]. 4-Bromo-3-hydroxybenzaldehyde with HNO_3 and H_2O (7 : 3) gives 4-*bromo*-2-*nitro*-3-*hydroxybenzaldehyde* (IV), m. p. 167° [p-*nitrophenylhydrazone*, m. p. 205°, (purple) (yellowish-brown)], and 4-*bromo*-6-*nitro*-3-*hydroxybenzaldehyde* (V), m. p. 72° [p-*nitrophenylhydrazone*, m. p. 271° (purple) (amber)], and with HNO_3 (*d* 1·42) 4-*bromo*-2 : 6-*dinitro*-3-*hydroxybenzaldehyde* (VI) [p-*nitrophenylhydrazone*, m. p. 226° (decomp.) (violet) (amber)]. 6-Bromo-3-hydroxybenzaldehyde gives 6-*bromo*-4-*nitro*-3-*hydroxybenzaldehyde* (VII), m. p. 118° [p-*nitrophenylhydrazone*, m. p. 236° (blue) (red)], and with HNO_3 (*d* 1·5) 6-*bromo*-2 : 4-*dinitro*-3-*hydroxybenzaldehyde*, m. p. 129° [p-*nitrophenylhydrazone*, m. p. 256° (greenish-blue) (red)]. VII with hot dil. HNO_3 yields III. 4 : 6-Dibromo- and 2 : 4 : 6-tribromo-3-hydroxybenzaldehyde give II. 2-Nitro-3-hydroxybenzaldehyde with Br in $CHCl_3$ gives IV, and in EtOH 4 : 6-*dibromo*-2-*nitro*-3-*hydroxybenzaldehyde*, m. p. 140° (decomp.) [p-*nitrophenylhydrazone*, m.p. 218° (decomp.) (purple) (amber)], which yields VI. 4-Nitro-3-hydroxybenzaldehyde cannot be monobrominated, but in suspension in H_2O gives 2 : 6-*dibromo*-4-*nitro*-3-*hydroxybenzaldehyde* (VIII), m. p. 95° [p-*nitrophenylhydrazone*, m. p. 242° (brownish-purple) (yellowish-brown)], also obtained by bromination of VII in EtOH, and transformed by HNO_3 into III. 6-Nitro-3-hydroxybenzaldehyde with Br in EtOH gives II. VI and III are obtained on bromination of 2 : 6- and 4 : 6-dinitro-3-hydroxybenzaldehydes, respectively; 2 : 6-dinitro-3-hydroxybenzaldehyde has m. p. 106°, previously assigned (A., 1927, 1075) to the 4 : 6-isomeride. A modified method of nitrating 6-nitro-3-hydroxybenzaldehyde is given. 4-Nitro-3-hydroxybenzaldehyde with HNO_3 (98%) gives 4 : 6-dinitro-3-hydroxybenzaldehyde, m. p. 104°, previously designated (*loc. cit.*) the 2 : 6-dinitro-compound. The group migrations are discussed on the basis of electronic theories. II exists in three isomeric forms, which are accounted for by co-ordination, or lack of it, between the bromo-hydroxy- and nitro-aldehydo-groups.
R. S. CAHN.

α-Amylcinnamaldehyde. A. A. ROSENTHAL (Deut. Parfümerieztg., 1931, **17**, 3—5; Chem. Zentr., 1931, i, 2047).—Condensation of PhCHO with heptaldehyde affords α-amylcinnamaldehyde (α-benzylideneheptaldehyde), b. p. 140°/5 mm., α-amylnonenaldehyde, b. p. 130°/5 mm., and products of condensation of these substances with heptaldehyde. When kept in contact with air PhCHO is oxidised five times, and α-amylnonenaldehyde twice, as rapidly as α-amylcinnamaldehyde, for which a specification is proposed.
A. A. ELDRIDGE.

Manufacture of odoriferous substances [cyclic acetals]. I. G. FARBENIND. A.-G.—See B., 1931, 710.

Manufacture of aromatic N-dialkylamino-alkylaminoaldehydes and derivatives. I. G. FARBENIND. A.-G.—See B., 1931, 622.

1-4-*iso*Propyl-Δ^2-*cyclo*hexen-1-one. R. S. CAHN, A. R. PENFOLD, and J. L. SIMONSEN (J.C.S., 1931, 1366—1369).—The oil from *Eucalyptus cneorifolia* contains 1-4-iso*propyl*-Δ^2-cyclo*hexen*-1-*one* (I), b. p. 98—100°/10 mm., α_D −59·3° to −66·4° (*semicarbazone*, decomp. 185°; p-*nitrophenylhydrazone*, m. p. 168—169°), the constitution of which is proved by its giving a H_2S compound, decomp. 82°, and on reduction electrolytically and catalytically in the presence of Pd-charcoal 4-*iso*propyl*cyclo*hexanone (A., 1908, i, 424) (*semicarbazone*, m. p. 188—189°; p-*nitrophenylhydrazone*, m. p. 123—124°), oxidised by CrO_3 to β-*iso*propyladipic acid. Electrolytic reduction gave also a little 4-*iso*propyl*cyclo*hexanol (A., 1906, i, 194) (*phenylurethane*, m. p. 75—77°). There is no means of separating I from cryptal (J.C.S., 1922, **121**, 266), which has been isolated only from *E. hemiphloia*. The oil of *E. polybractea* contains (I). I may be derived from β-phellandrene or cryptal.
R. S. CAHN.

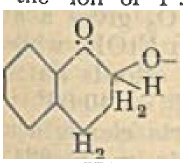
***cyclo*Hexane-*spiro*-*cyclo*butanone.** G. A. R. KON (J.C.S., 1931, 1604).—The statements of Vogel this vol., 727) regarding the prep. of *cyclo*hexane-*spiro*-*cyclo*butane and the corresponding *cyclo*heptane derivative are incorrect (cf. J.C.S., 1922, **121**, 513).
R. S. CAHN.

Preparation of hydrobenzoin, and the system benzoin–hydrobenzoin. P. CARRE and P. MAUCLERE (Compt. rend., 1931, **192**, 1393—1395).—Benzoin is not reduced by $SnCl_2$ and HCl in EtOH at 100° (cf. A., 1904, i, 510), and is converted by Sn and aq. HCl into deoxybenzoin. It is readily reduced to hydrobenzoin in good yield by Ni (formed by reduction at 280°) and H in EtOH at 125—160°/150 atm. if carefully freed from cyanide, which poisons the catalyst. Data are given for the m. p.-composition relationship of benzoin and hydrobenzoin. During the reduction of PhCHO to hydrobenzoin by Zn and HCl (cf. A., 1928, 64) a *substance*, $C_{14}H_{12}O$, m. p. 85°, which differs from both of the known stereoisomeric forms of diphenylethylene oxide, is formed.
H. A. PIGGOTT.

Formation of mixed benzoins. Influence of the nature of the cyclic radicals. TIFFENEAU and (MLLE.) J. LEVY (Bull. Soc. chim., 1931, [iv], **49**, 725—740).—Of seven pairs of aldehydes only the two pairs, PhCHO-*m*-methoxybenzaldehyde and anisaldehyde–piperonal, in which the aryl radicals are equal or similar in their affinity capacity, yield a mixture of two isomeric benzoins. Except the pair PhCHO-*o*-anisaldehyde, the other pairs yield a single mixed benzoin in which the radical with the higher affinity capacity is linked to the CO group, and this is regarded as the general rule when the aryl radicals differ considerably in affinity capacity. In the simple benzoin condensation aromatic aldehydes in which the aryl radical has a high affinity capacity give low yields of the benzoin.

PhCHO and *o*-methoxybenzaldehyde with alcoholic KCN yield benzoyl-*o*-methoxyphenylcarbinol (semicarbazone, m. p. 175—176°) and very small quantities of benzoin, the former with alcoholic KOH yielding BzOH and on hydrogenation *o*-methoxyphenylacetophenone. PhCHO and *m*-methoxybenzaldehyde similarly afford a mixture of two isomeric benzoins, m. p. 184°, semicarbazones, m. p. 99—102° and 80°, which could not be separated, and with alcoholic KOH yield a mixture of BzOH and *m*-methoxybenzoic acids. PhCHO and anisaldehyde yield anisobenzoin, m. p. 105·5—106·5° (semicarbazone, m. p. 185—186°; oxime, m. p. 136—138°); PhCHO and piperonal, piperobenzoin, m. p. 120—121° (semicarbazone, m. p. 181—182°; oxime, m. p. 156°), converted into *benzyl piperonyl ketone* (*semicarbazone*, m. p. 171°) on hydrogenation, together with a little benzoin. PhCHO and furfuraldehyde yield furobenzoin (furoylphenylcarbinol), m. p. 135° (*semicarbazone*, m. p. 192—193°; *oxime*, m. p. 165—166°), and a little benzoin, and anisaldehyde and *o*-methoxybenzaldehyde give 70% of p-*anisoyl*-o-*methoxyphenylcarbinol*, m. p. 101—102° (*semicarbazone*, m. p. 204°; *oxime*, m. p. 138—139°), also obtained from Mg anisyl bromide and *o*-methoxybenzaldehydecyanohydrin. Anisaldehyde and piperonal yield a little piperoanisoin, anisopiperoin, m. p. 110—111°, and a substance, m. p. 75°, probably a mixture of the anisopiperoin and piperoanisoin. R. BRIGHTMAN.

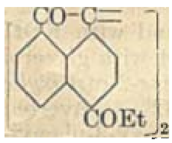
Oxidation processes. V. Autoxidation of 2-hydroxy-1-ketotetrahydronaphthalene. A. WEISSBERGER and W. SCHWARZE (Annalen, 1931, **487**, 53—61).—The autoxidation of 2-hydroxy-1-ketotetrahydronaphthalene (I) in alkaline solution is a unimol. reaction similar in velocity, and in the linear relationship of velocity to alkali concentration, to that of other α-hydroxyketones (cf. A., 1930, 475), and therefore most probably proceeds in the stages: (1) formation of the ion (II), (2) rearrangement into the ion of 1 : 2-dihydroxy-3 : 4-dihydronaphthalene



(II.)

(III), (3) oxidation of this to 1 : 2-diketotetrahydronaphthalene (IV), (4) enolisation to 1 : 2-dihydroxynaphthalene (V), and (5) oxidation to 2-hydroxy-1 : 4-naphthoquinone (VI). The final velocity is determined by stage 1. The presence of excess of O_2 is necessary for the final stage, which proceeds at 5—7 times the velocity of the overall reaction and is dependent on alkali concentration. The indigo-blue coloration observed in aq. Na_2CO_3 but not in aq. NaOH and destroyed by shaking with air is probably due to quinhydrone formation from III and IV, its non-appearance in NaOH being the result of rapid enolisation of III. The formation of dinaphthyl derivatives in presence of insufficient O_2 for complete oxidation (cf. A., 1925, 1155) is due to the oxidation of V to 1 : 2 : 1′ : 2′-tetrahydroxy-4 : 4′-dinaphthyl (VII) by the H_2O_2 produced in the second stage; in presence of excess of O_2 oxidation to VI occurs without intermediate formation of VII on account of the greater rapidity of this reaction. The autoxidation of V to VII also produces H_2O_2, and to explain the yield of VII in relation to the O_2 used the activation of mol. O_2 is suggested (cf. this vol., 604). H. A. PIGGOTT.

Syntheses and transformations of 3-propionyl- and 3:4-dipropionyl-acenaphthene. K. DZIEWOŃSKI and J. MOSZEW (Rocz. Chem., 1931, **11**, 415—425).—3-*Propionylacenaphthene*, m. p. 69·5—70° (*picrate*, m. p. 109°: 4-*nitro*-derivative, m. p. 164—165°), is prepared from EtCOCl and acenaphthene in the presence of $AlCl_3$. 3-*Propionamidoacenaphthene*, m. p. 150—151°, and 3-*aminoacenaphthene*, m. p. 108—109°, are prepared from its *oxime*, m. p. 185—186°; on oxidation it yields 3 : 3′-*dipropionylbisacenaphthenedione* (I), m. p. 286°, and 4-*propionylnaphthalic acid*,



m. p. 152—153° (*imide*, m. p. 221—222°; *diphenylhydrazone*, m. p. 192—193°). 2-*Acenaphthyl-3-methylindole*, m. p. 179° (*dipicrate*, m. p. 148°), is prepared from the *phenylhydrazone* of 3-propionylacenaphthene, m. p. 107°. 3 : 4-*Dipropionylacenaphthene*, m. p. 122—123° (*picrate*, m. p. 129°), formed together with the monopropionyl derivative, yields a *dioxime*, m. p. 143°, from which 3 : 4-*dipropionyldiaminoacenaphthene*, m. p. 181—182°, is obtained by the Beckmann change. R. TRUSZKOWSKI.

Manufacture of [1 : 4 : 5 : 8-tetra-amino-] derivatives of anthraquinone. SOC. CHEM. IND. IN BASLE.—See B., 1931, 623.

Vitamin of growth. I. Separation of carotene into its components. R. KUHN and E. LEDERER (Ber., 1931, **64**, [*B*], 1349—1357: cf. this vol., 733).—Optically active carotene preparations are obtained from *Daucus carota*, *Sorbus aucuparia*, and *Aesculus hippocastanum*. Almost inactive preparations are derived from fresh-winter spinach and preserved stinging nettle. Fractional precipitation of carotene with I removes a large proportion of the inactive material as the iodide; the residual hydrocarbon is purified by adsorption with Al_2O_3. Inactive carotene (β-carotene) is isolated by adsorption of feebly active initial materials or, less readily, from the di-iodide. α-Carotene has m. p. 174—175°, $[\alpha]_{Cd}$ +380°, whilst β-carotene has m. p. 181—182°, $[\alpha]^{20}_{Cd}$ +0°; the absorption bands in CS_2 are respectively 511 and 478 mμ and 521 and 485·5 mμ. Crystallographic data are given. Karrer's formula in which two β-ionone residues are placed at the ends of a dehydrogenated chain of isoprene residues may be

applicable to β-carotene. In α-carotene the ends of the polyene chain are probably attached to α-ionone rings, the asymmetric C atoms of which are responsible for the optical activity of the hydrocarbon.

H. WREN.

Carotene isomerides. P. KARRER, H. VON EULER, and H. HELLSTRÖM (Arkiv Kemi, Min., Geol., 1931, **10**, B, No. 15, 6 pp.; cf. this vol., 846).—Carotene from carrots is a mixture of two isomerides distinguishable by solubility, optical activity, and m. p. β-*Carotene*, m. p. 181—182° (uncorr.), $[\alpha]_{6680}^{22}$ +4·2° in $CHCl_3$, has a symmetrical structure $\left| CH_2{<}{CH_2\cdot CMe_2 \atop CH_2-CMe}{\gg}C\cdot[CH{:}CH\cdot CMe{:}CH]_2\cdot CH{:} \right|$. α-*Carotene*, m. p. 170° approx., $[\alpha]_{6680}^{23}$ +68° in $CHCl_3$, is asymmetric. The $SbCl_3$ reagent with the two isomerides gives solutions with the same absorption spectrum directly after mixing, but after 1 hr. there is a considerable difference. The spectrum of the β-isomeride is nearer to the red end than that of the α-isomeride both in true (CS_2) and colloidal solution.

F. O. HOWITT.

Constitution of hydrangenol and phyllodulcin. IV. Synthesis of phyllodulcin dimethyl ether. Y. ASAHINA and J. ASANO (Ber., 1931, **64**, [*B*], 1252—1256; cf. A., 1930, 1442).—Homoveratric acid is converted by 3-methoxyphthalic anhydride and NaOAc at 180—190° into 7 : 3′ : 4′-*trimethoxybenzylidene-phthalide*, m. p. 184°, reduced by Na and aq. EtOH to 7 : 3′ : 4′-*trimethoxybenzylphthalide*, m. p. 142°. Hydrolysis of the last-named compound with KOH in MeOH and treatment of the product with glycerol at 180° affords 3 : 3′ : 4′-*trimethoxystilbene-2-carboxylic acid*, m. p. 172° (*Me* ester, m. p. 142°), converted by conc. H_2SO_4 into 8 : 3 : 4′-trimethoxy-3-phenyl-3 : 4-dihydro*iso*coumarin, m. p. (unstable form) 105°, (stable variety) 125°, identical with *dl*-phyllodulcin dimethyl ether. *dl*-Phyllodulcin is transformed by KOH in glycerol at 180—200° into 6-*hydroxy*-2 : 3′-*hydroxy*-4′-*methoxystyrylbenzoic acid*, m. p. about 165° after softening at 130°, converted by diazomethane into *Me* 3 : 3′ : 4′-*trimethoxystilbene-2-carboxylate*, m. p. 142°, hydrolysed to 3 : 3′ : 4′-trimethoxystilbene-2-carboxylic acid, m. p. 172°. Optically active phyllodulcin is racemised by hot aq. or alcoholic HCl. Only *d*- and *dl*-phyllodulcin occur in *Amatscha* leaves; the name *iso*phyllodulcin should be deleted from the literature.

H. WREN.

Shellac. VI. Separation of aleuritic and shellolic acids. W. NAGEL (Wiss. Veroff. Siemens-Konz., 1931, **10**, [2], 108—118; cf. B., 1928, 376).—The finely-divided resin is kept mixed with NaOH for 2 days. The resulting solution is diluted, saturated with CO_2, and evaporated. The residue is extracted with 96% EtOH, the solvent distilled off, and steam blown through the residual liquid, which is then diluted and treated several times with a 5% solution of $Ba(OH)_2$ followed by a current of CO_2 and filtration of the $BaCO_3$ etc. The resulting solution of Na salts is evaporated and the acids are liberated by addition of H_2SO_4; the pasty mass is extracted with Et_2O, which removes all the decomp. products of the shellac with the exception of aleuritic acid. The residue is therefore purified by recrystallisation and the shellolic acid recovered from the Et_2O solution is purified by direct esterification of the ether-moist acid. The following derivatives of aleuritic acid are described: *triacetylmethyl* ester, b. p. 232—234° (0·2 mm.), *hydrazide*, m. p. 139—140°, *azide*, decomp. 50°, *NN′-bistrihydroxypentadecylcarbamide*, m. p. 122—123°, *trihydroxypentadecylurethane*, m. p. 73—74°, *trihydroxydecylamine*, m. p. 110—120° (not sharp). The *Zn*, *Ba*, and K salts of aleuritic and shellolic acid have also been prepared.

A. R. POWELL.

Theelin. Physical and chemical properties. S. A. THAYER, L. LEVIN, and E. A. DOISY (J. Biol. Chem., 1931, **91**, 791—801).—In agreement with Butenandt (A., 1930, 1480), the follicular hormone, theelin, highest m. p. 254—257°, I val. 95·1 (*ibid.*, 1069) (*monomethyl ether*, m. p. 165°), is a ketomonohydric alcohol $C_{18}H_{21}O(OH)$ containing one double linking. The Ac derivative, m. p. 125·3°, and oxime, m. p. 229° (decomp.), are described.

J. W. BAKER.

Resin of *Garcinia mangostana*. II. O. DRAGENDORFF (Annalen, 1931, **487**, 62—79).—The freshly extracted sap of the stem and unripe fruits of *G. mangostana* do not contain β-mangostin (cf. A., 1930, 1578); that from the latter is also free from the sterol and essential oil. Analyses of the *tetrabromide*, $C_{21}H_{25}O_5Br_4$, decomp. 200°, p-*nitrobenzoate*, m. p. 147°, and *nitrohexahydromethylmangostin*, m. p. 127° (prepared with HNO_3 of *d* 1·1), agree better with the formula $C_{21}H_{24}O_5$ than that already proposed (*loc. cit.*). The Ac derivative previously described is actually the Ac_3 derivative, m. p. 133—134°, and is converted by H_2 and PtO in AcOH into a *hexahydro*-derivative, m. p. 123—124°; as Zerevitinov's method indicates only two active H in mangostin, and one in methylmangostin, the introduction of the third Ac group must be due to enolisation. The action of perbenzoic acid on mangostin indicates three double linkings, in accordance with the above formula. Oxidation of hexahydromethylmangostin with CrO_3 in AcOH gives *iso*hexoic acid and neutral substances, and of mangostin or methylmangostin with cold alkaline $KMnO_4$ α-hydroxy*iso*butyric acid. Methylmangostin is converted by O_3 in CCl_4 into a cryst. *ozonide* and acetone peroxide; the former on hydrolysis gives a *substance*, $C_{15}H_{14}O_6$, m. p. 199° (*oxime*, m. p. 207°), unaffected by CH_2N_2 or Br, but oxidised by alkaline $KMnO_4$.

H. A. PIGGOTT.

Elemic acid from Manila elemi resin. II. H. LIEB, M. MLADENOVIC, and (in part) F. GSTIRNER and M. SOBOTKA (Monatsh., 1931, **58**, 59—68).—Reduction of elemic acid, m. p. 221°, with H_2 and Pd in AcOH at 960 mm. gives dihydroelemic acid, $C_{30}H_{50}O_3$, m. p. 238°, $[\alpha]_D^{19}$ −12·36° in $CHCl_3$ (not $C_{27}H_{44}O_3$; cf. A., 1928, 412). Other derivatives also confirm the C_{30} constitution. Thus O_3 gives a *di-ozonide*, decomp. 199°, $[\alpha]_D^{19}$ −30·17° in EtOH, whilst with Ac_2O and pyridine, elemic acid affords an *Ac* derivative $C_{32}H_{50}O_4$, m. p. 225° $[\alpha]_D^{20}$ −40·06° in $CHCl_3$. Anhyd. HBr in Et_2O converts elemic acid into *bromohydroelemic acid*, $C_{30}H_{49}O_3Br$, m. p. 224°, whilst Br in Et_2O affords *dibromoelemic acid*, m. p. 207°, $[\alpha]^{20}$ −17·14° in $CHCl_3$, converted by KOH in

MeOH into *bromoelemic acid*, $C_{30}H_{47}O_3Br$, m. p. 285°. Since analysis of elemic acid itself even after repeated crystallisation corresponds with the C_{27} formula, it must be contaminated with another acid of lower C content which can be removed only by conversion into derivatives (cf. following abstract).

J. W. BAKER.

New resin acid from Manila elemi resin. I. M. MLADENOVIC and H. LIEB (Monatsh., 1931, **58**, 69—72).—Fractional crystallisation of elemic acid from EtOH affords the less sol. *γ-elemic acid*, $C_{30}H_{50}O_3$, m. p. 281°, $[\alpha]_D^{20}$ +68·76° in MeOH (*K* salt $+2H_2O$; *Ac* derivative, m. p. 180°, $[\alpha]_D^{20}$ +59·17° in EtOH), which contains one OH and one CO_2H group, does not add Br, and is differentiated from the α-acid by its ready solubility in most org. solvents except MeOH and EtOH.

J. W. BAKER.

Reactions of *g*- and *k*-strophanthin. L. EKKERT (Pharm. Zentr., 1931, **72**, 388—389).—The addition of a few drops of aq. Cl, aq. Br, an acid solution of NH_2Cl, or a solution of neomagnol to an alkaline solution of *g*- or *k*-strophanthin in presence of β-naphthol produces successively a wine-red, a ruby-red, and in 15 sec. a yellow colour. At the junction of an alcoholic solution of α-naphthol and conc. H_2SO_4 *g*-strophanthin produces an intense reddish-violet ring; after mixing, the liquid is carmine, whereas *k*-strophanthin gives a garnet-red ring, and after mixing a violet-red liquid.

C. C. N. VASS.

Microchemistry of artemisin and santonin sublimates. C. VAN ZIJP (Pharm. Weekblad, 1931, **68**, 526—535, 615—616).—Reactions and methods of differentiation of artemisin and santonin are discussed. If the sublimate is liquid, gently breathing upon it causes the appearance of quadratic crystals only if artemisin is present, whilst if a drop of water is added to the sublimate santonin crystallises much more readily than does artemisin. The product of the reaction between HI containing I and santonin is sparingly sol. in H_2O, whilst that derived from artemisin is readily sol. Finally, cryst. artemisin, but not santonin, when treated with 10% KI + I solution, yields dichroic brown–dark brown prismatic crystals.

H. F. GILLBE.

Isoprene and caoutchouc. XXXIII. Terminal groups in caoutchouc. H. STAUDINGER (Ber., 1931, **64**, [*B*], 1407—1408).—The determination of mol. wt. by the behaviour of terminal groups is not possible in the case of caoutchouc in which they form only an insignificant part of the mol.

H. WREN.

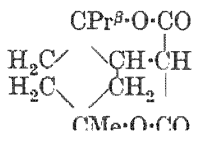
Polymorphism of guttapercha hydrocarbons. H. MARK and G. VON SUSICH (Naturwiss., 1931, **19**, 399—400).—For the α- and β-modifications of the isoprene complex occurring in guttapercha and balata, the "rontgenographic m. p.," *i.e.*, temp. at which crystal interference patterns disappear, are 64—66° and 55—57°, respectively. The phase diagram, determined rontgenographically, indicates that the polymorphism of guttapercha hydrocarbons is monotropic and that under suitable conditions of heating and cooling both changes, α β, can be realised.

F. O. HOWITT.

Optical activity and the polarity of substituent groups. XIX. *l*-Menthyl esters of benzenesulphonic acids, and of benzoic acids with sulphur-containing *o*-substituents. H. G. RULE and G. SMITH (J.C.S., 1931, 1482—1490).—l-*Menthyl* o-*nitrobenzenesulphonate*, m. p. 66°, has a low rotation and anomalous dispersion, whilst l-*menthyl toluene*-p-*sulphonate*, m. p. 91—92°, *toluene*-o-*sulphonate*, m. p. 78°, m-*nitrobenzenesulphonate*, m. p. 80°, and p-*nitrobenzenesulphonate*, m. p. 70·5°, resemble the corresponding benzoic esters, and differ little from the unsubstituted compound. In the series, l-*menthyl* o-*thiolbenzoate*, b. p. 202—205°/0·2 mm., and o-*methylthiolbenzoate*, b. p. 210°/0·3 mm., l-*menthyl* ester of o-*carboxyphenylmethylsulphone*, b. p. 190—193°/0·2 mm. (o-*carboxyphenylmethylsulphone monohydrate*, m. p. 73°), *K* salt of *l*-menthyl *o*-sulphobenzoate, and *Me* o-*carbomenthoxybenzenesulphonate*, the influence of substitution is given by SMe>SH>H>SO_2Me>SO_2·OMe>SO_2·OH. Ionisation of the SH or SO_3H group depresses the rotatory power, and the characteristic effect of the *o*-substituents is in every case more pronounced in C_6H_6 than in EtOH.

F. R. SHAW.

Constitution of citrylidenemalonic acid. R. KUHN and M. HOFFER (Ber., 1931, **64**, [*B*], 1243—1252).—Whereas Et citrylidenemalonate absorbs 3 mols. of H_2 in accordance with the structure CMe_2:CH·CH_2·CH_2·CMe:CH·CH:C(CO_2Et)$_2$ the acid is indifferent towards H, and does not add Br. The acid is shown to be *menthane*-3-*malono*-1 : 4-*dilactone* (I).



It is converted by aq. NaOH (1 mol.) into *menthan*-1-*ol*-3-*aceto*-4-*lactone*, m. p. 123—123·5° (corr.), and by an excess of boiling, aq. KOH into *menthan*-4-*ol*-3-*aceto*-1-*lactone*, m. p. 118—119°, also derived by similar treatment of the first-named lactone. The OH group of both lactones is esterified with difficulty, but easily replaced by Cl, yielding respectively 1-*chloromenthan*-3-*aceto*-4-*lactone*, m. p. 89—90°, and 4-*chloromenthan*-3-*aceto*-1-*lactone*, m. p. 59·3—60·5°. Either lactone is transformed by HCl in MeOH into *Me* 1 : 4-*dichloromenthane*-3-*acetate*, m. p. 123·5—124° (decomp.), converted by KOH in EtOH into an acidic oil containing Cl. When heated at 290°, 1-chloromenthan-3-aceto-4-lactone loses HCl and yields *menthene*-3-*aceto*-4-*lactone*, b. p. 160—162°/11 mm., d_4^{19} 1·041, hydrogenated to *menthane*-3-*aceto*-4-*lactone*, b. p. 156—158°/11 mm., d_4^{20} 1·015. For purposes of comparison, synthetic menthol," $[\alpha]_D^{20}$ —14·7° in EtOH, is oxidised to menthone, which is condensed with Me bromoacetate to *Me menthol-acetate*, b. p. 138—139°/12 mm. Treatment of the last-named compound with $KHSO_4$ at 150—160° affords menthane-3-aceto-4-lactone, b. p. 154—159°/11 mm., d_4^{20} 1·015, isomerised by P and HI in AcOH to the cryst. lactone, m. p. 93·5—95°, identical with that derived from citrylidenemalonic acid.

H. WREN.

Hydration of turpentine terpenes to terpin hydrate by mineral acids. A. PARIS (Acta Comm. Univ. Tartu. [Dorpat], 1930, **16**, No. 1, 3—28; Chem. Zentr., 1931, i, 1607).—Pinene fractions of different age and history show small indefinite

differences on hydration. Terpin hydrate was employed as homogeniser for the turpentine–aq. acid mixtures, since it forms a hydrophobic layer on the droplets of the aq. phase. Hydration in presence of H_2SO_4, HCl, or HNO_3 (0·5—6 mol.) proceeds relatively rapidly at first, then ceases (presumably owing to the formation of a film of solid terpin hydrate around the drops of the aq. phase) or appears retrogressive. At higher temp. and acid concentration dehydration, and with HCl addition of HCl, also occur. The reaction system is regarded as a macro-emulsion; the interfaces are relatively small and saturated with pinene. The reaction velocity is proportional to the square of the acid concentration or, at 25°, to the square of the activity of the acid. The temp. coeff. is 3·4—3·8 per 10°. A. A. ELDRIDGE.

Dependence of optical rotatory power on chemical constitution. XI. Rotatory dispersion of stereoisomeric trans-*oo'*-stilbene and *oo'*-dibenzyl derivatives of bisimino-, bisamino-, and bisaminomethylene-camphors. B. K. SINGH and B. BHADURI (J. Indian Chem. Soc., 1931, **8**, 181—198; cf. A., 1930, 1441).—Condensation of the appropriate camphorquinone with *trans-oo'*-diaminostilbene and *s*-di-*o*-aminophenylethane affords d- and l-, m. p. 231—232°, $M[\alpha]_{5461}^{5}$ ±456°, and dl-, m. p. 238—239°, -oo'-*stilbene-bisimino-* (I), reduced by Zn dust and 12% KOH to d- and l-, decomp. 220°, m. p. 240—241°, $M[\alpha]_{5461}^{35}$ ±45·6°, and dl-, m. p. 210—212°, -oo'-*stilbenebisamino-* (II), d- and l-, m. p. 187—188°, $M[\alpha]_{5461}^{35}$ ±684°, and dl-, m. p. 194—195°, -oo'-s-*diphenylethanebisimino-* (III), reduced to d- and l-, m. p. 214—216°, $M[\alpha]_{5461}^{31}$ ±157°, and dl-, m. p. 204—205°, oo'-s-*diphenylethanebisamino-* (IV) -*camphor.* Similar condensation of oxymethylenecamphor affords d- and l-, m. p. 295—296°, ±394°, and dl-, m. p. 295—296°, -oo'-*stilbenebisaminoethylene-* (V), d- and l-, m. p. 266—268°, $M[\alpha]^{35}{}_{1}$ ±392°, and dl-, m. p. 272—273°, oo'-s-*diphenylethanebisaminoethylene-* (VI) -*camphor.* All rotations are in $CHCl_3$, but they are also recorded in various other solvents. Whilst destruction of conjugation at a distance from the asymmetric centre causes only a small depression in rotatory power (*e.g.*, I ⟶ V; III —— VI), breaking it near that centre results in a large depression (*e.g.*, I ⟶ II; III ⟶ IV). Apparent anomalies to this conclusion in certain solvents are probably explained by the existence of the compound in the completely conjugated *o*-quinonoid–enol form. With the exception of IV in pyridine and C_6H_6, all these derivatives exhibit simple rotatory dispersion. In pyridine, V exhibits mutarotation 435·4° ⟶ 413·3° in 15 hr. J. W. BAKER.

Essential oil of Taiwania cedar. K. KAFUKU and R. KATO. **Essential oil of leaves of *Chamæcypyrasis obtusa*, Sieb. et zucc., f. *Formosana*, Hayata, or Arisan "Hinoki." II.** K. KAFUKU and T. NOZOE.—See B., 1931, 698.

Synthesis of *dl*-pilopic acid. K. N. WELCH (J.C.S., 1931, 1370).—The successive action of CH_2O and HCl on Et butane-ααβ-tricarboxylate gives 2-keto-3-ethyltetrahydrofuran-4-carboxylic acid, m. p. 86—87°, which appears to be identical with that obtained by Tschitschibabin and Preobraschenski (A., 1930, 452). F. R. SHAW.

Relation between odour and chemical behaviour. A. ANGELI and A. POLVERINI (Gazzetta, 1931, **61**, 276—280).—Determination of the oxidisability of the double linking $\cdot CH_2{:}CH\cdot CO\cdot$ in coumarin and its alkyl derivatives shows parallelism between this property and strength of odour, coumarin itself and its 7- and 3-Me derivatives, which have a strong odour, being readily oxidised, whilst the practically odourless 4-Me derivatives resist oxidation. E. E. J. MARLER.

Synthesis of coumarins from phenols and β-ketonic esters using phosphorus pentoxide. I. Coumarins from resorcinol and ethyl acetoacetates. D. CHAKRAVARTI (J. Indian Chem. Soc., 1931, **8**, 129—136).—Contrary to Simonis and Remmert (A., 1914, i, 980), the product obtained by condensation of Et methylacetoacetate and resorcinol in the presence of P_2O_5 or NaOEt is not 7-hydroxy-2 : 3-dimethylchromone (A., 1901, i, 735), but is 7-hydroxy-3 : 4-dimethylcoumarin, m. p. 256° (not m. p. 262°, as given by Simonis and Remmert) (cf. A., 1884, 66) (*Ac* derivative, m. p. 165°; *Me*, m. p. 140°, and *Et*, m. p. 121°, *ethers*). This explains the failure of Heilbron and others (J.C.S., 1923, **123**, 2569) to condense the Et ether with MeCHO, their suggestion that failure was due to the presence of the 7-OH group being incorrect, since 7-methoxy-2 : 3-dimethylchromone readily condenses with PhCHO to give 7-*methoxy*-2-*styryl*-3-*methylchromone*, m. p. 152°, whilst 7-methoxy-2-methyl*iso*flavone (Baker and Robinson, A., 1925, i, 1299) and PhCHO afford 7-methoxy-2-styryl-3-phenylchromone identical with a specimen differently prepared by these authors. Thus the formation of coumarins, rather than chromones, by condensation of resorcinol with substituted acetoacetic esters is a general reaction. Contrary to Jacobson and Ghosh (J.C.S., 1915, **107**, 1053), resorcinol and Et benzylacetoacetate afford only 7-hydroxy-3-benzyl-4-methylcoumarin, m. p. 224°, the other product, m. p. 186°, obtained by these authors being an impure specimen. Similarly are prepared 7-*hydroxy*-3-*ethyl*-, m. p. 194—198° (*Ac* derivative, m. p. 110°; *Me ether*, m. p. 93°); -3-n-, m. p. 169—171° (*acetyl* derivative, m. p. 119°), and -3-*iso*-, m. p. 224° (*Ac* derivative, m. p. 124°), -*propyl*-; -3-iso*butyl*-, m. p. 153° (*Ac* derivative, m. p. 109°); -3-*phenyl*- (Me ether, m. p. 104°; lit. m. p. 87°), and -3-chloro- (A., 1901, i, 210) -4-*methylcoumarin.* J. W. BAKER.

Hydroxy-carbonyl compounds. III. Preparation of coumarins and 1 : 4-benzopyrones from phloroglucinol and resorcinol. F. W. CANTER, F. H. CURD, and A. ROBERTSON (J.C.S., 1931, 1255—1265).—Phloroglucinol and resorcinol condense with Et acylacetates in presence of P_2O_5 forming coumarins instead of the expected 1 : 4-pyrones (cf. A., 1913, i, 890; 1914, i, 424, 980). The following are prepared: (*a*) from phloroglucinol: 5 : 7-dihydroxy-4-methyl- [*Me_2 ether*, m. p. 171°, also formed when phloroglucinol Me_2 ether is condensed with $CH_2Ac\cdot CO_2Et$ in presence of P_2O_5 (not with conc. H_2SO_4)]; 5 : 7-*dihydroxy*-3 : 4-*dimethyl*-, m. p. 291—292° (*diacetate,*

m. p. 130°; *Me_2 ether*, m. p. 157—158°, also obtained from phloroglucinol dimethyl ether and $CHMeAc{\cdot}CO_2Et$ as above); 5 : 7-*dihydroxy-4-methyl-3-ethyl-*, m. p. 217° (*diacetate*, m. p. 124°; *Me_2 ether*, m. p. 112°), and 5 : 7-dihydroxy-4-phenylcoumarin (also prepared from 2 : 4 : 6-trihydroxybenzophenone, Ac_2O, and NaOAc at 170—180°); (*b*) from resorcinol: 7-hydroxy-4-methyl-; 7-hydroxy-3 : 4-dimethyl-, m. p. 258° (*Ac* derivative, m. p. 164°; *Me*, m. p. 142·5°, and Et ethers, m. p. 120°) [the 7-hydroxy-2 : 3-dimethylbenzo-1 : 4-pyrone of Simonis and Remmert (A., 1914, i, 980) is this coumarin], and 7-*hydroxy-4-methyl-3-ethyl-coumarin*, m. p. 198° (*Ac* derivative, m. p. 107°; *Me_2 ether*, m. p. 93°). All the above coumarins were prepared also using conc. H_2SO_4 as the condensing agent.

Treatment of phlor-propiophenone and -butyrophenone with Ac_2O and NaOAc at 170—180° gives 5 : 7-*dihydroxy-2 : 3-dimethyl-*, m. p. 215° (*diacetate*, m. p. 141—142°), and 5 : 7-*dihydroxy-2-methyl-3-ethyl-1 : 4-benzopyrone*, m. p. 206—207° (*diacetate*, m. p. 124°), respectively. Similar acetylation of phloroacetophenone affords nuclear acetylated *compounds*, m. p. 127° and 131° (hydrolysed to *substances*, m. p. 226° and 274° after sintering at 269°, respectively), whilst respropiophenone and resbutyrophenone afford 7-hydroxy-2 : 3-dimethyl- and 7-*hydroxy-2-methyl-3-ethyl-1 : 4-benzopyrones*, m. p. 238°, respectively. 5 : 7-*Dihydroxy-3-methyl-*, m. p. 262° (*diacetate*, m. p. 132°), 5 : 7-*dihydroxy-3-ethyl-*, m. p. 243°, and 7-*hydroxy-3-methyl-flavones*, m. p. 278° (*acetate*, m. p. 137°), are prepared by the action of Bz_2O and NaOBz at 180—190° on phlorpropiophenone, phlorbutyrophenone, and respropiophenone, respectively.

H. BURTON.

Condensation of α-formylphenylacetonitriles with phenols. I. I. C. BADHWAR, W. BAKER, B. K. MENON, and K. VENKATARAMAN (J.C.S., 1931, 1541—1546).—Condensation of α-formylphenylacetonitrile (I), its *O*-Bz and some other derivatives on the one hand with resorcinol and other phenols and their derivatives on the other under the conditions of the Hoesch reaction produces 3-phenylcoumarins in poor yields and not, as usually, 3-phenylchromones. Unless otherwise stated, the following condensations were performed by saturating a solution of the components in dry Et_2O with HCl at 0° in the presence of $ZnCl_2$. Resorcinol and I gave 7-hydroxy-3-phenylcoumarin (II) (cf. A., 1928, 70) and an amorphous *substance*, m. p. about 245—255° (amorphous *Ac* derivative, m. p. 150—156°). Resorcinol Me ether and I gave 7-methoxy-3-phenylcoumarin (replaced in one experiment by 7-methoxy*iso*flavone) and an amorphous substance. Phloroglucinol and I gave 5 : 7-dihydroxy-3-phenylcoumarin. *p*-Methoxyphenylacetonitrile, Na, abs. EtOH, and $H{\cdot}CO_2Et$ gave p-*methoxyphenylacetonitrile* (III), m. p. 120—121°. 3 : 4 : 5-Trimethoxyphenylacetonitrile similarly gave α-*formyl-3 : 4 : 5-trimethoxyphenylacetonitrile* (IV), dimorphous, m. p. 83—85° and then 114—115°. Phloroglucinol Me_2 ether and III gave 5 : 7 : 4′-trimethoxy-3-phenylcoumarin. 3 : 4 : 5-Trimethoxyphenol and IV gave 5 : 6 : 7 : 3′ : 4′ : 5′-*hexamethoxy-3-phenylcoumarin*, m. p. 157°. Phenylacetonitrile, $H{\cdot}CO_2Et$, Na, and dry Et_2O, followed by BzCl and aq. NaOH gave benzoyloxymethylenephenylacetonitrile (V), which with resorcinol yielded II and a non-phenolic *substance*, m. p. 145—146°. V gave with pyrogallol 7 : 8-dihydroxy-3-phenylcoumarin, and with orcinol 7-hydroxy-3-phenyl-5-methylcoumarin (previously described as the chromone, J.C.S., 1916, **109**, 117). V with resorcinol diacetate, $ZnCl_2$, and HCl in AcOH gave 4 : 6-diacetylresorcinol and a little II, and with resorcinol Me ether yielded 7-methoxy-3-phenylcoumarin. No reaction occurred with V and quinol, pyrocatechol, or phenol under the conditions stated, nor in conc. H_2SO_4.

R. S. CAHN.

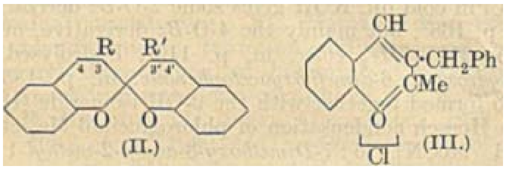
Hydroxy-carbonyl compounds. II. Benzoylation of ketones derived from phloroglucinol. F. W. CANTER, F. H. CURD, and A. ROBERTSON (J.C.S., 1931, 1245—1255).—Treatment of 2 : 4 : 6-trihydroxyacetophenone (*tribenzoate*, m. p. 117—118°) with BzCl in cold dil. KOH gives some 2-*O*-*Bz* derivative, m. p. 168°, but mainly the 4-*O*-*Bz* derivative, m. p. 210—211° [*Me_2 ether*, m. p. 119°, hydrolysed to 4-*hydroxy-2 : 6-dimethoxyacetophenone*, m. p. 185·5°, also formed together with the 2-OH-isomeride (I) by the Hoesch condensation of phloroglucinol Me_2 ether and MeCN]. 5 : 7-*Dimethoxy-3-acetyl-2-methyl-1 : 4-benzopyrone*, m. p. 169°, is obtained from I, Ac_2O, and NaOAc at 180°. Hoesch condensation of phloroglucinol and EtCN affords 2 : 4 : 6-*trihydroxypropiophenone* ($+H_2O$), m. p. 174—175°, benzoylated to the 2-*O*-*Bz*, m. p. 191—192° after sintering at 187—188°, and 4-*O*-*Bz* derivatives, m. p. 193° after sintering at 188° (main product) [*Me_2 ether*, m. p. 103°, hydrolysed to 4-*hydroxy-2 : 6-dimethoxypropiophenone*, m. p. 180° (*acetate*, m. p. 76°), also formed with 2-*hydroxy-4 : 6-dimethoxypropiophenone* (II), m. p. 111°, from phloroglucinol Me_2 ether and EtCN by the Hoesch reaction]. 5 : 7-*Dimethoxy-2 : 3-dimethyl-1 : 4-benzopyrone*, m. p. 189—190°, and 5 : 7-*dimethoxy-3-methylflavone*, m. p. 178—179°, are prepared from II and Ac_2O and Bz_2O, respectively. 2 : 4 : 6-Trihydroxybutyrophenone, m. p. 183° (lit. 179—180°), is benzoylated to the 4-*O*-*Bz* derivative, m. p. 164° (*Me_2 ether*, m. p. 86°, hydrolysed to 4-*hydroxy-2 : 6-dimethoxybutyrophenone*, m. p. 107°, which is formed with 2-*hydroxy-4 : 6-dimethoxybutyrophenone*, m. p. 70°, by a Hoesch condensation). 5 : 7-*Dimethoxy-2-methyl-3-ethyl-1 : 4-benzopyrone* has m. p. 118°. 2 : 4 : 6-Trihydroxybenzophenone (*tribenzoate*, m. p. 125—126°) affords the 4-*O*-*Bz* derivative, m. p. 186° (*Me_2 ether*, m. p. 170—171°).

H. BURTON.

Chromone group. II. 1 : 4-α-Naphthapyrones. A. S. BHULLAR and K. VENKATARAMAN (J.C.S., 1931, 1165—1170).—2-Acetyl-α-naphthol (I) [benzoate, m. p. 128° (lit. 96·5°)] reacts more readily with acid anhydrides than any of the ketones previously used (A., 1926, 1149; 1929, 325, 1459); mixtures of 1 : 4-α-naphthapyrones and their 3-acyl or -aroyl derivatives are produced. The following are prepared: 2-methyl-1 : 4-α-naphthapyrone (3-acetyl derivative), from I and Ac_2O; α-naphthaflavone (3-*Bz* derivative, m. p. 218°), from I and Bz_2O; 4′-methoxy-α-naphthaflavone (3-*anisoyl* derivative, m. p. 211—212°). 1-*Acetoxy-2-naphthyl αβ-dibromo-β-3 : 4-dimethoxyphenylethyl ketone*, m. p. 161°, is converted by aq.-alcoholic KOH into 3′ : 4′-*dimethoxynaphthaflavone*,

m. p. 192° after sintering at 184°, demethylated to 3′ : 4′-*dihydroxynaphthaflavone*, m. p. 317—319° (*diacetate*, m. p. 204°). H. BURTON.

Styrylpyrylium salts. XIII. Reactivity of methyl β-phenylethyl and γ-phenylpropyl ketones. I. M. HEILBRON, R. N. HESLOP, F. IRVING, and J. S. WILSON (J.C.S., 1931, 1336—1342; cf. A., 1929, 822).—Condensation of methyl β-phenylethyl ketone (I) (from ethyl α-benzylacetoacetate) with salicylaldehyde in the presence of piperidine or NaOH gave 2-*hydroxystyryl* β-*phenylethyl ketone*, m. p. 128—129°, which with β-naphthol-1-aldehyde and HCl yielded non-ionising 3′-*benzylbenzo*-β-*naphtha*spiro-*pyran* (II; R=H, R′=CH_2Ph), m. p. 129—130°, colourless in boiling xylene, rapidly giving a wine-red colour in AcOH (contrast benzyl methyl ketone, *loc. cit.*). Condensation in the presence of HCl gave the



pyrylium salt (III) (hydrolysed to 3-benzyldibenzo-*spiro*pyran), which on condensation with β-naphthol-1-aldehyde and hydrolysis yielded 3-*benzylbenzo*-β-*naphtha*spiro*pyran* (II; R=CH_2Ph, R′=H), m. p. 157° to a purple liquid, colourless in cold xylene, reddish-purple when boiling, and slowly giving a blue colour in AcOH. Methyl γ-phenylpropyl ketone (IV) [from Et α-(β-phenylethyl)acetoacetate] gave similarly 2-*hydroxystyryl* γ-*phenylpropyl ketone*, m. p. 114°; 3′-β-*phenylethylbenzo*-β-*naphtha*spiro*pyran*, m. p. 180°, colourless in boiling xylene or veratrole, wine-red in AcOH; 3-β-*phenylethylbenzo*-β-*naphtha*spiro*pyran*, m. p. 140—141° to a deep purple liquid, colourless in cold xylene, deep purple when heated, and slowly giving a blue colour in AcOH. I and IV with β-naphthol-1-aldehyde and HCl gave the pyrylium salts, from which 3-benzyldi-β-naphtha*spiro*pyran and 3-β-*phenylethyldi*-β-*naphtha*spiro*pyran*, m. p. 219—220° (bluish-purple in boiling xylene), respectively, were obtained. I with PhCHO yielded either styryl β-phenylethyl ketone, m. p. 53—54° (cf. this vol., 92; A., 1904, i, 427) (*semicarbazone*, m. p. 135°) [the structure of which is proved by its prep. from *benzylidene-α-benzylacetoacetic acid*, m. p. 157° (decomp.) (from PhCHO and ethyl benzylacetoacetate)], or *di*(*styryl* β-*phenylethyl ketone*), m. p. 184°, according to the experimental conditions. IV gave similarly *styryl* γ-*phenylpropyl ketone*, m. p. 51°, and *di*(*styryl* γ-*phenylpropyl ketone*), m. p. 138° (contrast benzyl methyl ketone, A., 1899, i, 140). R. S. CAHN.

Formation of phlobaphens. M. BERGMANN and G. POJARLIEFF (Collegium, 1931, 244—247).—Phlobaphens were formed by boiling tetramethylcatechin with alcoholic HCl, from which it is inferred that phenolic OH groups are not essential to phlobaphen formation, but that probably unsaturated linkings in close proximity with OH groups, as in pyran rings, cause a tendency to acid condensation. This view is supported by the behaviour of glucal. Pyrocatechol tannins are therefore related structurally to the sugars. D. WOODROFFE.

Organic compounds of sulphur. XIX. Novel intramolecular atomic displacement (migration of a chlorine atom from carbon to sulphur). Tautomerism and desmotropy of thiocarbonic esters. A. SCHONBERG and L. VON VARGHA (Ber., 1931, **64**, [*B*], 1390—1399; cf. A., 1930, 1574).—Diphenyldiazomethane and Ph chlorothionformate in Et_2O afford β-*chloro*-β-*phenoxy*-αα-*diphenylethylene sulphide*, m. p. 78°, which passes at 100—130° into 2-*phenoxy*-3-*phenylthionaphthen*, m. p. 116°, stable to heat, acids, and alkali, but decomposed by molten KOH with production of PhOH. Similarly, diphenyldiazomethane and Ph chlorodithioformate give β-*chloro*-β-*phenylthiol*-αα-*diphenylethylene sulphide*, m. p. 99—100° (decomp.) when rapidly heated, converted by LiPh into ββ-diphenylthiol-αα-diphenylethylene, m. p. 112° (Ph_2S, b. p. 156°/16 mm., is obtained in the same manner from LiPh and chlorothiolbenzene), and passing at 95—100° into 2-*phenylthiol*-3-*phenylthionaphthen*, m. p. 123°. Di-*p*-tolyldiazomethane and Ph chlorothionformate give a non-cryst. product which is transformed at 110—120° into 2-*phenoxy*-3-p-*tolyl*-6-*methylthionaphthen*, m. p. 102°. *Me* β-*phenoxy*-αα-*diphenylvinylsulphenate*, $CPh_2{:}C(OPh){\cdot}S{\cdot}OMe$, m. p. 117°, is obtained by the action of boiling MeOH on β-chloro-β-phenoxy-αα diphenylethylene sulphide; the corresponding *Et* ester has m. p. 105—106°. *Me* β-*phenylthiol*-αα-*diphenylvinylsulphenate*, m. p. 127°, is prepared analogously from β-chloro-β-phenylthiol-αα-diphenylethylene sulphide, but the main product is 2-phenylthiol-3-phenylthionaphthene when boiling EtOH is used. Reduction of β-chloro-β-phenoxy-αα-diphenylethylene sulphide with Al–Hg in moist Et_2O affords *Ph diphenylthionacetate*, $CHPh_2{\cdot}CS{\cdot}OPh$, m. p. 67°, hydrolysed by H_2SO_4 to diphenylacetic acid. β-Chloro-β-phenylthiol-αα-diphenylethylene sulphide is converted by similar means into β-*thiol*-β-*phenylthiol*-αα-*diphenylethylene*, m. p. 112°, hydrolysed to diphenylacetic acid and PhSH. H. WREN.

Reactivity of conjugated systems. III. Condensation of αβ-unsaturated esters with cyanoacetamide. C. BARAT (J. Indian Chem. Soc., 1931, **8**, 37—44).—αβ-Unsaturated esters and amides react with cyanoacetamide in presence of NaOEt to form 4-alkyl-2 : 6-diketo-3-cyanopiperidines, which on acid hydrolysis form β-alkylglutaric acids. The reactivity decreases from αβ-unsaturated ketones, through the acids to amides (A., 1930, 925). Et acrylate, crotonate, cinnamate, and *p*-nitrocinnamate give respectively 2 : 6-*diketo*-3-*cyanopiperidine*, m. p. 206—207°, 2 : 6-*diketo*-3-*cyano*-4-*methylpiperidine*, m. p. 140—142°, 2 : 6-*diketo*-3-*cyano*-4-*phenylpiperidine*, m. p. 224—225°, and 2 : 6-*diketo*-3-*cyano*-4-p-*nitrophenylpiperidine*, m. p. 279—280°, the amides giving the same products in better yield. G. DISCOMBE.

Condensation of an amine and formaldehyde with quinaldine and picoline. T. HEOU-FÉO (Compt. rend., 1931, **192**, 1242—1244).—Condensation of $NHEt_2$,HCl, CH_2O, and quinaldine in aq. solution affords 2-β-*diethylaminoethylquinoline*, b. p. 181°/12

mm. (*monopicrate*, m. p. 122°; *dipicrate*, m. p. 153°; *chloroplatinate*, decomp. 185°; *chlorozincate*, m. p. 230°; *hydrochloride*), and a little bisdiethylaminomethane. Similar condensation with NH_2Et,HCl affords a product, b. p. 160—180°/0·2 mm., converted by BzCl into 2-(β-*benzethylamidoethyl*)*quinoline*, $C_9H_7N\cdot[CH_2]_2\cdot NBzEt$, m. p. 130°, whilst α-picoline, $NHEt_2$, and CH_2O give 2-(β-*diethylaminoethyl*)*pyridine*, b. p. 153°/16 mm. (*picrate*, m. p. 164°; *methiodide*, m. p. 183°; *chloroplatinate*, decomp. 205°; *cadmichloride*, m. p. 186°; *hydrochloride*).

J. W. BAKER.

Quinoline derivatives. XIX. β-Diethylaminoethyl 2-phenylquinoline-4-carboxylate and β-diethylaminoethyl 6-methoxy-2-phenylquinoline-4-carboxylate. XX. Derivatives of 2-phenylquinoline-4-carboxylic acid and 6-methoxy-2-phenylquinoline-4-carboxylic acid. XXI. 4-Amino-6-hydroxy-2-phenylquinoline. XXII. Decomposition of 6-methoxy-2-phenylquinoline-4-carboxylic acid. XXIII. 4-Halogeno-6-methoxy-2-phenylquinolines. XXIV. 6-Ethoxy-2-phenylquinoline-4-carboxylic acid and 4-amino-6-ethoxy-2-phenylquinoline. H. JOHN [with H. LUKAS] (J. pr. Chem., 1931, [ii], **130**, 289—292, 293—304, 304—313; 314—327, 328—331, 332—341).—XIX. β-*Chloroethyl 2-phenylquinoline-4-carboxylate*, m. p. 72° (from the acid chloride) gives with $NHEt_2$ the corresponding β-*diethylaminoethyl* ester (*dihydrochloride*, m. p. 160°). β-*Chloroethyl*, m. p. 98°, and β-*diethylaminoethyl 6-methoxy-2-phenylquinoline-4-carboxylate*, m. p. 78°, are similarly prepared.

XX. 2-Phenylquinoline-4-carboxyl chloride condenses to give with (*a*) 0·5 mol. of carbamide, 2-*phenyl-4-quinoloylcarbamide*, m. p. 232°; (*b*) 1 mol. of carbamide, NN'-*bis*-(2-*phenyl-4-quinoloyl*)*carbamide*, m. p. 215°; (*c*) β-aminoethyl alcohol, β-2-*phenyl-4-quinoloylamidoethyl alcohol*, m. p. 165°; and (*d*) ethylenediamine, NN'-*bis*-(2-*phenyl-4-quinoloyl*)*ethylenediamine*, m. p. above 300°. 6-*Methoxy-2-phenyl-4-quinoloylcarbamide*, m. p. 245°, NN'-*bis*-(6-*methoxy-2-phenyl-4-quinoloyl*)-*carbamide*, m. p. 181°, β-6-*methoxy-2-phenyl-4-quinolyl-amidoethyl alcohol*, m. p. 243°, -*ethylenediamine*, m. p. 105°, and -*diethylamide*, m. p. 163° (*picrate*, m. p. 141°), NN'-*bis*-(6-*methoxy-2-phenyl-4-quinoloyl*)*ethylenediamine*, m. p. above 300°, 6-*methoxy-2-phenyl-4-quinoloyl*)-p-*phenetidine*, m. p. 230°, and (6'-*methoxy-2'-phenyl-4-quinoloyl*)-4-*aminoantipyrine*, m. p. 280° (decomp.) (*picrate*), m. p. 126°, are similarly prepared.

XXI. 6-Hydroxy-2-phenylquinoline-4-carboxylic acid, m. p. above 300°, prepared from benzylidene-*p*-aminophenol and pyruvic acid or from the corresponding OMe-compound, affords the following derivatives: *Me* ester, m. p. 183°; *Et* ester, m. p. 176°; *hydrazide*, m. p. 242°; iso*propylidenehydrazide*, m. p. 218°; *benzylidenehydrazide*, m. p. 287°; *azide*, decomp. at 100°. *Et* 6-*hydroxy-2-phenyl-4-quinolylaminoformate* has m. p. 208°; NN'-*bis*-(2-*phenyl-6-hydroxy-4-quinoloyl*)*carbamide*, m. p. 166°; 4-*amino-6-hydroxy-2-phenylquinoline*, m. p. 153° (*hydrochloride*, m. p. 215°, from the urethane).

XXII.—6-*Methoxy-2-phenylquinoline-4-carboxylic acid*, m. p. 237° (*salts* described), obtained from benzylidene-*p*-anisidine and pyruvic acid, affords the *chloride*, m. p. 237°; *amide*, m. p. 246°; *Et* ester, m. p. 106°; *Pr* ester, m. p. 85°; *Pr*$^\beta$ ester, m. p. 80°; *hydrazide*, m. p. 200°; *benzylidenehydrazide*, m. p. 223°; *methylbenzylidenehydrazide*, m. p. 218°; *azide*. *Et* 6-*methoxy-2-phenyl-4-quinolylaminoformate* has m. p. 164°; NN'-*bis*-(6-*methoxy-2-phenyl-4-quinolyl*)*carbamide*, m. p. 273° (decomp.); 6-*methoxy-2-phenyl-4-quinolylcarbimide*, m. p. 221°, which is converted by alcoholic KOH into 6-*methoxy-2-phenyl-4-aminoquinoline*, m. p. 143° (*hydrochloride*, m. p. 258°, from the urethane); and 4-*diacetamido-6-methoxy-2-phenylquinoline*, m. p. 100°.

XXIII. 4-*Chloro-6-methoxy-2-phenyl-*, m. p. 109°, 4-*bromo-*, m. p. 157°, and 4-*iodo-quinoline*, m. p. 178°, are prepared from the corresponding amine.

XXIV. 6-*Ethoxy-2-phenylquinoline-4-carboxylic acid*, m. p. 203°, obtained from benzylidene-*p*-phenetidine and pyruvic acid, affords a *Me* ester, m. p. 118°; *Et* ester, m. p. 114°; *hydrazide*, m. p. 195°; iso*propylidenehydrazide*, m. p. 183°; *benzylidenehydrazide*, m. p. 218°; *azide*, decomp. 108°. *Et* 6-*ethoxy-2-phenylquinolylaminoformate* has m. p. 135°; 6-*ethoxy-2-phenylquinolylcarbimide*, m. p. 213°, reacts with alcoholic KOH to give 4-*amino-6-ethoxy-2-phenylquinoline*, m. p. 187° [*Ac_2* derivative, m. p. 108°; *hydrochloride*, m. p. 292° (also obtained from the urethane)]; N : N'-*bis*-(6-*ethoxy-2-phenyl-4-quinolyl*)-*carbamide*, m. p. 275°.

F. R. SHAW.

Optical activity and the polarity of substituent groups. XVIII. *l*-Menthyl and *d*-β-octyl esters of picolinic, quinaldinic, nicotinic, and cinchoninic acids. H. G. RULE, J. B. MILES, G. SMITH, and (MISS) M. M. BARNETT (J.C.S., 1931, 1478—1482).—The rotatory powers of l-*menthyl quinaldinate*, m. p. 141—142°, and *picolinate*, b. p. 170°/1 mm., d-β-*octyl quinaldinate*, b. p. 168°/0·6 mm., *picolinate*, b. p. 170—173°/12 mm., *nicotinate*, b. p. 142—145°/0·02 mm., and *cinchoninate*, b. p. 154—156°/0·3 mm., in EtOH and in EtOH and HCl are discussed with reference to the polar changes involved on conversion into their salts.

F. R. SHAW.

Acridine. VI. *ms*-Acridine derivatives. II. K. LEHMSTEDT (Ber., 1931, **64**, [*B*], 1232—1239; cf. A., 1930, 926).—Acridine-9-carboxylamide is converted by Br and NaOMe (2 mols.) into 9 : 10-*dihydroxy-9 : 10-dihydroacridine-9-carboxylamide*, decomp. 169° when introduced into a bath preheated at 167°; under similar conditions acridine affords acridone. With 1 mol. of Br and 3 mols. of NaOMe in MeOH the amide yields *Me* 9-*acridylcarbamate*, m. p. 203·5° (slight decomp.) [*hydrochloride*]; the corresponding *Et*, m. p. 193°, *Bu*$^\alpha$, m. p. 148—150°, and *CH_2Ph*, m. p. 193—194°, esters are described. 4-Nitroacridine-9-carboxylamide yields the corresponding red *$(OH)_2$* derivative and *Me* 4-*nitro-9-acridylcarbamate*, m. p. 218° (slight decomp.). 9-Cyanoacridine is converted by H_2SO_4 and HNO_3 into 4-*nitro-9-cyanoacridine*, m. p. 216° (decomp.), hydrolysed by 90% H_2SO_4 to 4-*nitroacridine-9-carboxylamide*, decomp. 280° [*sulphate*, m. p. 275° (decomp.)], which with H_2SO_4 and $NaNO_2$ yields 4-*nitroacridine-9-carboxylic acid*, decomp. 203°, decarboxylated to 4-nitroacridine. Me 9-acridylcarbamate and $Ca(OH)_2$ at 220° give 9-*aminoacridine*, m. p. 234°; with conc. H_2SO_4 at 110—120° the carbamate yields a dehydrated 9-*aminoacridine*-

disulphonic acid, m. p. above 350° (K salt). 9-Phenylacridine with Br and KOH in MeOH affords *dibromo-9-phenylacridine*, m. p. 267—269° (*hydrochloride*). 9-*Cyanoacridine* is prepared from 9-chloroacridine, KCN, CuCN, and MeOH at 160—170°.

H. WREN.

Chloride, esters, and amides of hydantoin-3-acetic acid, and their use in the identification of alcohols and amines. R. LOCQUIN, V. CERCHEZ, and (in part) A. A. POLICARD (Bull. Soc. chim., 1931, [iv], **49**, 595—600, 600—602, 602—607, 607—612).—When hydantoin-3-acetyl chloride (I) in tetrachloroethane is treated with alcohols, preferably in presence of pyridine, quant. yields of the corresponding well-cryst. acetates are obtained. Since I is readily obtained from the acid and $SOCl_2$ and these esters are readily hydrolysed by dil. HCl they have advantages for identifying primary and secondary alcohols and certain phenols. They cannot be used for identifying *tert.* or terpene alcohols; the extreme solubility of the geranyl and citronellyl esters makes purification difficult. The esters may in many cases also be obtained quantitatively by normal esterification of hydantoin-3-acetic acid. I with dry NH_3 in tetrachloroethane yields hydantoin-3-acetamide. With amines and other NH_2-compounds N-substituted hydantoin-3-acetamides are similarly obtained, and are suitable for the identification of the parent compounds, especially of pyrazolines.

The following esters of hydantoin-3-acetic acid are described: *Pr*, m. p. 116°, *Bu*, m. p. 95°; *Bu*$^{\beta}$, m. p. 124°; sec.-*Bu*, m. p. 142°; iso*amyl*, m. p. 104°; sec.-*octyl*, m. p. 84°; *benzyl*, m. p. 142°, and cyclo*hexyl*, m. p. 184° (all obtained by esterification); *Me*, m. p. 91° (from hydantoin-3-acetic acid and diazomethane, and not from I); *Ph*, m. p. 205—206°; *cholesteryl*, m. p. 304—305° (together with substances, m. p. 131° and 185—186°).

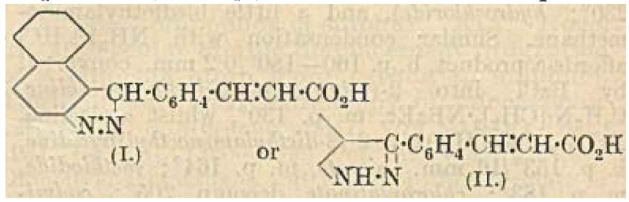
The following are described: *hydantoin-3-acetanilide*, m. p. 215°; N-*benzyl-*, m. p. 209—210°; N-*piperidyl-*, m. p. 160°; N-*methyl-*, m. p. 223° (together with a substance, m. p. 173°); and N-m-*xylyl-hydantoin-3-acetamide*, m. p. 242°. Et aminoacetate yields an *amide*, m. p. 168°, Et aminomalonate an *amide*, m. p. 172—173°, and 3-methyl-5-*iso*propylpyrazoline a *derivative*, $C_3H_3O_2N_2\cdot CH_2\cdot CO\cdot N<\begin{matrix}CHPr^{\beta}\cdot CH_2\\ N{=\!=\!=}CMe\end{matrix}$, m. p. 185°.

R. BRIGHTMAN.

Diagnosis of "veronalides" [derivatives of malonylcarbamide] by micro-crystalloscopy. G. DENIGÈS (Mikrochem., 1931, **9**, 316—323).—The substance is dissolved in a drop of aq. NH_3 on the microscope slide and a drop of 10% H_2SO_4 is placed at the side of the first drop and allowed to diffuse into it, when characteristic crystals of the derivative are formed. Illustrations and descriptions of the following are included: veronal, soneryl, rutonal, luminal, dial, allonal, and allyl*iso*propylmalonylcarbamide.

A. R. POWELL.

Anomalous decomposition of the tetrazo-derivative of 2 : 2′-diamino-1 : 1′-dinaphthyl. A. CORBELLINI and L. BARBARO (Atti R. Accad. Lincei, 1930, [vi], **12**, 445—451).—Purification of the acid substance, m. p. 250—252° (A., 1929, 1172), yields [4 : 5-(*naphtho*-1′ : 2′)-*pyrazole*(3)]-o-*cinnamic acid*, m. p. 269·5° (decomp.), which forms a *Me*, m. p. 158°,



and an *Et* ester, m. p. 143—143·5°; the latter yields an unstable *dibromide*, m. p. about 205° (crude). On sublimation, the acid gives [4 : 5-(*naphtho*-1′ : 2′)-*pyrazole*(3)]-o-*styrene* ($:CH_2$ for $:CH\cdot CO_2H$ in II), m. p. 154°, which forms an unstable *dibromide*, m. p. about 255—258° (crude). Oxidation of the acid by alkaline $KMnO_4$ yields [4 : 5-(*naphtho*-1′ : 2′)-*pyrazole*(3)]-o-*benzaldehyde*, m. p. 230° (p-*nitrophenylhydrazone*, m. p. 258°), an *acid*, m. p. about 287°, and another acid not obtained pure.

T. H. POPE.

Existence of true semiquinones. L. MICHAELIS (Naturwiss., 1931, **19**, 461).—Although reduction of pyocyanin (I), α-hydroxyphenazine (II), and rosinduline-GG (III) with Pd and H_2 proceeds normally in alkaline solution, in acid solution true semiquinones are formed intermediately, since determination of the oxidation–reduction potential of the completely reduced dye gives two values of this potential for each value of p_H below certain limits (I, p_H 5; III, p_H 1—2), the region between the fork of the curve being that in which the semiquinone is in equilibrium with the other form of the dye.

J. W. BAKER.

Reduction products of certain cyclic methylene-amines. J. GRAYMORE (J.C.S., 1931, 1490—1494).—Reduction of hexamethylenetetramine with Zn dust in acid solution gives chiefly NH_3 and trimethylamine. The action of CH_2O on *hexamethylenetetramine picrate*, m. p. 179° (decomp.), yields *dimethylpentamethylenetetramine picrate*, m. p. 196° (decomp.). Reduction of trimethyltrimethylenetetramine affords mainly $NHMe_2$ and some NH_2Me, and of triethyltrimethylenetetramine, NHMeEt (*picrate*, m. p. 196°) and some NH_2Me. Tripropyltrimethylenetetramine (*urate*; *di-iodide*, m. p. 85°; *dibromide*) is reduced to NHMePr only (*picrate*, m. p. 43°; *oxalate*, m. p. 155°; *hydrochloride*, m. p. 140°). The mechanism of the reaction is discussed.

F. R. SHAW.

Phyllobombycin: the biological degradation of chlorophyll. H. FISCHER and A. HENDSCHEL (Z. physiol. Chem., 1931, **198**, 33—42).—A new chlorophyll derivative, $C_{34}H_{36}O_6N_4$, named *phyllobombycin*, can be isolated from silk-worm fæces and detected in the fæces of the death's-head caterpillar. It is free from Mg, phytol, and OMe groups, forms a *Mg* salt and an *Et* ester, m. p. 209°, gives with NaOEt choline (spectroscopically identified) and with HBr–AcOH (cf. this vol., 496) phylloerythrin (spectroscopically identified). Reduction with HI–AcOH gives a *porphyrin*, spectroscopically identical with phæoporphyrin a_5, the ester of which does not depress the m. p. of phæoporphyrin a_5 ester. With HBr–AcOH a mixture of porphyrins, spectroscopically identical with chloroporphyrin e_6 and chloroporphyrin e_4, respectively, is obtained. Chlorophyll is converted by the intestinal

cells of the worm into a red *dye*, which can be detected microscopically.

Penicillium glaucum and *Aspergillus oryzæ* have no action on coproporphyrin I, hæmin, or phæophorbid *a*, but act on chlorin *e* giving a porphyrin spectroscopically identical with phylloerythyrin (the cryst. form of the ester supports the identity) and on rhodin *g* giving an unknown *porphyrin*, which is the first biologically prepared derivative of chlorophyll b_1. A *compound* spectroscopically identical with choline can be extracted from human fæces. A. RENFREW.

Synthesis of deuteroætioporphyrin, deuterorhodin, and two tetramethylmonoethyldicarboxyethylporphins: synthesis of hæmoporphyrin. H. FISCHER and A. KIRSTAHLER (Z. physiol. Chem., 1931, **198**, 43—81).—Hæmoporphyrin is a mixture of mesoporphyrin, deuteroporphyrin, and porphyrins *A* and *B* (see below).

4 : 5 : 3′ : 5′-*Tetramethyl*-4′-*ethylpyrromethene hydrobromide* (methene I), m. p. 214° (*perbromide*, m. p. 138°, which when crystallised from AcOH gives a *dibromomethene hydrobromide*, m. p. above 300°), condenses (succinic acid method) with methene II (A., 1926, 1256) to give 1 : 3 : 5 : 8-*tetramethyl*-4-*ethyl*-6 : 7-*dicarboxyethylporphin* (porphyrin *A*) {Me_2 ester, m. p. 213° [*Fe* salt, m. p. 259° (corr.); *Cu* salt, m. p. 220° (corr.)], which depresses the m. p. of mesoporphyrin IX dimethyl ester by 23°; *hæmin*; *Cu* salt}. Bromination of porphyrin *A* and its Me_2 ester gives amorphous *perbromides*, converted into the *monobromo*-derivatives by aq. $COMe_2$. The *bromodimethyl* ester, m. p. 270° (corr.) [*Cu* salt, m. p. 230° (corr.)], can also be prepared by the succinic acid method. Acetylation of the Me_2 ester Fe salt is accompanied by much decomp. Removal of the Fe gives, with difficulty, 1 : 3 : 5 : 8-*tetramethyl*-4-*ethyl*-2-*acetyl*-6 : 7-*dicarboxyethylporphin* {Me_2 ester, m. p. 261° (corr.) [*Fe* salt, m. p. 260° (corr.); *Cu* salt, m. p. 227° (corr.)]}. The entry of the Ac group displaces the first spectrum band towards the red. The Ac group can be replaced by both the $OH{\cdot}C_2H_4$ and vinyl groups.

Condensation (succinic–pyrotartaric acid method) of 4′-*bromo*-4 : 3′ : 5′-*trimethyl*-3-*ethyl*-5-*bromoethylpyrromethene hydrobromide*, m. p. 315° (decomp.) (prepared by brominating 4 : 5 : 3′ : 5′-tetramethyl-3-ethylpyrromethene hydrobromide), and 5 : 5′-dibromo-4 : 4′-dimethyl-3 : 3′-dicarboxyethylpyrromethene hydrobromide yields 1 : 3 : 5 : 8-*tetramethyl*-2-*ethyl*-6 : 7-*dicarboxyethylporphin* (porphyrin *B*) {Me_2 ester, m. p. 214° [*Fe* salt, m. p. 220° (corr.); *Cu* salt, m. p. 230° (corr.)]}, which depresses the m. p. of both the Me_2 ester of the isomeric porphyrin, m. p. 213°, and the Me_2 ester of mesoporphyrin: *Fe* salt; *Cu* salt; cryst. *perbromide*, giving on partial debromination 4-*bromo*-1 : 3 : 5 : 8-*tetramethyl*-2-*ethyl*-6 : 7-*dicarboxyethylporphin* [*Cu* salt: *Me*$_2$ ester, m. p. 259° (corr.) (*Cu* salt, m. p. 276°)].

Porphyrins *A* and *B* are spectroscopically identical and give the same HCl no. Projection of the ether spectrum of one on that of the other gives a spectrum identical with that of hæmoporphyrin (A., 1913, i, 1251). The HCl nos. of mesoporphyrin (0·5), porphyrins *A* and *B* (0·4), and deuteroporphyrin (0·3) depend on the no. of free methine groups in the porphin nucleus. A modification of Willstatter's method for determining HCl nos. is described. Mixed m. p. of various combinations of the Me_2 esters of the above four porphyrins show that hæmoporphyrin ester is a mixture of these esters.

2 : 3-Dimethylpyrrole and 5-formyl-3-carbethoxy-2 : 4-dimethylpyrrole give, with HBr, 4′-*carbethoxy*-4 : 5 : 3′ : 5′-*tetramethylpyrromethene hydrobromide* (methene IV), m. p. 216° (corr.), giving, on bromination, 3-*bromo*-4′-*carbethoxy*-4 : 5 : 3′ : 5′-*tetramethylpyrromethene hydrobromide*, m. p. above 300°, which condenses (succinic acid method) with 5 : 5′-dibromo-4 : 4′-dimethyl-3 : 3′-dicarboxyethylpyrromethene hydrobromide to give 4-*carbomethoxy*-1 : 3 : 5 : 8-*tetramethyl*-6 : 7-*dicarboxyethylporphin* (*Me*$_2$ ester, m. p. 205°), spectroscopically identical with rhodoporphyrin. Another porphyrin, probably deuteroporphyrin, since the Me ester, m. p. 212°, does not depress the m. p. of deuteroporphyrin Me ester and gives a bromo-derivative, m. p. 274°, which does not depress the m. p. of dibromodeuteroporphyrin Me ester, is formed in small amounts.

[With O. GUNTHER.] At least three porphyrins (*tetramethylmonocarboxylic acid porphin*; *tetramethyldicarboxylic acid porphin*, m. p. 275—280°; and *tetramethylporphin*) can be synthesised by heating 3 : 5-dicarbethoxy-4-methyl-2-bromoethylpyrrole with AcOH–HBr mixture in a sealed, Ag-lined tube. 3 : 4′ : 5-Tribromo-4 : 3′ : 5′-trimethylpyrromethene hydrobromide (methene VI) gives when similarly treated 1 : 3 : 5 : 7-*tetramethylporphin* (*Cu* salt). The same compound is formed, also in poor yield, from 3 : 4′ : 5-tribromo-4 : 3′ : 5′-trimethylpyrromethene hydrobromide (succinic acid method).

3 : 4 : 5-*Tribromo*-3′ : 4′ : 5′-*trimethylpyrromethene hydrobromide* (formed by brominating 3′ : 4′ : 5′-*trimethylpyrromethene hydrobromide*, which results from the action of HBr on a mixture of pyrrole-2-aldehyde and trimethylpyrrole) gives either by the succinic acid method or by heating with HBr–AcOH mixture under pressure very small amounts of a porphyrin $C_{24}H_{21}N_4Br$ (*Cu* salt).

3 : 4′-Dibromo-4 : 5 : 3′ : 5′-tetramethylpyrromethene hydrobromide (A., 1926, 621) yields a free *base*, m. p. 182° (corr.), giving, on oxidation, bromocitraconimide, m. p. 176° (corr.), *Et*$_2$ ester, m. p. 204°, which does not depress the m. p. of *deuteroporphyrin Et*$_2$ ester, m. p. 204°, obtained by the resorcinol fusion of hæmin. The corresponding deuterorhodin gives a *Me* ester, m. p. 245° (corr.).

Deuteroætioporphyrin, m. p. 282° (corr.) [*Cu* salt, m. p. 280° (corr.); *monobromo*-derivative; *dibromo*-derivative, m. p. 368°; *hæmin*], is formed by condensing (succinic acid method) 3 : 4′-dibromo-4 : 5 : 3′ : 5′-tetramethylpyrromethene hydrobromide with 5 : 5′-dibromo-4 : 4′-dimethyl-3 : 3′-diethylpyrromethene hydrobromide. A. RENFREW.

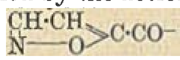
Bile pigments. V. Syntheses of bilirubic and xanthobilirubic acids and their isomerides, also of tripyrrans and bilirubinoid pigments. H. FISCHER and E. ADLER (Z. physiol. Chem., 1931, **197**, 237—280; cf. this vol., 853).—5-Bromo-4 : 3′ : 5′-trimethyl-3-ethyl-4′-carboxyethylpyrromethene hydrobromide (I) when heated with AgOAc

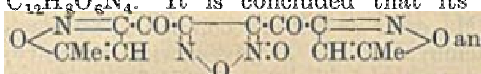
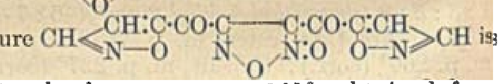
or KOAc in AcOH gives xanthobilirubic acid (II), reduced by Na–Hg or HI to bilirubic acid (III). II may also be obtained from I by means of NaOMe. The Br of I may be replaced by OMe to form an *ether*, m. p. 145—146° (*Me* ester, m. p. 62°), hydrolysable by NaOMe or resorcinol fusion. 5-Bromo-3 : 3′ : 5′-trimethyl-4-ethyl-4′-carboxyethylpyrromethene hydrobromide (IV) heated with AgOAc gives a xanthobilirubic acid *isomeride* (V), m. p. 289—290° (*Me* ester, m. p. 197°), yielding a bilirubic acid *isomeride* (VI), m. p. 207°. Hæmopyrrolecarboxylic acid and 2-formyl-4-methyl-3-ethylpyrrole-5-carboxylic acid give 5-carboxy-4 : 4′ : 5′-trimethyl-3-ethyl-3′-carboxyethylpyrromethene hydrobromide, which, by way of the 5-*bromo*-derivative, m. p. 214°, gives another xanthobilirubic acid *isomeride* (VII), m. p. 289—290° (*Me* ester, m. p. 205°; corresponding bilirubic acid *isomeride*, m. p. 174°). 5-Bromo-3 : 4′ : 5′-trimethyl-4-ethyl-3′-carboxyethylpyrromethene hydrobromide gives another xanthobilirubic acid *isomeride* (VIII), m. p. 265° (*Me* ester, m. p. 173°; corresponding bilirubic acid *isomeride*, m. p. 171°).

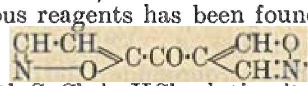
5-Carbethoxy-4-methyl-2-bromomethylpyrrole-3-propionic acid gives a 2-*ethoxy*-derivative (IX), m. p. 151° (2-*methoxy*-, m. p. 75°). 5-Carbethoxy-4-methyl-2-bromomethyl-3-ethylpyrrole gives a 2-*methoxy*-, m. p. 73°, and a 2-*ethoxy*-derivative (X), m. p. 54°. 5-Carbethoxy-2-ethoxymethyl-4-ethylpyrrole and methyl cryptopyrrolecarboxylate form *5-carbethoxy-4 : 3 : 5′-trimethyl-3-ethyl-4′-carbethoxyethylpyrromethane*, m. p. 96—97°. IX with opsopyrrole yields *1 : 8-dicarbethoxy-2 : 4 : 7-trimethyl-5-ethyl-3 : 6-dicarboxyethyltripyrran*, m. p. 217°, giving a tetracarboxylic acid on hydrolysis. Opsopyrrole and X give *1 : 8-dicarbethoxy-2 : 4 : 7-trimethyl-3 : 5 : 6-triethyltripyrran*, m. p. 195°. 5-Hydroxy-3-carbethoxy-2 : 4-dimethylpyrrole with 1 mol. of SO_2Cl_2 yields *5-hydroxy-3-carbethoxy-4-methyl-2-chloromethylpyrrole* (XI), m. p. 186°, with 3 mols. *5-hydroxy-3-carbethoxy-4-methyl-2-trichloromethylpyrrole* (XII), m. p. 117°. Et α-methyl-ββ-diacetylpropionate with NH_3 affords *5-hydroxy-3-acetyl-2 : 4-dimethylpyrrole*, m. p. 143° (XIII) (*isomerides*, m. p. 196° and 173°; 5-*acetoxy*-derivative, m. p. 202—203°). XIII with 3 mols. of SO_2Cl_2 furnishes *5-hydroxy-3-acetyl-4-methyl-2-trichloromethylpyrrole* (XIV), m. p. 152° (5-*acetoxy*-derivative, m. p. 151—152°); XII with aq. NaOH loses HCl and gives a product, m. p. 185°; XIV with aq. NaOH loses HCl and gives a *product*, m. p. 141°. XI with aniline yields a *substance* (probably Schiff's base), m. p. 241°, XII a *substance*, m. p. 227°.

5-Hydroxy-3-carbethoxy-2 : 4-dimethylpyrrole with Br gives *5-hydroxy-3-carbethoxy-4-methyl-2-bromomethylpyrrole* (XV), decomp. 169° (excess of Br gives a *dibromo*-compound, m. p. 146°), which was used to prepare the following methenes: (*5-hydroxy-3-carbethoxy-4-methylpyrryl*)-(*3-carbethoxy-2 : 4-dimethylpyrryl*)*methene*, m. p. 266°; (*5-hydroxy-3-carbethoxy-4-methylpyrryl*)-(*2 : 4-dimethyl-3-ethylpyrryl*)*methene*, m. p. 250° (3-*carboxy*-derivative, m. p. 296°); *5-hydroxy-3-carbethoxy-4-methylpyrryl*)-(*2 : 4-dimethylpyrryl*)*methene*, m. p. 264°; (*5-hydroxy-3-carbethoxy-4-methylpyrryl*)-(*3-acetyl-2 : 4-dimethylpyrryl*)*methene*, m. p. 286°; *5-hydroxy-3-carbethoxy-4-methylpyrryl*)-(*2 : 4-dimethylpyrryl-3-carboxyethyl*)*methene* (XVI), m. p. 286° [*Ac* derivative, m. p. 241°; 3-*carboxy*-derivative, m. p. 294° (decomp.)]. XI and opsopyrrolecarboxylic acid give *5-hydroxy-3-carbethoxy-4 : 3′-dimethyl-4′-carbomethoxyethylpyrromethene* (XVII), m. p. 198° [corresponding 4′-*ethylpropionate* (XVIII), m. p. 159°]. XVIII condenses with CH_2O to the *di-*(XVIII)-*methane*, m. p. 244°, with PhCHO to *di-*(XVIII)-*phenylmethane*, m. p. 184°.

Chloromethyl ether reacts with substituted pyrroles to give methenes (cryptopyrrolemethene, 2 : 4-dimethylpyrrolemethene); with opsopyrrole, ætioporphyrin; with opsopyrrolecarboxylic acid, coproporphyrin. J. H. BIRKINSHAW.

Structure of products of reaction of nitric acid on acetonylacetone. IV. Action of nitric acid on acetylene. A. QUILICO (Gazzetta, 1931, **61**, 265—276; cf. A., 1930, 622).—The action of HNO_3 on C_2H_2 containing $COMe_2$ vapour gives, besides 4 : 5′-di*iso*oxazolyl ketone (I), small amounts of a *ketone*, $C_5H_2O_3N_2$, m. p. 161° (decomp.), which dissolves in alkali with evolution of heat, evolving CO_2 and HCN on acidification and giving on extraction with Et_2O *iso*oxazole-5-carboxylic acid, identical with that obtained by the action of alkali on I, showing that the group  is present.

The action of HNO_3 on acetonylacetone (A., 1891, 890) gives a ketone $C_6H_4O_3N_2$, m. p. 128—129° (decomp.), which behaves with alkali like the C_5 ketone, of which it is probably the Me homologue, giving 3-methyl*iso*oxazole-5-carboxylic acid (A., 1901, i, 499). The mol. wt. of the C_6 ketone shows it to be $C_{12}H_8O_6N_4$. It is concluded that its structure is  and by analogy the structure  is assigned to the ketone, m. p. 161°, obtained from C_2H_2. E. E. J. MARLER.

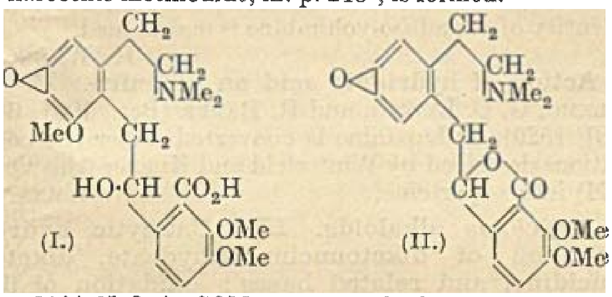
4 : 5′-Di*iso*oxazolyl ketone. M. FRERI (Gazzetta, 1931, **61**, 312—320).—The behaviour of this substance with various reagents has been found to confirm the structure,  (I) (this vol., 622). With $SnCl_2$ in HCl solution it gives 4 : 5′-*diisooxazolylcarbinol*, m. p. 88°, with EtMgBr 4 : 5′-*diisooxazolylethylcarbinol*, m. p. 68—69°, and with cold alcoholic NH_3 in a sealed tube a *compound* which very readily loses NH_3, re-forming I. Analysis of a freshly prepared specimen gives the formula $C_7H_7O_3N_3$, and the structure ⋗C·C(OH)(NH_2)·C⋖ is suggested. Prolongation of treatment with NH_3 for two months gives 4 : 5′-*diisooxazolylketimine*, m. p. 88—89°. Heating I in a sealed tube with alcoholic NH_3 causes scission, giving a small amount of the *amide*, m. p. 142°, of *iso*oxazole-5-carboxylic acid. On boiling I with NH_2Ph (4 mols.) and excess of EtOH, the Schiff's base, ⋗C·C(NPh)·C⋖, m. p. 99°, is obtained. Use of excess of NH_2Ph with a small amount of EtOH gives a *compound*, m. p. 125°, regarded as a stereoisomeride of the Schiff's base, into which it is converted by prolonged heating in an inert solvent. The

anilide, m. p. 142°, of *iso*oxazole-5-carboxylic acid is described. E. E. J. MARLER.

Unsaturation and tautomeric mobility of heterocyclic compounds of the thiazole type in relation to modern electronic conceptions. G. M. DYSON, R. F. HUNTER, J. W. T. JONES, and E. R. STYLES (J. Indian Chem. Soc., 1931, 8, 147—180).—An attempt to summarise and explain the authors' published results on the lines indicated in the title. The following compounds appear to be new. s-p-*Tolylethylthiocarbamide*, m. p. 97° (from *p*-tolylthiocarbimide and NH_2Et), with Br affords the *hydrotetrabromide*, m. p. 78° (decomp.), of 1-*ethylamino-5-methylbenzthiazole*, m. p. 129° [3-*bromo*-derivative, m. p. 150° (*hydrotribromide*, m. p. 147°)]. Similarly are obtained s-p-*tolyl*-n-*propyl*-, m. p. 70°, -iso*butyl*-, m. p. 87°; s-p-*chlorophenyl-ethyl*-, m. p. 119°, -n-*propyl*-, m. p. 110°, -iso*butyl*-, m. p. 122°; s-o-*tolyl-ethyl*-, m. p. 90°, -n-, m. p. 53°, and -iso-, m. p. 68°, -*butyl*-, -n-, m. p. 74°, and -iso-, m. p. 57°, -*amyl*-, -n-*hexyl*-, m. p. 76°; p-*fluorophenyl*-, m. p. 164° (*thiocarbimide*, b. p. 228°/760 mm.); s-p-*fluorophenylmethyl*-, m. p. 70°; s-p-*iodophenylmethyl*-, m. p. 169°, -*thiocarbamide*: 1-n-*propylamino*-, m. p. 116° [*hydrotetrabromide*, m. p. 61°; 3-*bromo*-derivative, m. p. 116° (*hydrotribromide*, m. p. 130°)], 1-iso*butylamino*-, m. p. 132° {*hydrotribromide*, m. p. 89° (decomp.); 3-*bromo*-derivative, m. p. 95° [*hydrotribromide*, m. p. 126° (decomp.)]}, -5-*methylbenzthiazole*: 5-chloro-1-aminobenzthiazole [*hydrodibromide*, m. p. 230—235° (decomp.), previously described (A., 1927, 680) as a *dibromide*, m. p. 82—83°] is converted by Br in $CHCl_3$ into its 3-*bromo*-derivative, m. p. 245° (*dibromide*), and similarly are obtained 5-*chloro-3-bromo-1-methylamino*-, m. p. 180° [*hydrotribromide*, m. p. 270° (decomp.); *dibromide*, decomp. 250°], -1-*ethylamino*-, m. p. 155° [*dibromide*, m. p. 190°; *hydrotribromide*, m. p. 181—183° (decomp.)] [from 5-*chloro-1-ethylamino*-, m. p. 159° (*hydrotetrabromide*, m. p. 64—66°)], -1-n-*propylamino*-, m. p. 190° (*dibromide*, m. p. 173°; *hydrotribromide*, m. p. 191°) [from 5-*chloro*-1-n-*propylamino*-, m. p. 129° (*hydrotetrabromide*, m. p. 87°)], -1-iso*butylamino*-, m. p. 93° (*dibromide*, m. p. 265°) [from 5-*chloro*-1-iso*propylamino*-, m. p. 138° (*hydrotribromide*, m. p. 101°)], -*benzthiazole*; 1-*ethylamino*-, m. p. 114° (*hydrotetrabromide*, m. p. 78°), 1-n-*butylamino*-, m. p. 50° (*hydrohexabromide*, m. p. 61°), 1-iso*butylamino*-, m. p. 58° (*hydrohexabromide*, m. p. 70—72°), 1-n-*amylamino*-, m. p. 48° (*hydrohexabromide*, m. p. 61°), 1-iso*amyl*-, m. p. 59° (*hydrohexabromide*, m. p. 57°), and 1-n-*hexylamino*-, m. p. 46° (*hydrohexabromide*, m. p. 58°); 5-*fluoro-1-amino*-, m. p. 182° (*Ac* derivative, m. p. 221°), -1-*methylamino*-, m. p. 174° (*Ac* derivative, m. p. 156°); 5-*fluoro-1-acetimino-2-methyl*-1 : 2-*dihydro*-, m. p. 197°; and 5-*iodo-1-amino*-, m. p. 210°, -1-*methylamino*-, m. p. 219° (*Ac* derivative, m. p. 185°; *picrate*, m. p. 245°), and -1-*imino-2-methyl*-1 : 2-*dihydro*- (*picrate*, m. p. 222°) -*benzthiazole*. Bromination of 2 : 4-dimethylthiazole [(*chloroplatinate*, m. p. 230—232° (decomp.)] gives the 5-*bromo*-derivative, b. p. 188—190°/745 mm. (*hydropentabromide*, m. p. 93—95°), and similarly are obtained 2-p-*toluidino*-, m. p. 127—128° {5-*bromo*-derivative, m. p. 142—143° [*hydrotribromide*, m. p. 128—129° (decomp.)]}, 2-o-*bromo*-p-*toluidino*-, m. p. 84—85°, and 2-p-*tolylmethylamino*-, m. p. 60°, -4-*methylthiazole*; and 2-p-*tolylimino*-3 : 4-*dimethyl*-2 : 3-*dihydrothiazole*, m. p. 107—108° (*hydriodide*, m. p. 224—226°). J. W. BAKER.

Quinoline derivatives. VIII. Photochemical oxidation of conchinine. H. JOHN and E. ANDRASCHKO (Ber., 1931, 64, [*B*], 1286—1287; cf. A., 1926, 525).—When conchinine dissolved in 10% H_2SO_4 is irradiated in presence of anthraquinone-2-sulphonic acid, quinic acid is obtained in 56% yield together with about 2·6% of a dark resin, insol. in dil. mineral acids, whilst 36% of the base and 90·9% of the sulphonic acid can be recovered. H. WREN.

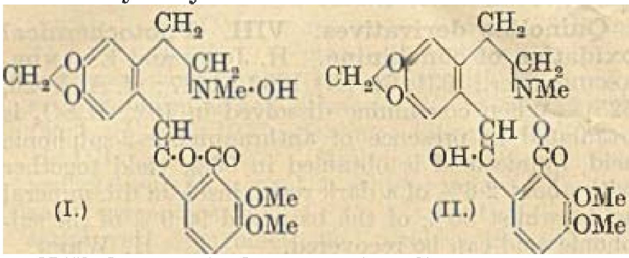
Some derivatives of narcotine. M. POLONOVSKI and M. POLONOVSKI (Bull. Soc. chim., 1931, [iv], 49, 542—550).—Reduction of narceine in aq. solution (Na–Hg) gives the secondary alcohol, *hydronarceine* (I), m. p. 154—155°, similarly obtained from narcotimethine and narcotine methiodide, which are intermediately converted into narceine. Reduction (Zn and HCl) of narceine and narcotimethine gives *hydronarcotimethine* (II) (*hydrochloride*, m. p. 200—210°; *nitrate*, m. p. 196°; *tartrate*, m. p. 140°; *chloroplatinate*, m. p. 192°; *methiodide*, m. p. 233—234°; *anil*). With narcotine methiodide the insol. $ZnCl_2$ compound of narcotine methiodide, m. p. 248°, is formed.



30% H_2O_2 in $COMe_2$ converts hydronarcotimethine into its *N-oxide*, m. p. 153°. On esterification in presence of HCl hydronarcotimethine and hydronarceine yield the same *Me*, m. p. 197°, and *Et*, m. p. 199—200°, esters of chlorohydronarceine. Nornarceine and excess of Ac_2O give *acetylnornarcomethine*, m. p. 120°, hydrolysed by alkali to acetylnornarceine, m. p. 130°. Reduction (Na–Hg and H_2O) of nornarceine yields *hydronornarceine*, m. p. 172°, which with HCl gives *hydronornarcotimethine*, m. p. 176°. R. BRIGHTMAN.

Amine oxides of alkaloids. VIII. Transformation of hydrastine *N*-oxide into dialkylhydroxylamine; *N*-hydroxynorhydrastimethine and *N*-hydroxyhydrasteine. M. POLONOVSKI and M. POLONOVSKI (Bull. Soc. chim., 1931, [iv], 49, 533—543; cf. A., 1930, 935).—Hydrastine *N*-oxide slowly in the cold or rapidly in boiling $CHCl_3$ loses H_2O, basicity, and optical activity, giving anhydro-*N*-hydroxynorhydrastimethine (I), m. p. 189° (*hydrochloride*, m. p. 196°). In HCl with SO_2 I yields a mixture of a *sulphamino*-derivative, $C_{21}H_{20}O_6N{\cdot}SO_3H$, m. p. 229° (*Ba* salt), and a *sulphone*, $C_{21}H_{20}O_6N{\cdot}SO_2$, m. p. 218°, which on alkaline hydrolysis both yield the same Na_2 salt of hydrasteinesulphamic acid, $C_{21}H_{21}O_5(CO_2Na)(SO_3Na)$; when kept for several months I becomes insol. in HCl and is converted into

anhydro-N-*hydroxyhydrasteine* (II), m. p. 192°. It therefore represents an intermediate stage in the conversion of hydrastine-*N*-oxide into the disubstituted hydroxylamine.



N-Hydroxynorhydrastimethine dissolves in warm aq. $Ba(OH)_2$, yielding on acidification and extraction with $CHCl_3$ 70% of N-*hydroxyhydrasteine*, m. p. 205° [*Et ether*, m. p. 125° (*hydrochloride*, m. p. 132°; *sulphanic acid*, m. p. 177°), from either *N*-hydroxynorhydrastimethine or *N*-hydroxyhydrasteine], which on reduction with alkaline $FeSO_4$ yields a small amount of a secondary base, m. p. 175°, probably hydrasteine, together with a secondary alcohol.

R. BRIGHTMAN.

Yohimbine and quebrachine. Identity of α-yohimbine and *iso*yohimbine. K. WARNAT (Ber., 1931, **64**, [*B*], 1408—1410; cf. this vol., 243).—Contrary to Hahn and Schuch (this vol., 243), the identity of α- and *iso*-yohimbine is maintained.

H. WREN.

Action of hydriodic acid on lupanine. G. R. CLEMO, G. C. LEITCH, and R. RAPER (Ber., 1931, **64**, [*B*], 1520).—*r*-Lupanine is converted under the conditions described by Winterfeld and Kneuer (this vol., 371) into *r*-sparteine.

H. WREN.

***Strychnos* alkaloids. LX. Catalytic hydrogenation of diketonucine dihydrate, diketonucidine, and related bases; oxidation of dihydrobrucidine and a second degradation of diketonucidine to hydroxy*apo*nucidine.** H. LEUCHS and F. KROHNKE (Ber., 1931, **64**, [*B*], 1307—1314).—Catalytic reduction of the pentahydrated Wieland acid in presence of PtO_2 or of 2-keto-3-hydroxynucine hydrate affords the acid $C_{17}H_{24}O_5N_2$, m. p. 224—225° (decomp.) (*perchlorate*). 2-*Keto*-3-*hydroxydihydronucidine* (*mono*- and *semi-hydrate*), m. p. (vac.) 257—259° after softening at 246°, $[\alpha]_D^{18}$ +67·7°/*d* in H_2O, is similarly derived from diketonucidine or 2-keto-3-hydroxynucidine; the *hydroperchlorate*, $[\alpha]_D^{18}$ +61·7°/*d* in H_2O, *hydrochloride*, $[\alpha]_D$ +68·4°/*d*, and *Ac* derivative, m. p. 143°, are described. 3-*Bromo*-2-*ketodihydronucidine* has m. p. 292° (decomp.). Dihydrobrucidine is oxidised by CrO_3 and H_2SO_4 at 75—80° to 2 : 3-*diketodihydronucidine*, $C_{17}H_{22}O_3N_2$, m. p. 252—252·5°, $[\alpha]_D^{15}$ +184·°/*d* in H_2O [*perchlorate*, $[\alpha]_D^{15}$ +136°/*d*; *semicarbazone*, m. p. (vac.) 252—254°], reduced (Clemmensen) to 2-keto-3-hydroxydihydronucidine. Catalytic reduction of the amino-acid $C_{16}H_{22}O_3N_2,4H_2O$ in presence of PtO_2 leads to *carboxydihydroaponucidine*, $C_{16}H_{24}O_3N_2$, m. p. 289—291° (decomp.), $[\alpha]_D^{1}$, −32·1°/*d* (*perchlorate*), decarboxylated by distillation at 280—340°/15 mm. to dihydro*apo*nucidine, also obtained by hydrogenation of *apo*nucidine and isolated as the *dipicrate* $C_{27}H_{30}O_{15}N_8$, m. p. 187—189°, decomp. 190°. Oxidation of 2 : 3-diketonucidine by H_2O in presence of aq. NH_3 and subsequent addition of $HClO_4$ gives a *perchlorate*, $C_{17}H_{20}O_4N_2,HClO_4,H_2O$, $[\alpha]_D^{12}$ +35°/*d* to +8·9°/*d* or 9·9 /*d*; the corresponding base is transformed by aq. $Ba(OH)_2$ into oxalic acid and *hydroxyaponucidine*, m. p. 216—218°, $[\alpha]_D^{12}$ −123°/*d* (*diperchlorate*).

H. WREN.

Sinomenine and disinomenine. XXVI. Decomposition of sinomenine with methyl sulphate. K. GOTO and K. TAKUBO (Bull. Chem. Soc. Japan, 1931, **6**, 126—132; cf. this vol., 635).—Sinomenine with Me_2SO_4 in aq. suspension gives *sinomenine methyl methosulphate*, m. p. 265° (decomp.), whilst with Me_2SO_4 and 33% NaOH added alternately in small portions at room temp. it gives *methylsinomenine methyl methosulphate*, m. p. 245°. At 45° and with more alkali and Me_2SO_4 the same reaction gives *methylsinomenine violeomethine methyl methosulphate*, m. p. 204°, $[\alpha]^{1}$, +478° in H_2O, $[\alpha]^{20}$ +581·6° in $CHCl_3$, also obtained by methylating at 0° the sinomenine violeomethine which results from the action of cold 10% alkali on the crude achromethine. The mother-liquors from this last methylation when boiled yield *tetramethylbis*-5 : 5′-*sinomenol*, m. p. 288°, also obtained when sinomenine is kept for 3 weeks with Me_2SO_4 and NaOH, some dimethylsinomenol being also formed. The mother-liquors from this prep. are oxidised by $KMnO_4$ to dimethylsinomenolquinone (A., 1929, 1187). Sinomenine with Me_2SO_4 and NaOH, and subsequent boiling of the neutralised solution with Na_2CO_3, gives *methylsinomenine roseomethine methyl methosulphate*, m. p. 178°. The above methylsinomenine violeomethine methyl methosulphate when boiled with 2% NaOH gives 4 : 4′-*dimethylbis*-5 : 5-*sinomenol*, m. p. 310° (*Ac*$_2$ derivative, m. p. 230°) (yield 20%), and NMe_3.

A. A. LEVI.

Preparation of 3-carbamido-4-hydroxyphenylarsinic acid. W. G. CHRISTIANSEN and A. E. JURIST (J. Amer. Pharm. Assoc., 1931, **20**, 544—545).—The compound is prepared by Ehrlich and Bertheim's method. It is about twice as toxic as stovarsol.

E. H. SHARPLES.

"Tryparsamide." G. GILTA (Bull. Soc. chim. Belg., 1931, **40**, 189—194).—Spontaneous evaporation of an aq. solution of sodium anilinoacetamide-4-arsinate ("tryparsamide") affords a trihydrate (crystallographic data given). This loses, and the anhyd. salt absorbs, H_2O in the air. Precipitation of aq. solutions by EtOH gives a mixture of the trihydrate and anhyd. form.

H. BURTON.

Quinoline compounds. III. A. N. BRAHMACHARI and T. BHATTACHARJEE (J. Indian Chem. Soc., 1931, **8**, 7—10).—As derivatives of quinoline cannot be obtained by Bart's reaction or by the $Hg(OAc)_2$ method. Chloroacetyl-*p*-arsanilic acid reacts with aminoquinolines in alkaline aq. EtOH solution to form quinolineaminoacetyl-*p*-arsanilic acids. *Quinoline*-8-, m. p. 171° (decomp.) [*nitroso*-derivative, m. p. 182° (decomp.)], 6-*methoxyquinoline*-5-, *quinoline*-6-, and 2-*methylquinoline*-6-*aminoacetyl*-p-*arsanilic acid*, and their *nitroso*-derivatives (all m. p. above 240°) are described. 8- and 6-Aminoquinoline *p*-arsanilates are prepared from the amine and atoxyl, and melt above 240°.

G. DISCOMBE.

Resolution of *trans*-tetrahydroselenophen-2 : 5-dicarboxylic acid. A. FREDGA (J. pr. Chem., 1931, [ii], **130**, 180—184).—*trans*-Tetrahydroselenophen-2 : 5-dicarboxylic acid (*quinine* salt $+2H_2O$) (A., 1930, 1196) is resolved by brucine and quinine into the l-, m. p. 173°, $[M]_D^{25}$ −649° in $0{\cdot}4N$-HCl (*brucine* and *brucine hydrogen* salts), and d-*forms*, m. p. 173°, $[M]_D$ +650·5° in $0{\cdot}4N$-HCl (*quinine hydrogen* salt $+1{\cdot}5H_2O$). H. BURTON.

Preparation of some new organo-thallium halides. F. CHALLENGER and (MISS) B. PARKER (J.C.S., 1931, 1462—1467).—$TlCl_3$ reacts immediately in hot aq. solution with phenylboric acid to give, according to the proportions of the reactants, *phenylthallium dichloride*, m. p. 235° (decomp.), and *diphenylthallium chloride*, m. p. above 310°. Similarly, $TlBr_3$ affords *phenylthallium dibromide*, m. p. 152° (decomp.). The dihalides are decomposed with H_2O and also give an immediate yellow ppt. with KI, which turns black, eliminating PhI. The black ppt. is $5TlI,TlI_3$. The presence of phenylthallium dihalides has also been detected in the product of the interaction of MgPhBr and ethereal $TlCl_3$. *p*-Tolylboric acid is converted by $TlBr_3$ into p-*tolylthallium dibromide*, m. p. 160—165° (decomp.), with some *p*-bromotoluene. The constitution of these compounds is discussed. F. R. SHAW.

Polymorphism of substances of high mol. wt. I. Amorphous and crystalline gelatin and the nature of the gelatinisation process in gelatin. J. R. KATZ, J. C. DERKSEN, and W. F. BON (Rec. trav. chim., 1931, **50**, 725—731).—Gelatin exists in a cryst. (β) form consisting of micelles, and in an amorphous (α) form. The reversible transformation of the two forms has been followed by *X*-ray examination. Ordinary air-dried gelatin (containing 18% H_2O) consists almost completely of the β-form, which is converted into the α-form by heating at 100° in a sealed tube. Stabilisation of the α-form is effected by cooling rapidly in liquid air. At room temp. and in the air the α-form is stable, but if it is allowed to swell in water and is then air-dried at 20°, it reverts to the β-form. It is concluded that the gelatinisation of gelatin sols consists in the transformation $\alpha \longrightarrow \beta$. J. D. A. JOHNSON.

Action of alkalis on the absorption spectrum of proteins. Dakin's theory of racemisation and enolisation of proteins. J. GRÓH and M. WELTNER (Z. physiol. Chem., 1931, **198**, 267—275; cf. A., 1930, 1460).—With egg-albumin and caseinogen in *N*-NaOH there was no change in the absorption spectrum at 25°; serum-globulin showed an increase in the extinction coeff. at the absorption max. in $0{\cdot}1N$-NaOH. At 100°, all the proteins examined showed considerable changes in absorption. The change, which is not reversible on acidification, is related to Dakin's enolisation theory of racemisation. In the large group of easily racemised proteins the enolisation is regarded as relatively slow and the re-formation of the inactive keto-compound as rapid, hence the enol form is not detected spectrophotometrically. When enolisation is still more difficult (second group), the enol form is probably more stable and hence detectable. J. H. BIRKINSHAW.

Micro-determination of carbon by wet combustion. H. LIEB and H. G. KRAINECK (Mikrochem., 1931, 9, 367—384).—The substance containing 1—3 mg. of C is heated at 130—135° with 3—4 c.c. of a solution of 20 g. of $Ag_2Cr_2O_7$ and 10 g. of $K_2Cr_2O_7$ in 200 c.c. of conc. H_2SO_4 in a current of O_2. The gases from the combustion vessel are passed through a tube containing platinised asbestos, Pt gauze, and Ag wool heated to dull redness, and then through a capillary tube into $0{\cdot}1N$-$Ba(OH)_2$ containing 1% $BaCl_2$ and sufficient phenolphthalein to give a pink solution. After 1 hr. the substance is completely decomposed and without stopping the O_2 current the $Ba(OH)_2$ solution is titrated with $0{\cdot}05N$-HCl containing 3% $BaCl_2$; filtration of the $BaCO_3$ ppt. is unnecessary. A. R. POWELL.

Organic ultra-micro-analysis. Determinations of carbon and hydrogen on fractions of a milligram of a substance. J. B. NIEDERL and J. R. MEADOW (Mikrochem., 1931, 9, 350—359).—The substance is burnt in O_2 in a Pregl tube; the H_2O is absorbed in a $CaCl_2$ tube and the CO_2 in 1 c.c. of saturated $Ba(OH)_2$ solution containing 0·1 c.c. of EtOH. The $Ba(OH)_2$ solution is contained in a tube protected from ingress of air by soda-lime tubes and so constructed that the $BaCO_3$ formed can be collected, washed, dried, and weighed in the tube without coming into contact with the air. A. R. POWELL.

Microchemical determination of nitrogen by Pregl's method (micro-Dumas). F. GOVAERT (Mikrochem., 1931, 9, 338—344).—The method of Pregl is modified in that the CO_2 is generated by heating magnesite in a hard glass tube connected to the combustion apparatus by means of a T-piece provided with glass stopcocks and a Hg valve. A. R. POWELL.

Micro-Dumas method. O. R. TRAUTZ (Mikrochem., 1931, 9, 300—312).—Possible sources of error in the determination of N by the micro-Dumas method are discussed. A. R. POWELL.

Detection of organic compounds. L. ROSENTHALER (Pharm. Ztg., 1931, 76, 775—776).—*p*-Toluenesulphonic acid is suggested as condensing agent for the detection of alcohols by the odour of their esters. The odour of the ester can easily be detected when 1 c.c. of 1% EtOH is heated for 5 min. at 100° with a little BzOH and 1 g. of *p*-toluenesulphonic acid. It may advantageously replace H_2SO_4 in the " flower odour " reaction of atropine. $Pr^{\beta}OH$ can be recognised in presence of EtOH by its reaction with aromatic aldehydes; if to a mixture of 5 c.c. of a 5% solution of protocatechualdehyde in EtOH and 2 c.c. of 2% $Pr^{\beta}OH$ in EtOH be added 10 c.c. of H_2SO_4, the liquid turns brown and on dilution with H_2O blue. Fusel oil behaves similarly. $COMe_2$ produces the sequence red and purple to green after addition of H_2O. The formation of CHI_3 occurs more readily with $Pr^{\beta}OH$ than with EtOH and the rate of formation under standard conditions from the sample and pure EtOH by the action of alkaline hypoiodite can be followed nephelometrically. Terpin hydrate forms a lilac colour when its mixture with H_2SO_4 is poured into vanillin–HCl mixture. Menthol with similar treatment gives a raspberry-red colour.

Microchemical reactions of atroscine are described. They show no difference from those of *r*-scopolamine.
E. H. SHARPLES.

Colour reactions of phenols in common use. M. FRANÇOIS and (MLLE.) L. SEGUIN (Bull. Soc. chim., 1931, [iv], 49, 680—684).—The characteristic colour reactions of phenol, α- and β-naphthol, thymol, pyrocatechol, guaiacol, resorcinol, orcinol, quinol, pyrogallol, phloroglucinol, gallic acid, and salicylic acid with phthalic anhydride and H_2SO_4, H_2SO_4 alone, and with $CHCl_3$ in presence of KOH in the cold are described. The slight colour and fluorescence formed by H_2SO_4 in absence of added phthalic acid are attributed to the formation of phthaleins, due to phthalic acid formed by oxidation of the phenol. The coloration produced with $CHCl_3$ is better marked in alcoholic solution, the colouring matters formed being mostly insol. in $CHCl_3$ but sol. in EtOH. Whilst the three reactions can be used for the characterisation of the commonest phenols, the colorations obtained must be reviewed with those tabulated to avoid errors in interpretation.
R. BRIGHTMAN.

Colour reactions in the system phenol–aldehyde–acid. V. E. LEVINE (J. Amer. Pharm. Assoc., 1931, 20, 537—543).—The use of this system for detecting phenols of all types, aldehydes, substances which easily form aldehydes such as alcohols, many carboxylic acids, carbohydrates, and alkaloids, and inorg. acids is illustrated by an exhaustive list of examples.
E. H. SHARPLES.

Determination of citronellol and rhodinol in presence of geraniol and nerol. L. S. GLICHITCH and Y. R. NAVES (Parfums de France, 1930, 8, 326—333; Chem. Zentr., 1931, i, 1842).—The oil (1 vol.) is refluxed with 90% formic acid (2 vols.) and is frequently shaken during 1 hr. on the water-bath; after cooling it is washed with NaCl solution (50 c.c., repeatedly), 2% $NaHCO_3$ solution, and H_2O and dried with Na_2SO_4. The product (2 g.) is hydrolysed during 45 min. with 30 (or 20) c.c. of 0·5*N*-KOH. Tiemann and Schmidt's method employing PCl_3 gives low results.
A. A. ELDRIDGE.

Colour reaction for quinones. R. CRAVEN (J.C.S., 1931, 1605—1606).—*p*-Benzoquinone, *p*-benzoquinone dichloride, *o*-toluquinone, chloranil, α-naphthaquinone, and thymoquinone yield a bluish-violet colour, changing to blue, green, and finally reddish-brown, on addition of 2—3 drops of $CN\cdot CH_2\cdot CO_2Et$ and excess of alcoholic NH_3. The reaction, which is intense with 0·1 mg. per c.c., and recognisable with 0·01 mg. per c.c., is not given by β-naphthaquinone, anthraquinone, chloranilamide, or phenanthraquinone.
R. S. CAHN.

Determination of morphine. L. DAVID (Pharm. Ztg., 1931, 76, 706—708).—Morphine, heroine, and physostigmine react with diazotised anæsthesin, forming orange-red colours which can be extracted from the reaction mixture with $CHCl_3$. Many morphine derivatives react similarly, but the colours are not extracted. The reaction has been adapted to the determination of morphine in its preps. Physostigmine can be distinguished separately and the method will detect 0 00002 g. of morphine.
E. H. SHARPLES.

Determination and buffer action of polypeptides. J. ENSELME (Bull. Soc. chim., 1931, [iv], 49, 723—725).—The quantity of 0·001*N*-NaOH necessary to produce a given p_H val. in a buffer solution to which glycylglycine or Witte's peptone has been added is, within certain limits, directly proportional to the quantity of polypeptide added.
H. F. GILLBE.

Triketohydrindene hydrate as a reagent for albumin, peptone, and amino-acids. H. GARDNER (Lancet, 1930, ii, 525—526).—Triketohydrindene hydrate is not a trustworthy reagent for the products of protein hydrolysis. The colour reaction is due to traces of free NH_3, or NH_3^+ ions, and is masked by NH_4OH or excess of alkali. H_2O containing 0·00865% NH_3 gives the characteristic blue colour.
L. S. THEOBALD.

Biochemistry.

Carbon dioxide compounds in hæmoglobin solutions. O. M. HENRIQUES (J. Biol. Chem., 1931, 92, 1—11).—Polemical. The author supports the formation of a mol. complex of hæmoglobin and CO_2 (cf. A., 1928, 1389) and refutes the view of Van Slyke and Hawkins (A., 1930, 1053) that catalytic acceleration of the reaction $HCO_3'+H^+ \quad H_2CO_3$ occurs.
F. O. HOWITT.

Action of aluminium hydroxide sol on blood. H. KÜHL (Z. ges. Getreidew., 1931, 18, 22—24; Chem. Zentr., 1931, i, 1936).—A hæmoglobin solution may be almost completely decolorised by addition of a suspension of $Al_2(OH)_6$. The toxic action of alum in flour depends therefore on the coagulation of serum-albumin and the precipitation of the colouring matter of the hæmoglobin.
A. A. ELDRIDGE.

Protein coagulation and its reversal. (*a*) Identity of normal hæmoglobin with hæmoglobin prepared by reversal of coagulation, as determined by solubility tests. (*b*) Globin. M. L. ANSON and A. E. MIRSKY (J. Gen. Physiol., 1931, 14, 597—604, 605—609; cf. this vol., 426).—(*a*) The solubilities in aq. $(NH_4)_2SO_4$ of amorphous methæmoglobin, whether (i) normal, (ii) prepared by reversal of coagulation, or (iii) prepared from hæmin and globin prepared by reversal of coagulation of globin, are the same within 2%.

(*b*) Globin prepared from hæmoglobin by the acid $COMe_2$ method (Hill and Holden, A., 1927, 67, 689) is denatured globin, but the denaturation is readily reversible, for sol globin can be obtained from denatured globin after precipitation with trichloroacetic acid or heating to 100°.
R. K. CALLOW.

Differences between the gas analysis and colorimetric hæmoglobin determinations on splenectomised dogs. F. HAUROWITZ and M.

Reiss (Z. physiol. Chem., 1931, **198**, 191—195).—The differences between the figures obtained by the two methods are ascribed to a lipæmia induced by splenectomy, since strongly lipæmic blood gives erroneous results by the colorimetric method.

J. H. Birkinshaw.

Relationship between sedimentation rate of red corpuscles and the protein spectrum. W. M. Bendien and I. Snapper (Biochem. Z., 1931, **235**, 14—34).—The sedimentation rate and cell vol. of erythrocytes, the protein spectrum of the plasma, and in many cases the sedimentation rate of the defibrinated blood of 119 patients are compared. The sedimentation rate is always proportional to the fibrinogen content of the plasma. In most cases showing high sedimentation rate, the fibrinogen content is increased much more than the globulin content. In a few cases (cirrhosis of the liver) fibrinogen is present in normal or decreased amount, but the sedimentation rate is increased, due to the presence of greatly increased amounts of globulin. In a few cases both the fibrinogen and globulin contents are increased and the sedimentation rate is extremely high (100 mm. per 30 min.). In defibrinated blood, increased sedimentation rate runs parallel with increased globulin content. An empirical formula gives sedimentation rate as a function of the albumin and fibrinogen contents and the cell vol.

P. W. Clutterbuck.

Effect of sunlight on human blood-cells. W. W. Lepeschkin (Science, 1931, **73**, 568).—Exposure to direct sunlight gradually disintegrates and hæmolyses red corpuscles. Diffuse sunlight increases susceptibility only to subsequent hæmolysis by direct sunlight. Resistance to poisons and hypotony is diminished by the visible rays, but this effect is counteracted by short exposures to ultra-violet light. Ultra-violet light (Hg) destroys the red corpuscles.

L. S. Theobald.

Importance of the medium in the study of catalase. II. Action of alkali on blood-catalase. U. Sammartino and G. Lucchetti (Arch. Farm. sperim., 1931, **52**, 149—180).—When the p_H of rabbits' blood is raised by injection of $NaHCO_3$ the catalase activity increases slightly when the increase of p_H is large, but otherwise shows no significant variation. The variation of catalase activity in pathological conditions is, therefore, not merely an effect of the alteration of p_H.

R. K. Callow.

Analysis of whole blood. I. Precipitation of the proteins. II. Determination of sugar and non-fermenting copper-reducing substances. S. R. Benedict. **III. Determination and distribution of uric acid.** S. R. Benedict and J. A. Behre (J. Biol. Chem., 1931, **92**, 135—139, 141—159, 161—169).—I. Blood is diluted with 7 vols. of H_2O, and 1 vol. of Na tungstomolybdate reagent (A., 1929, 1189) is added followed by 1 vol. of $0{\cdot}62N$-H_2SO_4. Any one or all of the non-protein constituents of the blood may be accurately determined by the use of a filtrate so prepared. The use of laked blood for analysis is upheld.

II. The use of a new Cu reagent (a solution of Na_2CO_3, $CuSO_4$, Na R tartrate, and alanine) to which is added a small amount of $NaHSO_3$ is described. By use of tungstomolybdate filtrates satisfactory vals. are obtained for the total and (after fermentation) the non-fermentable Cu-reducing sugars (for which the term " saccharoids " is advocated). Zn filtrates contain non-fermentable reducing substances (cf. A., 1930, 801) the distribution and nature of which are discussed. By the use of the reagent without addition of $NaHSO_3$ the true sugar content is ascertained. Human blood (10 samples) contains 0·012—0·031% of non-fermentable Cu-reducing substances. The application of the method to 0·1 c.c. of blood is described.

III. The tungstomolybdate filtrate is mixed with a HCl–LiCl reagent followed by $AgNO_3$ solution and centrifuged. The supernatant fluid (free from thioneine) is treated with NaCN solution and arsenotungstate reagent (A., 1922, ii, 405) and the colour compared with appropriate standards. Corpuscular uric acid averages 72% of the plasma content. A micro-technique is also given.

F. O. Howitt.

Ionic equilibria in the serum in relation to the critical temperature. P. L. Du Noüy (Science, 1931, **73**, 595—597).—The precipitation by H_2O of the globulins in horse-serum has been followed optically. The instability of the serum reaches a max. at 0·33% of salts. Heating above 55° increases the instability of the system, but at 60° no sedimentation of the globulins occurs.

L. S. Theobald.

Lactic acid determination in blood. O. Jervell (Biochem. Z., 1931, **235**, 101—103).—The $K_2Cr_2O_7$ method of Hansen (A., 1926, 444) for determination of lactic acid in pure solutions is somewhat modified and applied to its determination in blood-filtrates.

P. W. Clutterbuck.

Influence of diet and avitaminosis on blood-glycolysis. I. Cholesterol and lecithin. Y. Kawashima and J. Chiwaki (J. Biochem., Japan, 1931, **13**, 107—132).—Cholesterol-feeding in rabbits results in an increase of blood-cholesterol, especially of the plasma, and, at a later period, in a decrease in glycolytic activity both of the serum and corpuscles. The fasting blood-sugar level is generally increased. Lecithin exhibits no such phenomena, but when administered to rabbits soon after discontinuance of cholesterol-feeding it induces a more rapid return of the glycolytic activity and blood-sugar to normal levels.

F. O. Howitt.

Calcium. IV. Blood-calcium changes following administration of calcium gluconate given subcutaneously to normal and parathyroidectomised dogs and *per os* to human beings. A. L. Lieberman (J. Pharm. Exp. Ther., 1931, **42**, 245—252).—In dogs subcutaneous administration of 10% solutions of Ca gluconate (25 mg. per kg. body-wt.) causes a rise in blood-Ca, max. in about 1 hr., followed by a fall which is steeper in parathyroidectomised than in normal animals. In man oral administration of Ca gluconate (10 g. in 250—375 c.c. H_2O) brings about a rise in blood-Ca (max. after 4 hr.) provided that it does not produce diarrhœa. Food may favour adsorption by decreasing peristaltic action.

W. O. Kermack.

Determination of iron in blood. F. REIS and H. H. CHAKMAKJIAN (J. Biol. Chem., 1931, **92**, 59—63).—Blood (0·2 c.c.) is oxidised by H_2SO_4 and $KClO_4$ and then treated with $K_4Fe(CN)_6$ in gum-ghatti solution. The colour due to the dispersed Prussian-blue is compared with suitable standards.

F. O. HOWITT.

Determination of phosphorus in small quantities of serum. G. POPOVICIU (Bull. Soc. Chim. biol., 1931, **13**, 548—551).—The serum (0·12 c.c.) is deproteinised by trichloroacetic acid and treated with an $(NH_4)_2MoO_4$ reagent containing strychnine nitrate. The ppt. is washed with H_2O, dissolved in NaOH, $K_4Fe(CN)_6$ and HCl are added, and the solution is compared colorimetrically with appropriate standards. F. O. HOWITT.

Bromide distribution in blood. I. Bromide and chloride distributions *in vitro*. A. B. HASTINGS and H. B. VAN DYKE. **II. Bromide and chloride distributions following oral administration of sodium bromide.** H. B. VAN DYKE and A. B. HASTINGS (J. Biol. Chem., 1931, **92**, 13—25, 27—32).—An electrometric method for the determination of Br′ and Cl′ in presence of each other is described. Addition of NaBr to dog's blood *in vitro* results in a distribution ratio of Br′ between corpuscles and serum 10% higher than the corresponding ratio for chloride. Br ions are freely diffusible between corpuscles and serum. Change in reaction or degree of oxygenation produces a change of distribution in agreement with the Donnan equilibrium theory.

II. The abnormally high (up to 2·0) Br′ distribution ratios between corpuscles and serum following oral administration of 40 g. of NaBr to dogs and the concomitant low vals. for the corresponding Cl′ ratios indicate that corpuscular Cl′ is present partly in non-ionic form which can be displaced by Br, a conclusion supported by the extent of diffusion of Br′ occurring when normal serum is mixed with Br-containing cells and *vice versa*. F. O. HOWITT.

Action of acids on blood coagulation. Neutralisation of acid character. R. DOURIS, C. MONDAIN, and M. PLESSIS (Compt. rend. Soc. Biol., 1930, **104**, 278—280; Chem. Zentr., 1931, i, 1936).—When H_2SO_4 (1 c.c.) is added to coagulated blood (10 c.c.) the titratable acidity diminishes rapidly, reaching a practically constant val. (76%) after 45 min. With HNO_3 the fall continues for 5 hrs., but a rise is observed on the fourth and fifth days. With HCl, H_3PO_4, AcOH, and oxalic acid the effect continues for 4—5 hr. A. A. ELDRIDGE.

Action of anticoagulants on serum-enzymes and -complement. K. YANAGISAWA (J. Biochem., Japan, 1931, **13**, 11—42).—Heparin exerts no influence on the action of the blood-enzymes except glycerophosphatase and lecithinase, the actions of which are slightly enhanced. The action of proteinogenic, but not of lipinogenic, hæmolysins is inhibited by heparin, whilst novirubin inhibits the action of both types. Hence the hæmolysis due to the complex hæmolysin system produced by injection of goat blood into rabbits is inhibited by novirubin but not by heparin. The mixtures of the globulin and albumin fractions separated from guinea-pig serum by normal methods retain their complement action for proteinogenic but not for lipinogenic hæmolysis.

F. O. HOWITT.

Chemical significance of immunohæmolysis. L. JARNO and L. SURANYI (Z. Immunitat., 1930, **69**, 298—304; Chem. Zentr., 1931, i, 1780).—Various amino-acids behave differently towards the normal amboceptors of various animals. Immunohæmolysis is increased by amino-acids, and particularly by glycine. The participation of cholate in hæmolysis is supported. A. A. ELDRIDGE.

Enzymic phosphatide fission and immune hæmolysis. E. BRUNIUS (Arkiv Kemi, Min., Geol., 1931, **10**, **A**, No. 8, 13 pp.).—Kidney- but not pancreatic lipase or guinea-pig serum splits off phosphoric acid from lecithin. Goat-blood erythrocytes treated with complement and amboceptor undergo hæmolysis with concomitant formation of free phosphate. Equal phosphate formation occurs with saponin in place of amboceptor, the results being in agreement with those on fat-splitting in immune hæmolysis (cf. A., 1924, i, 784). The theory of complement action being of a lipolytic nature is not upheld.

F. O. HOWITT.

Saponin hæmolysis. E. GORTER, F. GRENDEL, and W. A. SEEDER (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 471—473).—Complete hæmolysis occurs when there is sufficient saponin available to cover the surface of the cells with a layer 1 mol. thick. J. W. SMITH.

Nature and specificity of antigens. P. CARNEIRO and W. KOPACZEWSKI (Compt. rend., 1931, **192**, 1595—1598).—Guinea-pigs can be sensitised to colloids, more particularly to positively-charged colloids. After sensitisation to horse serum positively-charged colloids induce anaphylactic shock. C. C. N. VASS.

Diminution in chloride measurement after drying blood and tissues. F. W. SUNDERMAN and P. WILLIAMS (J. Biol. Chem., 1931, **92**, 99—107).—The Cl content of dried blood and tissues as determined by normal analytical methods is up to 31% less than that given by the moist samples. Soaking of the dry samples in water for some hrs. results in a recovery equal to that for the original wet samples. This retention of Cl is due to fats or fatty acids.

F. O. HOWITT.

Iodometric titration of glutathione. E. J. KING and C. C. LUCAS (Biochem. Z., 1931, **235**, 66—69).—Accurate vals. for the glutathione content of any solution by this method can be obtained only when the I titration is carried out in acid solution and at temp. below 25°. P. W. CLUTTERBUCK.

Tribasic acid present in liver, convertible into pyrrole derivatives. H. D. DAKIN and R. WEST (J. Biol. Chem., 1931, **92**, 117—133).—An aq. solution of liver extract powder is precipitated by basic Pb acetate, the filtrate, freed from Pb, is treated with picric acid and extracted with $BuOH-Et_2O$ mixture. The aq. layer is precipitated by phosphotungstic acid and the ppt. is treated according to the technique previously described (A., 1930, 1309). This yields

a water-sol., EtOH-insol., *Ba* salt of a tribasic acid, $C_{11}H_{15}O_7N,H_2O$, probably

$$\begin{array}{l}CO_2H\cdot CH_2\cdot CH\cdot CHMe \\ \qquad\qquad\ \ \vert \\ \qquad\qquad NH \text{——} CO\end{array}\!\!>\!CH\cdot CH_2\cdot CH(CO_2H)_2$$

(*quinine* salt, $C_{11}H_{15}O_7N,H_2O,1\cdot5C_{20}H_{24}O_2N_2$, m. p. 149—150°, $[\alpha]^{20}$ −147°). Intravenous administration of the acid in a single dose of 0·25—0·75 g. results in a distinct rise in reticulocytes, which, however, is not considered identical with that produced by liver extract. Heating the acid in a sealed tube with excess of $Ba(OH)_2$ at 120—130° yields an Et_2O-sol. pyrrolecarboxylic acid, whilst at 155—165° hæmopyrrole is produced. The possibility of the acid being a precursor of hæmoglobin is discussed. F. O. Howitt.

Preparation of egg-yolk lecithin. Y. Sueyoshi (J. Biochem., Japan, 1931, **13**, 145—154).—The ethereal extract of egg-yolk is evaporated in vac. and the residue repeatedly extracted with cold $COMe_2$. The wax-like, colourless residue is treated with 5—6 vols. of EtOH and the extract cooled to −14°, when cephalins are precipitated. The fluid portion is evaporated in a vac. and precipitated by $COMe_2$. Digestion with $COMe_2$ at 55° removes fats, yielding a product containing 3·84% P and 1·74% N. The Cd compound contained 11·13% Cd. F. O. Howitt.

Fatty acids of egg-yolk lecithin. I. Saturated acids. II. Unsaturated acids. Y. Sueyoshi and T. Furukubo (J. Biochem., Japan, 1931, **13**, 155—175, 177—183).—I. Small amounts of stearic and palmitic acids are present. The main constituent is *iso*palmitic acid, m. p. 56—57°.

II. The unsaturated acids include oleic acid (73·2%), clupanodonic acid (5·1%), and linoleic acid (2·1%). F. O. Howitt.

Fatty acids and unsaponifiable substances in tissue. T. Furukubo (J. Biochem., Japan, 1931, **13**, 185—209).—An increase of the muscle-fatty acids is produced in rabbits by administration of vitamin-*A* in excess, of adrenaline and of insulin in small amounts, whereas starvation, injection of insulin in large doses, and thyroid-feeding cause a decrease. The unsaponifiable fraction is increased by starvation and decreased by hunger, by injection of insulin in large doses, and by thyroid-feeding. Thus insulin in small amounts brings about a change of sugar to fat, whilst large doses have the opposite effect. The relation of the unsaponifiable fraction to the carbohydrate metabolism is discussed. F. O. Howitt.

Cholesterol of protoplasm. VIII. Ox spinal chord. G. Pfeiffer (Biochem. Z., 1931, **235**, 97—100).—The percentage oxy- and esterified- of the total cholesterol of ox spinal chord is greater than with brain. The esters are exclusively formed from oleic acid and oxycholesterol. P. W. Clutterbuck.

Insect wax. III. Wax of the wool louse (*Pemphigus xylostei*). F. N. Schulz and M. Becker (Biochem. Z., 1931, **235**, 233—239).—Wax of *Pemphigus xylostei*, $C_{68}H_{136}O_4$, m. p. 108—109°, on hydrolysis gives a dialcohol, $C_{34}H_{70}O_2$, m. p. 100—105°, and a hydroxy-acid, $C_{33}H_{67}(OH)\cdot CO_2H$, m. p. 101—102° (cf. this vol., 642). P. W. Clutterbuck.

Phosphatase activity of transplants of the epithelium of the urinary bladder to the abdominal wall producing heterotopic ossification. C. B. Huggins (Biochem. J., 1931, **25**, 728—732).—In heterotopic osteogenesis with transplants of the urinary bladder epithelium to the abdominal fibrous tissue in the dog, the ratio of phosphatase activity to dry wt. was very high, at least 2·5 to 8 times the max. and 10—20 times the mean vals. of the control tissues without bone. S. S. Zilva.

Soluble enzymes in the spleen. E. Laborde and H. Wyler (Bull. Soc. Chim. biol., 1931, **13**, 552—554).—The presence of the following enzymes in extracts of spleen was demonstrated: amylase, glycogenase, invertase, inulase(?), lipase, lecithase, pepsin, trypsin, erepsin, urease, hippuricase, salicylase, peroxidase, and catalase. Lactase, glycolase, nuclease, deamidase, oxidases, tyrosinase, and phosphatase could not be detected. F. O. Howitt.

Modification of Mallory's triple stain. B. Krichesky (Stain Tech., 1931, **6**, 97—98).—An improvement in detail of the technique of staining connective tissue is described. H. W. Dudley.

***iso*Hæmatein as a biological stain.** E. C. Cole (Stain Tech., 1931, **6**, 93—96).—*iso*Hæmatein has a staining power greater than that of hæmatoxylin, but is not so selective for nuclei. The dye may be useful as a differential stain for nerve-cell bodies.
H. W. Dudley.

Rapid methods for tissue diagnosis. A. M. Hjort and C. H. Moulton (Stain Tech., 1931, **6**, 83—91).—Two new methods for staining fixed and fresh frozen tissue sections are presented.
H. W. Dudley.

Vapour pressures of aqueous solutions with special reference to the problem of the state of water in biological fluids. A. Grollman (J. Gen. Physiol., 1931, **14**, 661—683).—Using Hill's method (A., 1930, 689, 1211) data for the depression of v. p. have been obtained for aq. solutions of NaCl (0·03—0·1*M*), KCl (0·03—0·1*M*), carbamide (0·05—0·5*M*), sucrose (0·05—0·1*M*), lactic and succinic acids, creatine, $CaCl_2$ (0·05*M*), and mixtures of these substances with one another and with certain other solutions, *e.g.*, gelatin, gum-acacia, sea-water, and LiCl. The relation of the depression of v. p. of a mixed solution to that of solutions of the individual constituents was investigated in order to see how far such methods could be applied to the determination of the degree of hydration or the state of water ("free" or "bound") in solutions. Org. substances showed anomalous results, unpredictable in mixed solutions, and in the case of LiCl and $CaCl_2$ the principle of the additive nature of colligative properties is only approx. true, and the determination of degree of hydration is possible only with certain limitations.

Using NaCl or KCl, hydration in gelatin is relatively small at p_H 7, and undetectable in gum-acacia solutions. The supposed high degree of hydration of hydrophilic colloids is, therefore, not substantiated. The change from sol to gel in gelatin or blood is not accompanied by appreciable change in the degree of hydration. R. K. Callow.

Cerebrospinal equilibrium of hydrogen carbonates. P. Cristol (Compt. rend., 1931, **192**, 1672—

1674).—If hydrogen carbonates obey Derrien's law, the ratio of the concentration of CO_2 in cerebrospinal fluid to that in blood is 1. In keto-acidosis the ratio is less than 1, the more so as acetoacetic acid accumulates in the blood. A decreased ratio is also given if the cerebrospinal fluid contains organisms which induce glycolysis. C. C. N. VASS.

***Post-mortem* changes in cerebrospinal fluid.** I. SÜMEGI and L. FINDEISEN (Magyar orvosi Arch., 1930, **31**, 464—467; Chem. Zentr., 1931, i, 1938).—Colloid reactions were normal for 9 hr., later changes being connected with the increase in total and non-protein-N, the change in the albumin : globulin ratio, and the shift of towards the acid side. A. A. ELDRIDGE.

Uric acid and allantoin in gastric juice. Y. INATSUGU (J. Biochem., Japan, 1931, **13**, 1—9).—Uric acid and allantoin are normal components of the gastric fluid of man and dog. Intravenous administration of uric acid in the dog results in a marked increase in the allantoin content of the juice. No relation exists between the quantity of either substance and the gastric acidity. F. O. HOWITT.

Polarimetric determination of bile acids in body-fluids and organs. F. ROSENTHAL (Arch. exp. Path. Pharm., 1931, **160**, 460).—Polemical against Jenke (this vol., 509; cf. *ibid.*, 251). W. O. KERMACK.

Influence of bile acids on the inorganic salts of the bile. Y. KAWADA (J. Biochem., Japan, 1931, **13**, 133—144).—Oral administration of Na cholate to dogs increases the relative and abs. contents of H_3PO_4 and Ca in the bile due to an increased nuclein catabolism. F. O. HOWITT.

Nature of the "ether reaction" of urine. W. J. BOYD (Biochem. J., 1931, **25**, 812—817).—Two substances responsible for the reaction have been isolated from the urine of asthmatic and normal subjects. One is an irreversibly coagulable protein possibly identical with serum-albumin and the other a mucoid containing 12·5% of N, possibly derived from the urinary passages. S. S. ZILVA.

New clinical method for determination of protein in urine. P. M. T. KERRIDGE (Lancet, 1931, i, 21—22).—Urine is mixed with a suspension of C, and C and protein are precipitated by $CCl_3{\cdot}CO_2H$. With a const. amount of C, the grey colour depends on the amount of protein. The error is 0·025—0·05 g. protein-N% and the accuracy is unaffected by artificial light. L. S. THEOBALD.

Micro-determination of allantoin. Application to human urine. R. FOSSE, A. BRUNEL, and P. E. THOMAS (Compt. rend., 1931, **192**, 1615—1619).—The absorption density of glyoxylic acid phenylhydrazone is proportional to its concentration. Allantoin in human urine is hydrolysed for 24 hr. in presence of KCN by allantoinase. After removal of the proteins, phenylhydrazine and HCl are added and the absorption spectrum is examined before and after hydrolysis. In 7 individuals the concentration of allantoin varied from 18 to 35 mg. per litre. C. C. N. VASS.

Occurrence of ethyl sulphide in dog's urine. A. A. CHRISTOMANOS (Z. physiol. Chem., 1931, **198**, 185—190).—A titrimetric method for the determination of Et_2S depends on the formation of an additive compound with I. Dogs excrete 4—7 mg. of Et_2S daily. With a diet rich in carbohydrate the Et_2S is higher than with a diet rich in protein. J. H. BIRKINSHAW.

Determination of sugar in urine by means of "glucophot." J. J. HOFMAN and J. DE KEUNING (Pharm. Weekblad, 1931, **68**, 584—589).—The method and apparatus are satisfactory for rapid approximations. S. I. LEVY.

Excretion of uric acid. V. B. WIGGLESWORTH (Nature, 1931, **128**, 116).—Evidence is given for the view that in *Rhodnius prolixus* the upper parts of the 4 Malpighian tubes secrete a solution of acid urates from the blood into the lumen and in the lower parts H_2O and base are re-absorbed and insol. uric acid is precipitated. A continuous circulation of H_2O and base results. L. S. THEOBALD.

Determination of uric acid. J. L. ST. JOHN and O. JOHNSON (J. Biol. Chem., 1931, **92**, 41—45).—Uric acid in avian excrement is determined by extraction with piperidine solution and formation of NH_4 urate which is converted into uric acid and weighed as such. The error does not exceed 0·22%. F. O. HOWITT.

Intraperitoneal iron. C. G. GRULEE and H. N. SANFORD (Amer. J. Dis. Children, 1931, **41**, 53—61).—Fe injected intraperitoneally into rabbits is deposited in the liver rather than the spleen; the hæmoglobin and erythrocyte contents of the blood are unchanged. Injection of colloidal $Fe(OH)_3$ into children with secondary anæmia increases the blood-hæmoglobin and -erythrocytes. CHEMICAL ABSTRACTS.

Value of determinations of iron content of whole blood. W. P. MURPHY, R. LYNCH, and I. M. HOWARD (Arch. Int. Med., 1931, **47**, 883—892).—The "iron index" (ratio of mg. of Fe per 100 c.c. of whole blood to millions of red cells per cu.mm.) is nearly const. for normal persons, and averages 8·46. In pernicious anæmia the index is above 10, and is generally below normal in secondary anæmia. A. COHEN.

Inhibitory effect of monoiodoacetic acid on lactic acid production by cancer tissue. S. T. HARRISON and E. MELLANBY (Biochem. J., 1931, **25**, 770—772).—The aerobic production of lactic acid by tumour slices is inhibited by iodoacetic acid. A single injection of a sublethal dose in mice did not produce an inhibition of lactic acid production. S. S. ZILVA.

Mineral metabolism in multiple inoculation-sarcoma in rats. F. EICHHOLTZ (Biochem. Z., 1931, **235**, 170—173).—The Ca content of this tissue for different animals is 70—350 mg. per 100 g. dry substance. The val. does not vary by more than 1—2% in different slices from the same animal. The Mg content of the tumour cells is also const. in the same animal (differences 5—10%). P. W. CLUTTERBUCK.

Tumour immunity. T. LUMSDEN (Amer. J. Cancer, 1931, **15**, 563—640).—The euglobulin fraction

of an anti-malignant-cell serum contains the anti-malignant-cell bodies; in the process of its precipitation most of the heterotoxins are destroyed. The cytolytic effects of the eu- and pseudo-globulin fractions on mouse and human cancer cells are described. The results demonstrate that antibodies which are specifically lethal to malignant cells exist; they are toxic to malignant cells of all varieties, which may therefore have a common constituent capable of acting as an antigen. CHEMICAL ABSTRACTS.

Malignant conditions. J. H. ROE and H. M. DYER (Amer. J. Cancer, 1931, **15**, 725—731).—Fowls bearing Rous sarcoma No. I have a reduced carbohydrate tolerance. The glycogenolytic activity of the blood is normal, but the glycolytic activity is double the normal. The glycolytic activity of the blood is of no clinical diagnostic value.
CHEMICAL ABSTRACTS.

Effect of ergotamine on the blood-sugar in normal and diabetic conditions and in disease of the liver. G. CORBINI (Policlinico, 1930, 11 pp.; Chem. Zentr., 1931, i, 2078).—In diabetes hyperglycæmia is produced; the other cases are unaffected.
A. A. ELDRIDGE.

Diabetes insipidus. F. MAINZER (Arch. exp. Path. Pharm., 1931, **160**, 461—478).—The ability to concentrate the body-fluids in diabetes insipidus is quant. similar for chlorides and hydrogen carbonates, although the basic equiv. is of greater significance than the actual concentration of Cl′. Previous findings with regard to the protein content of the serum in diabetes insipidus (Arch. klin. Med., 1930, **169**, 1) are confirmed. P. G. MARSHALL.

Creatinine metabolism in diabetes insipidus. L. D'ANTONA (Arch. Ist. Biochim. Ital., 1931, **3**, 187—204).—Contrary to Pakodzy (Z. klin. Med., 1930, **112**), excretion of creatinine in the urine is not necessarily augmented in diabetes insipidus. Records are given of the excretion of urine and creatinine of four patients, and of the effects of administering pituitary extract or mercurials (*e.g.*, "salyrgan"), which sometimes have a notable antidiuretic effect accompanied by retention of creatinine.
R. K. CALLOW.

Carbamide content of cerebrospinal fluid in status epilepticus. O. R. BINYON and J. T. FOX (Lancet, 1930, ii, 1233—1234).—Carbamide and dextrose contents are high. L. S. THEOBALD.

Guanidine-like substances in the blood in experimental yellow fever. G. M. FINDLAY and E. HINDLE (Lancet, 1930, ii, 678—679).—In experimental yellow fever in monkeys the guanidine-like substances in the blood are increased. Ca lactate reduces this increase, tends to prevent hæmorrhages, but does not prevent death. L. S. THEOBALD.

Gallstone formation. I. Determination of streaming potential and applicability of Schultze–Hardy rule; relation between ζ-potential and coagulation. II. Lyotropic series and influence of acids and alkalis; relation between ζ-potential and adsorption. III. Influence of anions and halogen group. N. FURUTANI, T. KUROKOCHI, and Y. ASODA (Japan. J. Gastroenterol., 1930, **2**, 148—157, 158—161, 162—165).—I. The e.m.f. was proportional to the pressure but independent of the diameter and length of the glass capillary. The potential decreases in the order (equiv. mol. conc.) KCl, $BaCl_2$, $AlCl_3$, $Th(NO_3)_4$. Lyophobic sols are coagulated by a solution of an electrolyte when the streaming potential of the latter becomes sufficiently low. Crystal-violet behaves like quadrivalent electrolytes.

II. The streaming potential decreases in the order (*a*) Li, Na, K, Rb, NH_4, Cs, (*b*) Mg, Ca, Ba, as chlorides. The max. potential of NaOH is much greater than that of HCl.

III. The streaming potential decreases in the order (*a*) $0{\cdot}25K_4Fe(CN)_6$, $0{\cdot}33K_3Fe(CN)_6$, $0{\cdot}5K_2SO_4$, KCl, (*b*) I, Br, Cl. CHEMICAL ABSTRACTS.

Ultra-violet light and goitre. T. VON FELLENBERG (Biochem. Z., 1931, **235**, 205—213).—The I contents of the thyroid glands of white rats kept in the dark and in bright light (Davos) did not show differences parallel with the histological changes obtained under similar conditions by Bergfeld (Strahlenther., 1930, **39**, 245). The I contents of the air, drinking water, milk, etc. of Davos and that of the urine of a few inhabitants are tabulated. The incidence of goitre is what would be expected from the I content of the environment, and no evidence could be obtained that ultra-violet irradiation decreased the incidence of goitre. P. W. CLUTTERBUCK.

Differential stain favourable to the diagnosis of Neisserian infection. S. A. SCUDDER (Stain Tech., 1931, **6**, 99—105).—Air-dried films are stained for 3—5 min. in 1% crystal-violet solution in 10 parts of phosphate buffer of p_H 6·6—7·0 and 90 parts of H_2O. They are then flushed with 2% I in 0·1*N*-NaOH, after which they are decolorised in $COMe_2$ for 10 sec. After air-drying they are counterstained for 1·5—2 min. in a mixture of 2 parts of 2% aq. Me-green and 1 part of 0·3% aq. pyronin-yellowish. They are then washed and air-dried. Bergamot oil is preferable to xylene as a clearing agent. H. W. DUDLEY.

Congestive heart failure. VIII. Effect of administration of dibasic potassium phosphate on the potassium content of certain tissues. J. A. CALHOUN, G. E. CULLEN, G. CLARKE, and T. R. HARRISON (J. Clin. Invest., 1931, **9**, 693—703).—The tissue-K was subnormal in heart failure; administration of K increases the tissue-K, the difference being most marked in skeletal muscle and least in heart muscle. CHEMICAL ABSTRACTS.

Hypoglycæmia. Clinical syndrome, etiology, and treatment: a case due to hyperinsulinism. G. D. GAMMON and W. C. TENERY (Arch. Int. Med., 1931, **47**, 829—854).—A clinical review. A. COHEN.

Analyses of the blood of idiots. S. S. NEGUS (Science, 1931, **73**, 449—450).—Abnormal amounts of inorg. phosphate were not found.
L. S. THEOBALD.

Biochemistry in relation to intelligence. H. D. POWERS (Science, 1931, **73**, 316).—In idiots, blood-Ca is normal but blood-P is high. L. S. THEOBALD.

[Nature of] two types of bilirubin diazo-reaction in serum. Hypothesis on nature of bilirubin in serum from hæmolytic jaundice.

G. Hunter (Brit. J. Exp. Path., 1930, **11**, 415—419).—The "direct" reaction is probably due to Na H bilirubinate, and the "delayed" reaction to free bilirubin in an undetermined solvent. The bilirubin may be combined with its solvent (lipin or sterol) or some other serum constituent so that it resists salt formation and oxidation. Chemical Abstracts.

Manganese in foodstuffs. Possible relation to cirrhosis of the liver. A. E. Boycott and G. R. Cameron (Lancet, 1930, ii, 959).—The Mn contents of various foodstuffs are recorded. Cloves, tea, spice, pepper, scallops, winkles, and ginger contain most Mn. No relation to cirrhosis is evident. L. S. Theobald.

Chemotherapeutic treatment by colloidal magnesium hydroxide of liver and kidney lesions produced experimentally by poisons. E. Pribyl (Arch. exp. Path. Pharm., 1931, **160**, 255—268).—Colloidal $Mg(OH)_2$ administered intravenously to rabbits suffering from kidney and liver lesions produced experimentally by As_2O_3, P, and $UO_2(NO_3)_2$ exerts a distinct beneficial effect on the animals. The action is probably due partly to the basic nature of the reagent and partly to the sp. action of $Mg^{\cdot\cdot}$. W. O. Kermack.

Plasma-protein loss with œdema but without proteinuria, and its bearing on the concept of nephrosis. T. I. Bennett, E. C. Dodds, and J. D. Robertson (Lancet, 1930, ii, 1006—1008).—Considerable protein loss may occur from blood by routes other than the kidney and œdema follows such loss. L. S. Theobald.

Role of the lipins and proteins of blood on water exchange in the organism. A. Machebœuf (Compt. rend., 1931, **192**, 1413—1415).—Serum-albumin from the blood of patients suffering from lipoid nephrosis has a greater combining capacity than normal serum-albumin on the basic but not on the acid side of the isoelectric point. It also exerts a greater osmotic pressure per g. in solution and, further, the lipins associated with it are more readily extracted with Et_2O than in the case of normal serum-albumin. An albumin fraction was obtained from horse serum of high lipin content showing abnormally high combining power on the alkaline side of the isoelectric point. W. O. Kermack.

Lipin nephrosis. I. Lipins carried down with serum-globulin and -albumin precipitates. M. A. Machebœuf and R. Wahl. **II. Lipins and lipin fractions of blood-serum.** M. A. Machebœuf, R. Wahl, and G. Sandor. **III. Fractionation of serum-albumin and the accompanying lipins.** M. A. Machebœuf and R. Wahl (Bull. Soc. Chim. biol., 1931, **13**, 486—503, 504—510, 511—515; cf. this vol., 759).—I. In lipin nephrosis, for which the globulin–albumin ratio is not characteristic, there occurs a diminution of protein in the serum. The increase in globulin-lipins is not so marked as with the albumin-lipins.

II. In lipin nephrosis there is an increase in total unsaponifiable matter, cholesterol, and phospholipins of the serum, whilst the cholesterol : phospholipin ratio is decreased and the free cholesterol : cholesteryl ester ratio unchanged. The division of the various lipins between the globulin and albumin fractions is given.

III. Lecithin–sterol–protein complexes were prepared by repeated precipitation of the albumin–lipin fraction at p_H 3·7—3·8 in presence of moderate concentrations of $(NH_4)_2SO_4$. For normal sera they contain approx. 60% of protein and 40% of lipins. Little unsaponifiable material is found in the complex from horse serum, whilst human serum has a higher content. The complexes are sol. at alkaline reactions. No marked variation in the amount or type of complex occurs in lipin nephrosis. F. O. Howitt.

Physical properties of blood-serum in lipin nephrosis. C. Achard and A. Boutaric (Compt. rend., 1931, **192**, 1611—1615).—The ratio of the total vol. of particles comprising 1 g. of dry matter to the mean vol. of these particles is fairly const. in normal sera. If the serum is warmed for 1 hr. at rising temp. the luminous absorption increases, but the ratio remains const. until gelation sets in at 64°. In lipin nephrosis the ratio is 1·25 instead of 6; warming induces clarification, and the ratio increases. At 64° after 5 hr. the luminous absorption and the viscosity were increased, and the ratio became equal to that of normal sera. Coupled with other pathological conditions the physical data obtained were not markedly different from those obtained in normal sera. C. C. N. Vass.

Case of animal ochronosis and experimental porphyria. G. Fink (Z. physiol. Chem., 1931, **197**, 193—205).—The colouring matter extracted from the bones of an ox with marked ochronosis coincided spectroscopically with uroporphyrin. The ultraviolet fluorescence of the teeth and bones of animals receiving daily injections (1 mg. dose) of various porphyrins varied widely with the nature of the porphyrin. *iso*Uroporphyrin was the most readily absorbed; deuteroporphyrin had no effect. J. H. Birkinshaw.

Physiology of the parathyroid glands. II. Relation of serum-calcium to serum-phosphorus at different levels of parathyroid activity. F. Albright, W. Bauer, J. R. Cockrill, and R. Ellsworth (J. Clin. Invest., 1931, **9**, 659—677).—The product Ca×inorg. P is approx. const. In parathyroid dysfunction the body-fluids exhibit normal Ca phosphate but abnormal Ca : phosphate. At high Ca levels the fluids contain a large amount of Ca phosphate. Chemical Abstracts.

Blood constituents in acute rheumatism before and after salicylate treatment. E. M. Hickmans and S. H. Edgar (Arch. Dis. Childhood, 1930, **5**, 387—396).—The blood-urea, -non-protein-N, and -uric acid are high in acute rheumatism, and remain high during treatment with salicylate. The urea tends to become increased. Chemical Abstracts.

Effect of phosphorus in rickets. I. Röntgenological changes in rickets following administration of phosphorus. II. Chemical changes. E. L. Compere (Amer. J. Dis. Children, 1930, **40**, 941—967, 1177—1192).—The effect of cod-liver oil is enhanced by a small amount of P; the serum-Ca and -P are markedly increased. The administration

of P alone neither cures severe rickets nor affects the serum-Ca or -P. The healing of rickets is not associated with changes in the of the blood-serum.

CHEMICAL ABSTRACTS.

Causes and origin of "incurable" forms of rickets and the amount of inorganic phosphorus in the serum of the afflicted animals. A. VAN HARREVELD (Arch. Neerland. physiol., 1931, **16**, 234—250).—Rats fed on a diet deficient in vitamin-*D* and also in other respects, viz., in P, vitamin-*B*, and in protein, develop severe rickets which is not cured by the administration of large doses of vitamin-*D*, even although the serum-P rises to a level equal to or exceeding the normal. When only one of the three defects is corrected, response to the administration of vitamin-*D* still fails to occur, but when two of the three defects are corrected, improvement is brought about by vitamin-*D* administration. When all three defects are corrected, marked healing occurs after administration of vitamin-*D*. Rat diets used in testing for vitamin-*D* should therefore not be deficient in any factor except vitamin-*D*. The conclusion of Hess *et al.* (A., 1930, 949) that rickets not curable by administration of vitamin-*D* is specifically produced by a diet deficient in P with a high Ca : P ratio is not supported. W. O. KERMACK.

Metabolism studies in tetany. S. MORRIS, A. M. WATSON, and N. MORRIS (Biochem. J., 1931, **25**, 786—798).—The following metabolic changes occur after parathyroidectomy or injection of guanidine. There is a marked retention of Cl in the tissues. In the late tetany stage there is an increase of volatile Cl in both the blood and tissues, whilst in the active period there is almost complete absence of volatile Cl. The urinary output of N, amino-acids, and purine-N rises, whilst that of creatinine and NH_3 falls. The percentage retention of Ca decreases as a result of relative excess in the urinary excretion. There is a correlation between the excess of Ca and amino-acid excreted. The retention of P is either slightly diminished or unchanged. S. S. ZILVA.

Adsorption in relation to some physiological phenomena. I. The physical problem. II. Meaning of the potentials determined at the surface of a tissue and at the surface of a wound by means of reversible electrodes. J. W. LANGELAAN (Arch. Néerland. physiol., 1931, **16**, 145—159, 160—167).—I. A discussion of the relation between adsorption, electrokinetic potential, and thermodynamic potential with special reference to the theory of Stern (Z. Elektrochem., 1924, **30**, 508) according to which the double layer in a liquid in the neighbourhood of a solid surface is partly unimol. and partly diffuse.

II. The general theory is applied to the interpretation of potential measurements made on the system muscle–tendon–lymphatic fluid.

W. O. KERMACK.

Metabolism of tissues growing *in vitro*. IV. Effect of lævulose, galactose, and xylose on ammonia and urea production of embryo kidney tissue. E. WATCHORN and B. E. HOLMES (Biochem. J., 1931, **25**, 843—848).—The addition of lævulose, galactose, and xylose tends to increase the growth of embryo kidney tissue, but whilst the first inhibits the production of NH_3 and urea (A., 1927, 479) by the growing cells, galactose does so only irregularly and xylose not at all. The added sugars were utilised by the tissue, the non-growing using less than the growing tissue. S. S. ZILVA.

Factors limiting the growth of tissue cultures *in vitro*. B. EPHRUSSI (Compt. rend., 1931, **192**, 1763—1765).—In fibroblastic tissues grown in a nutrient medium but washed free from stimulating substances, small initial cultures grow faster to attain the same development as larger initial cultures, which suggests that the arrest of growth is not due to metabolites but rather to the exhaustion of certain substances in the initial culture. The glutathione reaction is positive during growth, but diminishes as the rate of growth decreases and is absent at cessation of growth. Elimination of substances which can yield SH radicals is the cause of arrest of growth, whilst addition of such substances, *e.g.*, embryonic extract, to a culture in which growth has ceased can induce growth. C. C. N. VASS.

Fat metabolism in muscular work. C. P. STEWART, R. GADDIE, and D. M. DUNLOP (Biochem. J., 1931, **25**, 733—748).—In normal men performing muscular work the blood-fat usually rose after about 8000 kg. of work. With greater rates of work the rise appeared earlier. After recovery it appeared more easily on the performance of a second period of work. A high fasting blood-fat in normal or diabetic subjects led on the other hand to a preliminary fall when work was performed. An abnormally low blood-fat was increased by relatively small amounts of work. This alteration in the blood-fat was confined to the glyceride fraction. Continuance of work led to a return of the blood-fat towards normal and later to a second rise. The CO_2-combining power of the blood was roughly the reciprocal of the blood-fat, but these changes preceded those in the blood-fat. The R.Q. for exercise and recovery was unity for amounts of work up to about 6000 kg. and thereafter fell steadily with increasing amounts of work. Protein was not used for work. Carbohydrate continued to be used throughout, although in decreasing amounts. Fat was used in increasing amounts. There was no relationship between the utilisation of fat and the changes in the blood-fat concentration. There was no diminution in efficiency at the lower R.Q. and no conversion of fat into carbohydrate. Diabetic subjects showed no less efficiency and no wastage of O. S. S. ZILVA.

Metabolic rate and respiratory quotients of rats following the ingestion of dextrin and during fasting. L. G. WESSON (J. Nutrition, 1931, **3**, 503—518).—With rats a low basal rate of 718 kg.-cal. per sq. in. per 24 hr. was reached 13 hr. after feeding dextrin. R.Q. values are recorded.

CHEMICAL ABSTRACTS.

Passage of carbohydrate through the animal organism. II. F. HOLTZ (Biochem. Z., 1931, **235**, 104—161).—The factors which vary and condition the blood-sugar curve are investigated (cf. A., 1930, 1312). The changes of sugar content of serum and corpuscles in man, dog, swan, goose, and goat do not always run parallel, but may be antagonistic. The

serum-sugar content of 325 dogs in the morning of the third day of fasting was between 60 and 130 mg. per 100 c.c., and showed considerable variation for the same dog under the same conditions of life and food. The typical alimentary serum-sugar curve rises, falls below the initial val., and then slowly rises again to normal. A large number of curves show the influence of diet, acidosis, and alkalosis on the course of the blood-sugar vals. Carbohydrate causes increased secretion not only of insulin, but also of an antagonistic secretion designated glycæmin—possibly adrenaline.

P. W. Clutterbuck.

Cyclic changes in the glycogen content of the liver and the muscles of rats and mice. Their bearing on the sensitivity of the animals to insulin and their influence on the urinary output of nitrogen. G. Ågren, O. Wilander, and E. Jorpes (Biochem. J., 1931, **25**, 777—785).—Glycogen accumulates in the liver of the rabbit, rat, and mouse during the night and disappears again to some extent during the next morning. This change is to a large extent independent of the intake of food. It occurs even in fasting animals. In the muscles the change is less marked. Mice show an increased resistance to insulin in the afternoon and particularly during the night. In rabbits the urinary N output is increased during the night. In fasting rabbits the excess of N thus eliminated is about 20% of the amount excreted during the day. S. S. Zilva.

Dietary deficiencies of milk. J. E. Becker and E. V. McCollum (Amer. J. Hyg., 1930, **12**, 503—510).—The best supplements (reproduction records) are ox liver, yeast, and a mixture of Fe^{III} citrate and $CuSO_4$. Chemical Abstracts.

Kidney metabolism. P. Gyorgy and W. Keller (Biochem. Z., 1931, **235**, 86—96).—The phosphatase content of the cortex of pig's kidney measured in terms of hydrolysis of hexose-mono- and -di-phosphoric acids is many times as great as that of the medullary tissue. Whereas with the cortical tissue, the liberation of phosphate is about the same for both hexose-mono- and -di-phosphates, with the medullary tissue phosphate liberation is about twice as great with the di- as with the mono-phosphate. NH_3 formation is greater with the cortical than with the medullary tissue and is increased by addition of adenosinephosphoric acid, the increase, however, being greater with the medullary tissue. P. W. Clutterbuck.

Conjugation of benzoic acid in man. A. J. Quick (J. Biol. Chem., 1931, **92**, 65—85).—Ingestion of prunes is followed by fairly prolonged excretion of hippuric acid (cf. A., 1924, i, 121) due to presence of quinic acid. Benzoic acid appears to be the stimulus for the synthesis of glycine, a max. (0·55—0·70 g. per hr.) of which is formed when 15 g. of BzOH are ingested. Addition of glycine increases the rate of hippuric acid excretion until the kidney leak max. (1·42—1·82 g. per hr.) is reached. Administration of BzOH produces a decrease in uric acid excretion which returns to normal levels on glycine feeding. With large doses of BzOH a part (10—12%) is excreted conjugated with glycuronic acid. F. O. Howitt.

Legal's reaction and the excretion of conjugated glycuronic acid. A. Meyer and J. Jeannin (Bull. Soc. Chim. biol., 1931, **13**, 542—547).—The transitory red colour formed on addition of Na nitroprusside to urine at alkaline reactions is due to conjugated glycuronic acid. A positive response is obtained following administration of asparagus (which results in excretion of MeSH), camphor and its derivatives, menthol, salicylic acid, antipyrine, aspirin, hexatone, etc. F. O. Howitt.

Simple methods for metabolic balance studies and their interpretation. E. Donelson, B. Nims, H. A. Hunscher, C. F. Shukers, and I. G. Macy (J. Home Econ., 1931, **23**, 267—272).—The mean difference between the computed and experimental compositions of a diet was 2—5% (variations, N 0·7—38, Ca 0—22, P 0—38%). Chemical Abstracts.

Condition of water in a marine aquarium. W. R. G. Atkins (J. Marine Biol. Assoc., 1931, **17**, 479—481).—The use of CaO is preferable to that of $NaHCO_3$ for the control of the p_H of water in marine aquaria. The conclusions of Breder and Howley (Zoologica, 1930, **9**, 403—442) in this connexion are disputed. C. W. Gibby.

Physiological significance of some inorganic elements. E. V. McCollum and E. Orent (J. Maryland Acad. Sci., 1931, **2**, 33—36).—Mn is an indispensable nutrient element for mammals.

Chemical Abstracts.

Biological function of zinc. D. Ganassini (Arch. Ist. Biochim. Ital., 1931, **3**, 131—138).—Basic Zn salts, or the hydroxide, act as catalysts in certain oxidation reactions *in vitro*. The evidence that Zn is an essential constituent of org. tissues and fluids is reviewed, and it is suggested that one of its functions is that of catalyst in oxidations. R. K. Callow.

Suffocation point in the horned lizard, *Phrynosoma cornutum*. G. E. Potter (Science, 1931, **73**, 314—315).—When confined in closed vessels these lizards survive until the O_2 content reaches 4—5·5% and that of CO_2 12—15%. When the CO_2 is continuously removed, they survive until the O_2 content reaches 4 or even 3·21%. L. S. Theobald.

Ether narcosis. [Determination of ether and regulation of dose.] G. Karber (Arch. exp. Path. Pharm., 1931, **160**, 428—439).—Et_2O is determined by a modified CrO_3 oxidation method, the error being $\pm$3% with 0·2—4·5 mg. Et_2O in 2 c.c. of blood or 20 c.c. of air. An apparatus is also described for supplying Et_2O–air mixtures of required concentrations. W. O. Kermack.

Action of ether on respiration. G. Karber and L. Lendle (Arch. exp. Path. Pharm., 1931, **160**, 440—459).—The breathing by rabbits of Et_2O–air mixtures of const. concentration results first in a stimulation of the respiration, but when the concentration is such as to bring about the disappearance of the corneal reflex respirations cease almost simultaneously. No concentration of Et_2O could be found which would cause the breathing to continue steadily at a diminished rate. The paralysing effect of Et_2O on respiration is irreversible, and is probably due to secondary toxic effects. W. O. Kermack.

Elimination of ethyl iodide after inhalation and its relation to therapeutic administration.

H. L. Blumgart, D. R. Gilligan, and J. H. Swartz (J. Clin. Invest., 1931, **9**, 635—650).—On inhalation of 1—3 c.c. EtI in air, 45% is exhaled immediately, 9% during the following 2 hr., and 31% by the kidneys as iodide. The percentage of EtI retained in the body is independent of the size of the dose.

Chemical Abstracts.

Occurrence of succinic acid in corpses and the detection of narcotics of the barbituric acid series in presence of succinic acid in toxicological cases. F. Weiss (Pharm. Zentr., 1931, **72**, 433—436).—A discussion of published work on the occurrence of succinic acid in human remains. Barbituric acid derivatives may be separated from aq. solution which also contains succinic acid by neutralisation to Me-red with Na_2CO_3 followed by Et_2O extraction. The extract is evaporated, redissolved in H_2O, decolorised, and the barbituric acid extracted with Et_2O.

E. H. Sharples.

Biological assay of ergot preparations. II. Use of the paralysis of the renal vasomotors as an assay method. G. A. Wulp and E. E. Nelson (J. Pharm. Exp. Ther., 1931, **42**, 143—154).—The method of Raymond-Hamet (Compt. rend., 1926, **182**, 1045) is not recommended.

W. O. Kermack.

Increase of calcium content of blood-serum during strychnine poisoning. A. von Beznak (Arch. exp. Path. Pharm., 1931, **160**, 397—400).—The rise in blood-Ca which occurs during the convulsions of strychnine poisoning is not diminished in dogs by parathyroidectomy or by cholecystectomy; the effect therefore is not due to stimulation of the parathyroids or of increased resorption of Ca from the gall-bladder. Intravenous administration of lactic acid to dogs produces no increase in blood-Ca, and thus the high blood-lactic acid resulting from the convulsions is not the cause of the increased blood-Ca. The additional Ca therefore probably comes from the muscles. W. O. Kermack.

Effect of atropine on blood-sugar in man. D. Danielopolu, S. Stoicescu, and Cimino-Berenger (Klin. Woch., 1931, **10**, 311—313; Chem. Zentr., 1931, i, 2078).—Stimulant doses increase, whilst paralytic doses diminish, the blood-sugar.

A. A. Eldridge.

Effect of nicotine and the components of tobacco smoke on the blood-sugar. A. S. Salischtschev (Z. ges. exp. Med., 1930, **74**, 14—19; Chem. Zentr., 1931, i, 2077).—Intravenous injection of nicotine (0·5 mg.) into rabbits caused hypoglycæmia (1·5—49·6%); with 1·0 mg. hyperglycæmia (7·7—51%) was followed by hypoglycæmia (2·5—10·9%). Tobacco smoke in toxic quantities leads in man to hypoglycæmia (18·3—61·7%). The changes are attributed to the action of nicotine on the sympathetic nervous system, whereby the production of adrenaline is increased. A. A. Eldridge.

Adsorption. I. Adsorption of physiologically active substances by activated charcoal. F. Saunders, J. E. Lackner, and S. S. Schochet (J. Pharm. Exp. Ther., 1931, **42**, 169—177).—Strychnine, brucine, adrenaline, histamine, and tyramine are quant. adsorbed or inactivated when aq. solutions of their salts are treated with activated charcoal for 20 min. In the case of acetylcholine and ephedrine inactivation is almost complete. W. O. Kermack.

Contractile poisons and different types of frog's muscle. F. Petermann (Arch. exp. Path. Pharm., 1931, **160**, 543—550).—The rectus abdominis muscle is the most sensitive to all poisons, followed by the gastrocnemius and the sartorius. The ratio of sensitivities to nicotine is 1,000,000 : 10,000 : 1 and for coniine 200 : 100 : 1. Caffeine and Nile-blue in small doses produce reversible histological changes in the muscle fibres. The sensitivity of *R. esculenta* to acetylcholine is greater than that of *R. temporaria*, although the sartorius muscle does not react in either even to high concentrations. *m*-Nitroaniline also produces a differential effect on the three types of muscle. P. G. Marshall.

Effect of ephedrine on the blood-sugar and -lactic acid and on the plasma-fat. H. E. Himwich, H. Henstell, and J. Fazikas (Proc. Soc. Exp. Biol. Med., 1930, **28**, 333—334; Chem. Zentr., 1931, i, 1779).—In the dog, injection of ephedrine (10 animals) caused a rise of blood-sugar in all cases, of -lactic acid in 5 cases, and of plasma-fat in 7 cases.

A. A. Eldridge.

Urinary phosphate following bile acid administration. K. Fuziwara (J. Biochem., Japan, 1931, **13**, 43—56).—Subcutaneous injection of Na cholate into dogs increases the excretion of the secondary, and lowers that of the primary, phosphate, the net result being an increased phosphate excretion and a rise in p_H. F. O. Howitt.

Behaviour of "germanin" *in vivo*. K. Lang (Arch. exp. Path. Pharm., 1931, **160**, 560—568).—"Germanin" on acid hydrolysis, yields *m*-aminobenzoic acid, 3-amino-4-methylbenzoic acid, and α-naphthylamine-4 : 6 : 8-trisulphonic acid. The NH_2 compounds liberated by heating the serum with HCl are diazotised and coupled with α-naphthol and the resulting colour is compared with that obtained from the amines liberated from pure "germanin." The max. error of the method for serum is +7·5%. Shaking with kaolin does not affect the result. Germanin is not hydrolysed in the animal body and is only slowly excreted by the kidneys. It is not absorbed by the liver, whilst its concentration in the blood is affected by the mode of injection.

P. G. Marshall.

Toxicity of salvarsan. W. Milbradt (Arch. exp. Path. Pharm., 1931, **160**, 489—526).—The toxicity of salvarsan is raised by alkaloids which paralyse the sympathetic, by bile salts and alkalis in high concentrations, by histamine-like substances, and by insulin and acetylcholine. In small doses salvarsan stimulates the sympathetic, whilst in larger doses it counteracts the rise of blood-sugar which follows the administration of a narcotic. The body itself detoxicates salvarsan, chemically by means of its Ca and dextrose metabolism, and mechanically by storage in the reticulo-endothelial system and elimination by the kidneys. Salvarsan poisoning can be cured by means of liver extract; its toxicity is increased where liver injury (phloridzin poisoning etc.) occurs.

P. G. Marshall.

Can the biological standardisation of arsenobenzene derivatives be replaced by a chemical method ? H. BAUER and M. ROTHERMUNDT (Z. Immunität., 1930, **69**, 213—220; Chem. Zentr., 1931, i, 1649).—Kielbasinski's " toxicity val." (*ibid.*, 1930, **69**, 346; A., 1930, 370) agrees with the results of biological (mouse) tests. When kept in contact with air, neosalvarsan solutions become more toxic.
A. A. ELDRIDGE.

Influence of boron compounds on tissue respiration. B. KISCH (Biochem. Z., 1931, **235**, 35—44).—The respiration of isolated mammalian tissues (kidney, heart, liver of cat, rabbit, and guinea-pig) is inhibited by H_3BO_3 in concentrations of 10^{-5} (about $2 \times 10^{-4}M$) and is increased at concentrations of 10^{-7} to 10^{-9} (2×10^{-5} to $2\times10^{-7}M$). $Na_2B_4O_7$ has a similar but smaller action. The respiratory power of old tissues is better maintained in presence of traces of H_3BO_3. P. W. CLUTTERBUCK.

Influence of aluminium salts on the respiration of isolated kidney tissue. B. KISCH and J. LEIBOWITSCH (Biochem. Z., 1931, **235**, 45—50).—$AlCl_3$ and $Al_2(SO_4)_3$ added to normal Ringer's solution in concentrations of 10^{-5} ($10^{-4}M$) inhibit and of 10^{-7} to 10^{-9} (10^{-6} to $10^{-8}M$) increase respiration of isolated mammalian kidney tissue. The accelerating effect is obtained better in neutral and faintly acid than in alkaline solution. P. W. CLUTTERBUCK.

Tissue respiration in calcium-free medium. B. KISCH (Biochem. Z., 1931, **235**, 51—65).—The action of $CaCl_2$ in increasing respiration is confirmed for old and fresh tissue, and a similar effect is obtained with certain tervalent cations ($AlCl_3$) and with H_3BO_3. $TlNO_3$ is inactive. High concentrations of $AlCl_3$ and H_3BO_3 which in normal Ringer's solution would inhibit respiration do not inhibit in Ca-free solution. Maximal increase of respiration is obtained with higher concentrations of these substances with Ca-containing than with Ca-free medium. " Omega " (the oxidation product of adrenaline) causes increased respiration in Ca-free Ringer's solution, but the action is not less than with normal Ringer's solution. Increased respiration is obtained in Ca-free solution with H_3BO_3 and $AlCl_3$ in concentrations of 1 in 10^{12}.
P. W. CLUTTERBUCK.

Human absorption of magnesium with and without aspirin and other adjuvants. J. E. WINTER and C. H. RICHEY (J. Pharm. Exp. Ther., 1931, **42**, 179—183).—The more efficient absorption of Mg from the alimentary tract brought about by the administration of aspirin, ginger, or alcohol together with MgO or $MgCl_2$ is probably to be correlated with the irritant action of these substances on the mucosa, resulting in an increased blood supply and also in the maintenance of an approx. normal level of gastric acidity. W. O. KERMACK.

Effect of sodium thiosulphate on mercury poisoning. A. G. YOUNG and F. H. L. TAYLOR (J. Pharm. Exp. Ther., 1931, **42**, 185—195).—In rabbits poisoned by $HgCl_2$, Hg succinimide, or Hg salicylate no beneficial results were produced by the administration of large and repeated doses of $Na_2S_2O_3$. In rabbits poisoned with K mercuri-tetraiodide a slight beneficial effect was noted. W. O. KERMACK.

Calcification due to bismuth. C. LEVADITI, A. VAISMAN, R. SCHOEN, and Y. MANIN (Compt. rend., 1931, **192**, 1768—1769).—Administration of toxic doses of fat- or H_2O-sol. Bi to the rabbit causes calcification of the kidney, and of the musculature at the site of injection. C. C. N. VASS.

Influence of orally administered iron on the animal organism. H. MATTIS and E. MANDRYSCH (Arch. Pharm., 1931, **5**, 289—291).—Colloidal Fe on a substrate of liver protein, administered orally to rabbits during 12 weeks, causes an increase in the number of blood corpuscles, whilst Fe is deposited in the liver and kidneys; excess over the normal is found in the spleen, but none is present in the spinal cord.
A. A. LEVI.

Toxicity of colloidal iodine. W. NYIRI and L. DUBOIS (J. Amer. Pharm. Assoc., 1931, **20**, 546—550).—Colloidal I (prepared by acidification at 0° of Na iodohypoiodite containing gum-acacia) has the same fatal dose as the U.S.P. tincture when administered intravenously, but the local corrosive action on the mucous membrane of the stomach is only about $\frac{1}{6}$—$\frac{1}{4}$ of that of the tincture. E. H. SHARPLES.

Iodine retention and distribution in rabbits. W. A. PEABODY (J. Amer. Pharm. Assoc., 1931, **20**, 551—555).—Continued doses of KI or iodised fatty acid ester fed to rabbits showed greater retention after the org. form and a marked increase of I in most tissues and organs, but the latter effect bore no relationship to the form of administration.
E. H. SHARPLES.

Osmium tetroxide poisoning. F. R. BRUNOT (Analyst, 1931, **56**, 451).—Inhalation of fumes of OsO_4 in high concentration results in pneumonia and consequent death in animals. T. MCLACHLAN.

Accumulation of strong electrolytes in living cells. S. C. BROOKS (Science, 1931, **73**, 589—590).—Osterhout's hypothesis concerning the mechanism of selective accumulation of ions by living cells is criticised. L. S. THEOBALD.

Hæmatopoietic power of carotene. L. BINET and M. V. STRUMZE (Compt. rend., 1931, **192**, 1758—1760).—Oral administration of carotene to anæmic dogs markedly facilitates the production of hæmoglobin. C. C. N. VASS.

Effect of high altitudes on cholesterol, lecithin, and fatty acids in plasma of healthy men. G. L. MULLER and J. H. TALBOTT (Arch. Int. Med. 1931, **47**, 855—860).—No significant changes were observed in the cholesterol, lecithin-P, fatty acids, and O_2 capacity of the blood of 4 healthy subjects at 10,000 and 14,000 ft. above sea-level. A. COHEN.

Comparative kinetics of the liquefaction and saccharification of starch. I. Soya-bean amylase. C. ARTOM and G. ORESTANO (Bull. Soc. Chim. biol., 1931, **13**, 516—541).—During the course of hydrolysis of 70% of the substrate the viscosity decreases in proportion to the square root of the reaction time, the relation between liquefaction and concentration of enzyme following the Schütz–Borissow law. The saccharification is a unimol. reaction, and is inversely and the liquefaction directly proportional to the concentration of substrate, the two reactions being

expressed by $k_s=(c/Et)\log 75/(75-x)$ and $k_l-x/c\sqrt{Et}$, respectively, where x is the amount of substrate transformed at time t, E the quantity of enzyme, and c the concentration of substrate. F. O. HOWITT.

Structure and enzyme reactions. IX. The systems amylase–starch–gelatin and urease–urea–gelatin. S. FREIBERGER (Biochem. J., 1931, **25**, 705—712).—The velocity of reaction in the system amylase–0·6% starch–gelatin sol is unaffected below 9% gelatin, and appears to be little dependent on the viscosity of the medium. With 0·3% starch there is no retardation of reaction below 5% gelatin, whilst at higher concentrations of gelatin increasingly great retardation of reaction takes place. The velocity of the reaction between urease and urea is the same in the presence or absence of gelatin. The rate of diffusion of starch and amylase in gelatin jellies is considerably smaller than in similar sols. The velocity of reaction between amylase and starch in gelatin solution is little greater than in gelatin only.

S. S. ZILVA.

Disaccharide fission by α-glucosidase. K. MYRBACK (Z. physiol. Chem., 1931, **198**, 196—200).—The autolysis products of a strain of *B. coli* hydrolyse maltose strongly, but have no action on sucrose (cf. this vol., 654). This contradicts Weidenhagen's hypothesis (A., 1930, 499) and observation (this vol., 873). J. H. BIRKINSHAW.

Determination of enzymic processes by dilatometer. I. P. RONA and N. NEUENSCHWANDER-LEMMER (Biochem. Z., 1931, **235**, 214—226).—During hydrolysis of sucrose both by enzymes and by acid, the decrease of vol. followed dilatometrically proceeds parallel with the polarimetrically determined decrease of sucrose. The vol. decrease in the enzymic hydrolysis of maltose is about half that of sucrose.

P. W. CLUTTERBUCK.

Emulsin. L. ROSENTHALER (Biochem. Z., 1931, **235**, 227—232).—Racemisation of *d*-mandelonitrile proceeds slowly in 50% EtOH, more quickly in presence of emulsin. It occurs at the same rate with heated as with unheated emulsin, and the reaction is not enzymic. The conversion of *r*- into *l*-mandelonitrile by emulsin is an enzymic process.

P. W. CLUTTERBUCK.

Effect of narcotics on some dehydrogenases. K. C. SEN (Biochem. J., 1931, **25**, 849—857).—Ethylurethane, phenylurethane, diethyl- and phenylcarbamide, propionitrile, valeronitrile, and vanillin had no effect on xanthine oxidase or Schardinger enzyme in ordinary concentrations both as regards O_2 absorption and anaerobic reduction of methylene-blue. In the case of succinic dehydrogenase there was an inhibiting effect which increased with higher homologues of the same series. The degrees of inhibition of O_2 uptake and methylene-blue reduction agreed with each other in the majority of cases. Nitriles have no effect on methylene-blue reduction, although they inhibit O_2 uptake strongly. There is a competitive inhibition of hypoxanthine oxidation in presence of vanillin and piperonal. S. S. ZILVA.

Kinetics of peroxidase action. P. J. G. MANN (Biochem. J., 1931, 918—930).—The temp. coeff. of peroxidase reaction is just below 2 at all H_2O_2 concentrations. The effect of variation of the concentrations of H_2O_2 and the reducing substrate (leucomalachite-green and guaiacol) on the velocity of peroxidase action suggests that both H_2O_2 and reducing substrate must be combined at the enzyme before catalysis can take place. S. S. ZILVA.

Nature of tyrosinase. D. NARAYANAMURTI and C. V. RAMASWAMI (Biochem. J., 1931, **25**, 749—751).—*Dolichos* tyrosinase purified by ultrafiltration is more active than the dialysed preparation. The addition of cathode or anode cell liquid to the middle cell liquid of tyrosinase subjected to electro-osmosis and of ultrafiltrate to the enzyme causes slight inhibition. Tyrosinase does not lose its activity on repeated precipitation. S. S. ZILVA.

Action of tannase on gallotannin. W. N. NICHOLSON, M. NIERENSTEIN, J. C. POOL, and N. V. PRICE (Biochem. J., 1931, **25**, 752—755).—*Aspergillus niger* produces in addition to tannase an enzyme (pyrogallase) which destroys gallic acid.

S. S. ZILVA.

Synthesis of a hydrocarbon chain with help of enzymes. III. Distribution of carboligase in plants. A. STEPANOV and A. KUSIN (Ber., 1931, **64**, [*B*], 1345—1349).—An enzyme is present in the green leaves of *Lactuca sativa*, which causes the formation of acetoin from pyruvic acid. The carboligase remains active in the rapidly dried leaves, whereas maceration affords only a feebly acidic extract. The absence of the enzyme from the internal leaves free from chlorophyll has led to the examination of plants of higher chlorophyll content. The leaves of *Urtica dioica* and *U. ureus* are appreciably more active, but dry preps. are difficult to secure by reason of the basic nature of the juice. The leaves of *Beta vulgaris* are extraordinarily active, and the activity persists after desiccation. Maceration of the dry leaves and subsequent addition of EtOH cooled to −20° to the extract yields a very active H_2O-sol. powder. The carboligase from yeast extract cannot be precipitated in a similar manner. Carboligase is also present in the leaves of *Rumex acetosa*, *Petroselinum sativum*, *Allium cepa*, *Prunus padus*, and in apples. H. WREN.

Action of dyes on enzymes. II. Fumarase. J. H. QUASTEL (Biochem. J., 1931, **25**, 898—913).—Many acid and basic dyes are toxic to cell-free fumarase. There is a marked specificity in action and toxicity which is not associated with any simple grouping, but depends on the arrangement of the mol. as a whole. Methylene-blue and toluidine-blue which have little toxic action on brain-fumarase inhibit fumarase prepared from *B. coli* and *M. lysodeikticus*. The addition of dyes has no inhibiting action on the activity of the enzyme from blood. This is due to the presence of protein, which protects fumarase by combining with the dyes. A mixture of acid and of basic dyes forms a compound which is inert towards fumarase. A mixture of two acid or two basic dyes, on the other hand, is not less toxic than the more active of the two dyes present. Fumarate protects the enzyme from Congo-red or methyl-violet. The actual inhibition decreases as the

amount of enzyme increases when a const. amount of dye is present. The combination of enzyme and dye is not easily reversible. Phosphates exert some protective action on the enzyme against toxic dyes.
S. S. ZILVA.

Enzymic hydrolysis of paired bile-acids. W. GRASSMANN and K. P. BASU (Z. physiol. Chem., 1931, **198**, 247—250).—Pancreatic, intestinal, and liver enzymes fail to hydrolyse tauro- and glyco-cholic acids, but kidney extract is active particularly with the latter acid, the optimum p_H being 8. *Aspergillus niger* extract and putrefactive organisms also attack glycocholic acid. J. H. BIRKINSHAW.

Influence of sodium taurocholate and copper sulphate on lipase. I. A. PARFENTJEV, W. C. DEVRIENT, and B. F. SOKOLOFF (J. Biol. Chem., 1931, **92**, 33—40).—The adrenal glands do not contain lipase. Neither Na taurocholate nor $CuSO_4$ has any influence on serum-lipase, whilst the former accelerates and the latter inhibits the actions of liver- and pancreas-lipase in concentrations as low as 1 : 500,000 of either substance. Some antagonism exists between the two salts in their action on liver- or pancreas-lipase. F. O. HOWITT.

Enzymic hydrolysis of lecithin. E. J. KING (Biochem. J., 1931, **25**, 799—811).—An enzyme "lecithinase" is described. The following is the relative activity of different tissues in decreasing order: kidney, small intestine, spleen, liver, testis, pancreas, large intestine, brain, ovary, bone, suprarenal, lung, blood vessels, cardiac muscle, skeletal muscle. The enzyme is fairly stable at neutral reaction, but is rapidly destroyed in acid or alkaline medium at 38°. Its optimal [H$^\cdot$] is at about p_H 7·5, and it acts more rapidly at body temp. The addition of inorg. phosphate and choline and of glycerol to hydrolysing mixtures of lecithin and the enzyme does not affect appreciably either the rate or amount of hydrolysis. S. S. ZILVA.

Nitrogen distribution in the liver and serum of sensitised animals. H. HABS (Arch. exp. Path. Pharm., 1931, **160**, 527—534).—Subcutaneous injection of a foreign serum does not affect N-distribution in the liver. Sensitised guinea-pigs show no difference in protein-N content of the serum from that of normal animals, nor is there any difference between the non-protein-N of the serum of allergic and non-allergic individuals. P. G. MARSHALL.

Liver autolysis and treatment with serum of sensitised animals and allergic individuals. H. HABS (Arch. exp. Path. Pharm., 1931, **160**, 535—542).—The serum of sensitised guinea-pigs has no effect on the rate of autolysis of liver-pulp, whilst that of allergic individuals delays autolysis.
P. G. MARSHALL.

Northrop's crystalline pepsin. P. A. LEVENE and J. H. HELBERGER (Science, 1931, **73**, 494).—After 5 crystallisations, the material contains only 3·3% of total N as basic N. L. S. THEOBALD.

Specificity of animal proteases. XXIII. Zookinase. E. WALDSCHMIDT-LEITZ and A. PURR (Z. physiol. Chem., 1931, **198**, 260—266; cf. this vol., 520).—Zookinase is obtained in greater yield from partly autolysed organs. The isolation of the cryst. substance, which corresponds with reduced glutathione, is described. J. H. BIRKINSHAW.

Enzymic proteolysis. V. Structure of protamines. I. Protaminase and the products of its action on clupeine and salmine. E. WALDSCHMIDT-LEITZ, F. ZIEGLER, A. SCHAFFNER, and L. WEIL (Z. physiol. Chem., 1931, **197**, 219—236; cf. A., 1928, 550).—Clupeine and salmine are purified by fractionation from conc. aq. solution. The oily ppt. has a N/NH_2 ratio of 104 (clupeine) and 340 (salmine), the smaller sol. fraction 35 and 32 respectively. A sp. protaminase from pancreas, which eliminates basic amino-acids from the carboxyl end of the substrate, removes $\frac{1}{4}$ of the total arginine from clupeine and $\frac{1}{4}$ from salmine. The residues, "clupean" and "salman," show the same high N/NH_2 ratios as the unchanged protamines, which therefore have no terminal NH_2 group, but a proline NH group.
J. H. BIRKINSHAW.

Polypeptide constitution and proteolytic enzymes. K. SUZUKI (J. Biochem., Japan, 1931, **13**, 57—80).—Erepsin but not papain, papain-HCN, pepsin, trypsin, or trypsin-kinase hydrolyses the tripeptides: glycylglycyl-*l*-asparagine (I), glycylglycyl-*l*-aspartic acid (II), glycyl-*dl*-asparagylglycine (III), and *dl*-asparagyldiglycine (IV), the peptides as given in this order exhibiting decreasing rates of hydrolysis. Thus lengthening of the chain of the glycylaspartic acid dipeptide does not result in a substrate acted on by trypsin. Balancing of the CO_2H group by an NH_2 group increases the rate of hydrolysis as shown by (I). *dl*-Asparagyldi-*l*-tyrosine is hydrolysed by trypsin-kinase, but not by pepsin, trypsin, papain, papain-HCN, or erepsin. This tripeptide has an optimum reaction for hydrolysis of approx. p_H 8·3. The proteinase and carboxypolypeptidase fractions of trypsin prepared by the Waldschmidt-Leitz adsorption method and activated by kinase effect a small hydrolysis in each case. The indispensability of kinase indicates, however, that the action is due to the proteinase and not to the carboxypolypeptidase. F. O. HOWITT.

Action of proteolytic enzymes on polypeptides. S. UTZINO (Z. physiol. Chem., 1931, **198**, 135—152).—The behaviour of various enzyme solutions was studied on the dipeptides *glycylsulphanilic acid* (I), darkens above 350° (from *chloroacetylsulphanilic acid*, blackens about 290°), glycyl-β-phenylalanine (II), *glycyl*-o-*aminobenzoic acid* (III), decomp. 235—236° (*chloroacetyl* derivative, m. p. 188—189°), -m-*aminobenzoic acid* (IV), decomp. 231—232° (*chloroacetyl* derivative, m. p. 230—231°), -*p*-aminobenzoic acid (V) and on the tripeptides diglycylanthranilic acid, *diglycylsulphanilic acid*, darkens above 300°, and *diglycyl*-o-*aminobenzoic acid*, m. p. 220—221° (decomp.) [*chloroacetylglycyl* derivative, m. p. 214—215° (decomp.)]. Glycylglycine and glycylphenylalanine were used as controls.

All the peptides were hydrolysed by kidney enzyme; intestinal and pancreatic enzyme were practically unable to hydrolyse II and III. Liver and spleen enzymes attacked II to a small extent, but not III. Enzymes of pig's liver and spleen, but not those of

ox and dog's liver, hydrolysed I. Pig's, intestinal, and ox testes enzymes attacked only IV and V. III is attacked only by kidney enzyme, IV and V by all the enzymes employed. All the tripeptides were hydrolysed by all the enzyme solutions.

J. H. BIRKINSHAW.

Kinetic theory of the velocity of biochemical processes. J. V. MEDVEDEV (Bull. Acad. Sci. U.S.S.R., 1931, 345—360).—A theoretical discussion of such points as Willstatter's results, indicating the possibility of the direct fermentation of polysaccharides without previous hydrolysis, and the disparity between the rates of fermentation by zymase and by living yeast. T. H. POPE.

Fermentation and growth in dry yeast cells. III. C. BARTHEL, H. VON EULER, and R. NILSSON (Z. physiol. Chem., 1931, **198**, 251—259; cf. A., 1929, 1199).—A prep. of dry yeast made by EtOH and Et_2O treatment from a sample showing no autofermentation (absence of reserve carbohydrate) contained no cells capable of reproduction, although the fermentative power was practically unchanged.

J. H. BIRKINSHAW.

Specific activators of enzymic carbohydrate fission. H. VON EULER and R. NILSSON (Arkiv Kemi, Min., Geol., 1931, **10**, **B**, No. 14, 6 pp.).—Dried bottom yeast (washed with $0{\cdot}1N$-KH_2PO_4) in presence of dextrose, phosphate, Na hexosediphosphate, and co-enzyme ferments only on addition of 10^{-4} to $10^{-1}M$-$MgCl_2$. Such a yeast reduces methylene-blue, the reduction being accelerated on addition of Mg. The decrease in the amount of MeCHO disappearing and the simultaneous increase in CO_2-evolution when Mg is added to a yeast fermentation appear to be related to the antagonism of the metal to fluorides. Mg also stimulates phosphoric ester formation. The degradation of both hexose-mono- and -di-phosphoric acid is activated by muscle-adenylic acid, which, however, cannot replace the co-zymase with either dextrose or hexosediphosphate as substrate. F. O. HOWITT.

Co-zymase. XVIII. H. VON EULER and K. MYRBACK (Z. physiol. Chem., 1931, **198**, 219—235; cf. A., 1930, 1318).—No separation of an adenylic acid fraction from highly active co-zymase was attainable with $Ba(OH)_2$. Uranyl acetate ppts. the whole of the active portion. The isolation from yeast of co-zymase of activity coeff. 100,000 in about 40% yield is described. The preps. have a composition closely related to those of the adenine nucleotides.

J. H. BIRKINSHAW.

Properties of highly purified co-zymase preparations. K. MYRBACK and H. VON EULER (Z. physiol. Chem., 1931, **198**, 236—246).—The reaction consts. for elimination of H_3PO_4 in acid solution, inactivation at 100°, and elimination of adenine from co-zymase are 2, 120, and 50×10^{-3}, respectively. The co-enzyme thus falls in the inosic acid group: hence hydrolysis of the nucleotide or elimination of H_3PO_4 does not explain the inactivation. Changes in optical rotation were followed under various conditions.

J. H. BIRKINSHAW.

Reactivation of reductase in washed yeast preparations. A. HARDEN and M. G. MACFARLANE (Biochem. J., 1931, **25**, 818—821).—The addition of lactate, succinate, or methylglyoxal restores the power of reducing methylene-blue to yeast preps. washed to a point at which no fermentation of hexosediphosphate occurs. Co-enzyme is probably not required for the action of the reductase in yeast preps.

S. S. ZILVA.

Fermentation by yeast preparations. I. Effect of monoiodoacetate on the fermentation of hexosediphosphate. II. Action of arsenate on the induction period of zymin. M. G. MACFARLANE (Biochem. J., 1931, **25**, 822—828).—The fermentation of hexosediphosphate by hexosephosphatase and arsenate (A., 1930, 1317) is inhibited by monoiodoacetate. The esterification of sugar by yeast-juice is inhibited by this compound in concentrations which only slightly inhibit that of glycogen. Arsenate does not accelerate the rate of fermentation by yeast-juice in presence of monoiodoacetate. The rate of liberation of inorg. phosphate during the induction period of zymin fermentation is not accelerated by arsenate. S. S. ZILVA.

Temperature-constant and -coefficient of the fermentation of press-juice and of maceration-juice. S. KOSTYTSCHEV and G. MEDVEDEV (Z. physiol. Chem., 1931, **197**, 213—218).—The temp. coeff. of fermentation by press-juice and maceration-juice increases rapidly as the temp. falls. This behaviour is similar to that of living yeast fermentation and is contrasted with the const. temp. coeff. shown by enzyme actions. J. H. BIRKINSHAW.

Decomposition of malic acid by various *Saccharomyces* from fruit and grape wines. A. OSTERWALDER (Landw. Jahrb. Schweiz, 1930, **44**, 515—516; Chem. Zentr., 1931, i, 1983—1984).—Yeast reproduced after cessation of fermentation, with access of air and disappearance of alcohol, decomposes malic acid, but without formation of lactic acid.

A. A. ELDRIDGE.

Enzyme formation in *Penicillium glaucum*. I.—III. S. WADA (Acta Schol. Med. Kioto, 1930, **13**, 128—144, 145—157, 158—161).—When the mould is grown on a protein- and carbohydrate-free medium (salts and glycerol) it contains deamidases, urease, a glucosamine-splitting enzyme, nuclease, pepsin- and trypsin-like enzymes, and erepsin. It does not show the relation between the nutrient medium and enzyme exhibited by bacteria. Lactase and glycolytic enzyme were absent. The culture liquid contains nuclease, pepsin, glycogenase, invertase, a glucosidase, a lipase, and a hippuric acid-splitting enzyme. When protein and carbohydrate are absent the pepsin, trypsin, and lipase content is greatly decreased.

CHEMICAL ABSTRACTS.

Production of gas and acid in the spontaneous fermentation of rye groats infusion. E. BECCARD (Z. ges. Getreidew., 1930, **17**, 128—134, 150—153; Chem. Zentr., 1931, i, 2072).—H_2, N_2, CO_2, and volatile acids are formed in irregularly varying quantities.

A. A. ELDRIDGE.

Bacterial chalk deposition in tropical seas. W. BAVENDAMM (Ber. deut. bot. Ges., 1931, **49**, 282—287).—In preference to the views that $CaCO_3$ is deposited by purely physico-chemical action, by the

action of bacterially produced CO_2 on CaC_2O_4 from higher plants, or by the interaction of bacterially produced $(NH_4)_2CO_3$ with $CaSO_4$, it is suggested that anaerobic bacteria reduce $CaSO_4$ to CaS, which reacts thus : $CaS+CO_2+H_2O=CaCO_3+H_2S$.
F. O. Howitt.

Nitrogen fixation and ammonia production by *Azotobacter*. S. Kostytschev and A. Scheloumov (Z. physiol. Chem., 1931, **198**, 105—114).—NH_3, the first detectable product of N fixation, is formed in presence of an excess of carbohydrate. *Azotobacter Winelandii* also produces NH_3 by dissimilation (probably deamination) of N compounds, but only in the absence of the N-free (*i.e.*, carbohydrate) material. Both types of NH_3 production are brought about only by living cultures. In an O_2-free atm. the *Azotobacter* cultures are not killed, but the N-fixation is strongly depressed. J. H. Birkinshaw.

Respiration studies on *Azotobacter* under controlled conditions. J. M. Fife (Science, 1931, **73**, 533—534).—Measurements of the metabolic activity of *A. chroococcum* under different partial pressures of O_2 showed that the rate of respiration increased linearly to a const. value at 78% O_2 (cf. A., 1929, 473). L. S. Theobald.

Nitrite formation by soil bacteria other than *Nitrosomonas*. D. W. Cutler and B. K. Mukerji (Proc. Roy. Soc., 1931, B, **108**, 384—394).—Four species of non-sporing soil bacteria differing widely from *Nitrosomonas* or *Nitrosococcus* were capable of oxidising NH_4 salts to nitrite, some being able to assimilate nitrites. Nitrite production was stimulated by aeration and by the presence of 0·1% of sucrose in the medium. A. G. Pollard.

Occurrence of porphyrins in cultures of *C. diphtheriæ*. C. B. Coulter and F. M. Stone (J. Gen. Physiol., 1931, **14**, 583—596).—A new complex porphyrin with absorption max. at 574 and 537 mμ has been detected in liquid cultures of *C. diphtheriæ*. It contains Fe and Cu and coproporphyrin and shows an oxidation–reduction change. The amount present is proportional to the biological titre of the culture filtrate. It is suggested that both porphyrin and toxin are derived from the cytochrome of the bacilli.
R. K. Callow.

Immunological relationships among the pneumococci. VI. Anaphylaxis and precipitation between antigens and antisera of yeast and of type II pneumococci. J. Y. Sugg and J. M. Neill (J. Exp. Med., 1931, **53**, 527—534).
Chemical Abstracts.

Oxidation–reduction potentials of hæmolytic streptococci. II. Effect of catalase. L. F. Hewitt (Biochem. J., 1931, **25**, 858—862).—Catalase inhibits peroxide formation in cultures of hæmolytic streptococci. When catalase is added reducing conditions are maintained after the logarithmic phase of growth, and the high level corresponding with peroxide formation is not reached in aerated cultures. In cultures containing peroxide catalase causes an immediate and rapid fall in potential despite the resulting vigorous oxygenation of the culture.
S. S. Zilva.

Decomposition of hemicelluloses by *Bacillus gelaticus*, Gran. W. Bavendamm (Ber. deut. bot. Ges., 1931, **49**, 288—290).—The bacillus, isolated from marine mud-banks, hydrolyses starch and mannan, whilst agar is readily decomposed, serving as a source of energy in presence of nitrates. F. O. Howitt.

Respiration of *B. coli communis*. R. P. Cook and J. B. S. Haldane (Biochem. J., 1931, **25**, 880—887; cf. this vol., 769).—The velocity of oxidition of dextrose, succinate, and lactate by *B. coli* at 16° does not reach a max. until more than 1 hr. has elapsed, owing to the gradual production of further metabolites. In the presence of formate the rate of O_2 uptake became const. after 30 min. as in the presence of PhMe. The effects of CO and HCN on these oxidations differ greatly. S. S. Zilva.

Mechanism of the antiseptic action of lactic acid for *B. coli*. D. Bach (Compt. rend., 1931, **192**, 1680—1682).—Superimposed on the inhibitor factor due to p_H produced in the glucose–peptone medium there is the toxic factor due to the undissociated lactic acid mol. C. C. N. Vass.

Action of acetone extracts of tubercle bacillus on pathogenic properties of the filtrate of the tubercle virus. L. Negre and J. Valtis (Ann. Inst. Pasteur, 1931, **46**, 587—597).—Repeated subcutaneous injections of $COMe_2$ extracts of *B. tuberculosis* into guinea-pigs inoculated with a T. B. filtrate restore its virulence. Acetone extracts of *B. paratuberculosis* or olive oil are inactive. This technique has been successfully used for diagnostic purposes.
C. C. N. Vass.

Filtrates containing the filtrable element of the tubercle virus. C. Ninni (Ann. Inst. Pasteur, 1931, **46**, 598—603).—Young, rapidly grown cultures only yield filtrates of the ultravirus. The cultures are mixed with a min. quantity of saline and sterile sand, diluted with saline, and kept at 0° for 2 or 3 days before filtering first through paper and then through a candle. C. C. N. Vass.

Action of pancreatic juice on tubercle bacilli. K. Vietorisz (Magyar Orvosi Arch., 1930, **31**, 546—560; Chem. Zentr., 1931, i, 1933—1934).—Destructive fermentation takes place. A. A. Eldridge.

Detachment of bacteriophage from its carrier particles. D. M. Hetler and J. Bronfenbrenner (J. Gen. Physiol., 1931, **14**, 547—562).—Diffusion experiments show that phage in lytic broth filtrate is associated with particles of mean radius 4·4 mμ; particles of radius 0·6 to 11·5 mμ can be separated by ultrafiltration. Under certain conditions the active agent can be transformed from larger into smaller particles. R. K. Callow.

Effects of ultra-violet light on *Paramecium*. L. B. Rentschler (Science, 1931, **73**, 480—481)—*Paramecium* gives a pale violet fluorescence when exposed to the light from a Hg-vapour lamp; the proteins of the cytoplasm are coagulated.
L. S. Theobald.

Electrosterilisation. I. II. Relative antibacterial effects of different electrodes. III. Single and multiple electrodes. L. I. Grossman and J. L. T. Appleton, jun. (Dental Cosmos, 1931,

73, 147—160, 250—253, 370—373).—Under the conditions tolerated, with oral bacteria, the anti-bacterial effect was greater at the anode; ZnI_2 was more efficient than KI. The effect depended on both the electrode and the electrolyte. The effect from a single electrode is greater than that of each member of a multiple electrode system. CHEMICAL ABSTRACTS.

Influence of soaps on the germicidal properties of certain mercurial compounds. B. HAMPIL (Amer. J. Hyg., 1931, **13**, 623—637).—The presence of Na oleate (1%) greatly increases the toxicity of $HgCl_2$ to virulent staphylococci at 37°; with other organisms different results were obtained. The toxicity of $Hg(CN)_2$ and *o*-chloromercuriphenol is increased by soap. A. A. ELDRIDGE.

Reality, nature, and localisation of "virtual" adrenaline. M. PAGET (J. Pharm. Chim., 1931, [viii], **13**, 617—626).—A modified colorimetric method (cf. A., 1929, 462) is described for determining adrenaline in suprarenal glands. The increase in adrenaline content observed when the glands are kept in a vac. over H_2SO_4 is confirmed by biological determinations. The nature of the "protoadrenaline" from which the "virtual" adrenaline is formed is undecided. Like the free adrenaline, it is concentrated in the medulla. R. K. CALLOW.

Preparation of adrenal extract. F. A. HARTMAN and K. A. BROWNELL (Science, 1931, **73**, 620).—Details are recorded. L. S. THEOBALD.

Cortico-adrenal hormone. S. W. BRITTON and H. SILVETTE (Science, 1931, **73**, 322—323).—Results obtained with cortico-adrenal extracts prepared by Swingle and Pfiffner's method and by Hartman's are discussed; they show that extracts prepared by the former method contain considerable amounts of the cortico-adrenal hormone, the presence of which is also indicated in some preps. made by the latter method. L. S. THEOBALD.

Influence of the adrenals on the residual nitrogen of the organism. G. WILL (Arch. exp. Path. Pharm., 1931, **160**, 317—328).—The residual N of the tissues of rabbits increases after adrenalectomy and after large doses of adrenaline, but this effect of adrenaline is exhibited only in presence of hormone produced by the adrenal cortex. Administration of uric acid causes a greater increase of residual N in adrenalectomised than in normal rabbits. W. O. KERMACK.

Blood-sugar response to intravenous insulin in normals and in diabetics. W. S. COLLENS and H. G. GRAYZEL (Proc. Soc. Exp. Biol. Med., 1931, **28**, 487—489).—Equiv. intravenous doses of insulin, on the basis of body-wt., produce a much greater fall in blood-sugar in diabetic than in normal man. CHEMICAL ABSTRACTS.

Distributions and concentrations of water and halides in the blood and urine during diuresis-inhibition by pituitary extract. A. R. MCINTYRE and H. B. VAN DYKE (J. Pharm. Exp. Ther., 1931, **42**, 155—168).—Administration of the extract of the posterior lobe of the pituitary to a dog so as to produce inhibition of diuresis causes a slight but definite increase in the water content of erythrocytes and serum and a slight fall in the concentration of halide, but has no effect on the distribution of Cl and Br between erythrocytes and serum. The extract produces no change on the serum-halide concentration of nephrectomised dogs. Posterior pituitary extract causes diuresis-inhibition in dogs probably solely through its direct action on the kidneys. W. O. KERMACK.

Inactivation by proteolytic enzymes of the anterior pituitary hormone from urine of pregnancy. M. REISS, A. SCHAFFNER, and F. HAUROWITZ (Endokrinol., 1931, **8**, 22—24; Chem. Zentr., 1931, i, 2075).—The hormone is inactivated by activated trypsin, but not by pepsin at p_H 3—4, polypeptidase, or protamine-splitting enzymes. A. A. ELDRIDGE.

Diffusibility of female sex hormone into the spinal fluid and its relationship to the oxytocic activity of spinal fluid. R. W. WHITEHEAD and O. L. HUDDLESTON (J. Pharm. Exp. Ther., 1931, **42**, 197—211).—The intravenous injection of œstrus-producing preps. into dogs results in the appearance of the active principle in the cerebrospinal fluid. When certain preps. which had oxytocic activity were employed, the cerebrospinal fluid developed an oxytocic action, but this did not occur when highly purified preps., themselves devoid of oxytocic activity, were injected. W. O. KERMACK.

Antagonism between follicular and corpus luteum hormones. R. COURRIER (Compt. rend. Soc. Biol., 1930, **104**, 280—282; Chem. Zentr., 1931, i, 2075).—Large doses of folliculin repress the decidual reaction of the corpus luteum in guinea-pigs. A. A. ELDRIDGE.

Ovarian hormone. Biological assay. A. NOVELLI (Anal. Farm. Bioquím., Supl., 1931, **2**, 69—87).—A review. R. K. CALLOW.

Influence of vitamin-*D* and parathyroid hormone on calcium economy. F. HOFF and E. HOMANN (Z. ges. exp. Med., 1930, **74**, 258—273; Chem. Zentr., 1931, i, 1938).—After 50 injections of 50 units of parathyroid hormone the blood-Ca and -K increase, and the K : Ca quotient and the alkali reserve fall. Calcification of bone produced by vitamin-*D* is prevented by parathyroid hormone, but deposition of Ca in organs produced by excessive administration of vitamin-*D* is increased by simultaneous administration of parathyroid hormone. A. A. ELDRIDGE.

Effect of thyroxine on the blood-sodium chloride. E. COELHO and J. C. OLIVEIRO (Compt. rend. Soc. Biol., 1930, **105**, 801—802; Chem. Zentr., 1931, i, 2076).—The corpuscular, and sometimes the plasma-, Cl is diminished. A. A. ELDRIDGE.

Effect of injection of thyroxine on the urinary carbon and nitrogen. G. FONTES and L. THIVOLLE (Compt. rend. Soc. Biol., 1930, **105**, 558—559; Chem. Zentr., 1931, i, 1778).—Daily injection into dogs of 1 mg. of thyroxine increases the urinary C and N, but the ratio C : N remains unchanged. A. A. ELDRIDGE.

Effect of thyroidectomy and subsequent injection of thyroxine on the urinary carbon and nitrogen. G. FONTES and L. THIVOLLE (Compt. rend. Soc. Biol., 1930, **105**, 559—561; Chem. Zentr., 1931, i, 1778).—After thyroidectomy a transitory increase in both C and N is followed by an increase in N

only; after injection of thyroxine (1—3 mg. daily) the excretion of C increases and the quotient C : N becomes normal, although the quantities excreted remain high. A. A. ELDRIDGE.

[Carotene and] vitamin-*A*. P. KARRER, B. VON EULER, H. VON EULER, H. HELLSTROM, and M. RYDBOM (Arkiv Kemi, Min., Geol., 1931, **10**, **B**, No. 12, 6 pp.).—Ox-blood corpuscles are poor in carotene even when the serum is rich in the pigment. Human serum has a carotene content averaging 0·8 Lovibond unit per 10 c.c. following isolation and treatment with $SbCl_3$ in $CHCl_3$. The serum-carotene varies considerably in different animals; in herbivorous animals it is higher than in man or rat and it is higher in the summer than in the winter. Calves fed on milk poor in vitamin-*A* have a low serum-carotene value. Absorption spectra of serum indicate the presence only of carotene; the Lovibond units ($SbCl_3$ reaction), however, do not agree with direct colorimetric determination. Examination by spectrophotometry and by the $SbCl_3$ reaction shows that in fish oils a growth factor different from carotene is present. Carotene is provitamin-*A* and is considered to be reduced to the vitamin by a liver-carotenase. Carotene is absent from barley shoots, extracts of which and also of the sea-weed *Fucus vesiculosus* were investigated spectrophotometrically. F. O. HOWITT.

Vitamin actions of carotene. H. VON EULER and M. RYDBOM (Arkiv Kemi, Min., Geol., 1931, **10**, **B**, No. 10, 6 pp.).—Carotene may be replaced by xanthophyll as a source of vitamin-*A* in chicks but not in rats owing to incomplete absorption by the latter. Injected intramuscularly, carotene dissolved in arachis oil results in less growth than when administered orally. Carotenoids occur in the eggs of the herring, perch, pike, cod, and to a smaller extent in pike spermatozoa where xanthophyll predominates. Fresh mature roe contains carotenoids equiv. to about 0·10 mg. of carotene per g. The gynæcium of the *Liliaceæ* and microspores of *Alnus glutinosa* are poor in carotenoids. F. O. HOWITT.

Antimony trichloride colour test for vitamin-*A*. W. R. BRODE and M. A. MAGILL (J. Biol. Chem., 1931, **92**, 87—98).—The normal $SbCl_3$ test (A., 1926, 870) for vitamin-*A* often produces a solution having two absorption bands, 578 mμ and 608 mμ, both of which fade and are replaced by bands at 472 and 532 mμ, there being a relation between the extinction coeff. of the two sets. By the use of a saturated (18·5%) $CHCl_3$ solution of $SbCl_3$ and of certain concentrations of cod-liver oil only the 608 mμ band is produced, the extinction coeff. of which is then proportional to the concentration of oil. F. O. HOWITT.

Growth-promoting vitamin in liver-fat. P. KARRER, H. VON EULER, and H. HELLSTROM (Svensk Kem. Tidskr., 1931, **43**, 138).—An absorption band at 328 mμ occurs in the ultra-violet spectrum of shark oil in agreement with liver-oil (A., 1928, 1058; 1930, 380). Reduced forms of carotene, some of which possessed growth-promoting properties, previously exhibited no well-marked bands in the ultraviolet spectrum. Reduction of carotene by Al–Hg has now given a substance with characteristic lines at 315, 328—330, and 370 mμ, supporting the suggestion that the vitamin-*A* of animal oils is a hydrogenation product of carotene (cf. A., 1929, 1202). F. O. HOWITT.

Vitamin-*A* in butter-fat. M. LUNDBORG (Biochem. Z., 1931, **235**, 1—13).—The colorimetric vals. ($SbCl_3$) for butter-fat give greater vals. for the carotene content than those obtained by direct colorimetric comparison with a solution of known carotene content. A known amount of added carotene can be determined in the hydrolysis residue by the colorimetric method, carotene being uninjured during hydrolysis of fat. During saponification a yellow colour is produced which makes it impossible to use direct colorimetric comparison except after addition of $SbCl_3$. P. W. CLUTTERBUCK.

Occurrence of vitamin-*A* in cocoa and its extraction products. H. LABBE, H. DE BALSAC, and R. LERAT (Bull. Soc. Ther., 1930, 12 pp.; Chem. Zentr., 1931, i, 2079).—The results of tests with $AsCl_3$ and $SbCl_3$ are tabulated. Cacao butter contains a small quantity of vitamin-*A*. A. A. ELDRIDGE.

Vitamin. XVIII. Biological assay of food materials for vitamin-*A* as influenced by yeast from various sources. H. E. HONEYWELL, R. A. DUTCHER, and J. O. ELY (J. Nutrition, 1931, 3, 491—498).—The vitamin-*A* response depends on the sample of yeast used as source of vitamin-*B*. Vitamin-*A* may consist of two factors, antiophthalmic and growth-stimulating. CHEMICAL ABSTRACTS.

Effect of vitamin-*B* deficiency on the vitamin-*A* reserves of the rat. W. J. DANN and T. MOORE (Biochem. J., 1931, **25**, 914—917).—There is no material diminution in the vitamin-*A* reserves of the liver of albino rats, previously fed on diets containing large amounts of carotene, when severely emaciated as a result of a dietetic deficiency in the vitamin-*B* complex. S. S. ZILVA.

Nutrition. X. Comparative vitamin-B_1 values of foodstuffs. Cereals. II. R. H. A. PLIMMER, W. H. RAYMOND, and J. LOWNDES (Biochem. J., 1931, **25**, 691—704).—The following are the comparative vitamin-*B* values obtained from the maintenance values for pigeons: dried yeast 100, marmite 67, wheat germ ("bemax") 62, middlings 40, baker's yeast 33, bran 20, buckwheat 20, millet 13, oatmeal 11, wheat 10, barley 10, malt 10, rye 10, dari 10, brown rice 10. S. S. ZILVA.

Preparation and behaviour of vitamin-B_1 concentrates from yeast. B. C. GUHA (Biochem. J., 1931, **25**, 931—944).—Preps. were obtained at the Pt stage (cf. A., 1929, 1496) which promoted good growth in rats in daily doses of 0·075—0·1 mg. The curative day dose for pigeons is about 0·047 mg. Vitamin-B_1 is not identical with co-zymase, secretin, or "bios," and the concentrates show no sp. absorption spectrum. Adenine, guanine, uracil, *dl*-thyroxine, histamine, and adrenaline cannot replace vitamin-B_1 in the diet of rats. S. S. ZILVA.

Vitamin-B_2. I. Sources. II. Stability. III. Chemistry. B. C. GUHA (Biochem. J., 1931, **25**, 945—959).—Milk powder, aq. extracts of brewer's yeast, baker's yeast, beef-muscle, Lilly's liver concen-

trate No. 343, and fresh ox-liver contain the vitamin. The last extract is the most potent. The stability of vitamin-B_2 depends on the source. An aq. extract of the liver concentrate autoclaved at p_H 9 for 30 min. at 124—125° is an excellent source of vitamin-B_2 free from vitamin-B_1. Picric acid, BzCl, phosphotungstic acid, and flavianic acid do not ppt. vitamin-B_2 from an aq. extract of liver. HNO_2 neither ppts. nor inactivates it. $Pb(OAc)_2$ and $AgNO_3$ ppt. it partly. Esterification inactivates it partly. It is not acted on by trypsin. Norite adsorbs it at p_H 4·6. It is not possible to elute it effectively by aq. EtOH, 30% PrOH, or saponin.

The vitamin is stable to SO_2, H_2O_2, and O_3. Rats not undergoing a drastic deprivation of vitamin-B_2 develop a form of depilation which is cured by the administration of the liver extract, but not by that of hæmin, hæmoglobin, or lactalbumin, which show no vitamin-B_2 activity. S. S. ZILVA.

Determination of vitamin-*C*. K. M. KEY and G. K. ELPHICK (Biochem. J., 1931, **25**, 888—897).—The method is based on the degree of protection afforded by the tested substance against the histological changes which take place in the teeth of young guinea-pigs subsisting on a scorbutic diet. The assessment is referred to a curve constructed from data obtained with different doses of orange-juice. S. S. ZILVA.

Fat-soluble vitamins. S. SCHMIDT-NIELSEN (Svensk Kem. Tidskr., 1931, **43**, 141—155; cf. A., 1930, 1222)—An examination of the following fishes: *Chimæra monstrosa, Somniosus microcephalus, Etmopterus spinax, Squalus acanthias, Cetorhinus maximus, Lamna cornubica, Raja fullonica, Raja oxyrhynchus, Gadus morrhua*, indicated that the vitamin-*D* content of the liver oils showed a relationship to the total Ca content of the fish. On the other hand, examination of the liver fat of various sea and land mammals (whales, oxen, pigs, etc.) showed no such corresponding relation, all these creatures having a very low content of vitamin-*D*. Liver oil from certain bony fish such as salmon, flounder, and tunny contains unusual amounts of vitamin-*D*; the last-named is especially rich in this constituent, and contains, in addition, the largest proportion of vitamin-*A* hitherto found. An explanation of the above irregular variations cannot as yet be given. H. F. HARWOOD.

Ultra-red absorption spectrum of ergosterol and of the antirachitic substance. W. HIRSCH and L. KELLNER (Biochem. Z., 1931, **235**, 162—169).—The ultra-red absorption spectrum of ergosterol has only one band at 3·71 μ, whilst that of irradiated ergosterol has two bands, one as above and a second, much fainter, at 0·976 μ. Irradiated ergosterol in this range has a greater absorption than ergosterol.

P. W. CLUTTERBUCK.

Toxicity of vitamin-*D*. J. B. DUGUID (Lancet, 1930, ii, 983—984).—A *résumé* of pathological effects in animals resulting from overdosage with vitamin-*D*.

L. S. THEOBALD.

Overdosage of vitamin-*D*. II. R. F. LIGHT, G. E. MILLER, and C. N. FREY (J. Biol. Chem., 1931, 92, 47—51; cf. A., 1930, 119).—Moderate daily administration (40 units) of vitamin-*D* to rats has no influence on the calcification or ash content of the bones when continued through to the fourth generation. Such animals are, however, more susceptible to massive overdosage than normal animals. Overdosage (2500 units daily) just insufficient to produce toxic symptoms in the first and second generations produces pathological changes (decalcification of the bones, calcification of the kidneys, and certain pellagra-like symptoms) in the third and fourth generations.

F. O. HOWITT.

Increasing the vitamin-*D* potency of cow's milk by the daily feeding of irradiated yeast or irradiated ergosterol. B. H. THOMAS and F. L. MACLEOD (Science, 1931, **73**, 618—620).—Addition of irradiated yeast or irradiated ergosterol to the diet increased the vitamin-*D* potency of cow's milk up to 16 times. L. S. THEOBALD.

Rickets. IV. [Non-]formation of protective substance in germination of various seeds in the dark. P. GYÖRGY and H. SCHALL (Jahrb. Kinderheilk., 1929, **124**, 260—267; Chem. Zentr., 1931, i, 2079—2080).—Seeds germinated in the dark and ergosterol exposed to Gurwitsch radiation possessed no vitamin-*D* activity. A. A. ELDRIDGE.

Vitamin-*D* in whole maize. H. GOLDBLATT (Science, 1931, **73**, 494—495.—The unexpected non-production of rickets occurring with certain diets may be due to the settling out of $CaCO_3$ and a fall in ratio Ca : P below the necessary val. A method of avoiding this is described. L. S. THEOBALD.

Certain factors necessary for the normal nutrition of the rat. B. C. GUHA (Biochem. J., 1931, **25**, 960—971).—Yeast contains a factor other than vitamin-B_1 or -B_2, and milk contains a factor other than those present in yeast. The latter is not identical with vitamin-*A*, -*D*, -*C*, or -*E*. It is inactivated by autoclaving and is also present in egg-yolk, egg-white, spinach, grass, lucerne, and to a smaller extent in pig- and sheep-liver. It is not replaceable by carotene or chlorophyll. Milk and "light white casein" vary in their content of the factor. Male rats are more responsive than females. S. S. ZILVA.

Conditions of assimilation in tropical rain forests. O. STOCKER (Ber. deut. bot. Ges., 1931, **49**, 267—273).—A study of the respiration and assimilation of the leaves of 3 tropical trees (*Stelechocarpus burahol, Cassia fistula*, L., and *Calophyllum inophyllum*, L.) shows an extensive adaptation for high temps. There is a fall in the optimum of assimilation but no abs. increase in the amount of assimilation. The CO_2 content of the air in rain forests is slightly less than in temperate forests. F. O. HOWITT.

Glutathione, growth, and cancer of plants. L. BINET and J. MAGROU (Compt. rend., 1931, **192**, 1415—1416).—The growing tumour of a plant (*Pelargonium zonale*) inoculated with *B. tumefaciens* contains more glutathione than does the green stem, the flower bud, or the open flower. A still higher content is, however, found in the rapidly growing terminal bud, whilst that in the tumour disappears after necrosis, and consequently it is considered that the glutathione content is a function of the rapidity of growth. H. A. PIGGOTT.

Effects of X-rays on the growth of wheat seedlings. W. Cattell (Science, 1931, **73**, 531—533).—Average results for hundreds of measurements are summarised graphically. The order of increasing effect is coleoptiles, leaves, primary roots, and lateral roots. Vitamin-*B* in the embryo is destroyed by excessive exposure to *X*-rays. L. S. Theobald.

Protein studies. X. Glutenin in different forms of wheat. XI. Gliadin in different forms of wheat. K. Kondo and T. Hayashi. **XII. Globulins of polished rice.** K. Kondo and T. Ito (Mem. Coll. Agric. Kyoto, 1931, No. 11, 1—19, 21—29, 31—35).—X. Glutenin from various sources was freed from globulin by stirring with 0·5*N*-NaCl solution (yields, 3·04—7·67 g. per kg. of flour; 17·30—17·66% N). The isoelectric points of different samples were identical in AcOH–acetate buffer (p_H 5·19—5·58) and in citric acid–phosphate buffer, although invariably more acid in the latter medium (p_H 4·57—4·98). Admixture of 10% of gliadin does not alter the isoelectric point.

XI. Gliadin was extracted from crude gluten by means of 70% EtOH. The amounts obtained from different sources were 5·42—17·94 g. per kg. of flour and its N content was 17·40—17·65%. The isoelectric point, determined by addition of phosphate or AcOH–acetate either to a 70% EtOH solution or to an alkaline solution of gliadin, is identical for different samples (p_H 6·41—6·59). The precipitation at the isoelectric point is greater in AcOH–acetate buffer (92·03%) than in phosphate buffer (80·76—81·75%).

XII. A cryst. globulin (p_H 3·98—4·61) was isolated from rice flour, which was poorer in diamino-acids than the non-cryst. globulin also obtained (p_H 3·89). P. G. Marshall.

Urea and ureides in the higher plants. I. Occurrence of urea in the vegetable kingdom and its transformation during the vegetative period. G. Klein and K. Taubock [with H. Linser] (Jahrb. wiss. Bot., 1930, **73**, 194—225; Chem. Zentr., 1931, i, 1298—1299).—The xanthhydrol reaction has been employed for the approx. determination of free or ureide-urea in plant organs and of its variation during the vegetative period. A. A. Eldridge.

Volatile nitrogenous bases in higher plants. M. Steiner (Beitr. Biol. Pflanzen, 1929, **17**, 247—258; Chem. Zentr., 1931, i, 1298).—In general, leaves contain gaseous NH_3; the occurrence of NMe_3 in *Amorphophallis Rivieri* was followed as regards stage of growth and organs. Previous observation of the occurrence of $NHMe_2$ and NMe_3 in the fruit of *Phallus impudicus* was confirmed. Nicotine was detected by means of the reaction with dinitronaphthol in various organs of *Nicotiana rustica*. *Allium ursinum* contains no amine in the flowers or leaves. A. A. Eldridge.

Nitrogenous bases in the protein synthesis of higher plants. II. Distribution and transportation of ammonia and volatile amines. M. Steiner and H. Loffler (Jahrb. Wiss. Bot., 1929, **71**, 463—532; Chem. Zentr., 1931, i, 1298).—NH_3 is liberated from the tissue preferably with 5% aq. Na_2CO_3 and 5% aq. NaCl; tests for various amines were critically examined. Numerous plants were tested histochemically. Amines, particularly NMe_3, *iso*amylamine, and *iso*butylamine, were found in 48 species. A. A. Eldridge.

Total nitrogen in Bartlett pear shoots. A. S. Mulay (Plant Physiol., 1931, **6**, 333—338).—Individual shoots, whether from the same or different trees, vary considerably in N content, the variations being of the same order in both cases. Bark and wood from green shoots have less total N than those from brown shoots. A sample of 35—40 shoots is necessary to obtain results with an experimental error of ±5%. A. G. Pollard.

Volatilisation of nicotine from the tobacco plant. J. Chaze (Compt. rend., 1931, **192**, 1268—1269).—Nicotine is identified by means of the cryst. ppt. deposited on passing air over the leaves into aq. silicotungstic acid. C. C. N. Vass.

F.-p. determination of physiological solutions. J. M Johlin (J. Biol. Chem., 1931, **91**, 551—557).—The f. p. of a small vol. of aq. solution is determined with a min. of supercooling by seeding with small metal rings cooled in solid CO_2 and covered with frost. R. K. Callow.

Acetate–veronal buffer. L. Michaelis (Biochem. Z., 1931, **234**, 139—141).—The prep. of this buffer solution is described and a table indicates the p_H range 9·64—2·62. P. W. Clutterbuck.

Oxidimetric determination of small amounts of alcohol. L. Smith (Svensk Kem. Tidskr., 1931, **43**, 83—98).—A modification of Widmark's micromethod for the determination of EtOH in blood (A., 1922, ii, 789). EtOH is absorbed in 2 c.c. of conc. H_2SO_4 in a stoppered flask maintained at 60° for 30—120 min. in a thermostat. 0·1 c.c. of 0·1*N*-$K_2Cr_2O_7$ is then added, and the flask replaced in the thermostat for 30 min. Water is added, followed by a slight excess of standard arsenite solution, and the excess of the latter is titrated with $KBrO_3$. The method has been employed to determine the concentration of EtOH in human breath. H. F. Harwood.

Colorimetric determination of potassium in small amounts of biological fluids. M. Dreguss (Biochem. Z., 1931, **233**, 375—380).—The K in 0·05—0·1 c.c. of biological fluid is precipitated as K Na cobaltinitrite, the ppt. is dissolved by addition of Griess–Ilosvay reagent, and the colour of the solution is compared with that of a standard. The results deviate, on the average, about 2·5% from those obtained by the method of Kramer and Tisdall (A., 1921, ii, 412). W. McCartney.

Determination of copper in biological material. J. M. Inouye and F. B. Flinn (J. Lab. Clin. Med., 1930, **16**, 49—51).—An electrolytic method is described. Chemical Abstracts.

Micro-determination of tungsten. L. Pincussen and B. Minz (Biochem. Z., 1931, **234**. 19—24).—A colorimetric method is described for the determination of 0·1—10 mg. of W depending on the production of a blue colour on alkalising the tungstate after reduction with quinol in acid solution. The presence of P and Fe invalidates the method. In blood and tissues the method is not as sensitive, owing to difficulties in ashing, and only detects amounts of the order of 5 mg. P. W. Clutterbuck.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

SEPTEMBER, 1931.

General, Physical, and Inorganic Chemistry.

Under-water spark spectra in the infra-red. B. SETNA (Indian J. Physics, 1931, 6, 29—34).—The spectra of condensed discharge under H_2O between Cu, Zn, Cd, Fe, W, and Mo electrodes have been studied in the visible and infra-red up to 0·85

A. J. MEE.

"Ultimate" radiations of condensed spark spectra. T. NEGRESCO (Bull. Mat. Phys. Ecole Poly. Bucarest, 1931, 11, 93—94).—High-potential radiations, not recorded among existing data for ultimate radiations, emitted by atoms in various states of ionisation have been found for many elements.

N. M. BLIGH.

Appearance of spectral lines in a condensed spark. H. V. KNORR (Physical Rev., 1931, [ii], 37, 1611—1621).—The variation of intensity of lines with time after the beginning of the spark, measured photometrically, gave results not in agreement with those obtained visually by the Kerr cell method. The order of appearance was, by the former method: air lines excited in the spark gap; spark lines; arc lines of Cd; arc lines of Zn. N. M. BLIGH.

Edge discharge and edge breakdown. L. INGE and B. WUL (Naturwiss., 1931, 19, 424—425).—The dependence of breakdown on edge discharge is experimentally investigated for glass plates 1·4 mm. thick in liquid media of differing dielectric const.

W. GOOD.

Quantitative spectral analysis by means of the negative glow of an arc. R. MANNKOPFF and C. PETERS (Z. Physik, 1931, 70, 444—453).—The spectrum of most substances is enhanced near the cathode of an arc, and this allows the measurement of smaller quantities than the ordinary method.

A. B. D. CASSIE.

Intensity and natural width of spectral lines. E. F. M. VAN DER HELD (Z. Physik, 1931, 70, 508—515).—Theoretical. A. B. D. CASSIE.

Field distribution and sources of error in the Stark effect using the Lo Surdo method. W. STEUBING (Ann. Physik, 1931, [v], 10, 296—310).—The relative advantage and disadvantages of the Lo Surdo method are discussed. Good spectrograms can be obtained only by keeping pressures, discharge voltage, current strength, and other conditions const. during the whole exposure. A. J. MEE.

Application of the slitless spectrograph to the measurement of the Doppler shift. N. DEISCH (J. Opt. Soc. Amer., 1931, 21, 248—249).—A supplementary note (cf. this vol., 135). W. GOOD.

Zeeman effect with high-frequency [discharge]. L. BLOCH, E. BLOCH, E. ESCLANGON, and P. LACROUTE (Compt. rend., 1931, 192, 1717—1720).—The electrodeless discharge was used. Good results were obtained with Hg and Ne in a field of 26,250 gauss.

C. A. SILBERRAD.

Temperature of the electric arc and the Saha theory. L. S. ORNSTEIN and H. BRINKMAN (Naturwiss., 1931, 19, 462—463).—Spectra from arcs of different composition are those to be expected from the Saha theory. W. R. ANGUS.

Widths of the lines in the *B* band, due to atmospheric oxygen in the solar spectrum. R. VAN DER R. WOOLLEY (Astrophys. J., 1931, 73, 185—193).—Measurements of lines in the *B* band in the solar spectrum show that the width is not in agreement with Unsold's formula.

L. S. THEOBALD.

Molecular spectra in sun-spots. R. S. RICHARDSON (Astrophys. J., 1931, 73, 216—246).—Many lines in certain bands of TiO, MgH, and CaH have been identified with lines in the solar spectrum. Evidence for the presence of SiF, AlO, AlH, ZrO, and H_2 in sun-spots and the reversing layer is also given. MgH probably exists in the reversing layer, whilst TiO is probably confined entirely to sun-spots. Both the Swan bands of C and the TiO bands are present in the spot spectrum. L. S. THEOBALD.

Interpretation of spectrophotometric observations of weak Fraunhofer lines. R. VAN DER R. WOOLLEY (Astrophys. J., 1931, 73, 194—204).—The legitimacy of inferring a number of atoms from observations of line width or equiv. breadth of a weak Fraunhofer line is discussed.

L. S. THEOBALD.

Emission spectrum of compressed hydrogen and some pressure phenomena in metal vapour spectra. W. FINKELNBURG (Z. Physik, 1931, 70, 375—394).—Spark discharges were observed in H_2 at pressures between 1 and 30 atm. Broadening of Balmer lines can be accounted for by the interat. Stark effect of fields between 2×10^5 and 2×10^6 volts per cm. Spectra due to Fe, Al, and Cu, vaporised from the electrodes, showed broadening proportional to the partial pressure of the metal vapour, and this is dependent on the total pressure.

A. B. D. CASSIE.

Continuous spectrum of the hydrogen molecule. D. CHALONGE (Compt. rend., 1931, 192, 1551—1553; cf. A., 1930, 1073).—A further elabor-

ation with illustrative curves of deductions previously arrived at. C. A. SILBERRAD.

Relationships between the continuous and the many-lined spectra of hydrogen. II. Y. HUKUMOTO (Sci. Rep. Tohoku, 1931, **20**, 178—196).—Apparatus, procedure, results, and discussion of spectroscopic examination of the light emitted from the various types of strata in the striated discharge in H_2. W. GOOD.

Stark effect in the Balmer series of hydrogen. K. SJOGREN (Naturwiss., 1931, **29**, 640).—A determination of the abs. value of the Stark effect in the Balmer series of hydrogen. A. B. D. CASSIE.

Asymmetry observed in the Stark components of H_α. D. R. MCRAE (Proc. Roy. Soc., 1931, **A**, **132**, 257—265).—With the exception of certain unexplained discrepancies, the asymmetry observed in the displacements of the Stark components of H_α is in qual. agreement with the calculations of Schlapp (A., 1928, 806). L. L. BIRCUMSHAW.

Excitation of the secondary and Balmer spectrum of hydrogen by electronic impact in molecular hydrogen and by protons of high velocity. L. S. ORNSTEIN, A. A. KRUITHOF, and W. A. M. DEKKERS (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 610—614).—Excitation curves for singlet and triplet lines in the secondary spectrum of H_2 and for Balmer lines excited in mol. H_2 are given and discussed. W. R. ANGUS.

Structure of the helium arc line 3888. R. C. GIBBS and P. G. KRUGER (Physical Rev., 1931, [ii], **37**, 1559—1561).—Three components, predicted by theory, were found. N. M. BLIGH.

Excitation potentials of metallic lithium. H. W. B. SKINNER (Nature, 1931, **128**, 114).—Photoelectric measurements give a val. of approx. 53·5 volts for the min. excitation potential for the *K*-radiation of Li metal. L. S. THEOBALD.

Intensity measurements in the band spectrum of lithium. W. R. VAN WIJK and A. J. VAN KŒVERINGE (Proc. Roy. Soc., 1931, **A**, **132**, 98—107).—The measured intensity ratio of the strong to the weak rotational lines in the bands 4900, 4838, and 6554 Å. is 1·63, in agreement with the value given by Harvey and Jenkins (A., 1930, 649). For band 4900 Å. the ratio of the *Q* to the *P* lines is 2·0. From the optical determination of the relative abundance of the isotopes the ratio of Li^7 to Li^6 atoms is 7·2 : 1; the ratio calc. from the at. wts. is 13 : 1.
L. L. BIRCUMSHAW.

Some "brush" bands of the negative nitrogen group. D. COSTER and H. H. BRONS (Z. Physik, 1931, **70**, 492—497).—Two N_2^+ bands degraded towards the red were photographed under high dispersion and are shown to belong to the same electronic transition as bands degraded towards the violet (cf. A., 1928, 808). A. B. D. CASSIE.

Absorption spectrum of oxygen at high temperatures. D. MALAN (Compt. rend., 1931, **192**, 1720—1721).—The absorption spectrum of O_2 at 1400° indicates no formation of O_3, but extension of the absorption bands as far as 2500 Å. The heads of 24 overlapping bands were observed between 2160 and 2360 Å. C. A. SILBERRAD.

Difference in the self-reversal of neon lines excited by direct and alternating currents. II. H. NAGAOKA and T. MISHIMA (Proc. Imp. Acad. Tokyo, 1931, **7**, 192—194). N. M. BLIGH.

Zeeman effect in the noble gas spectra in connexion with "anomalous" coupling of quantum vectors. C. J. BAKKER (Arch. Neerland., 1931, [III A], **13**, 121—195).—Experimental details for investigating the Zeeman effect in the spectra of ionised inert gases are described. Results for the Zeeman effect in the spectra of Ne II, A II, Kr II, and Xe II are given and discussed. W. R. ANGUS.

Intensity anomalies in rare gas spectra. E. RASMUSSEN and H. SWENSON (Nature, 1931, **128**, 188).—Intensity irregularities parallel with deviations in term values have been observed in the spectra of A and Kr. L. S. THEOBALD.

Spectrum of Na II. S. FRISCH (Z. Physik, 1931, **70**, 498—507).—The spark spectrum due to Na II was excited in a discharge tube and investigated under high dispersion. A. B. D. CASSIE.

Resonance spectrum of sulphur vapour. J. FRIDRICHSON (Z. Physik, 1931, **70**, 463—467).—Investigation of the variation with pressure of the relative intensity of the 3132 and 3126 Å. doublet series suggests that the accepted allocation of this doublet is incorrect. A. B. D. CASSIE.

Accommodation coefficients of positive ions of argon, neon, and helium. C. C. VAN VOORHIS and K. T. COMPTON (Physical Rev., 1931, [ii], **37**, 1596—1610; cf. A., 1927, 1001).—The heat produced by positive ions striking a collector and being neutralised at its surface is much less than the equiv. of the kinetic energy which they should acquire from the attracting field. Correcting for energy scattering at collisions and the effect of secondary electron emission, the accommodation coeffs. are: A 0·75$\pm$0·05, Ne 0·65$\pm$0·05, He 0·35—0·55$\pm$0·05.
N. M. BLIGH.

Band spectra of zinc hydride. M. FUKUDA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, **15**, 227—245).—The results of investigations on the band spectrum of ZnH are given and discussed.
W. GOOD.

Multiplets in the spark spectrum of bromine (Br II). L. BLOCH, E. BLOCH, and P. LACROUTE (Compt. rend., 1931, **193**, 232—233).—By the method previously described (cf. this vol., 991) two triplets belonging to the system of quintuplets of Br II have been measured. Deb's results are not confirmed (cf. A., 1930, 651). C. A. SILBERRAD.

Third spark spectrum of krypton. D. P. ACHARYA (Indian J. Physics, 1931, **6**, 35—39).—Some of the lines previously published in the list of the second spark spectrum of Kr are classified, and are due to the different transitions of Kr^{+++}. Only quadruplets have been discovered. A. J. MEE.

Absorption spectrum of rubidium vapour. S. DATTA and H. S. MAITRA (Z. Physik, 1931, **70**, 548—551).—The absorption spectrum of Rb vapour was

measured between 3000 and 8000 Å., and is arranged in term series. A. B. D. CASSIE.

Interferometric wave determinations of the Bergmann series and secondary series of rubidium. R. RAMB (Ann. Physik, 1931, [v], **10**, 311—324).—The Rb spark spectrum was investigated within the range 5169—10075 Å. From the course of the $\Delta\nu$ of the Bergmann series it may be concluded that the F-term is also inverted. A. J. MEE.

Structure of the F-term of rubidium. K. W. MEISSNER and O. MASAKI (Ann. Physik, 1931, [v], **10**, 325—328).—The conclusion of Ramb (cf. preceding abstract) on the inversion of the F-term is further investigated. A. J. MEE.

Hyperfine structure of spectrum lines of silver arc in the visible and ultra-violet regions. W. MOHAMMAD and P. N. SHARMA (Indian J. Physics, 1931, **6**, 75—80).—The lines are classified and a term scheme is drawn up. A. J. MEE.

Vibrational analysis of antimony oxide bands. B. C. MUKHERJI (Z. Physik, 1931, **70**, 552—558).—The band spectrum of Sb_2O_3 was photographed between 3300 and 8000 Å. and analysed; the heat of dissociation of the ground state is 3·5 volts. A. B. D. CASSIE.

Nuclear moment of cæsium and lead. H. KOPFERMANN (Naturwiss., 1931, **19**, 675—676).—The spectrum of Cs^+ has been investigated in the visible; it has a complicated hyperfine structure. The lines of wave-lengths 5371, 4953, 4527, and 5274 Å., however, have especially simple hyperfine structure. The rotation impulse of the Cs nucleus, i, must either be equal to or greater than 2. From the interval rule it is either 7/2 or 9/2, but it is not possible to say with certainty which of the two is correct. The spectrum of Th-Pb is also mentioned. The extraordinarily great displacement of the hyperfine structure of Pb^{206} is definitely proved. A. J. MEE.

Arc spectrum of rhenium. W. F. MEGGERS (Bur. Stand. J. Res., 1931, **6**, 1027—1050).—The arc and spark spectra from 2100 to 8800 Å. have been photographed, and more than 3000 new lines have been recorded. Hyperfine structure is observed. About 500 lines have been classified as combinations of 115 levels belonging to quadruplet, sextet, and octet systems. The ultimate line is that at 3460·47 Å. The lowest term corresponds with an ionisation potential of 7·85 volts. H. F. GILLBE.

Luminous vapours from the mercury arc. M. RAM and K. C. NANDA (Indian J. Physics, 1931, **6**, 15—27).—The luminosity of the Hg vapour distilled from the Hg arc is due to the presence of positively-charged Hg atoms. The life of the afterglow is 0·03 sec., so that the particles present in the afterglow are probably metastable Hg atoms. A. J. MEE.

Bands near the resonance line of mercury. H. HULUBEI (Compt. rend., 1931, **193**, 154—156).—Re-examination of spectrograms of the emission of a Hg lamp burning in H_2O has shown numerous bands near the resonance line (cf. this vol., 276). C. A. SILBERRAD.

Nuclear moment and explanation of hyperfine structure of mercury. H. SCHULER and J. E. KEYSTON (Naturwiss., 1931, **19**, 676).—The nuclear moment of Hg^{199} is 0·5; that of Hg^{201} is 1·5. The theoretical hyperfine structure is worked out, and the results agree with experiment. A. J. MEE.

Intensity of absorption of the 2537 Å. line by dissolved mercury. H. REICHARDT (Z. Physik, 1931, **70**, 516—518).—Hg absorbs the 2537 Å. line with equal intensity whether free or dissolved in hexane. A. B. D. CASSIE.

Hyperfine structure of Tl II. J. C. MCLENNAN and M. F. CRAWFORD (Proc. Roy. Soc., 1931, **A**, **132**, 10—21).—From a consideration of the observed intensities and separations of the components of the hyperfine multiplets, an interpretation of the hyperfine structure of Tl II has been deduced. The analysis confirms the term classification previously given (A., 1929, 1354). No evidence is found for the existence of isotopes. L. L. BIRCUMSHAW.

Applications of the differential filter method of obtaining monochromatic X-rays. H. KUSTNER (Z. Physik, 1931, **70**, 468—491; see below).—The method was applied to determination of the absorption coeff. of Sn and to determination of electron emission by Ta and W at different wave-lengths, and to an investigation of the relative intensities of the Cu series. A. B. D. CASSIE.

Relation between the K-absorption edge and the $K\beta_2$ line of nickel, copper, and zinc. S. KAWATA (Mem. Coll. Sci. Kyoto, 1931, **A**, **14**, 55—57).—Experimental. W. GOOD.

Influence of temperature on K-absorption of iron. J. D. HANAWALT (Z. Physik, 1931, **70**, 293—305).—Fine structure at 10—20 volts on the short-wave side of the Fe K-absorption edge moves away from the edge as temp. is raised, and disappears completely at 800°. Monat. gases show no such effect. A. B. D. CASSIE.

Absorption coefficient for X-rays near the K-absorption edge of Cu and Zn. D. COSTER and J. VELDKAMP (Z. Physik, 1931, **70**, 306—316).—K-Absorption edges of Cu and Zn show max. and min. which diminish in intensity and become further apart as the distance from the edge increases. A. B. D. CASSIE.

Fine structure in X-ray absorption spectra. R. DE L. KRONIG (Z. Physik, 1931, **70**, 317—323).—Fine structure described in the two preceding abstracts does not arise in double electronic transitions, but in the discrete zones that an electron may occupy when moving in the periodic potential field of a crystal. A. B. D. CASSIE.

Intense monochromatic X-ray beams obtained without a spectrometer. H. KUSTNER (Z. Physik, 1931, **70**, 324—347).—A difference method of distinguishing characteristic from scattered radiation by means of filters is described. A. B. D. CASSIE.

X-Ray wave-length change by partial absorption. J. M. CORK (Physical Rev., 1931, [ii], **37**, 1555—1558; cf. this vol., 277).—The change of wave-length reported by Ray (cf. A., 1930, 1334) on

passing an X-ray beam through an absorber was not observed in L-radiation through B, Be, C, N_2, and O_2. N. M. BLIGH.

Effect of chemical combination on the X-ray spectra of copper. E. A. OWEN and T. E. WILLIAMS (Proc. Roy. Soc., 1931, **A.**, **132**, 282—295).—No change is found in the wave-length of the Cu-K line or in the width of the Cu-$K\alpha_1\alpha_2$ doublet when the Cu atom is present in the element, the oxides, or in Cu_3As, Cu_3Sn, Cu_2Sb, CuSn, Cu_3P, CuZn ($\alpha+\beta$) or ε. In the case of the oxides, any change that might occur would be masked by the decomp. that takes place when the oxide is placed on the target. The positions of the K absorption edges of Cu in the above substances and in CuCl, $CuSO_4$, $Cu(NO_3)_2$, $CuCO_3$, and $CuCl_2$ have been determined. In Cu, the Cu^I salts, and the alloys, the edge corresponds with the wave-length 1377·4X, whereas in all the inorg. Cu^{II} salts the edge moves about 1X towards the shorter wave-lengths. The results indicate that if a chemical linking exists between the elements in the intermetallic compounds considered, not more than one electron is supplied by the Cu atom in each case. The Cu atom is in the Cu^I state, agreeing with the views of Hume-Rothery (A., 1926, 356). L. L. BIRCUMSHAW.

Ionisation of air by X-rays of different hardnesses and degrees of homogeneity in cylindrical chambers of 2—70 cm. diameter. H. KUSTNER (Ann. Physik, 1931, [v], **10**, 616—648).—The accuracy of the method is discussed. For accurate results, neither the photo-electrons nor the reflected electrons must reach the chamber walls. The harder and more homogeneous the radiation, the greater must be the diameter of the chamber. The smaller the chamber the greater is the error. A. J. MEE.

Atomic photo-effect with hard exciting rays. F. SAUTER (Ann. Physik, 1931, [v], **9**, 217—248).—Theoretical. W. GOOD.

Photo-electric properties of cadmium, especially the effect of gases on them. H. BOMKE (Ann. Physik, 1931, [v]. **10**, 579—615).—The prep. of thin Cd layers and their photo-electric properties are described. By vaporisation at a pressure of about 10^{-4} mm. in a non-heated cell, Cd layers are obtained with a long-wave limit of 320—330 mμ. The photo-electric sensitivity of the cell is greatly affected by the adsorption of gases. Dry gases (O_2, H_2, N_2, A, CO_2) invariably reduced the sensitivity, whilst moist gases (air and A were tried) may increase or diminish the sensitivity, according to circumstances. The increased sensitivity for moist gases is ascribed to the H_2O vapour present. A. J. MEE.

Course of activation of thoriated tungsten and molybdenum. A. GEHRTS (Z. tech. Physik, 1931, **12**, 66—71; Chem. Zentr., 1931, i, 2172).

Directional distribution of electrons liberated from potassium vapour by polarised light. A. KRAUS (Naturwiss., 1931, **19**, 617—618).—The directional distribution of electrons set free from K vapour by polarised light was investigated, K being chosen because it has a comparatively long-wave limit for ionisation, and the K atom is similar to that of H. The theoretical distribution curve was followed. A. J. MEE.

Loss of energy by slow electrons in hydrogen. H. RAMIEN (Z. Physik, 1931, **70**, 353—374).—Electrons of less than 9 volts lose energy proportional to the number of collisions with H_2 mols., due to excitation of vibrational levels. No dissociation energy loss of 4·2 volts was observed. A. B. D. CASSIE.

Electron interference produced by thin sheets of celluloid and collodion. F. KIRCHNER (Naturwiss., 1931, **19**, 463—464).—Three different types of electron interference diagram are found; their origin is discussed. W. R. ANGUS.

Analogy of crack and electron. T. TERADA (Proc. Imp., Acad. Tokyo, 1931, **7**, 215—217). A. J. MEE.

Temperature function in the gas equation and the properties of the electron. R. D. KLEEMAN (Z. Elektrochem., 1931, **37**, 371—373).—It is shown theoretically that the equation of state of a perfect gas is $pv^{1+\alpha}$—$RMT^{1+\beta}$, where p, v, R, M, and T have their usual significance and α and β are positive quantities, the latter being independent of the nature of the gas (cf. this vol., 406). It is deduced that when the internal energy of a charged or an uncharged gas particle decreases with decrease in v the excess energy must be lost by a process of radiation of a type as yet unknown. R. CUTHILL.

Influence of magnetic fields on "polarised" electron beams. E. RUPP and L. SZILARD (Naturwiss., 1931, **19**, 422—423).—An electron beam (220 kv.) after reflexion on Au was passed through a magnetic field in the direction of the lines of force. The Debye–Scherrer diagram was photographed and a rotation was observed in it the magnitude of which is approx. proportional to the magnetic field strength and the length of the field traversed by the electrons. W. GOOD.

Polarisation of a beam of electrons by scattering. E. G. DYMOND (Nature, 1931, **128**, 149—150).—Predicted polarisation (A., 1929, 861) has been detected with Au foil. L. S. THEOBALD.

Emission of electrons under the influence of chemical action. A. K. DENISOFF and O. W. RICHARDSON (Proc. Roy. Soc., 1931, **A**, **132**, 22—50).—The electron emission from NaK, under the action of $COCl_2$ has been investigated over the pressure range 2×10^{-7} to $\sim10^{-3}$ mm. Full details are given of the methods of obtaining const. pressure of $COCl_2$ in the reaction chamber, of measuring p, and of obtaining a uniform flow of drops of the liquid alloy into the chamber. The total emission varies as p at the lowest pressures, but the rate of increase falls at 10^{-5} mm. A sharp max. of electron current occurs near 3×10^{-5} mm.; with increase in p a steadily diminishing decrease of i_0 takes place, until at about 10^{-3} mm. i_0 is approx. const. The effective temp. of the emitted electrons is 2370° abs. over the range 2×10^{-7} to 10^{-2} mm. L. L. BIRCUMSHAW.

Constitution of lithium. F. W. ASTON (Nature, 1931, **128**, 149).—A provisional value now found for

the ratio of the relative abundance of Li^6 and Li^7 is $10 \cdot 2 \pm 0 \cdot 5$; this gives an at.wt. $>6 \cdot 923 \pm 0 \cdot 006$.
L. S. THEOBALD.

Periodic regularity in atomic nuclei. G. I. POKROVSKI (Naturwiss., 1931, **19**, 573).—When the number of isotopes existing in an interval $N \pm 5$ is plotted against the at. wt. N, a curve is obtained analogous to the at. vol. curve. J. W. SMITH.

Method of recording coincidences between Geiger counters. J. C. JACOBSEN (Nature, 1931, **128**, 185). L. S. THEOBALD.

Thyratrons for high-speed automatic counting of physical phenomena. C. E. WYNN-WILLIAMS (Proc. Roy. Soc., 1931, **A**, **132**, 295—310).—A number of circuits are described whereby thyratron valves can be used for recording voltage impulses separated by as little as 0·002 sec. L. L. BIRCUMSHAW.

Magnetic spectrum of α-rays of active deposit of actinon. (MME.) P. CURIE and S. ROSENBLUM (Compt. rend., 1931, **193**, 33—35).—Using a specially intense source (cf. A., 1930, 517), the complexity of the 5·5-cm. particles from actinium (cf. A., 1930, 1338) is confirmed by the magnetic spectrum in a field of 24,000 gauss. The velocities of the rays α, α_1, α_2 of Ac-C, Ac-C'', and Ac-C' are respectively as 1 : 0·973 : 1·062. C. A. SILBERRAD.

Number of pairs of ions produced in air by an α-particle of polonium. GRÉGOIRE (Compt. rend., 1931, **193**, 42—44).—The ratio I/i (I the ionisation current produced by a bundle of α-particles for the solid angle 2π, i the current due to the charge carried by them) for α-particles of Po is $0 \cdot 765 \times 10^5$. Assuming the α-particles to be practically all doubly charged, the number of pairs of ions $=2I/i=(1 \cdot 53 \pm 0 \cdot 02) \times 10^5$. From this and other results (cf. A., 1930, 8) the number of α-particles emitted by Ra per g. per sec. is $3 \cdot 56 \times 10^{10}$ (cf. A., 1929, 6). C. A. SILBERRAD.

Homogeneous groups of long-range α-particles from radium-*C*. K. PHILIPP (Naturwiss., 1931, **19**, 618—619).—The Wilson cloud method provides a further method of analysis of the long-range α-particles from Ra-C. A. J. MEE.

α-Particles of the actinium series. P. MISCIATTELLI (Atti III Cong. Naz. Chim., 1929, 388—394; Chem. Zentr., 1931, i, 2164).—Measurements have been made of the range of α-particles from Ra, Ac, and Ac-X. A. A. ELDRIDGE.

Absorption and scattering of γ-rays. J. C. JACOBSEN (Z. Physik, 1931, **70**, 145—158).—Measurements of the relative absorption of γ-radiation from Ra and mesothorium" indicate that absorption per electron increases continuously with the at. no. of the absorbing atom, and that the increase is greater for radiation from Th-C'' than from Ra.
A. B. D. CASSIE.

Determination of niton in the atmosphere. W. MESSERSCHMIDT (Physikal. Z., 1931, **32**, 548—549).—Apparatus for measuring the amount of niton in the atm. is described. Results during different weather conditions are illustrated. W. R. ANGUS.

Method of atomic disintegration. H. POSE (Physikal. Z., 1931, **32**, 584).—The dependence of the vagueness of the observed groups of protons emitted on disintegration (cf. this vol., 783) on the experimental conditions or on vagueness of nuclear levels is discussed. In the case of Al it is certain that the first is the case. A. J. MEE.

Artificial disintegration of aluminium. M. DE BROGLIE and L. LEPRINCE-RINGUET (Compt. rend., 1931, **193**, 132—133).—By the method previously referred to (cf. this vol., 889) the "velocity" spectrum (measured by the range) of the H-particles (protons) emitted by Al on bombardment with monokinetic groups of α-particles of Po have been determined. There is no continuous spectrum, only a series of groups of range varying with the energy of the incident particles. C. A. SILBERRAD.

Radioactive disintegration. F. STÖBER (Chem. Erde, 1931, **6**, 368—375).—Disintegration of radioactive elements may be due to the action of cosmic rays. L. J. SPENCER.

Microcalorimetric determination of the life period of polonium. A. DORABIALSKA (Rocz. Chem., 1931, **11**, 469—476).—The value of the half-life period of Po, calc. from determinations of the variation in heat production of a sample with time, is of the same order as that determined by different methods. The rate of decay is, contrary to Bogoiavlenski (A., 1929, 737), unaffected by the altitude at which the sample is kept. R. TRUSZKOWSKI.

Evidence for the spin of the photon from light scattering. (SIR) C. V. RAMAN and S. BHAGAVANTAM (Nature, 1931, **128**, 114—115).—Under certain conditions of encounter between a mol. and a photon, a change in sign of the circular polarisation of the photon will occur. L. S. THEOBALD.

Neutron. R. M. LANGER and N. ROSEN (Physical Rev., 1931, [ii], **37**, 1579—1582).—The explanation of at. and cosmic phenomena is simplified by assuming the existence of a neutron, of small size and low energy, formed by the combination of a proton and an electron. N. M. BLIGH.

Nomenclature and standards for biologically effective radiation. M. LUCKIESH and L. L. HOLLADAY (J. Opt. Soc. Amer., 1931, **21**, 420—427).

Ideal gases at the highest temperatures; a discussion of the problem: matter and radiation. K. BENNEWITZ (Z. Physik, 1931, **70**, 429—443).—Theoretical. A. B. D. CASSIE.

New light source for investigations in the blue and ultra-violet. W. M. COHN (Physikal. Z., 1931, **32**, 559—561).—When Th, under certain conditions, is bombarded by cathode rays a blue light is emitted which can be used as a source of light for absorption measurements and radiation in the blue and ultraviolet. This blue light gives a continuous spectrum between 2200 and 6000 Å. with max. intensity at 4500 Å. W. R. ANGUS.

Ultra-violet radiation. J. H. CLARK (J. Opt. Soc. Amer., 1931, **21**, 240—247).—A ZnS method of measuring ultra-violet radiation is described and the results of 3 years' observations on Baltimore sunshine are given. W. GOOD.

Band spectrum of boron hydride. W. Lochte-Holtgreven and E. S. van der Vleugel (Z. Physik, 1931, **70**, 188—203).—Two bands at λ 4332·7 and 4367·1 Å., due to BH, were photographed under high dispersion and analysed. Faint satellites were ascribed to the isotopic mol. $B^{10}H$. A. B. D. Cassie.

Spectrum of flame of carbon disulphide. A. Fowler and W. M. Vaidya (Proc. Roy. Soc., 1931, **A**, **132**, 310—330).—The most characteristic bands of the CS_2 flame, extending from the blue to the near ultra-violet, are due to S_2 mols. Many of the ultra-violet bands are also due to S_2, whilst fainter bands in this region are attributed to SO. When the flame is enclosed in a chimney, strong absorption bands of SO_2 appear. Similar results are obtained in experiments on S and H_2S flames, the latter also showing bands of HO. The spectrum of the "phosphorescent flame" of CS_2, as photographed by Emeléus (A., 1926, 777), has been re-examined and found to include bands of S_2, SO, and CS, the SO bands being relatively much stronger than in the normal flame. Preliminary investigations have been made of a group of bands in the ultra-violet which have been provisionally attributed to COS. These have not been found in any of the flame experiments. L. L. Bircumshaw.

Absorption spectra in relation to the colour of solutions of iodine monochloride. A. E. Gillam and R. A. Morton (Proc. Roy. Soc., 1931, **A**, **132**, 152—167; cf. A., 1929, 977).—ICl solutions show two colours, yellow (in AcOH and AcOEt) and brown (in CCl_4), corresponding with brown and violet I solutions. Yellow solutions of ICl in CCl_4, $CHCl_3$, AcOH, HCl, Et_2O, and AcOEt are characterised by an absorption max. about 360 mμ, the brown about 460 mμ, mol. extinction coeff. being 150—160 in each case. The most important factor influencing the colour and absorption spectrum of ICl solutions is dichroism, conditioned by the occurrence or non-occurrence of solvation. Aq. NaCl and HCl solutions of ICl have a higher extinction coeff. than the others, and there is a slight displacement of the max. towards the shorter wave-lengths. This is considered to indicate the formation of the compounds ICl,HCl and ICl,NaCl. The analogy with I solutions extends to the variation of the colours in certain solvents with temp., and to the fact that traces of EtOH in $CHCl_3$ cause the 460 mμ max. to be replaced by that at 360 mμ. L. L. Bircumshaw.

Comparative absorption spectra of complex chromic and cobaltic salts. (Mme.) M. Chatelet-Lavollay (Compt. rend., 1931, **193**, 30).—The difference in the frequencies (Δν) of the max. of the absorption band in the ultra-violet of corresponding luteo-, roseo-, and purpureo-chromic and -cobaltic salts is const. (120 mm.$^{-1}$). For the xantho-chromic and -cobaltic salts Δν is 340, but for the *iso*xantho-cobaltic it is 120 mm.$^{-1}$ The xanthochromic salt belongs therefore to the *iso*xantho-series and is $[Cr(NH_3)_5ONO]Cl_2$. C. A. Silberrad.

Radiation accompanying hydration of quinine sulphate. M. Curie and M. Prost (Compt. rend., 1931, **192**, 1729—1730).—By working in a vac. (save for H_2O vapour from ice at −15°), it is shown that the range of radiation emitted on hydration of quinine sulphate exceeds 1 mm. at a pressure of H_2O vapour of 1 mm. (cf. A., 1911, ii, 356; 1926, 910). C. A. Silberrad.

Absorption in liquid and solid solutions of rhodamine-*B* in a mixture of alcohol and collodion. A. A. Dixon (J. Opt. Soc. Amer., 1931, **21**, 259—261).—Experimental curves showing absorption in relation to wave-length are given. W. Good.

Zeeman effect of the absorption lines of potassium chromium selenate. K. Schnetzler (Ann. Physik, 1931, [v], **10**, 373—392).—$KCr(SeO_4)_2,12H_2O$ crystallises in the alum type, and has at −190° a sharp doublet at 6710 Å. The transverse Zeeman effect for this doublet was investigated. A. J. Mee.

Ultra-violet absorption of benzene derivatives and the theory of induced alternate polarity. K. L. Wolf and W. Herold (Z. physikal. Chem., 1931, **B**, **13**, 201—231).—The ultra-violet absorption spectra of dil. solutions of a number of mono- and di-substituted C_6H_6 derivatives are described. The displacement of the first absorption band caused by introduction of polar substituents may be calc. additively for the *p*-disubstituted compounds without regard to the charge, relative to the C_6H_6 ring, of the central atoms of the groups. The oscillation bands are most marked in *m*-substituted compounds if the charges in the substituents are similar, and in *p*-compounds if the charges are of opposite sign; it appears, therefore, that the strengthening or weakening of the induced alternate polarity caused by the introduction of one polar substituent, according to the nature and position of the second substituent, is in accordance with Vorländer's theory. H. F. Gillbe.

Spectral region 20—40 μ. J. Strong (Physical Rev., 1931, [ii], **37**, 1565—1572).—% transmission and reflexion are tabulated for several substances. SO_2 shows zero reflectivity at 20·75 and 8·7 μ, where it has strong absorption bands. β-MgO has a max. reflectivity at 23 μ. KI is transparent above 33 μ. N. M. Bligh.

Infra-red region of spectrum. III. Absorption spectrum of carbon disulphide. IV. Monochromator method in the infra-red. C. R. Bailey and A. B. D. Cassie (Proc. Roy. Soc., 1931, **A**, **132**, 236—251, 252—257; cf. this vol., 144).—III. Four bands, ν 878, 1523, 2179, 2330 cm.$^{-1}$, have been located in the region 1—22 μ; of these, the first three have been resolved into *P* and *R* branches with a frequency difference of 12—13 cm.$^{-1}$ The infra-red has been co-ordinated with the Raman spectrum, and the fundamental frequencies of the mol. are deduced. The mol. is rectilinear with one moment of inertia, I_0 264×10^{-40} g.-cm.^{2} The doublet structure of the Raman spectra of CS_2 and CO_2 is attributed to the excitation of two types of vibration associated with slightly different amounts of energy and corresponding with two types of linking. The force consts. characteristic of the linkings in CS_2 and similar mols. have been calc. CS_2 differs from CO_2 in having single linkings, the C atom being apparently bivalent.

IV. The monochromator method eliminates from the absorption tube all radiation emitted by the

Nernst filament except the small range of wavelengths passing through the telescope slit.

L. L. BIRCUMSHAW.

Raman effect in some gases. P. DAURE and A. KASTLER (Compt. rend., 1931, **192**, 1721—1723).—The Raman spectra of H_2, C_2H_2, C_2N_2 (at atm. pressure), and H_2O (saturated vapour at 130°) have been determined with 4358·3, 4046·7, and 3650·1 of the Hg arc. The two last give respectively $\Delta\nu=2330\pm5$ and $3655+5$ cm.$^{-1}$; former results are confirmed.

C. A. SILBERRAD.

Anomalous polarisation of Raman radiation. R. BAR (Naturwiss., 1931, **19**, 463).—Conditions under which anomalous polarisation of Raman lines is manifested are discussed and the polarisation factors for $CHCl_3$, CCl_4, and C_6H_6 are given.

W. R. ANGUS.

Polarisation of Raman scattering by hydrogen gas. S. BHAGAVANTAM (Nature, 1931, **128**, 70).—Raman lines representing the rotational transitions $0\longrightarrow2$ and $1\longrightarrow3$ in H_2 are polarised only to an extent of approx. 25%; polarisation of the vibration lines appears to be complete.

L. S. THEOBALD.

Circular polarisation in the Raman effect. W. HANLE (Physikal. Z., 1931, **32**, 556—558).—Apparatus for investigating circular polarisation of Raman lines is described. The character and amount of circular polarisation are the same for all Raman lines arising from similar mol. vibrations. Linear polarisation effects are compared with those obtained. Comparisons of the effects with CCl_4 and $CHCl_3$, and with C_6H_6 and PhMe and $C_6H_4Me_2$, are made. Corresponding lines of different substances show the same circular polarisation. W. R. ANGUS.

Intensity problems connected with the Raman effect. J. REKVELD (Arch. Neerland., 1931, [III A], **13**, 73—120).—The ratio of the intensities of Stokes and anti-Stokes Raman lines is expressed by an equation derived on the assumption of thermodynamic equilibrium between radiation and matter; experimental values agree well with this theory. A new optical method of determining h/k is based on these intensity measurements. The dependence of the scattered energy on frequency is discussed and experimental data on CCl_4, MeOH, and $COMe_2$ are given. A method of heterochromatic photometry in the ultra-violet is described. W. R. ANGUS.

Raman effect. A. CARRELLI (Rend. Accad. Sci. fis. mat. Napoli, 1930, **36**, 61—68; Chem. Zentr., 1931, i, 2169).—Raman rotation frequencies are emitted with much smaller (0·001) intensity than the Tyndall frequency. For substances which absorb in the ultra-violet the intensity of the Raman frequency increases with diminishing wave-length more rapidly than accords with the λ^{-4} law. A. A. ELDRIDGE.

Intensity of rotation lines in the Raman effect of diatomic molecules. E. SEGRE (Nuovo Cim., 1930, **7**, 380—387; Chem. Zentr., 1931, i, 2169).—A quantum-theoretical study. A. A. ELDRIDGE.

Continuous Raman spectrum and its behaviour at the critical point. G. PLACZEK and W. R. VON WIJK (Z. Physik, 1931, **70**, 287—292).—Determination of depolarisation of Rayleigh and Raman radiation in liquids shows that the increase of continuous radiation near a Raman line at the crit. point is due to an increase of continuous Raman radiation and not to an increase in Rayleigh scattering.

A. B. D. CASSIE.

Effect of pressure on Raman spectra. S. BHAGAVANTAM (Nature, 1931, **128**, 188).—Estimated pressures at which distinctness of quantisation of the different rotations would disappear in the commoner gases are in agreement with observed pressures above which lines in the rotational Raman spectrum are replaced by a continuous spectrum.

L. S. THEOBALD.

Raman effect for liquid hydrazine. S. IMANISHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, **16**, 1—7).—The spectra are nearly the same under low dispersion, showing the NH_3 N–H triplet frequency (3210, 3289, 3339 Å.), and two lower frequencies due to the N–N linking. The appearance of this triplet in the N_2H_4 spectrum supports the polymerisation theory of liquid NH_3. A value of 1000 cm.$^{-1}$ is obtained for the N–N linking in liquid N_2H_4. This may be halved in the vapour state. Gaseous N_2H_4 dissociates into two NH_2 groups on absorption of light of a certain wave-length.

A. J. MEE.

Raman effect in amorphous solids. S. BHAGAVANTAM (Indian J. Physics, 1931, **6**, 1—6).—Flint glass shows the effect much more strongly then crown. All the glasses show bands at about 500, 800, 1080, and 1330 cm.$^{-1}$ The most prominent are at 500 and 1080. A. J. MEE.

Raman spectra of inorganic crystals. III. P. KRISHNAMURTI (Indian J. Physics, 1931, **6**, 7—13).—The Raman spectrum of S crystals at the temp. of liquid air, excited by 4358 Å., was investigated. The crystals absorb this radiation completely at room temp., but at the temp. of liquid air they become much lighter in colour, and the Raman lines appear sharply. $HgCl_2$ crystals give a very strong line at 313 cm.$^{-1}$ and a weaker one at 3·1 cm.$^{-1}$, whilst $HgBr_2$ gives only one intense line at 187 cm.$^{-1}$ The MeOH solution of $HgCl_2$ gives a slightly broadened out line. $(NH_4)_2HgCl_4$ powder gave a line at 273 cm.$^{-1}$ A conc. aq. solution gave a broad line in a similar position. A. J. MEE.

Raman spectra of sulphuric acid. R. M. BELL and W. R. FREDRICKSON (Physical Rev., 1931, [ii], **37**, 1562—1564; cf. A., 1930, 978).—As concentration decreases the lines decrease in number and intensity and disappear; at this point a broad line 4817 Å. appears, and persists in dil. solution. An exception is 4566 Å., present at all concentrations and of increasing intensity with decreasing concentration. HNO_3 gives a line of the same wave-length and intensity variation. N. M. BLIGH.

Raman effect in solutions of inorganic complex salts. G. JOOS and I. DAMASCHUN (Physikal. Z., 1931, **32**, 553—554).—Complex salts containing co-ordinated H_2O or NH_3 groups were examined. None of the aquo-co-ordinated complex salts exhibited Raman displacements. Sulphates of hexammines gave displacements corresponding with 9·1, 10·2,

16·6, and 23·3 μ, agreeing with infra-red data on solid sulphates. A displacement is assumed to arise from the ammine complex, and its value is determined by the metallic radical, viz., $Cu(NH_3)_4SO_4$ −24·8 μ; $Cu(NH_3)_4Cl_2$ −24·5 μ; $Zn(NH_3)_6SO_4$ and $Zn(NH_3)_6Cl_2$ −23·4 μ; $Cd(NH_3)_6Cl_2$ −29·5 μ. Ni and Ag ammines gave no shifts and Co ammines are unsuitable for investigation because of their colour. Solutions of NH_3 exhibit three displacements corresponding with (in order of sharpness) 3·0, 2·9, 3·1 μ; $Zn(NH_3)_6SO_4$ showed only two displacements, 3·1 (sharper) and 3·0 μ (weaker). The shift corresponding with 36·5 μ shown by $Zn(NH_3)_6Cl_2$ is explained as due to the formation of $(NH_4)_4(ZnCl_6)$ and the subsequent dissolution of $ZnCl_6^{----}$ in $ZnCl_2$ gives rise to the displacement. W. R. ANGUS.

Depolarisation of the lines of the CO_3'' ion in the spectrum of light diffused by calcite. J. CABANNES and (MLLE.) D. OSBORNE (Compt. rend., 1931, **193**, 156—158).—Revised figures for the Raman lines of calcite are +28·13, +15·45, −15·74, −28·38, −71·21, −108·73, −143·66, and −175·20 mm.$^{-1}$ 71·21, 108·73, and 143·66 are three of the four fundamental frequencies of the CO_3'' ion (assumed plane). The polarisation of 108·73 differs from that of the other two, confirming the authors' view (cf. A., 1930, 15) in opposition to Schaefer's (cf. *ibid.*, 1499). C. A. SILBERRAD.

Raman spectra of some organic sulphides. S. VENKATESWARAN (Indian J. Physics, 1931, **6**, 51—74).—The Raman spectra of Me, Et, Pr, Bu^{α}, Bu^{β}, and allyl sulphides, and of Me_2S_2 and Et_2S_2 have been examined. The Me_2S model is triangular. There are two frequencies associated with the C–S linking, one sharp and intense at Δν 691, and one diffuse at Δν 746. These frequencies are not appreciably affected by changes in the group attached to the C atom, or by the difference in the chemical linking between the S and C atoms. The disulphides show a prominent line at Δν 512 due to the S–S linking. There is a difference between the linking of S atoms in S_2 and in the disulphides, for this frequency is a good deal lower than that obtained from fluorescence and absorption bands for S vapour. The C–S and S–S oscillations have a tendency to split into components in Et and higher members of the series. There is a slight shift in the C–S oscillation of Me_2S in Me_2S_2. Allyl sulphide shows a prominent line at Δν 1634, characteristic of the ethylenic linking. There are also differences in the nature of the C–H band in the normal and corresponding *iso*-compounds. A. J. MEE.

Raman effect. XI. Raman spectra of cyanogen compounds. A. DADIEU (Monatsh., 1931, **57**, 437—468).—Method and results are given. Constitutional relations in carbimides, thiocarbimides, carbylamines, and HCN are discussed. W. GOOD.

Raman effect. XII. Raman spectra of chlorinated hydrocarbons. M. PESTEMER (Monatsh., 1931, **57**, 469—487).—The results of an experimental study of the Raman effect in 15 chlorohydrocarbons are given and discussed. W. GOOD.

Raman effect. XIII. Raman spectra of halogen derivatives. A. DADIEU and K. W. F. KOHLRAUSCH (Monatsh., 1931, **57**, 488—511).—6 org. halogen compounds are examined for the first time. The results, as well as those for 5 other compounds, are given and discussed. W. GOOD.

Thermoluminescence excited by exposure to radium. F. G. WICK (J. Opt. Soc. Amer., 1931, **21**, 223—231).—This has been experimentally studied in $CaSO_4$ containing a small amount of Mn and in fluorite. The effect of subjecting these materials to high pressure before and after exposure to Ra was also studied. W. GOOD.

Radiation from phosphors in strong varying electric fields. H. HINDERER (Ann. Physik, 1931, [v], **10**, 265—295).—The behaviour of different phosphors in const. and changing electric fields is investigated. For a ZnS–Mn phosphor the intensity of the light is dependent on the metal content for both types of field. A new method of determining the duration of the luminescence of phosphors in an electric field is described. The duration of the luminescence for ZnS–Mn phosphors is independent of the centre size and field strength and lies between 9 and 10 sec. A. J. MEE.

Fluorescence of bonellin. C. DHÉRE and M. FONTAINE (Compt. rend. Soc. Biol., 1931, **105**, 843—846; Chem. Zentr., 1931, i, 2218).—Solutions of bonellin (from *Bonellia viridis*) in EtOH, Et_2O, and pyridine exhibit 3 fluorescence bands. The living animal fluoresces (red) only in intense violet and ultra-violet light. A. A. ELDRIDGE.

Additive colouring of alkali halide crystals. I. Macroscopic diffusion. E. REXER (Z. Physik, 1931, **70**, 159—187).—Diffusion of Na into rock-salt was studied at different temps. and for different samples of crystal. A. B. D. CASSIE.

Molecular association and optimum of fluorescence: influence of salts. E. PERRIN (Compt. rend., 1931, **192**, 1727—1729).—The more rapid decrease of fluorescence with increasing concentration and the smaller optimum concentration of a solution of fluorescein in one of KCl (3·9*N*) as compared with one in H_2O support the view that the decrease in fluorescence on increasing concentration beyond the optimum is due to association of mols. (cf. A., 1889, 554). The mechanism of the deactivation is discussed (cf. A., 1930, 133). C. A. SILBERRAD.

Phosphorescence of zinc sulphide. I. Explosion method. R. COUSTAL (J. Chim. phys., 1931, **28**, 277—298).—A mixture of Zn powder and flowers of S, with S slightly in excess of mol. proportions, on explosion yields ZnS. The phosphorescence of the pure substance is similar to that of ZnS prepared by older methods and activated by Cu. The presence of Pb has no effect on the phosphorescence, but Mn, Fe, Co, Ni, and Cu are extremely active. Other metals change the phosphorescence slightly, nonmetals very little, whilst compounds frequently displace the phosphorescence towards a longer wavelength. J. W. SMITH.

Phosphorescence of zinc sulphide. II. Physical study. R. COUSTAL (J. Chim. phys., 1931, **28**, 345—361; cf., preceding abstract).—Two phosphorometers are described; one aims at rapidity of measure-

ment and the other at accuracy. The decrease of intensity I of pure, phosphorescent ZnS with the time t is given by $I = C/t^n$, where C is a const. depending on the size of the crystals of ZnS and n is a function of the temp. E. S. HEDGES.

Relation of the intensity of fluorescence to the concentration in solid solutions. A. A. DIXON (J. Opt. Soc. Amer., 1931, **21**, 250—258).—Experimental investigation of fluorescence in both liquid and solid solutions (rhodamine-*B* in EtOH–collodion) shows that the intensity of fluorescence increases exponentially with a decrease in concentration over a wide range. W. GOOD.

Accuracy obtainable with gas-filled photo-electric cells. W. R. G. ATKINS (Sci. Proc. Roy. Dublin Soc., 1931, **20**, 67—73).—A gas-filled CsH cell, after a momentary glow discharge, showed 33% variation in emission at 143 volts anode potential. The sensitivity decreases about 2% per min. and subsequently rises. A KH gas-filled cell similarly tested varied 2% at 5 microamp. and 59 volts and more at 166 volts. Measurements should be made immediately after a discharge, which should be momentary, as the sensitivity falls 2% at 166 volts and more than 3% at 59 volts. C. W. GIBBY.

Influence of water in photo-electric cells. R. AUDUBERT (Compt. rend., 1931, **193**, 165—166).—The explanation of the photo-electric effect as due to the photolysis of H_2O (cf. A., 1930, 173) is supported by the fact that electrodes of CuI, Cu_2O, CuO, Ag_2S, or Hg_2I_2 in various non-aq. solvents, *e.g.*, $COMe_2$, Et_2O, MeOH, MeOAc, etc., rendered conducting by NaI, give relative to a Hg_2Cl_2 electrode, a const. potential, but no photopotential. The presence of very little H_2O causes such to appear, its influence being chiefly exerted as an adsorbed layer on the electrode. C. A. SILBERRAD.

Photo-electric effect in Cu_2O–Cu rectifier. E. PERUCCA and R. DEAGLIO (Ann. Physik, 1931, [v], **10**, 257—261).—The general photo-electric phenomena occurring in a Cu_2O–Cu cell are described, complicating factors being pointed out. A. J. MEE.

Photo-electric effect in the Cu_2O–Cu rectifier. O. VON AUWERS and H. KERSCHBAUM (Ann. Physik, 1931, [v], **10**, 262; cf. preceding abstract).—The work of the two sets of investigators is compared, and differences are indicated. A. J. MEE.

Photo-electromotive force in cuprous oxide crystals. H. DEMBER (Physikal. Z., 1931, **32**, 554—556).—An e.m.f. within a crystal can be originated by a light source only if the light is able to liberate electrons so that these may diffuse in the interior of the crystal. Observations preclude the contributory effect of a unidirectional layer. W. R. ANGUS.

Electric spectrum of water. M. ALIMOWA (Ann. Physik, 1931, [v], **9**, 176—178).—Using the method of damped oscillations a value 9·004±0·001 was found for n^{17} of H_2O in the range of wave-lengths 2200—2900 mm. W. GOOD.

Dielectric strength of degassed liquids. L. INGE and A. WALKER (Z. tech. Physik, 1930, **11**, 369—372; Chem. Zentr., 1931, i, 2022).—At temp. and pressures sufficiently removed from the vaporisation temp. and pressure the dielectric strength of well-degassed xylene is independent of pressure. For a.c. the val. decreases with rise of temp., but remains const. for d.c. or discharge. A. A. ELDRIDGE.

Dipole moment and spatial configuration of some inorganic halides. E. BERGMANN and L. ENGEL (Z. physikal. Chem., 1931, **B**, **13**, 232—246).—The dipole moments of a number of halides and of $Fe(CO)_5$, dissolved in C_6H_6 or CCl_4, have been determined. $SbCl_5$ possesses a definite moment, and one Cl atom therefore occupies a position in the mol. different from that of the other 4; a similar condition obtains for $Fe(CO)_5$. The moments of $SiCl_4$ and $TiCl_4$ are zero and the compounds are therefore of tetrahedral structure, but $SnCl_4$ is anomalous in possessing a moment of $0{\cdot}8\times10^{-18}$; the possible structure of the mol. is discussed. Measurements with trihalides indicate a pyramidal structure. H. F. GILLBE.

Reactions of atoms. M. PÓLANYI (Z. angew. Chem., 1931, **44**, 597—602).—The general problem of the reaction of atoms with mols. is discussed and the "rarefied flame" (A., 1928, 1339) and the diffusion methods for the study of the action of Na atoms on the halogens, halogen acids, and Hg halides are outlined. The investigation has been extended to the Me halides. H. INGLESON.

Internal structure of solid inorganic compounds at high temperatures. III. Electrical conductivity, diffusivity, and reactivity of some spinels in the solid state. W. JANDER and W. STAMM (Z. anorg. Chem., 1931, **199**, 165—182; cf. A., 1930, 1351).—The conductivity of ZnO at 400—1030° and of MgO at about 1000° shows these compounds to be electronic conductors, and Al_2O_3 is probably of the same type. In $ZnAl_2O_4$ and $MgAl_2O_4$ the conductivity at 900—1100° is mainly ionic, whereas in $MgCr_2O_4$ and $ZnCr_2O_4$ it is electronic. Measurements of the rate of diffusion of these compounds into each other and the rate of reaction with MgO, Cr_2O_3, and Al_2O_3 at 1230° show that Al and Cr exchange places more rapidly than Mg and Zn. From these results it is concluded that $MgAl_2O_4$ and $ZnAl_2O_4$ have ionic lattices at 900—1250°. R. CUTHILL.

Electric conductivity and optical absorption in metals. E. H. HALL (Proc. Nat. Acad. Sci., 1931, **17**, 392—401).—A theoretical discussion. J. W. SMITH.

Electric conductivity and optical absorption in metals (supplementary). E. H. HALL (Proc. Nat. Acad. Sci., 1931, **17**, 427—430).—Transit conductivity in optical experiments is dependent on the ratio wave-period/transit period in the same general way in which, according to both the Thomson formula and the Wilson–Jeans formula, free-electron conductivity is dependent on the ratio wave-period/free-path period. E. S. HEDGES.

Dispersion of aluminium in the range 1·1—2·3 A. H. STEPS (Naturwiss., 1931, **19**, 617).—The dispersion curve for Al is normal within this range. A. J. MEE.

Indices of refraction of liquids. M. MASIUS and W. E. LAWTON (J. Opt. Soc. Amer., 1931, **21**, 232—

239).—A theoretical treatment of the determination of the index of refraction of a liquid enclosed in a hollow prism. W. GOOD.

Invariant of magnetic rotation of some fused organic substances. C. SALCEANU (Compt. rend., 1931, **193**, 161—162).—If Λ is Verdet's constant, n refractive index, and d density, the expression $\Lambda nd/(n^2-1)^2$ should be independent of the physical state (cf. A., 1927, 8; this vol., 148). From m. p. to 180° for 2-$MeC_{10}H_7$, $CHPh_3$, and phenanthrene it increases slowly with rise of temp. This is probably connected with the effect on the strong magnetic dispersion of these substances of change in position of the absorption bands with temp.

C. A. SILBERRAD.

Magneto-electric rotatory power. J. BECQUEREL and L. MATOUT (Compt. rend., 1931, **193**, 158—161; cf. this vol., 787).—An alternative explanation of the phenomenon. With xenotime two kinds of absorption bands, quite distinct from each other, were observed. C. A. SILBERRAD.

Rational system of symbols for organic and inorganic compounds. W. MADELUNG (Z. Elektrochem., 1931, **37**, 377—378).—Supplementary to a previous paper (this vol., 548). R. CUTHILL.

Exact partitioning [of space] and co-ordination number. F. LAVES (Z. Krist., 1931, **78**, 208—241).—The connexion between 11 possible methods of partitioning of space and the relations between the co-ordination numbers of the constituents of a compound A_mB_n are discussed. C. A. SILBERRAD.

Single electron linking. J. H. SIMONS (J. Physical Chem., 1931, **35**, 2118—2124).—A discussion. The hypothesis of a single electron linking as a valency force is regarded as invalid and in direct opposition to electronic theories of valency. The parachor cannot be employed to establish the existence of such a linking. H. F. GILLBE.

Quantum mechanics applied to benzene problems. I. Electron configurations of benzene and its derivatives. E. HUCKEL (Z. Physik, 1931, **70**, 204—286).—Six detached electrons determine the aromatic character of ring systems. Wave mechanics is applied first to a system with one electron associated with each CH group, and, secondly, to an electron moving in the potential field due to the ring and remaining detached electrons. The second method indicates that the ring may be regarded as a quasi-at. core, and that the detached electrons form completed groups of 2, 6, 10, etc. electrons: 2 electrons form an ordinary covalent linking, and 6 the C_6H_6 ring. These groups are complete even when the number of detached electrons does not equal the number of members of the ring, *e.g.*, Ph^-K^+. Term values due to different electron configurations are determined, and details of the different hydrobenzenes are discussed.

A. B. D. CASSIE.

Energy relationships of inorganic halides. Determination of atomic radii. E. BERGMANN and L. ENGEL (Z. physikal. Chem., 1931, **13**, **B**, 247—267).—By assuming that the direction of operation of a valency force is governed by the polarisation of the atoms concerned, and that the homopolar linking approximates to an extremely deformed ionic linking, it is shown that the configuration of trihalides must be pyramidal, and not planar, and that $SnCl_4$ also, unlike CCl_4 and $SiCl_4$, is of pyramidal structure (cf. this vol., 999). A method for calculating from the electronic polarisation the distance between the central and outer atoms in such compounds is described; the vals. of the at. radii, calc. from the results so obtained, are in close agreement with those in the lit. The formula used is applicable both to dil. solutions and to gases. H. F. GILLBE.

Theoretical magneton numbers in Weiss units. C. J. GORTER (Nature, 1931, **128**, 68—69).—Theoretical values given by various authors for the rare earths and the Fe group are compared.

L. S. THEOBALD.

Magnetic susceptibility, absorption spectra, and constitution of iron nitrososulphides. L. CAMBI and L. SZEGO (Atti R. Accad. Lincei, 1931, [vi], **13**, 168—172).—The magnetic susceptibility of the tetra- and hepta-nitroso-salts indicates that they are ferrous–ferric compounds containing halogenoid NO groups, and this structure is supported by the absorption spectra of the two series of salts in the visible and ultra-violet regions. O. J. WALKER.

Oxide hydrates and active oxides. XLIII. Magnetic susceptibilities of preparations of hydrated ferric oxide. G. F. HUTTIG and H. KITTEL (Z. anorg. Chem., 1931, **199**, 129—148; cf. this vol., 804).—Goethite and anhyd. Fe_2O_3 are paramagnetic. Variations in the susceptibility, κ, of anhyd. Fe_2O_3 are due to the presence of varying amounts of the unstable γ form, to incomplete crystallisation, and to deviations of the ratio Fe : O from the value 2 : 3, an excess of either Fe atoms or dissolved O causing a marked increase in κ. The hydrohæmatites are ferromagnetic, κ decreasing with increase in the field strength. The products formed by reaction of ferric salts with aq. NH_3 are initially paramagnetic, but tend to become ferromagnetic on ageing.

R. CUTHILL.

Number of magnetons in ferromagnetic substances. A. WOLF (Z. Physik, 1930, **70**, 519—538).—Theoretical. The number of magnetons per ferromagnetic element is calc. assuming the constituent atoms in possible states of different multiplicity.

A. B. D. CASSIE.

Diamagnetism and the colloidal state. S. R. RAO (Nature, 1931, **128**, 153).—With colloidal C, diamagnetic susceptibility, χ, decreases in proportion to an increase in surface area of a given mass. With Sb and Bi, the decrease of χ can be explained by a fall due to reduced particle size and to oxidation (cf. A., 1930, 673). L. S. THEOBALD.

Diamagnetism of liquid mixtures. V. C. G. TREW and J. F. SPENCER (Nature, 1931, **128**, 152).—A reply to criticism (this vol., 900).

L. S. THEOBALD.

Valency and diamagnetism of titanium in the tetrachloride. V. I. VAIDYANATHAN (Nature, 1931, **128**, 189).—The diamagnetism of $TiCl_4$ ($-0{\cdot}287\times10^{-6}$ at 35°) suggests that the paramagnetism of Ti is due to the two pairs of valency electrons being in different orbits. In Ti compounds, paramagnetism

is due to the unsymmetrical nature of the valency linkings. L. S. THEOBALD.

New relation between electrical resistance and energy of magnetisation. W. GERLACH and E. ENGLERT (Nature, 1931, **128**, 151—152).—Above the Curie point the decrease of resistance of ferromagnetic wires is proportional to the square of the true magnetisation, and at temp. just above this point the external field produces true magnetisation and a form of ferromagnetic magnetisation. True magnetisation diminishes electrical resistance proportionately to the true magnetic energy. L. S. THEOBALD.

Sugden's parachors. V. Mercaptans. B. SINGH and R. SINGH (J. Indian Chem. Soc., 1931, **8**, 209—213; cf. A., 1930, 1349).—The parachors of various mercaptans indicate absence of association. R. CUTHILL.

Heat of evaporation of water and specific volume of saturated steam up to 310° (100·7 atm.). M. JAKOB and W. FRITZ (Tech. Mech. Thermodyn., 1930, **1**, 173—183, 236—240; Chem. Zentr., 1931, i, 2028).—Values correct to 0·25% are given. A. A. ELDRIDGE.

Exchange of energy between organic molecules in a molecular beam and metallic surfaces. F. O. RICE and H. T. BYKE (Proc. Roy. Soc., 1931, A, **132**, 50—66).—No decomp. of $COMe_2$ or $HgMe_2$ was observed when a mol. beam of these substances collides with a Pt target at temp. up to 1600°, from which it is concluded that no adsorption of any appreciable fraction of the mols. or the trapping of mols. in surface crevices occurs. When $COMe_2$ vapour or $HgMe_2$ comes into temp. equilibrium with a target at 1600°, the fraction of mols. having the energy of activation 65,500 g.-cal. is too small to be detected. It is concluded that the transfer of energy from a heated target to the internal degrees of freedom of an org. mol. is not 100% efficient. When $COMe_2$ or $HgMe_2$ in a mol. beam collides with a heated W target no decomp. takes place up to 1085°, after which a surface reaction occurs with formation of WC and liberation of CO and H_2. With a Ta target a similar reaction begins at 1400°. L. L. BIRCUMSHAW.

A tetrahedrally symmetrical field of influence as a general structure unit of all crystal lattices. R. REINECKE (Z. Krist., 1931, **78**, 334—362).

Lattice distance of bismuth and its reflective power for *X*-rays. E. ADINOLFI (Rend. Accad. Sci. fis. mat. Napoli, 1930, **36**, 69—75; Chem. Zentr., 1931, i, 2163—2164).—The value 3·970±0·005 Å. is recorded. A. A. ELDRIDGE.

Crystal structure of silicon. A. G. NASINI and A. CAVALLINI (Atti III Cong. Naz. Chim., 1929, 463—470; Chem. Zentr., 1931, i. 2163).—Specimens of Si prepared in various ways always possessed a structure of the diamond type; *a* 5·21 Å. Differences in the interference lines in accord with Laue's formula were observed. A. A. ELDRIDGE.

Lattice constants of rhenium. K. MOELLER (Naturwiss., 1931, **19**, 575).—Using a precision method, the following values have been obtained: *a* 2·755, *c* 4·450 Å., *c/a* 1·615 (cf. A., 1929, 382; this vol., 448). J. W. SMITH.

Cold-working of platinum wires and fibrous texture thereby produced. G. GREENWOOD (Z. Krist., 1931, **78**, 242—250).—Cold-working of Pt wire produces a fibrous structure, the crystallites arranging themselves so that [111] is approx. parallel to the direction of drawing (cf. A., 1929, 743). The effect is more marked towards the centre of the wire. The unit cell has *a* 3·912 Å. (cf. A., 1925, ii, 447). C. A. SILBERRAD.

Crystal structure of anhydrous halides of bivalent metals. A. FERRARI (Atti III Cong. Naz. Chim., 1929, 452—460; Chem. Zentr., 1931, i, 2162).—A tabulation and discussion. A. A. ELDRIDGE.

Apparent hemihedrism of crystals of lead chloride and some other salts. F. D. MILES (Proc. Roy. Soc., 1931, A, **132**, 266—281).—The fact that etch figures on the faces of a crystal may indicate a symmetry lower than that usually ascribed to the crystal is discussed. The phenomenon is probably due to the asymmetry of the etching agent. In certain conditions $PbCl_2$ (normally showing holohedral orthorhombic symmetry) can be obtained from hot solutions containing dextrin in microscopic crystals consisting of a single form (bisphenoid) which can have only axial symmetry. The same phenomenon is shown to a smaller extent by $PbBr_2$ and $HgBr_2$. In each case the identity of the anhyd. normal crystal and of the modification was confirmed by chemical analysis and by *X*-ray powder diagrams. The four Pb atoms in the $PbCl_2$ structure lie in the planes of simple symmetry (100) and (200), in an approx. hexagonal close packing. L. L. BIRCUMSHAW.

Spinel structure: example of variate atom equipoints. T. F. W. BARTH and E. POSNJAK (J. Wash. Acad. Sci., 1931, **21**, 255—258).—Comparisons of the observed and calc. intensities on $MgFe_2O_4$ and $MgGa_2O_4$ show that, instead of having Mg in 8*f* and (Fe, Ga) in 16*c*, 8 (Fe, Ga) ions occupy positions in 8*f* and 8 (Fe, Ga) ions and 8 Mg ions are in 16*c*. The possibility that different atoms replace one another in structurally equiv. positions of a crystal in this way is probably not confined to spinels. It is proposed to call unit cells of such crystals "cuts with variate atom equipoints." N. H. HARTSHORNE.

Structure of Tutton's salts. II. W. HOFMANN (Z. Krist., 1931, **78**, 279—333; cf. this vol., 415).—The following values are now given for *a*, *b*, *c*, for the series $M^IM^{II}(SO_4)_2,6H_2O$: $M^IM^{II}=(NH_4)_2Zn$, 9·205, 12·475, 6·225; $(NH_4)_2Cd$, 9·35, 12·705, 6·27; $(NH_4)_2Fe$, 9·28, 12·57, 6·22; K_2Mg 9·04, 12·24, 6·095; Tl_2Mg 9·22, 12·42, 6·185; $(NH_4)_2Mg(SeO_4)_2,6H_2O$, 9·42, 12·72, 6·30. The unit cell contains 2 mols.; space-group C_{2h}^5. A complete structure is deduced indicating physical properties in good agreement with the facts. The small effect of change in M^{II} is explained by the ion being surrounded by an octahedron of $6H_2O$. The structure can be represented as pseudocubic, closely resembling that of the alums. C. A. SILBERRAD.

Crystal structure of lithium iodate. W. H. ZACHARIASEN and F. A. BARTA (Physical Rev., 1931, [ii], **37**, 1626—1630).—The crystals are hexagonal with 2 mols. per unit cell; space-group D_6^6;

a 5·469±0·003, *c* 5·155±0·005 Å. Atom positions and grouping are detailed. N. M. BLIGH.

Crystal structure of tysonite. I. OFTEDAL (Z. physikal. Chem., 1931, B, **13**, 190—200).—Tysonite has *a* 7·124±0·007, *c* 7·280±0·007 Å.; space-group D_{6h}^3, or possibly D_6^6; the unit cell contains 6 mols. The structure appears to be simpler than that previously described (A. 1929, 1223). H. F. GILLBE.

Lattice dimensions and space-group of braunite. G. AMINOFF (K. Svensk. Veten. Handl. Stockholm, 1931, [iii], 9, No. 5, 14—22).—The space-group is probably D_{4h}^{20}. The unit cell, *a* 13·28, *c* 18·58, contains 8 mols. of $3MnMnO_3,MnSiO_3$. L. J. SPENCER.

***X*-Ray diffraction by incandescent carbon.** M. HIRATA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, **15**, 219—226).—The positive and negative incandescent electrodes of a C arc were examined by *X*-rays. The thermal expansion of graphite takes place in the direction perpendicular to the (002) plane. Reflexions due to the oblique planes and to second order (002) in the incandescent state are much diminished in intensity. W. GOOD.

Nature of the specific properties of molecular surface fields. Structure of active charcoal and the inversion effect for heats of adsorption and wetting. II. B. ILJIN and J. SIMANOV (Z. Physik, 1931, **70**, 559—561; cf. this vol., 421).—Debye photographs which showed no difference in structure between hydrophobic and quasihydrophilic C detected 2% of graphite deposited on the hydrophilic form. A. B. D. CASSIE.

***X*-Ray investigations of the crystals of copper formate dihydrate.** M. PRASAD and H. M. MAPARA (Indian J. Physics, 1931, **6**, 41—49).—The rotating-crystal method gives *a* 8·952, *b* 6·726, *c* 8·235 Å.; the unit cell contains 4 mols.; they are asymmetric. A. J. MEE.

Crystal form of paraffin hydrocarbons. G. H. GRAVES (Ind. Eng. Chem., 1931, **23**, 762).—Photomicrographs of synthetic hydrocarbons containing 22, 23, 30, and 40 C atoms are given. The cryst. plates are similar in form to the waxes $C_{18}H_{38}$ to $C_{43}H_{88}$ obtained from paraffin wax. T. A. SMITH.

Crystal structure of methane. H. H. MOOY (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 660—662).—The separation of the C and H atoms in solid CH_4 at 20·5° abs. is 0·09 Å., whereas the value deduced from infra-red data is 1·13 Å. The space-group structure is T_d^2. W. R. ANGUS.

Crystal structure of natural amino-acids and related compounds. J. D. BERNAL (Z. Krist., 1931, **78**, 363—369).—The following data are given: dimensions of unit cell, *a*, *b*, *c*, (where not 90°) β, no. of mols. therein. and space-group: α-glycine 5·04, 12·1, 5·41, 111° 38′, 4, $C_{2h}^5 2_1 n$; β-glycine 5·18, 6·18, 5·29, 114° 20′, 2, $C_2^2 n$; *l*-cystine 5·40, 57·8, 5·40, 120°, 6, $D_6 6_1 2$; *dl*-alanine 6·0, 12·0, 5·8, 4, $C_{2v}^9 bn$ (pseudo *bnm*); *d*-alanine 6·0, 12·1, 5·75, 4, $V^4 2_1 2_1 2_1$ (pseudo *bnm*); *d*-phenylalanine 30·8, 11·0, 4·8, 8, $V^4 2_1 2_1 2_1$; *l*-aspartic acid 5·1, 6·9, 15·1, 96°, 4, $C_2^2 2_1$; asparagine 5·6, 11·8, 9·86, 4, $V^4 2_1 2_1 2_1$; *l*-glutamic acid 7·06, 10·3, 8·75, 4, $V^4 2_1 2_1 2_1$; diketopiperazine 5·19, 11·5, 3·96, 83°, 2, $C_{2h}^5 2_1 a$; α-glycylglycine, 7·7, 9·56, 9·5, 125° 20′, 4, $C_{2h}^5 2_1 a$; β-glycylglycine, 17·3, 4·65, 8·4, 125° 20′, 4, $C_{2h}^5 2.a$; γ-glycylglycine, 8·1, 9·36, 7·7, 4, $C_2^5 bc$; diglycylglycine dihydrate 22·0, 9·8, 4·7, 4, $C_{2v}^5 ca$; $BaCl_2$–glycine 7·96, 14·7, 9·21, 4, $V_h^{16} cmn$. β-Glycine is obtained by adding EtOH to a glycine solution. Diglycylglycine was obtained in only one form, whether crystallised from H_2O or aq. EtOH. The positions of the atoms are sketched. C. A. SILBERRAD.

Physico-chemical researches on amino-acids. VII. T. YAGINUMA and K. HAYAKAWA. **VIII.** T. YAGINUMA (J. Soc. Chem. Ind. Japan, 1931, **34**, 215—216B, 216—218B).—I. The identity of a substance isolated in a biochemical research by S. Shiraishi, and believed to be histamine picrate, has been confirmed by comparing its crystallographic properties with those of chemically prepared histamine picrate. The latter is monoclinic, sphenoidal, β 100° 39′, $a:b:c=1·2216:1:1·2266$. Values of n_α, n_β, n_γ, and ν for three wave-lengths are given.

II. *d*- and *l*-Leucine have the following crystallographic properties: orthorhombic, $a:b:c=1·5139:1:1·0025$, n_α 1·5331, n_β 1·5361, n_γ 1·5514. *d*- and *l*-Norleucine are orthorhombic, $a:b:c=1·3924:1:2·8662$; n_α 1·5100, n_β 1·5104, n_γ 1·5385. N. H. HARTSHORNE.

Theory of *X*-ray interference in *p*-azoxyanisole. E. BUCHWALD (Ann. Physik, 1931, [v], **10**, 558—578).—Simple models are proposed for the explanation of the interference of *X*-rays in *p*-azoxyanisole observed by Hermann and others. In a magnetic field all the aggregates are arranged in the same direction, and the max. are perpendicular to the N–S direction; without the field the aggregates are irregularly disposed, and the max. are given, not by Bragg's formula, but by that of Keesom. A. J. MEE.

***X*-Ray diffraction of organic substances in the solid and liquid state.** S. TANAKA, G. OKUNO, and A. TSUJI (Mem. Coll. Sci. Kyoto, 1931, A, **14**, 67—71).—From a study of the relation of the crystal lines to the liquid bands it is concluded that the crystal planes which produce intense reflexion seem to maintain their properties when the crystal becomes liquid. W. GOOD.

Relation between m. p. and crystal structure. A. FERRARI (Atti III Cong. Naz. Chim., 1929, 449—451; Chem. Zentr., 1931, i, 2162—2163).—The m. p. is considered to depend on the number, mass, and distance of the atoms surrounding a given atom. Increasing distance should depress the m. p. The m. p. of halides of univalent metals falls with increasing radius of the negative ion. A regular depression of m. p. is not observed when the crystal structures of the halides differ, as in halides of bivalent metals. For elements of similar structure and nearly equal at. radii (V, Mo, W, Ta) the m. p. is given approx. by the formula $2700\sqrt{\text{at. wt.}}/a^2$, where *a* is the length of side of the unit cell. In body-centred lattices the m. p. is approx. proportional to at. wt. For Al, Ag, and Au the formula $400\times\text{at. wt.}^{\frac{1}{2}}$ holds. A. A. ELDRIDGE.

Micelle structure of the wool fibre. J. B. Speakman (Proc. Roy. Soc., 1931, A, **132**, 167—191; cf. A., 1930, 1370).—On immersion in H_2O, dry Cotswold wool fibres increase in length and diameter by 1·19 and 17·5%, respectively. The inter-micellar distance in the dry fibre is of the order of 6 Å., but in fibres swollen in H_2O it is 41 Å. The internal surface of the fibre is estimated as $0·77\times10^6$ sq. cm./g. approx. The total inter-micellar H_2O adsorbed by wool from saturated air is 20·5% of the dry wt. The value deduced from a study of the change in rigidity of wool with H_2O adsorption is 21·6%. The energy required to stretch wool fibres is less in HCO_2H and AcOH than in H_2O, and observations on swelling in the two acids suggest that their action on wool is due to a reversible destructive action on the micelle structure, the long-chain protein mols. being partly freed from one another. Aq. solutions of a number of other acids have the same action on wool.

L. L. Bircumshaw.

Relation of ferromagnetism to conductivity. H. Sachse (Z. Physik, 1931, **70**, 539—547).—The difference in electrical conductivity of Fe_2O_3 and Fe_3O_4 observed by Ghosh (this vol., 673) is too great, and probably bears no relation to their different magnetic properties. A. B. D. Cassie.

Anisotropy of magnetisation in ferromagnetic single crystals. F. Bloch and G. Gentile (Z. Physik, 1931, **70**, 395—408).—Theoretical. An investigation of interaction of elementary magnets in ferromagnetic single crystals. A. B. D. Cassie.

Cohesion of natural fluorite crystals. E. Rexer (Z. Krist., 1931, **78**, 251—256).—Using Blank's method (cf. A., 1930, 845) the mean tensile strength perpendicular to an octahedral face of fluorite varied from 1323 to 4930 g. per sq. mm. for crystals of various origins, the purest giving the lowest figures. Variations are due to impurities (cf. A., 1930, 675).

C. A. Silberrad.

Deformation of crystals at high pressures and temperatures. F. Heide (Z. Krist., 1931, **78**, 257—278).—Using Rose and Mugge's apparatus (cf. A., 1923, ii, 852) pressures up to 17,000 atm. and temps. to 400° applied to crystals of barytes, cœlestite, and anglesite caused translations along (001), (011), (102), (010), and probably (110), and slipping with K_1=(110), K_2=$(1\bar{1}0)$. Heat greatly facilitates the action of pressure. The production of Grahmann's modifications of barytes and cœlestite by heat (cf. A., 1913, ii, 586) is confirmed. C. A. Silberrad.

Mutual orientation and the forces at crystal faces. C. A. Sloat and A. W. C. Menzies (J. Physical Chem., 1931, **35**, 2005—2021).—KCN, KBr, RbCl, and RbBr, when deposited on PbS, are oriented if contamination of the surface of the substrate by oil is prevented. Royer's results with the substrate NaCl have been confirmed, except for RbCl. In salts which exhibit orientation the ratio of the radius of the anion to that of the cation is relatively large; the tendency to orientation therefore increases with decrease of symmetry of the field of the ion pair. Mutual orientation is readily obtained by using an org. solvent, and is favoured by solvents of low dielectric const. The apparent hydrophobia of galena is due merely to the affinity of the mineral for grease. The orientation of salts on Ag demands a smaller difference of parameter than does that on a salt substrate; the results described are attributed to the presence of a positive charge on the Ag crystal. The change of habit observed when crystals grow in presence of a foreign substance is not due to preferential adsorption. The forms of NH_4Cl and NH_4Br which are stable at high temp. are oriented when deposited from the vapour phase on NaCl or KCl. Mutual orientation does not apparently occur between electrovalent and covalent compounds. H. F. Gillbe.

Dimorphism of certain higher aliphatic compounds. J. W. C. Phillips and S. A. Mumford (J.C.S., 1931, 1732—1737).—Cetyl and octadecyl acetates, cetyl chloride, and Et cetylmalonate show monotropic dimorphism. The large and transparent crystals first obtained when the liquid is cooled are transformed into a finer, more opaque, and higher-melting form when seeded with crystals which have been cooled below 0°. Cetyl bromide, cetyl iodide, margaronitrile, Et margarate, and Et cetyl ether can only be said with certainty to exist in one form, although it is possible that another is produced momentarily. In the first three cases the modification obtained corresponds with the β-variety of the first substances mentioned, and in the case of the latter two compounds to the α-form. The margaric ester on further cooling changed into a more opaque form, the transition temp. being 14·5±3°. This behaviour is not shown by the palmitic and stearic esters. The cooling curves of the other compounds and also of n-hexadecane show no discontinuity down to −10°, although that of cetyl alcohol showed a well-defined discontinuity at about 40°. A. J. Mee.

Physics of real crystals. A. Smekal (Physikal. Z., 1931, **32**, 581—583).—A summary of recent work.

A. J. Mee.

Calculation of the latent heat of fusion of camphor from vapour pressure–temperature data. R. J. W. Le Fèvre and C. G. Tideman (Nature, 1931, **127**, 972—973).—Attention is directed to errors in Jouniaux's calculation (A., 1912, ii, 625).

L. S. Theobald.

Glass. VI. Specific heat of boron trioxide. S. B. Thomas and G. S. Parks. **VII. Conductivities and dielectric constants of dextrose and boron trioxide glasses.** S. B. Thomas (J. Physical Chem., 1931, **35**, 2091—2102, 2103—2111).—VI. The sp. heat (±4%) of B_2O_3 glass and liquid has been determined at temp. from 35° to 350° by a specially designed calorimeter. The temp.–sp. heat curves are analogous to those obtained with org. glasses, but exhibit variations according to the rate of cooling during the prep. of the glass.

VII. The conductivities and dielectric consts. of dextrose and of $Na_4B_2O_7$–B_2O_3 mixtures throughout the interval of transition from a viscous liquid to a glass are functions of the viscosity, and vary continuously. H. F. Gillbe.

Specific heats of five pure organic liquids and of ethyl alcohol–water mixtures. F. E. Blacet, P. A. Leighton, and E. P. Bartlett (J. Physical Chem., 1931, **35**, 1935—1943).—The sp. heats of PhEt,

CH_2Ph_2, NH_2Ph, and $C_{10}H_8$ over a range of temp. have been determined. NH_2Ph and PhEt yield anomalous temp.–sp. heat curves, but those of the other substances are linear. The max. deviation from the ideal law of the sp. heat of EtOH–H_2O mixtures at 30° occurs at 30% EtOH, and with rise of temp. the max. moves regularly, until at 70° it occurs at 55% EtOH. H. F. GILLBE.

Melting curve of hydrogen to 450 kg. per sq. cm.[2] W. H. KEESOM and J. H. C. LISMAN (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 598—601).—Previous work is repeated and extended (A., 1929, 387). Good agreement between experimental and theoretical values of p is obtained. W. R. ANGUS.

F. p. of platinum. W. F. ROESER, F. R. CALDWELL, and H. T. WENSEL (Bur. Stand. J. Res., 1931, **6**, 1119—1129).—The f. p. of Pt, determined with the optical pyrometer, is 1773·5°±1°. H. F. GILLBE.

Gas thermometric determination of the fixed points below 0° in combination with vapour pressure and resistance thermometers. W. HEUSE and J. OTTO (Ann. Physik, 1931, [v], **9**, 486—504).—Using a He thermometer the following points on the thermodynamic temp. scale have been fixed: m. p. H_2, −38·832°, sublimation pt. CO_2, −78·483°, b. p. O_2, −182·962°, b. p. H_2, −252·780°. The first two temps., measured by two Pt resistance thermometers, showed values less than 0·05° lower than the above. J. W. SMITH.

Molecular association and internal pressure. G. G. LONGINESCU and I. N. LONGINESCU (Bul. Chim. Soc. Romane, 1930, **33**, 1—7).—The phenomena attributed to mol. association may be considered as due to high internal pressure. C. W. GIBBY.

Mathias' coefficient and the formula of G. G. Longinescu. I. N. LONGINESCU (Bul. Chim. Soc. Romane, 1930, **33**, 1—3).—Theoretical. Mathias' reduced coeff., in his equation dealing with the relative densities of substances in the liquid and gaseous states, is four times that of Longinescu. C. W. GIBBY.

Thermal properties of toluene. K. NESSELMANN and F. DARDIN (Wiss. Veroff. Siemens-Konz., 1931, **10**, [2], 129—154).—Curves have been constructed for the vapour tension, sp. heat of the vapour and liquid, sp. gr. and vol. of the liquid, and latent heat of vaporisation of PhMe at temps. up to 250° and pressures up to 10 atm. A. R. POWELL.

Behaviour of the two modifications of liquid helium under pressure. W. H. KEESOM and K. CLUSIUS (Naturwiss., 1931, **19**, 462).—The pressure–temp. curve for the two modifications of He is reproduced and discussed. W. R. ANGUS.

Transition under pressure of liquid helium I to liquid helium II. W. H. KEESOM and K. CLUSIUS (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 605—609).—The temp. of transition is lowered as the pressure is increased. By a linear extrapolation the transition curve intersects the pressure–temp. curve at 30 atm. and 1·75° abs. W. R. ANGUS.

Vapour-pressure measurements. I. Vapour pressure of nitrobenzene. H. BRÜCKNER (Z. anorg. Chem., 1931, **199**, 91—92).—The v. p. has been measured between 0° and 50°. R. CUTHILL.

Gaseous state. C. ZENGHELIS (Chim. et Ind., 1931, **26**, 3—8).—A discussion. The conditions under which a substance is gaseous at the ordinary temp. and pressure are (1) great stability of the peripheral electrons of the atoms or of the mols. if the substance is diatomic; (2) electronegative properties; (3) diat. constitution, unless the substance is non-reactive; and (4) a low chemical equiv. H. F. GILLBE.

Temperature coefficient of gaseous friction. M. TRAUTZ (Ann. Physik, 1931, [v], **10**, 263—264).—Mathematical. A. J. MEE.

Molecular composition of binary liquid mixtures. G. TAMMANN (Z. anorg. Chem., 1931, **199**, 117—119; cf. A., 1928, 698).—If the formation of a compound in a binary liquid mixture involves a decrease in the mol. wt. a min. or point of inflexion may appear on the viscosity–composition curve. R. CUTHILL.

Variations in the azeotropic concentration of ethyl alcohol–benzene mixtures in relation to pressure. W. SWIENTOSŁAWSKI and R. KOPCZYNSKI (Rocz. Chem., 1931, **11**, 440—448).—The composition of azeotropic mixtures of EtOH and C_6H_6 is determined for pressures of 760—1743 mm., using a differential ebullioscope. R. TRUSZKOWSKI.

Application of resistance thermometers to ebullioscopy and tonometry. II. Azeotropy of ethyl alcohol–benzene mixtures. A. ZMACZYNSKI (Rocz. Chem., 1931, **11**, 449—468).—A modification of Swientosławski's differential ebullioscope for work at high pressures is described. For azeotropic mixtures at different pressures the composition and b. p. are: 760 mm., 32·38% EtOH, b. p. 68·02°; 3460 mm., 51·30% EtOH, b. p. 116·75°; 5920 mm., 58·97% EtOH, b. p. 137·75°. Azeotropy persists at pressures up to 7500 mm., but is probably absent at higher pressures. R. TRUSZKOWSKI.

Refractive index, atomic size, and packing in glasses. J. T. RANDALL and N. GEE (J. Soc. Glass Tech., 1931, **15**, 41—53T).—Using Wasastjema's values for ionic refractivities with slight modifications, the calc. values of n_D for a series of glasses are shown to agree satisfactorily with recorded data. From the ionic diameters given by Bragg, it is shown that the mol. vol. of a glass bears an almost const. ratio to the sum of the at. vols. The degree of packing of the glasses examined is more nearly const. than that of the crystals. M. PARKIN.

Thermal expansion of alloys of iron, nickel, and cobalt. H. MASUMOTO (Sci. Rep. Tohoku, 1931, **20**, 101—123).—The mean coeff. of thermal expansion (α) between 30° and 100° in binary and ternary alloys of Fe, Ni, and Co has been measured and the relation between α and the equilibrium diagrams of these systems studied. Alloys of small expansibility were investigated between the temp. of liquid air and the crit. point and the range of temp. available for this small expansibility was determined.

The smallest value of α found was 10^{-7}. A theory is advanced to explain the small expansibility of invar.
W. GOOD.

Thermal measurement of latent energy in cold-worked metal and alloys. S. SATO (Sci. Rep. Tohoku, 1931, **20**, 140—177).—The thermal changes which occur during the heating of cold-worked metals and alloys have been investigated and the energy retained as internal energy has been determined. The apparatus and procedure used are described.
W. GOOD.

Dependence of magnetic properties of cobalt–chromium mixed crystals on temperature. F. WEVER and H. LANGE (Mitt. Kaiser-Wilh. Inst. Eisenforsch., 1930, **12**, 353—363; Chem. Zentr., 1931, i, 2178).—Solid solutions containing up to 20% Cr were studied. The polymorphic transformation shows a large temp. hysteresis. Both modifications possess a characteristic temp.–concentration curve for the loss of magnetisability.
A. A. ELDRIDGE.

System aluminium–silver. E. CREPAZ (Atti III Cong. Naz. Chim., 1929, 371—379; Chem. Zentr., 1931, i, 2158).—The phase diagram of Al–Ag alloys has been studied thermally, and the solubility of Ag in solid Al has been investigated microscopically. The compounds Ag_3Al, Ag_2Al, and Ag_3Al_2 are formed. The eutectic temp. for a saturated solution of Ag in Al and the compound Ag_3Al_2 is 567° (39·5% Al); the solubility of Ag in Al is 45% Ag at the eutectic, and $<$0·5% at room temp.
A. A. ELDRIDGE.

Equilibrium diagram of the chromium–carbon system. K. HATSUTA (J. Study Met., 1931, **8**, 81—88).—Four carbide phases, ε, η ξ, and κ, correspond respectively with Cr_4C (cubic), Cr_7C_3 (trigonal), Cr_3C_2 (orthorhombic), and (?) CrC. A eutectic ($\alpha+\varepsilon$) lies at 1485°, 3·7% C. The ε and η phases are peritectically formed thus: $\eta+\text{melt}\longrightarrow\varepsilon$ (1530°); $\xi+\text{melt}\longrightarrow\eta$ (above 1600°). The ξ phase probably has the max. m. p. on the liquidus curve, and forms a eutectic with the κ phase; a transformation takes place at 1505° in this phase.
CHEMICAL ABSTRACTS.

Improvement of eutectic structures. F. DE CARLI (Atti III Cong. Naz. Chim., 1929, 432; Chem. Zentr., 1931, i, 2157—2158).—Addition of small quantities of metals or alkali fluorides leads to homogeneous distribution of the crystal particles; alkali metals retard the growth of crystals on solidification.
A. A. ELDRIDGE.

Atomic size and isomorphism. G. NATTA and L. PASSERINI (Atti III Cong. Naz. Chim., 1929, 365—370; Chem. Zentr., 1931, i, 2159—2160).—Systems of oxides and hydroxides of bivalent metals with ionic radius 0·70—1·06 Å. were studied by the X-ray powder method. The systems NiO–CoO, CoO–MgO, CoO–MnO, CoO–CdO, $Co(OH)_2$–$Mn(OH)_2$, $Mn(OH)_2$–$Cd(OH)_2$, $Ca(OH)_2$–$Cd(OH)_2$, $Ni(OH)_2$–$Co(OH)_2$, $Mg(OH)_2$–$Co(OH)_2$, and $Ni(OH)_2$–$Mg(OH)_2$ form solid solutions in all ratios; with CdO–MnO, NiO–MnO, MgO–MnO, CoO–MnO, ZnO–MgO, NiO–ZnO, CoO–ZnO, $Zn(OH)_2$–$Mg(OH)_2$, $Zn(OH)_2$–$Ni(OH)_2$, and $Zn(OH)_2$–$Co(OH)_2$ there is partial, and with NiO–CdO, NiO–CaO, MgO–CaO, CoO–CaO, MgO–CdO, CrO–CdO, $Mg(OH)_2$–$Ca(OH)_2$, and $Ni(OH)_2$–$Ca(OH)_2$ no, formation of solid solutions. Two cubic oxides of bivalent metals give solid solutions in all ratios only when the difference between the cationic radii is not much greater than 13% of the radius of the smaller cation. Partial solid solutions are obtained when the difference of the cationic radii is less than 25% of the smaller radius; solid solutions were not observed when the difference was $>$30%. The hydroxides show an increase in solubility limits with increasing dimensions of the unit cell. Carbonates are also considered.
A. A. ELDRIDGE.

Liquid ammonia and lithium nitrate. N. KAMEYAMA (J. Soc. Chem. Ind. Japan, 1931, **34**, 236B).—The vapour pressures of saturated $LiNO_3$ solutions between 10° and 50° are higher than those previously recorded.
C. IRWIN.

Solubility of sodium fluosilicate in aqueous sodium sulphate solutions and the activity coefficients of sodium fluosilicate and the fluosilicate ion. (MISS) A. G. REES and L. J. HUDLESTON (J.C.S., 1931, 1648—1652).—Solubility data are given for 17° and 20·8°. The activity coeffs. of Na_2SiF_6 and SiF_6'' have been determined; comparison of the results with those of Lewis and Randall for K_2SO_4 indicates that the latter should be multiplied by 1·033.
H. F. GILLBE.

Solubilities of metallic cyanides. K. MASAKI (Bull. Chem. Soc. Japan, 1931, **6**, 143—147).—The ionic conductance of CN′ has been measured and from it the solubilities of the cyanides of Cd, Ni, Zn, and Co have been calc.
F. J. WILKINS.

Crystallisation of anhydrous sodium acetate from aqueous solution at room temperature. W. W. CONNER (J. Amer. Chem. Soc., 1931, **53**, 2806—2807).—Complete dissolution of NaOAc occurs when $NaOAc,3H_2O$ is heated at 80° in a sealed tube. Anhyd. NaOAc crystallises when the tube is cooled to 0°, and is not converted into $NaOAc,3H_2O$ until cooled in liquid NH_3.
J. G. A. GRIFFITHS.

Molasses formation. I. Equilibrium of the system sucrose–water–alkali chloride at 30° and the viscosity of the liquid phase. K. NISHIZAWA and M. AMAGASA (J. Soc. Chem. Ind. Japan, 1931, **34**, 236—238B).—Equilibria between NaCl and KCl, sucrose, and H_2O at 30° have been examined. Chloride and sucrose mutually increase the solubility, but the effect of the former on the latter is very slight until the chloride concentration reaches 25 g. per 100 c.c. KCl has a greater influence than NaCl. No compound of sucrose and chloride exists in the solid state. There is a very marked increase in the viscosity of the solutions saturated with sucrose consequent on the presence of NaCl. This does not occur with KCl, and the formation of some metastable compound in the liquid phase is suggested.
C. IRWIN.

Discontinuities in adsorption isotherms. A. F. BENTON and T. A. WHITE (J. Amer. Chem. Soc., 1931, **53**, 2807—2808; cf. A., 1930, 990).—Many of the adsorption isotherms for H_2, N_2, and CO at pressures between 0 and 1 atm. on Ni, Cu, and Fe, in the range −200° to 200°, exhibit stepwise increases of adsorption with pressure which are characteristic of physical or

" secondary " adsorption and occur under conditions precluding liquid or multimol. films. It is suggested that the steps represent the formation of concentric rows of adsorbed mols., first at the edges of each crystal face with successive building up towards the centre. J. G. A. GRIFFITHS.

Adsorption of hydrogen. II. Maintenance of a unimolecular layer and liberation of recombined atoms with emission of energy. M. C. JOHNSON (Proc. Roy. Soc., 1931, **A**, **132**, 67—82; cf. A., 1929, 639).—Numerical values are obtained for the several processes contributing to the maintenance of a loosely-packed layer of adsorbed H by the analysis of curves of the fall of pressure in an electrodeless discharge. The chance that a collision between an atom in the adsorbed layer and an atom from the gaseous phase should result in recombination and desorption decreases exponentially as the concentration of neighbouring at. H in the layer is increased. This is interpreted as indicating that the valency of a H atom in the adsorbed state is not completely unsaturated (unless it be the only atom present on the surface), and that therefore the adsorbed layer possesses the character of a lattice. It is shown theoretically, and verified experimentally by measurement of the heating of a W wire, that for a given partial pressure of at. H in the gaseous phase, the total emission of energy by recombination of atoms leaving the layer increases with rise in the initial temp. of the surface, and passes through a max. L. L. BIRCUMSHAW.

Electrical condition of hot surfaces during the adsorption of gases. IV. Carbon and copper surfaces at temperatures up to 850°. G. I. FINCH and J. C. STIMSON (Proc. Roy. Soc., 1931, **A**, **132**, 192—200).—A C rod does not become " normalised " (*i.e.*, show const. and reproducible surface potential values) until the initial evolution of occluded gases has ceased. Such gas is regarded as chemically bound by the surface, which suffers structural alteration on its removal. A Cu sheet is not fully " normalised " until some time after the initial gas evolution has ceased. In this case sintering is probably occurring. O_2 forms a stable oxide completely blanketing the surface, which does not exhibit a surface potential either in vac. or in contact with O_2. Previous results obtained for Au, Ag, Ni, and Pt (A., 1927, 1135; 1928, 1087; 1929, 875) are discussed. The surface potentials acquired by any of the surfaces under similar experimental conditions tend to approach zero as the " normalisation " temp. is raised. At 850° the surface potentials fall into 3 groups: (1) O_2; (2) in vac., N_2, A, and CO; and (3) H_2. At this temp. the sp. effect of the surface is much reduced. L. L. BIRCUMSHAW.

Critical increment of the adsorption of hydrogen on amorphous carbon at 400—520°. F. E. T. KINGMAN (Nature, 1931, **128**, 272).—The rates of adsorption of H_2 by amorphous C for pressures from 1 cm. to 10^{-3} cm. Hg are given by $-dp/dt=k(Ap+p^2)$, where k is the velocity coeff. and A is a const. containing the area. A is practically doubled by a rise in temp. from 400° to 520°. Log k plotted against T^{-1} gives a straight line and a calc. crit. increment of 3×10^4 g.-cal. The results are discussed. L. S. THEOBALD.

Porosity of charcoal and the time required for the attainment of adsorption equilibrium. M. DUBININ (Z. physikal. Chem., 1931, **155**, 116—122).—The time required for the attainment of the equilibrium state in the adsorption from aq. solution of propionic, valeric, and heptoic acids, HCl, H_2SO_4, and H_3PO_4 on charcoal of varying porosity has been investigated. The reversal of the order of the adsorption series in the fatty acids, observed with fine-pore charcoals, becomes less pronounced when time is allowed for equilibrium to be established. J. W. SMITH.

Adsorption of aliphatic acids by " gas-free " charcoal. L. LEPIN (Z. physikal. Chem., 1931, **155**, 109—115).—The adsorption of the lower fatty acids on charcoal decreases with outgassing. The difference between the quantities adsorbed in air and in a vac. decreases with increasing length of the C chain, and becomes practically zero at C_5. According to the views of Schilov and Tschmutov (A., 1929, 1140; 1930, 991), this decrease in the adsorption with outgassing is explained by the removal from the C of surface basic oxides, which would cause chemical combination with the surface as well as mol. adsorption. This additional adsorption can occur only when the acid chain is oriented with its CO_2H group towards the charcoal. Hence with the higher acids for which the total surface energy becomes const. and which are oriented only with the Me group towards the charcoal, outgassing does not affect the adsorption. J. W. SMITH.

Adsorption by silica and carbon from binary organic liquid mixtures over the entire concentration range. F. E. BARTELL and G. H. SCHEFFLER (J. Amer. Chem. Soc., 1931, **53**, 2507—2511; cf. A., 1929, 757, 999).—MeOH, EtOH, PrOH, BuOH, and *iso*amyl alcohol are preferentially adsorbed by SiO_2 from C_6H_6 over the greater portion of the concentration range and in an order decreasing with increase of mol. wt. The positive preferential adsorption by blood charcoal is much less and is limited to a much smaller range of concentrations. S-shaped adsorption curves are obtained in all cases except in the systems MeOH–C_6H_6–SiO_2 and *iso*amyl alcohol–C_6H_6–C which exhibited no preferential adsorption of C_6H_6 and alcohol, respectively (cf. A., 1930, 1110). The modified Freundlich equation applies to all cases. The greater is the solubility, in a given solvent, of a member of a series of compounds with similar adhesion tensions against an adsorbent, the smaller is the tendency for the solute to be adsorbed. J. G. A. GRIFFITHS.

Adsorption by silica from non-aqueous binary systems over the entire concentration range. F. E. BARTELL, G. H. SCHEFFLER, and C. K. SLOAN (J. Amer. Chem. Soc., 1931, **53**, 2501—2507; cf. A., 1929, 999).—The binary systems of Et_2CO_3 with C_6H_6, MeOBz, and $NPhMe_2$, and of EtOH with C_6H_6 have been investigated interferometrically and the results represented by the equation previously developed. The component with the higher adhesion tension against SiO_2 is preferentially adsorbed over the greater portion of the concentration range and for each system an S-shaped adsorption curve is obtained which is very nearly the inverted and reverse form of that obtained with the same binary system and C as ad-

sorbent. This result is related to the general rule that the order of increasing adhesion tensions of a series of liquids against C is the reverse of the order of increasing values against SiO_2. J. G. A. GRIFFITHS.

Hysteresis effects in the absorption of water by human hair. N. H. CHAMBERLAIN and J. B. SPEAKMAN (Z. Elektrochem., 1931, **37**, 374—375, 376—377).—It is claimed that, contrary to the observations of Fricke and Luke (A., 1930, 542, 1118), the absorption of H_2O by hair exhibits hysteresis. R. CUTHILL.

[**Hysteresis effects in the absorption of water by human hair.**] R. FRICKE and J. LUKE (Z. Elektrochem., 1931, **37**, 375—376).—A reply to Chamberlain and Speakman (cf. preceding abstract). R. CUTHILL.

Theory of static and dynamic displacement. III. D. REICHINSTEIN (Z. Elektrochem., 1931, **37**, 365—371; cf. A., 1928, 132).—The application of the theory to adsorption is described and adsorption isotherms are deduced. It is shown that the Freundlich isotherm is in substantial agreement with the theory, and that it is probable that in many cases of adsorption saturation is not reached in a finite time. R. CUTHILL.

Topochemistry of contact catalysis. VI. Detection of adlineation by radioactive indicators. G. M. SCHWAB, E. PIETSCH, and (FRL.) E. JOSEPHY (Z. physikal. Chem., 1931, **B**, **13**, 13—17; cf. this vol., 919).—Further evidence has been obtained to show that the adsorption of Th-*B* by crocoisite (A., 1929, 1399) is due to adlineation at the edges of the crystals. R. CUTHILL.

Adsorption method for determination of area of a powder. W. D. HARKINS and D. M. GANS (J. Amer. Chem. Soc., 1931, **53**, 2804—2806).—The area is computed from the decrease in concentration of a solution of oleic acid in very dry C_6H_6 after establishing adsorption equilibrium with the powder (*e.g.*, TiO_2 or SiO_2 dried at high temp. in vac.) and assuming that the area per mol. of adsorbed acid is 20·0 sq. Å. The adsorption becomes almost const. at concentrations greater than 0·01—0·02 g.-mol. of acid per kg. of C_6H_6. J. G. A. GRIFFITHS.

Micro-method for the measurement of surface tension. H. MOUQUIN and S. NATELSON (J. Physical Chem., 1931, **35**, 1931—1934).—The very simple method described is based on measurement of the pressure necessary to force a drop of the liquid along a conical capillary in the direction of the larger cross-section; a microscope is the only special apparatus required, and the accuracy is comparable with macro-methods. H. F. GILLBE.

Variability of surface tension of water with increasing thickness of the glass plate. (Experiments with Searle's tensiometer.) B. N. SRIVASTAVA (Kolloid-Z., 1931, **56**, 45—49).—In surface-tension determinations using the Searle tensiometer, the values obtained increase linearly with the thickness of the glass plate used. E. S. HEDGES.

Theory of variability of surface tension with the thickness and section of the glass plate as measured with the Searle tensiometer. S. RAY. (Kolloid-Z., 1931, **56**, 49—51).—A theoretical treatment (cf. preceding abstract). E. S. HEDGES.

Capillary activity in aqueous solutions. H. MILLS and P. L. ROBINSON (J.C.S., 1931, 1629—1648).—On the basis of surface tension measurements two groups of capillary-active compounds are recognised. For those which show only slight interfacial adsorption the surface tension depression at equimol. concentration is proportional to the fourth power of the parachor; the proportionality const. is $7{\cdot}9\times10^{-8}$ approx. for a number of acids, alcohols, ketones, and amines. The rule breaks down if the surface concentration is relatively great, but is apparently valid if the bulk concentration alone is considered. A bubbling method for determining the rate of interfacial adsorption in such solutions is described. The rate diminishes with dilution and increases with increase of the ratio of max. adsorption concentration to bulk concentration; initially it is very small. H. F. GILLBE.

Unimolecular layers of proteins. F. HERČIK (Kolloid-Z., 1931, **56**, 1—7).—The properties of unimol. films of serum, serum- and egg-albumins, and myoprotein, as determined by the surface tension min. method of du Noüy, bear no relation to those recognised by the spreading method of Langmuir and Adam, probably because the latter method gives rise to films of denatured proteins. E. S. HEDGES.

Capillary systems. XI. Dialytic behaviour of canal-like capillary systems. (Collodion membranes, cellophane, parchment.) E. MANEGOLD and K. VIETS (Kolloid-Z., 1931, **56**, 7—40).—A mathematical investigation is made of the dependence of dialysis on the size of cross-section of the capillaries and of the dialysing mols. In the case of membranes of collodion, the H_2O content of the membrane has a considerable influence on the velocity of dialysis of carbamide, urethane, sucrose, HCl, KCl, and LiCl, and in H_2O-rich membranes the mobility of these substances is practically equal to that calc. for free diffusion through the available space in the membrane. Dialysis with cellophane membranes leads to calc. diffusion consts. which are only 20% of the values of the free diffusion consts., suggesting that only a fraction of the capillary space is permeable to the dissolved mols. The results obtained with parchment are similar on the whole, although the possibility of adsorption forces hindering the dialysis, particularly in the early stages, is recognised. E. S. HEDGES.

Membrane and osmosis. II. F. A. H. SCHREINEMAKERS (Rec. trav. chim., 1931, **50**, 883—899; cf. this vol., 422).—In the system H_2O–membrane–solution, the direction in which H_2O diffuses depends on the nature of the membrane, the solute, and (sometimes) the concentration of the solution. Through a membrane of cellophane, H_2O flows into solutions of tartaric or succinic acid. Through a membrane of pig's bladder, H_2O flows into solutions of Na_2CO_3, out of solutions of oxalic acid, and into conc. but out of dil. solutions of tartaric or succinic acid. Through a membrane of parchment, H_2O flows into solutions of succinic acid. These results are discussed in the light of general theoretical considerations. R. S. CAHN.

Freezing of dilute, still solutions. V. GIAMBALVO (Z. tech. Physik, 1931, 12, 111—113; Chem. Zentr., 1931, i, 2160).—The f. p. (t_c) and the temp. of max. d (t_M) of an aq. solution are linear functions of the percentage content p. When $t_c=t_M$, $p=a$; the typical cases $p>a$, $t_M<t_c$ and $p<a$, $t_M>t_c$ were studied for NaCl solutions as regards change of concentration and crystallisation phenomena. A. A. ELDRIDGE.

Precision cryoscopy; f.-p. depressions of potassium cobalticyanide and potassium ferricyanide. C. ROBERTSON and V. K. LA MER (J. Physical Chem., 1931, 35, 1953—1984).—The sources of error inherent in cryoscopic measurements are critically reviewed, and an apparatus with an error of $1° \times 10^{-5}$ is described; the f. p. is determined by using a Cu–Ni thermocouple in conjunction with a high-sensitivity galvanometer and a special potentiometer circuit. From a consideration of the magnitude of the individual errors involved a new type of apparatus has been designed. Measurements with 0·0003—0·005M-$K_3Co(CN)_6$ and $K_3Fe(CN)_6$ solutions agree with the form of the osmotic deviation function derived by Gronwall, La Mer, and Sandved by extension of the Debye–Huckel theory. H. F. GILLBE.

Effect of small amounts of impurities on f. p. of organic compounds (apparent and true f.-p. depression). C. WEYGAND and W. GRUNTZIG (Naturwiss., 1931, 19, 660).—Small amounts of impurities in certain triglycerides which exhibit polymorphism may result in the separation on freezing of a metastable modification, the apparent f.-p. depression being abnormally large in consequence. R. CUTHILL.

Observation by the ultra-microscope of smoke particles falling on liquid films. P. D. WATSON and A. L. KIBLER (J. Physical Chem., 1931, 35, 2125—2128).—A practical note. Direct evidence has been obtained of the existence of a H_2O film on smoke particles. The reactions between smoke particles and Cl_2 and the influence of Na oleate on the solubility of moist smoke particles in olive oil have been studied. H. F. GILLBE.

Measurement of particle size for cellulose nitrate dispersion. H. B. DE VORE and W. P. DAVEY (J. Physical Chem., 1931, 35, 2129—2131).—The thickness of a cellulose nitrate film on water bears a linear relationship to the log. of the concentration of the dispersion used. The ultimate particle size is not greater than $1·7 \times 10^{-7}$ cm., and is therefore not very different from that of the unit cell of cellulose nitrate. H. F. GILLBE.

Phenomenon shown by highly-charged aerosols. W. CAWOOD and H. S. PATTERSON (Nature, 1931, 128, 150).—The formation of a spherical cluster of highly-charged particles in the centre of the discharge vessel in which aerosols are produced is described and explained. L. S. THEOBALD.

Rontgenographic examination of internal structure of soap micelles. R. SPYCHALSKI (Rocz. Chem., 1931, 11, 427—439).—The X-ray diagrams of hydrosols of the Na salts of nonoic, decoic, undecoic, myristic, and oleic acids are identical with those of the corresponding dehydrated gels, indicating that the structure of the micelle is unaffected by gelation. The micelles are microcryst., consisting of rectangular prisms, the width and depth of which are const. for all soaps examined (5·0 and 3·7—4·0 Å., respectively), whilst the length varies from 22·8 Å. for nonoic acid to 44·8 Å. for oleic acid; the Na atoms are placed at the corners of the prism. During gelation in polar liquids the prisms join at their ends, yielding long threads, whilst in non-polar liquids they join at their edges, forming laminæ. R. TRUSZKOWSKI.

Apparatus for the rapid measurement of the osmotic pressure of colloidal solutions. P. VAN CAMPEN (Rec. trav. chim., 1931, 50, 915—920).—An apparatus with which the osmotic pressure of 10 c.c. of a solution can be determined in <0·5 hr. is described. The wt. of the micelle of commercial (Merck) hæmoglobin is found to be approx. 18,000, 16,900, and 16,130 in H_2O at the concentrations 9·8, 15·3, and 23·9 g. per litre, respectively. R. S. CAHN.

Structure-viscosimetric measurements of cellulose derivatives in organic solvents and the influence of additions on their viscosity. I. Y. NISIZAWA (Kolloid-Z., 1931, 56, 59—67).—Measurements with the overflow viscosimeter show that sols of cellulose nitrate, cellulose acetate, and ethylcellulose in $COMe_2$, $CH_2Ph·OH$, and mixtures of EtOH and Et_2O exhibit structure viscosity. The strongest effects were observed with cellulose nitrate in EtOH–Et_2O mixtures rich in Et_2O, with cellulose acetate in $CH_2Ph·OH$, and with ethylcellulose in EtOH–C_6H_6 mixtures. As a rule, the structure viscosity increases with the addition of a medium having a pronounced solvent power. E. S. HEDGES.

Action of water on cellulose derivatives. J. DUCLAUX and J. BARBIERE (J. Chim. phys., 1931, 28, 313—315).—When small quantities of H_2O (less than 5%) are added to sols of cellulose dinitrate or cellulose acetate in $COMe_2$ the viscosity is diminished, but larger quantities of H_2O increase the viscosity and act as a coagulant. The different behaviour is ascribed to the state of association of the H_2O, which seems to act as single mols. when present in small quantity and as complex mols. when present in larger amount. That the apparent solvent action of small amounts of H_2O is due to interaction of OH radicals with those in the cellulose derivative is confirmed by the fact that when H_2O is added to cellulose trinitrate solutions in $COMe_2$ the viscosity increases from the start. E. S. HEDGES.

Protective effect of salts of organic hydroxy-acids on cupric oxide sol. S. K. BASU and G. NARASHINA-MURTY (Kolloid-Z., 1931, 56, 51—59).—The protective effect of Na salicylate, gallate, and tannate on CuO sols has been studied by experiments on adsorption and cataphoresis and by spectroscopic observations in the visible and ultra-violet regions. These independent lines of investigation indicate the formation of a complex. E. S. HEDGES.

Photophoresis in suspensions and suspensoids. G. FACHINI (Kolloid-Z., 1931, 56, 40—45).—Photophoresis has been observed in isodisperse suspensions of lamp-black in H_2O in the presence of a protective colloid. E. S. HEDGES.

Swelling of gelatin in solutions of calcium salts. W. von Moraczevski and S. Grzycki (Biochem. Z., 1931, **236**, 432—443).—In presence of Ca salts, which become less sol. as the temp. rises, gelatin experiences a greater swelling at low temp. than at high, especially with more conc. gelatin solutions. With $Ca(SCN)_2$ the gel contains a greater proportion of Ca than the residual fluid. An excess of Ca occurs in the residual fluid with higher concentrations of most org. or inorg. Ca salts, whilst with more dil. solutions excess of $Ca^{\cdot\cdot}$ is found in the gel. This partition of the Ca depends, not only on the dilution, but also on the reaction of the medium with reference to the isoelectric point of gelatin.

F. O. Howitt.

Isoelectric point of a standard gelatin preparation. D. I. Hitchcock (J. Gen. Physiol., 1931, **14**, 685—699).—Values obtained for the isoelectric point are (*a*) p_H 4·86, the limiting val. of the p_H of aq. solutions of gelatin of increasing concentration, (*b*) p_H 4·85, at which point addition of gelatin does not affect the p_H of acetate buffers, (*c*) p_H 4·85 by observing max. turbidity of gelatin gels, and (*d*) p_H 4·80 by determining the p_H corresponding with zero cataphoretic velocity of suspensions of collodion in gelatin solution.

A. Cohen.

Effect of addition of salts on the isoelectric point of proteins. S. J. Przyłecki (Biochem. J., 1931, **25**, 713—727).—Serum-albumin solutions coagulate when heated at 100° above p_H 4·7 and below p_H 1. Various mineral salts produce coagulation at a certain crit. concentration (C_K) for each p_H. The C_K is at a max. at p_H about 2 and varies in accordance with the Hardy–Schulze rule. The ratios of C_K for ter-, bi-, and uni-valent anti-ions are as 1 : 30 : 500. The value of C_K of anti-ions depends on the valency of the accompanying iso-ion. The C_K of salts is less in solutions containing acids giving rise to bivalent as compared with univalent ions. The coagulative action of two or more anti-ions at concentrations below the crit. is additive. Salts possessing a univalent anti-ion and a multivalent iso-ion exert in certain concentrations a peptising action. Analogous results are obtained at p_H vals. higher than those of the isoelectric point. Coagulation can be effected by the addition of salts to systems containing 85% EtOH at any p_H. The Hardy–Schulze rule is followed in such systems and the max. vals. of C_K are at p_H 2. The C_K of Na_2SO_4 for caseinogen hydrochloride at p_H 2 has practically the same val. at 20°, 100°, and in 85% EtOH systems; that of SO_4'' is considerably higher. Gelatin in 80% EtOH can be flocculated at any p_H by crit. concentrations of anti-ions, the value of C_K varying according to the Hardy–Schulze rule. It varies inversely with the concentration of EtOH. The C_K of Na_2SO_4 increases with the free charge on the gelatin particles up to a certain max., after which it again falls as for albumin. The C_K of anti-ions increases with the valency of the iso-ions. The crit. concentration of EtOH necessary to flocculate gelatin at a given concentration of Na_2SO_4 is higher in the presence of $MgCl_2$ than in its absence and conversely at a given concentration of EtOH. The C_K of Na_2SO_4 is considerably higher in the presence of multivalent iso-ions. The peptising action of multivalent iso-ions is not apparent in high concentrations of EtOH in which salts possessing a multivalent iso-ion and univalent anti-ions exert a coagulative action. Isostable proteins can be converted into isolabile proteins by heating at 100° or by addition of EtOH. The C_K of Na_2SO_4 for a given p_H is practically the same for serum-albumin, gelatin, and caseinogen in presence of HCl in 85% EtOH. Salts possessing multivalent anti-ions are able to discharge protein particles at any p_H, C_K being different at each p_H for each salt. The coagulum differs from that obtained at the isoelectric point.

S. S. Zilva.

Effect of hydrogen-ion concentration on the precipitating and protective actions of proteins on colloidal gold and gum-benzoin. R. H. Hopkins, W. O. Kermack, and W. T. Spragg (Biochem. J., 1931, **25**, 829—842).—The effect of gelatin, ovalbumin, serum-albumin, pseudoglobulin, euglobulin, and oxyhæmoglobin has been studied. In very low concentration of protein, precipitation occurs on the acid side of the isoelectric point, but as the concentration increases the zone of precipitation approaches the isoelectric point and when sufficient protein is present the centre of the zone, except in the case of hæmoglobin, is at the isoelectric point. In the presence of 1·25% NaCl min. protection by these proteins except oxyhæmoglobin is at the isoelectric point. With Au the ppts. are usually red in the neighbourhood of the isoelectric point. Oxyhæmoglobin behaves as if its isoelectric point lay below its real value of about p_H 6·8. This is more pronounced with Au than with gum-benzoin. Michaelis and Nakashima's method for the determination of the isoelectric point of protein is therefore not of general application.

S. S. Zilva.

Electrokinetic properties of proteins. I. Isoelectric point and solubility of wheat proteins in solutions of alcohol. W. M. Martin (J. Physical Chem., 1931, **35**, 2065—2090).—Proteins are readily adsorbed on the porous diaphragms of filter crucibles, and a streaming potential method based on this fact has been developed for determining the isoelectric point of various proteins. The solubility of the protein extracted by aq. EtOH from wheat gluten is a max. at about 57% EtOH, whilst the relative isoelectric point falls continuously with increase of the EtOH concentration; the rate of change is small at concentrations between 40 and 70%.

H. F. Gillbe.

Generalised thermodynamics including the theory of fluctuations. G. N. Lewis (J. Amer. Chem. Soc., 1931, **53**, 2578—2588).—The laws of thermodynamics and of fluctuations are shown to constitute a generalised thermodynamics developed from a single postulate which is a new statement of the second law of thermodynamics.

J. G. A. Griffiths.

Stability of nitrogen pentoxide at 1000 atm. of oxygen in presence of nitrogen tetroxide. L. Lewon and H. Eyring (J. Amer. Chem. Soc., 1931, **53**, 2801—2802).—The reaction $N_2O_5 = N_2O_4 + \frac{1}{2}O_2$ in CCl_4 at 25° in presence of O_2 at 1000 atm. proceeds to completion. The equilibrium const. is greater than $1{\cdot}48 \times 10^4$ (atm.), from which the free energy change is

less than -5600 g.-cal., and ΔH is less than 1600 g.-cal. J. G. A. GRIFFITHS.

Dissociation of strong electrolytes. IV. M. B. JACOBS and C. V. KING (J. Physical Chem., 1931, **35**, 1922—1930).—The evidence of crystal structure data, transference no., conductivity, and concentration cell measurements, data employed for testing the Debye–Hückel theory, and the additive properties of ions are discussed in relation to the theory of complete dissociation; indisputable evidence of the presence of undissociated mols. in solutions has not yet been obtained, but is essential if the latter theory is to be accepted. H. F. GILLBE.

Hydrolysis of cupric sulphate. (MLLE.) QUINTIN (Compt. rend., 1931, **193**, 163—164).—Previous results (cf. A., 1927, 729) for $CuSO_4$ are confirmed and amplified by measurements with the quinhydrone electrode. C. A. SILBERRAD.

First dissociation [constant] of phosphoric acid in aqueous salt solutions at 18°. J. W. H. LUGG (J. Amer. Chem. Soc., 1931, **53**, 2554—2560; cf. this vol., 308).—Negligible liquid junction potential exists between dil. solutions of HCl and H_3PO_4 in a neutral chloride solution, and the e.m.f. is an exact measure of the relative H' activities (cf. A. 1929, 140). From determinations of the e.m.f. of the cell quinhydrone electrode 10·0015—0·006M-HCl or 0·002—0·01M-H_3PO_4 in 0·01—1·6M-XCl|KCl(sat.)|calomel electrode, the first dissociation const. of H_3PO_4 is computed to be $pK_1=2·09-\mu^{\frac{1}{2}}/(1+x\mu^{\frac{1}{2}})$, where x=1·6, 2·12, 1·14, or 0·93 when X=Na, K, Mg, or Ca, respectively. HCl is completely dissociated even in solutions containing much metal chloride. J. G. A. GRIFFITHS.

Classical dissociation constant of benzoic acid and the activity coefficient of molecular benzoic acid in potassium chloride solutions [at 25°]. E. F. CHASE and M. KILPATRICK, jun. (J. Amer. Chem. Soc., 1931, **53**, 2589—2597; cf. this vol., 566).—From determinations of the solubility of BzOH in KCl solutions and the values of [H'] (this vol., 811), the solubility of mol. BzOH has been calc. and the activity coeff. is given by $\log f=0·138c$, where c=0·1—3M-KCl. The classical dissociation const. of BzOH is given by $\log K_c=-4·2-0·14c+c^{\frac{1}{2}}/(1+1·7c^{\frac{1}{2}})$. The salting-out consts. of the ions of the solvent salts (this vol., 431) decrease with increasing crystal radius of the ions. J. G. A. GRIFFITHS.

Thermodynamic constants of iodine monobromide. J. MCMORRIS and D. M. YOST (J. Amer. Chem. Soc., 1931, **53**, 2625—2631).—From an investigation of the equilibrium $CuBr_2(s)+\frac{1}{2}I_2(g)=CuBr(s)+IBr(g)$ at 115°, 151·2°, and 176°, the free energy equation for the reaction $\frac{1}{2}I_2(g)+\frac{1}{2}Br_2(g)=IBr(g)$ is computed to be $\Delta F°=-1270-1·7449T$. The standard free energy of formation of IBr(g) is $\Delta F°_{298}$=903 g.-cal., and the heat of sublimation of IBr(s) is 12,545 g.-cal. The entropy of IBr(g) (60·6) lies between that of $I_2(g)$ and $Br_2(g)$. The increase in $\Delta F°$ and heat content at 25° attending the formation of IBr(g) from the atoms lie between those attending the formation of $I_2(g)$ and $Br_2(g)$ from atoms. These relationships may be general for gaseous interhalogen compounds. J. G. A. GRIFFITHS.

Energy of solvation and partition. Extension of Karl Fredenhagen's theory of electrolytic solubility. H. HAMMERSCHMID and E. LANGE (Z. physikal. Chem., 1931, **155**, 85—99; cf. this vol., 430).—The thermodynamic significance of the energy of solvation and of partition is discussed from the point of view of Fredenhagen's theory. J. W. SMITH.

Misleading equilibria encountered in the measurement of dissociation pressures in salt-hydrate systems. A. W. C. MENZIES and C. S. HITCHCOCK (J. Physical Chem., 1931, **35**, 1660—1665).—The dissociation pressures of salt hydrates can be quickly measured by allowing equilibrium to be reached with the solid phases in contact with a liquid in which H_2O is, at least, slightly sol. and then determining the aq. partial pressure by means of the authors' apparatus for measuring v. p. lowering of a solvent (cf. this vol., 901). Results for $BaCl_2,2H_2O$ $BaCl_2,H_2O+H_2O$ and $CuSO_4,H_2O \rightleftharpoons CuSO_4+H_2O$ are recorded. In salt hydrate systems genuine equilibrium pressures may be reached; these, however, are due to adsorbed H_2O and not to true dissociation pressures. L. S. THEOBALD.

X-Ray study of the system Fe_2O_3–SiO_2. P. SJOMAN (Tekn. Samf. Handl., 1930, No. 7, 24 pp.; Chem. Zentr., 1931, i, 1737).—When quartz and Fe_2O_3 are heated together, Si atoms in the SiO_2 lattice are partly replaced by Fe atoms within limits of temp. wherein there is a tendency of conversion of quartz into cristobalite. Further, new Fe^{III} silicates are produced. X-Ray examination shows no interaction when Fe_2O_3 is heated with excess of cristobalite or tridymite. A. A. ELDRIDGE.

System Cr_2O_3–Al_2O_3. E. N. BUNTING (Bur. Stand. J. Res., 1931, **6**, 946—949).—Cr_2O_3 which has not previously been fused (cf. A., 1930, 847; this vol., 41) has m. p. 2275°±25°, and its v. p. at this temp. is relatively low. Cr_2O_3 and Al_2O_3 are completely miscible in the liquid state, and form a continuous series of mixed crystals, but no compounds. H. F. GILLBE.

Compounds of the system calcium oxide–ferric oxide and their role in Portland cement. I. J. KONARZEWSKI (Rocz. Chem., 1931, **11**, 516—528).—Fe_2O_3 evolves O_2 at 1380°, yielding Fe_3O_4, with which it forms solid solutions; as a consequence, the partial pressure of O_2 depends not only on the temp., but also on the composition of the solid solution. The m.-p. diagram of the system CaO–Fe_2O_3 shows the existence of two compounds, $2CaO,Fe_2O_3$, m. p. 1440°, and CaO,Fe_2O_3, m. p. 1215°. R. TRUSZKOWSKI.

Phase diagram of system lead iodide–silver iodide. F. E. E. GERMANN and C. F. METZ (J. Physical Chem., 1931, **35**, 1944—1952).—AgI has m. p. 558±1° and PbI_2 412±1° (lit. 402°). Solid solutions exist within the limits 18·5—57·5 mol.-% and 85—100 mol.-% PbI_2, and in the liquid state the compounds are miscible up to 15 mol.-% AgI. The compound $4AgI,PbI_2$ does not exist, but $5AgI,PbI_2$ may be formed. The formation of solid solutions and the low crystallisation velocity render the ordinary methods of thermal analysis inapplicable to the determination of the composition of the compound formed.

The phase diagram of the system is the first of its type to be reported. H. F. GILLBE.

Reactions of amines with sulphur dioxide. I. Aniline and sulphur dioxide. A. E. HILL (J. Amer. Chem. Soc., 1931, **53**, 2598—2608).—The absorption of SO_2 by NH_2Ph affords the yellow crystals NH_2Ph,SO_2, m. p. 65° (approx.) at 3·5 atm. The heat of vaporisation, 19,630 g.-cal., is computed from v.-p. data between 3·5° and 50°. A phase diagram for the binary compound above the m. p. of its components, showing temp., composition, and pressure as variables, is discussed. NH_2Ph affords the white normal and acid sulphites with H_2O and SO_2. NH_2Ph,SO_2 in moist air loses some SO_2 and absorbs H_2O with the formation of a mixture of the sulphites (cf. A., 1891, 715). J. G. A. GRIFFITHS.

Molecular lowering of f. p. for camphor. R. J. W. LE FEVRE and (MISS) C. G. TIDEMAN (J.C.S., 1931, 1729—1732).—The f.-p. depression const. of camphor is 396. The fusion diagram of the system salicylic acid–camphor indicates the existence of a *compound* $2C_{10}H_{16}O,C_7H_6O_3$, m. p. 56°. H. F. GILLBE.

Ternary system zinc oxide–nitric acid–water. H. G. DENHAM and D. A. DICK (J.C.S., 1931, 1753—1757).—The system has been studied at 25° and 50°; the diagrams obtained at the two temps. are of similar form. The solid compounds indicated are the basic nitrates, $Zn(NO_3)_2,5ZnO,3H_2O$ and $Zn(NO_3)_2,ZnO,3H_2O$, and the normal hexa- and tetra-hydrates. H. F. GILLBE.

Ternary system lead oxide–nitrogen pentoxide–water. H. G. DENHAM and J. O. KIDSON (J.C.S., 1931, 1757—1762).—The system has been studied at 25° and 50°. The only stable solid phases are $Pb(NO_3)_2,PbO,2{\cdot}5H_2O$ and $Pb(NO_3)_2$. H. F. GILLBE.

Ternary system K_2O–CaO–SiO_2: a correction. G. W. MOREY, F. C. KRAČEK, and N. L. BOWEN (J. Soc. Glass Tech., 1931, **15**, 57—58T).—The compound (A., 1930, 1374) having the optical consts. $\gamma = 1{\cdot}59$, $\alpha = 1{\cdot}575$, is not $K_2O,2CaO,6SiO_2$, but $K_2O,3CaO,6SiO_2$; it crystallises in two enantiomorphic modifications, the β-form having the optical and crystallographic properties previously given for $K_2O,3CaO,6SiO_2$. Transition from α- to β-form is slow, but from β to α is rapid. *X*-Ray powder photographs confirm the individuality of the compounds. M. PARKIN.

Transformation of marine salts from a quaternary to a quinary system, in connexion with the treatment of langbeinite. D. LANGAUER (Rocz. Chem., 1931, **11**, 477—489).—The system K_2SO_4–$MgSO_4$–H_2O–$NaCl$ has been examined from the point of view of the phase rule. The liquid phase was unsaturated with respect to NaCl, but saturated with respect to the remaining components. The solid phases consisted at 25° of schonite, K_2SO_4, and astrakhanite, and at 55° and 83° of leonite, K_2SO_4, and loeveite. R. TRUSZKOWSKI.

Heat of dissociation of oxygen, determined from its thermal conductivity. E. JENKEL (Z. physikal. Chem., 1931, **155**, 100—108).—The energy consumption of a Nernst filament glowing in N_2 and in O_2 has been measured at different temps. At about 2450° abs. the consumption in O_2 becomes somewhat greater than that in N_2, owing to dissociation, and from the difference the heat of dissociation is calc. according to the method of Nernst to be 120 kg.-cal. The degree of dissociation of O_2 for temps. between 1800° and 2800° abs. is also calc. J. W. SMITH.

Apparent and partial molal heat capacities in aqueous solutions of 19 uni-univalent strong electrolytes. F. D. ROSSINI (Bur. Stand. J. Res., 1931, **7**, 47—55).—The apparent mol. heat capacity of the solute, ϕ_c, is shown to be a linear function of the square root of the mol. concentration for aq. solutions of uni-univalent strong electrolytes from infinite dilution to about 2·5*M*. Consequently, the partial mol. heat capacity of the solute, C_{p_2}, and the partial mol. heat capacity of the H_2O, C_{p_1}, are linear functions of the square root of the mol. concentration and the 3/2 power of the mol. concentration, respectively. Data are tabulated, from which may be computed values of ϕ_c, C_{p_2}, and C_{p_1} for aq. solutions of the chlorides, bromides, iodides, nitrates, and hydroxides of H, Li, Na, and K for any concentration in the given range at 18°, 21·5°, and 25°. E. S. HEDGES.

Heats of neutralisation at constant concentration and heat of ionisation of water [at 20°]. R. H. LAMBERT and L. J. GILLESPIE (J. Amer. Chem. Soc., 1931, **53**, 2632—2639).—The heat of neutralisation at const. concentration is the heat effect ($-\Delta H$) of the reaction $MOH,xH_2O+HA,xH_2O=MA,xH_2O+(x+1)H_2O$. By employing the data of Richards and co-workers in the plot of $1/x^{\frac{1}{2}}$ against $-\Delta H$ for the chlorides and nitrates of K, Na, and Li, a family of curves is obtained which affords the extrapolated value 13,650 g.-cal. (20°) for the heat of neutralisation at infinite dilution and the heat of formation of H_2O from its ions (cf. A., 1929, 511). The temp. coeff. of the latter ($-d\Delta H/dt$) is computed to be -52 g.-cal. per 1° at 20°. J. G. A. GRIFFITHS.

Heat of combustion of methyl alcohol. F. D. ROSSINI (Proc. Nat. Acad. Sci., 1931, **17**, 343—347).—The heat of combustion of liquid MeOH to CO_2 (gas) and H_2O (liquid) at 25° and 1 atm. is $173{\cdot}63\pm0{\cdot}05$ kg.-cal. per mol. J. W. SMITH.

Heat of combustion of methylglyoxal. C. FROMAGEOT and M. E. EMAMI (Bull. Soc. chim., 1931, [iv], **49**, 929—936).—The bomb-calorimetric method has given the following data. Heat of formation of methylglyoxalhydrazone -38 kg.-cal.; heat of formation of dinitrophenylhydrazine in 0·33*N*-HCl $+6$ kg.-cal.; heat of formation of methylglyoxal, aq. $+179$ kg.-cal.; heat of combustion of methylglyoxal $+326$ kg.-cal. E. S. HEDGES.

Change of transference number of a salt with change of concentration. Modification of the moving-boundary method. E. R. SMITH (Bur. Stand. J. Res., 1931, **6**, 917—926).—The moving-boundary method has been modified by observing the vol. through which a junction between two solutions of the same salt at different concentrations moves during the passage of a known quantity of electricity. Satisfactory results are obtained for NaCl

and LiCl solutions; the transference number of KCl is practically const. for the range 0·05—4·7M.

H. F. GILLBE.

Dissociation constants of organic acids. IV. Mobilities of the sodium, potassium, and hydrogen ions at 25°, and the determination of cell constants at 25°. G. H. JEFFERY and A. I. VOGEL (J.C.S., 1931, 1715—1729).—Conductivity measurements in 0·0001—0·001N solutions yield for Λ_c of KCl (25°), NaCl (25°), and KIO_3 (18°) the expressions $149·83-101·6c^{0·547}$, $126·18-117·4c^{0·551}$, and $115·45-58·7c^{0·384}$, respectively. The c–Λ_c curve for HIO_3 passes through a max. at c 0·001N, but at concentrations above 0·002N $\Lambda_c=351·0-384·1c^{0·577}$. The curves are compared with those obtained by application of the Debye–Hückel–Onsager equation. The mobilities of $H^{\cdot}$, $K^{\cdot}$, $Na^{\cdot}$, and IO_3' at 25° and of $H^{\cdot}$ at 18° have been calc. SiO_2 vessels must be used for conductivity measurements with acids at concentrations below 0·001N.

H. F GILLBE.

Effect of voltage on the conductivity of strong and weak acids. M. WIEN (Physikal. Z., 1931, **32**, 545—547).—With weak acids the effect of voltage on conductivity, although small, is 10 times that with strong acids, arising probably from an increase of ions due to ionic bombardment within the liquid. Data are given for HCl, H_2SO_4, AcOH, propionic and tartaric acid, $CH_2Cl·CO_2H$, and $CHCl_2·CO_2H$. The degree of dissociation can be computed and this is shown by reference to KI and LiBr.

W. R. ANGUS.

Influence of sucrose on the conductivity of electrolytes. J. PELLER (Z. Zuckerind. Cechoslov., 1931, **55**, 643—650).—Measurements of the conductivity of a number of acids and salts in presence of sucrose show that the decrease of conductivity is less the stronger is the acid, and is greater the stronger is the base. The conductivity of solutions of NH_3, $(NH_4)_2CO_3$, and NH_4OAc is increased by the addition of sucrose up to about 16%, further addition of sucrose causing a decrease. The influence of successive additions of sucrose on the depression of the conductivity decreases with increasing concentration of the sucrose.

E. S. HEDGES.

Constitution of sucrose solutions. E. LANDT and C. BODEA (Naturwiss., 1931, **19**, 660).—The product of the viscosity and mol. conductivity at infinite dilution of solutions of NaCl, KCl, $BaCl_2$, and NEt_4 picrate in aq. solutions of sucrose increases with the sucrose concentration too rapidly to be accounted for entirely by diminishing hydration of the ions. It is suggested that sucrose solutions contain aggregates of sugar mols., or of sugar mols. and H_2O mols. These complexes greatly increase the viscosity and vary in number and size with the temp. and concentration. Their influence on ionic migration is the more pronounced the larger are the ions.

R. CUTHILL.

Electrical conductivity of crystalline and vitreous silicates in the system sodium oxide–silica. R. SCHWARZ and J. HALBERSTADT (Z. anorg. Chem., 1931, **199**, 33—47).—Conduction through cryst. Na_2SiO_3 follows Faraday's law. With rise in the temp. the sp. conductivity, κ, increases up to about 800°, and then a period of more rapid rise extends to about 840°, beyond which the rate of increase is normal. Preheating at 870° causes a marked decrease in κ at 730—790°, probably in consequence of the formation at about 800° of a polyeutectic, with subsequent recrystallisation of the Na_2SiO_3. With $Na_2Si_2O_5$ glasses the log κ–$1/T$ curve is discontinuous near the transformation point, the temp. coeff. beyond this point increasing with increase in the SiO_2 content. The temp. coeff. for a glass is always less than for crystals of the same composition. The high conductivities of glasses containing 30—34% of SiO_2 indicate the absence of any material complex formation, but when the glass contains only 20% of SiO_2 κ is comparatively small and there is probably pronounced complex formation and adsorption of $Na^{\cdot}$. An attempt has been made to utilise conductivity data in constructing the equilibrium diagram.

R. CUTHILL.

Single potential of iron and steel electrodes. H. ENDO and S. KANAZAWA (Sci. Rep. Tohoku, 1931, **20**, 124—139).—The electrode potentials of pure Fe (single crystal), electrolytic Fe in various conditions, Armco Fe, and pearlitic steel (0·1—1·4% C) have been measured. The effect of the grain boundary and slight straining was investigated. The former increases the electrode potential and the latter causes the electrode to become more electropositive.

W. GOOD.

Diffusion of hydrogen through an iron cathode. A. H. W. ATEN and P. C. BLOKKER (Rec. trav. chim., 1931, **50**, 943—950; cf. A., 1930, 1125).—Purification of NaOH and H_2SO_4 does not entirely stop the diffusion of H_2 developed at an Fe cathode, but poisoning increases the rate of diffusion and the speed with which it sets in. Results with $HgCl_2$ in 0·1N-H_2SO_4 are similar to those previously obtained with As_2O_3. Addition of too much poison decreases the diffusion, particularly with higher c.d. These phenomena are explained as follows: the concentration of H atoms is greater where Hg has been deposited on the Fe, and consequently, using a little $HgCl_2$, diffusion through the Fe is more rapid. When sufficient $HgCl_2$ is used entirely to cover the surface, the Fe is cut off from the liquid and diffusion ceases; with higher current densities the ability of the Hg to form individual drops is diminished, and the effective covering power of a given amount of Hg thus increased. H_2SO_4 solutions show considerable diffusion after several days without poisoning, but alkaline solutions are more const. and, therefore, more suitable for study. Diffusion is greatly increased by addition of a little $HgCl_2$ to 0·1N-NaOH at 0·1—3 amp., and only slightly decreased by further addition of a large excess, whilst there is a rough parallelism between the cathode potential and the rate of diffusion. Results with these substances at 0·01 amp. are abnormal. Figures are given for diffusion through various Ni– and Cr–Fe alloys, using As_2O_3 in H_2SO_4. The connexion between current, potential, and rate of diffusion cannot be arrived at from these results, and the considerations of other authors are inadequate or erroneous.

R. S. CAHN.

Poisoning of hydrogen electrodes. A. H. W. ATEN and P. C. BLOKKER (Rec. trav. chim., 1931, **50**, 951—956).—The reaction between O_2 and H_2 at a Pt surface is less influenced by poisoning by As_2O_3 or

$HgCl_2$ in $0{\cdot}1N$-H_2SO_4, or by As_2O_3 in $0{\cdot}1N$-NaOH, than is the potential of the electrolytic gas electrode (cf. this vol., 171). It follows that the catalytic action of Pt is only slightly, if at all, due to transformation of H_2 into H atoms. The results may be due either to preferential poisoning of the catalytically most active portions of the surface, or to equal poisoning of the whole surface. When large additions of $HgCl_2$ in H_2SO_4 have completely stopped the catalytic action, the electrode shows the potential of a Hg electrode.

R. S. CAHN.

Electromotive force of liquid–liquid cells, and the variation on dilution. L. BOUCHET (Compt. rend., 1931, **193**, 149—151; cf. A., 1929, 769).—For cells $M_1|N\text{-}M_1SO_4$,aq.$||N$,aq.$|M_2$, where M_1–M_2 are Mg–Zn, Mg–Cu, Mg–Ag, Zn–Cu Zn–Ag, and Cu–Ag, respectively, the e.m.f. are 0·709, 1·810, 2·275, 1·089, 1·502, and 0·444 volts; with M_1–M_2=Zn–Cu, and the solutions of $ZnSO_4$ $0{\cdot}1N$, $0{\cdot}02N$, and $0{\cdot}01N$, and that of $CuSO_4$ N, the e.m.f. are 1·095, 1·114, and 1·128. All these values are in good agreement with calc. figures. Similar but less regular results are obtained with chlorides, acetates, and nitrates.

C. A. SILBERRAD.

Reaction between sodium nitroprusside and sulphides. III. G. SCAGLIARINI and P. PRATESI (Atti R. Acad. Lincei, 1931, [vi], **13**, 199—201; cf. A., 1930, 726).—The oxidation–reduction potential of the reaction $[Fe(CN)_5NO)''+S+2\ominus=[Fe(CN)_5NOS]''''$ with a Hg electrode is 0·348 volt at 20° for $0{\cdot}1N$ solutions of the reactants.

O. J. WALKER.

Potentiometric study of adrenaline. E. G. BALL and W. M. CLARK (Proc. Nat. Acad. Sci., 1931, **17**, 347—351).—The characteristic potentials of the adrenaline system are close to those of the related pyrocatechol system. The inherent instability of *o*-benzoquinone is enhanced by the presence of a side-chain with oxidisable groups. The reduction potential of the adrenaline system and the chemically undefined "reduction potentials" of the tissues must be such that the cells tend to protect this hormone from an oxidation which would result in its very rapid destruction.

J. W. SMITH.

Oxidation–reduction. XVI. The oxazines: Nile-blue, brilliant-cresyl-blue, methyl-Capri-blue, and ethyl-Capri-blue. B. COHEN (U.S. Publ. Health Serv. Suppl. No. 92, 1—67).—The oxidation–reduction potentials of the above oxazines have been measured at 30° in buffers of various p_H values and the results compared with theory. Methyl- and ethyl-Capri-blue are strongly basic, cresyl-blue is rather stronger than NH_3, and Nile-blue about equal to NH_3. Nile-blue sulphate corresponds with $C_{20}H_{20}N_3O{\cdot}SO_4H$ and aq. solutions of Nile-blue are colloidal. Relatively small but definite concentration and salt effects occur with cresyl-blue, and methyl- and ethyl-Capri-blue. Oxazines react readily with H_2O forming oxazones, and this reaction is accelerated by moderate acidity or alkalinity. They can be used as oxidation–reduction indicators within the range bounded by methylene-blue and indigo-carmine.

J. W. SMITH.

Oxidation–reduction of pyocyanine. II. Redox potentials of pyocyanine. B. ELEMA (Rec. trav. chim., 1931, **50**, 807—826; cf. this vol., 684).—The oxidation–reduction potential of pyocyanine was determined for the range p_H 1·3—11·5, using $TiCl_3$, $K_3Fe(CN)_6$, or benzoquinone in buffered solutions. Within the range p_H 6—9 pyocyanine is intermediate between methylene-blue and indigotrisulphonate. For p_H >7 the titration curves are normal, two electrons are involved in the change, and the colour of the solution changes gradually from blue to colourless. Pyocyanine thus exists in the unimol. form in dil. aq. solution. At p_H >12 the reaction is not reversible, a red pigment being formed on oxidation. Below p_H 7 the shape of the titration curves changes gradually until at p_H <3·5 a sharp discontinuity is observable, the system behaving as if it were associated with two consecutive reactions, each involving one electron. Simultaneously, a colour change, red–green–colourless, replaces the normal one. The abnormality is due to the formation, at p_H <about 7, of a half-way reductant, which is shown to be a free radical rather than a *meri*quinone.

R. S. CAHN.

Potential of solutions of sugars. III. R. WURMSER and J. GELOSO (J. Chim. phys., 1931, **28**, 260—276; cf. A., 1928, 846; 1929, 1393).—If O_2 is excluded, a solution of dextrose develops slowly an oxidation–reduction equilibrium, and this determines the potential of the solution, which at p_H 7·2 and at 20° is given by $E_{H_2}=-0{\cdot}05\pm0{\cdot}02$ volt.

J. W. SMITH.

Photodynamic studies. III. Photogalvanic phenomena with irradiated cupric oxide electrodes. M. KARSCHULIN (Biochem. Z., 1931, **236**, 312—325).—Using the photogalvanic cell fitted with CuO electrodes (A., 1930, 865) the spectral sensitivity with aq. NaF, NaI, and NaCN as electrolytes was determined. The general light absorption of the electrode and the electrical energy radiated were measured when the element was filled with aq. NaI. The photogalvanic effect does not disappear with positively-charged electrodes, and it follows that the Becquerel effect cannot be explained as a simple photo-electrical phenomenon.

F. O. HOWITT.

Physical chemistry of corrosion. F. GIORDANI (Giorn. Chim. Ind. Appl., 1931, **13**, 275—281).—In the corrosion of Sn-plated containers variations in the nature of the contents may change the relative behaviour of the local couples Fe–Sn. Observations show that in acid and alkaline solutions the potential of Sn is lower than that of Fe, whilst for intermediate solutions the behaviour of the couples Fe–Sn is in conformity with the position in the electrochemical series.

O. F. LUBATTI.

Energy yield and decomposition voltage in the electrolysis of sodium and potassium chloride solutions. H. RAMSTETTER and O. KAHN (Z. angew. Chem., 1931, **44**, 610).—When the energy yield in the electrolysis of NaCl and KCl solutions is taken as 100 × theoretical energy/energy used and the usual method of calculating the val. for the separation of equivs. of K and Na from the equation (Na/K)Cl+aq.=(Na/K)OH,aq.+Cl+H is used, very different vals. are found for the two metals. This is due to the circumstance that solid, and not dissolved, chlorides are considered. If correctly used, the avail-

able data lead to vals. which agree, whilst the decomp. voltages are also the same, viz., about 2·3 volts. These conclusions have been confirmed by experiments on an industrial scale. H. INGLESON.

The Leclanche cell. A. KELLER (Z. Elektrochem., 1931, **37**, 342—348).—Determination of the discharge curves of the positive electrode of the Leclanche cell has shown that for discharge down to 0·7 volt the current yield with an acid electrolyte is 7—10 times that with a neutral or alkaline electrolyte, and that electrodes which have been "run down" may be regenerated by being placed in an acid electrolyte. The rapid fall in voltage during discharge is ascribed to the formation of solid solutions of MnO_2 and Mn_2O_3, the conversion of the Mn_2O_3 into a manganous salt and MnO_2 by acid being responsible for the regenerative action of the latter. Experimental evidence has been obtained in favour of the theory that the e.m.f. of the electrode depends on the power of the MnO_2 to behave as an element and pass into solution as the MnO_2' ion. According to this view the reaction giving rise to the current is $2MnO_2+2H^{\cdot}=Mn_2O_3+H_2O+2\oplus$ in neutral and alkaline solution and $MnO_2+4H^{\cdot}=Mn^{\cdot\cdot}+2H_2O+2\oplus$ in acid solution. R. CUTHILL.

Reaction inertia of excited atoms. G. B. KISTIAKOWSKY and P. E. MILLINGTON (Z. physikal. Chem., 1931, **B**, **13**, 155—156; cf. this vol., 174).—Inertia has been observed in the reaction of excited O atoms with H_2 and with CH_4. R. CUTHILL.

Kinetics of unimolecular reactions. J. K. SYRKIN (Z. anorg. Chem., 1931, **199**, 28—32).—The velocity coeff., k, of many unimol. gas reactions and reactions in solution may be expressed as a function of the temp., T, by the empirical equation $k=e^{A/C-A/RT}$, where A is the energy of activation and C is a const. for all reactions of a given type. R. CUTHILL.

Experimental methods in the study of the kinetics of gaseous reactions. H. DOHSE and W. FRANKENBURGER (Z. angew. Chem., 1931, **44**, 605—610).—Some of the practical difficulties met with in the study of gaseous reactions are mentioned, *e.g.*, the prep. of pure materials, the prevention of the entry and formation of small traces of substances which give rise to irregularities. The methods adopted to overcome them are briefly sketched. H. INGLESON.

Effect of foreign gases on the lower critical oxidation limit of phosphorus vapour. H. W. MELVILLE and E. B. LUDLAM (Proc. Roy. Soc., 1931, **A**, **132**, 108—126).—The effects of N_2, H_2, He, A, Ne, CO_2, N_2O, H_2S, SO_2, C_6H_6, C_6H_{14}, C_2H_4, C_2H_2, $COMe_2$, $C_6H_3Me_3$, and CH_2Cl_2 on the lower crit. oxidation limit of P vapour have been studied. Although Semenov's equation, $p_P p_0[1+p_x/(p_0+p_P)]d^2$=const. (where p_0 is the lower crit. oxidation pressure, p_P and p_x are the pressures of P vapour and the foreign gas, respectively, d is the diameter of the vessel), represents the results satisfactorily, the slope of the curve connecting $1/p_0$ with the quantity in the bracket depends on the nature of the gas. The equation is modified to $p_0 p_P[1+Dp_x/(p_0+p_P)]$=const., where D is the diffusion coeff. of the chain propagators into the foreign gas. The slope of the curve is independent of the nature of the surface of the reaction tube. Evidence from the variation of the slope with temp. confirms the view that variation of D is the predominating cause of the differences observed. The results show no correlation with those obtained at the upper pressure limit (cf. A., 1930, 876). L. L. BIRCUMSHAW.

Explosion waves and shock waves. I. Wave-speed camera and its application to the photography of bullets in flight. W. PAYMAN and D. W. WOODHEAD (Proc. Roy. Soc., 1931, **A**, **132**, 200—213).—An account is given of the continuous (as opposed to the instantaneous or kinematographic) method of Schlieren photography, and its value in investigations in exterior ballistics is indicated. L. L. BIRCUMSHAW.

Kinetics of the oxidation of hydrogen sulphide. I. H. W. THOMPSON and N. S. KELLAND (J.C.S., 1931, 1809—1827).—The kinetics of the oxidation of H_2S has been studied at temps. in the vicinity of the ignition point, *i.e.*, 220—300°. The reaction proceeds almost entirely according to the equation $2H_2S+3O_2=2H_2O+2SO_2$, although traces of S were formed. There is an initial induction period which decreases either at a given temp. with increase of pressure or at a given pressure with rise of temp. If the pressure is below the ignition pressure, the subsequent reaction was of a low order which appeared to increase from a value slightly in excess of unity at low temp. to about two at high temp. Excess of O_2 facilitates reaction, whilst H_2S has the opposite effect; N_2 causes a slight retardation. Reaction is much retarded by a decrease in the dimensions of the reaction vessel. It is concluded that the reaction is of the chain type, propagation of the chains being favoured by excess of O_2. Chains are probably broken by a physical deactivation at the wall and a chemical deactivation by H_2S. The heat of activation is about 18,000 g.-cal. Above the ignition pressure the above measurable reaction becomes an explosion. The ignition pressure increases with fall of temp. and satisfies Semenov's equation. A peculiar phenomenon of successive explosions in the same reaction mixture has been observed. F. J. WILKINS.

Flame propagation through dry carbon monoxide-oxygen mixtures in an electric field. W. A. BONE, R. P. FRASER, and W. H. WHEELER (Proc. Roy. Soc., 1931, **A**, **132**, 1—10; cf. A., 1929, 771).—A comparison is made of the movements of flame, initiated near one of the closed ends of a tube, through intensively (P_2O_5) dried $2CO+O_2$ media (*a*) with no imposed electrostatic field, and (*b*) as the flame entered and passed into a strong electrostatic field, the polarity being reversed in successive experiments. The resistance to combustion offered by the dryness of the gases is overcome by the electrostatic field, the conditions near the negative pole being much more, and near the positive pole rather less, favourable to the continuance and propagation of flame than those in the control experiment. A series of similar experiments, but with the flame initiated midway between the boundaries of a field, is described. L. L. BIRCUMSHAW.

Kinetics of the combustion of methane by means of copper oxide. T. S. WHEELER (Rec. trav. chim., 1931, **50**, 874—882).—Equations are derived to explain the results of Campbell and Gray (J.S.C.I., 1930, **49**, 432T), and it is tentatively suggested that the reaction takes place at the Cu–CuO interface, and that it is inhibited in the collision area of one or both kinds of resultant mols. on the interface. The heat of activation is 32,000 and 41,000 g.-cal. per g.-mol., as determined by the static and stream experiments, respectively. R. S. CAHN.

Explosion limit of crude acetylene mixed with oxygen and nitrogen. S. YAGI and K. TAKEOKA (J. Soc. Chem. Ind. Japan, 1931, **34**, 205—207B).—The limits of the region of explosibility in mixtures of C_2H_2, O_2, and N_2 have been determined with the view of estimating the danger of explosion in storage tanks of CaC_2. To reproduce the conditions prevailing in practice crude gas (C_2H_2 97·69, H_2O 2·20, H_2S 0·0540, PH_3 0·0571 vol.-%) was used. There is no risk of explosion when the O_2 content is less than 8%, and the C_2H_2 content less than 2·5%. The lower limit of the explosion region runs parallel to the O_2–N_2 line (the results being plotted on a triangular diagram), attributable to the equality of the mol. heats of O_2 and N_2. The upper limit runs parallel to the N_2–C_2H_2 line, although the heat capacity of the mixture increases with the C_2H_2 content. N. H. HARTSHORNE.

Slow combustion of acetylene. R. SPENCE (Nature, 1931, **128**, 153).—Experiments which show that C_2H_2 and O_2 form a reaction chain of considerable length are described (cf. this vol., 572). L. S. THEOBALD.

Explosibility of acetylene–steam mixtures. RIMARSKI, PLEUS, FRIEDRICH, STREB, NOACK, KEMPER, HOFFMANN, and KONSCHACK (Jahresber. Chem.-tech. Reichsanst., 1930, **8**, 43—47; Chem. Zentr., 1931, i, 2418).—Mixtures of C_2H_2 and steam in the ratios 10 : 1 and 1 : 1·5 are not explosive whether the total pressure is 5 or 6 atm. Explosion occurs at a ratio 1·63—1·61 : 1, and becomes more violent with increasing C_2H_2 content. A. A. ELDRIDGE.

Direct oxidation of hydrocarbons by air. P. MONDAIN-MONVAL and B. QUANQUIN (Ann. Chim., 1931, [x], **15**, 309—424).—The inflammation of mixtures of hydrocarbons and air at relatively low temp. is caused by the explosive decomp. of the peroxides which have been described (A., 1930, 167, 1157; B., 1930, 803). This property is not confined to pure hydrocarbons, but is also observed in mixtures, such as paraffin, mineral oils, and motor spirit, and further in ethers, alcohols, and aldehydes. It is probably a property of all compounds possessing a saturated hydrocarbon chain. These views are applied to the processes occurring in the internal-combustion engine. E. S. HEDGES.

Aminolysis of alanine. S. MOLINARI (Helv. Chim. Acta, 1931, **14**, 671—687)—An extension of Wunderly's study of the hydrolysis of alanine to NH_4 lactate in presence of bone charcoal (A., 1924, ii, 841). The reaction ceases before all the alanine is hydrolysed, but the amount of hydrolysis depends on the quantity and sample of charcoal used. The charcoal may be completely regenerated by filtering and washing. Experiments in closed and in evacuated vessels, and using charcoal ignited in a current of CO_2, show that atm. O_2 plays no part in the reaction. The velocity of hydrolysis of solutions containing initial concentrations of 1, 2, and 3% of alanine is unimol. in the sense that it is expressed by the equation $0{\cdot}43K = 1/t \log \xi/(\xi - x)$, where ξ is the amount of alanine which has decomposed at the end of the reaction. With a 0·5% solution of alanine, however, the val. of K decreases as the reaction proceeds. The ratio $[NH_4^{\cdot}]^2/[A]$ (where $[NH_4^{\cdot}]$ and $[A]$ represent the concentrations of NH_4 and unchanged alanine, respectively, at the end of the reaction), is not const. over a wider range than that studied by Wunderly, nor is the ratio $[NH_4^{\cdot}][L']/[A]$, where $[L']$ is the concentration of lactate. $[L']$ is different from $[NH_4]$ because of secondary decomp. of the former, giving MeCHO, $H{\cdot}CO_2'$, EtOH, and CO_3'', all of which have been detected and determined. The ratio $[L']/M$ (where M is the wt. of charcoal) is, however, approx. const., but is little affected by the ratio A/M, where A is the amount of alanine adsorbed on the charcoal. It is suggested that the lactate, as it is formed, is adsorbed on the specially active parts of the charcoal surface, and that when it has occupied all these the reaction stops. The adsorbed lactate sends free lactate into the solution. It is assumed that the charcoal possesses virtually a concentration due to these active parts, the number of which depends on the wt. and specimen of charcoal used. Increase in this number increases the "dissociation tension" of the adsorbed lactate and more free lactate is sent into the solution. The addition of a salt with a common ion to the reaction mixture does not, however, lead to the expected results; NH_4Cl has scarcely any effect, whilst Na and NH_4 lactates, although markedly reducing the hydrolysis, do not do so to the extent required by the above theory. N. H. HARTSHORNE.

Kinetic study of some reactions of diazoacetic ester in benzene solution. J. N. BRONSTED and R. P. BELL (J. Amer. Chem. Soc., 1931, **53**, 2478—2498).—The velocity of the reaction of 0·0025—0·011N-diazoacetic ester with several substances in C_6H_6 solution has been measured at 15° by means of the N_2 evolved. The velocity coeff., k, of the reaction with a monocarboxylic acid, in large excess, is expressed by $k = \alpha c^2 + \beta c$, where α and β are consts. specific to a particular acid and c is its concentration. The effect of mixtures of these acids has been investigated. The results are consistent with the view that the addition of an acid mol. to the ester is catalysed by the presence of either a similar or a different acid mol., allowing for the progressive dissociation of double acid mols. with increasing dilution. The velocity of addition of picric acid to the ester is directly proportional to the concentration.

The rate of addition of PhOH to the ester is very strongly catalysed by the carboxylic acids, and the catalytic const. l is given, approx., by $l = GK^x$, where K is the electrolytic dissociation const. of the acid in aq. solution and x approaches unity. Picric acid is less catalytically active than is represented by the above relation. J. G. A. GRIFFITHS.

Chemical inertia. M. LEMARCHANDS and (MME.) M. LEMARCHANDS (Compt. rend., 1931, **193**, 49—50).—Two explanations of the difficulty in effecting interaction between some solids and gases, *e.g.*, some metals and Cl_2 or Br_2, CaO and Cl_2, Zn, Al, Mg, or Na and CO_2, SO_3, N_2O or P_2O_3, are suggested : (*a*) Formation of a protecting film, supported by the fact that only metals, *e.g.*, K, Hg, and Sn, the chlorides of which are volatile under the conditions of the experiment, are attacked by Cl_2. (*b*) Adsorption of the gas is a necessary preliminary to chemical action, and like it is exothermic, but rise in temp. checks adsorption and this cannot occur again until the surface has cooled. This explains the failure of a solid to catalyse such a reaction if that solid itself unites with the gas with considerable evolution of heat. C. A. SILBERRAD.

Dissolution velocity of oxygen into water. V. Oxidation velocity of sodium sulphite solution by oxygen in the presence of a molecular film of fatty acid. S. MIYAMOTO, T. KAYA, and A. NAKATA (Bull. Chem. Soc. Japan, 1931, **6**, 133—142).—The rate of dissolution of O_2 into aq. Na_2SO_3 increases to a max. val. as the $[SO_3']$ is increased. Whilst this max. val. is proportional to the area of the liquid–gas interface, covering the surface of the solution with a unimol. film of palmitic or stearic acid has no effect. In these experiments the main portion of the solution is stirred vigorously. Whilst the surface of the solution is not broken, the stirring may cause the fatty acid film to be covered with the solution. F. J. WILKINS.

Rate of combustion of charcoal and graphite as a function of the temperature. G. TAMMANN and G. BANDEL (Z. anorg. Chem., 1931, **199**, 109—116).—If the log of the rate of combustion, v, of charcoal in air is plotted as ordinate against the temp., T, as abscissa, the resulting graph consists of two straight lines intersecting at 175°, that corresponding with temps. below 175° having the greater slope. The probable explanation is that up to 175° the gas adsorbed by the C hinders its combustion, but at 175° the amount has become so small that the formation of a unimol. film is no longer possible. The retardation of the combustion is not, however, proportional to the amount of gas adsorbed. For the combustion of graphite between 340° and 480° the log v–T curve consists of a single straight line. Evidence has been obtained to show that the economy in fuel obtained by using a hot blast in the blast-furnace is due, not to an increase in the rate of combustion of the C, but to the increased rate of combustion of the CO at the tuyeres. R. CUTHILL.

Transformation of white into grey tin. G. TAMMANN and K. L. DREYER (Z. anorg. Chem., 1931, **199**, 97—108).—The linear rate of transformation is a max. at −30°, and decreases with increase in size of the crystallites, but is independent of their orientation. Cold-working increases the rate. The conversion between 0° and −20° can be suppressed by adding 0·5% Bi or Sb. R. CUTHILL.

Significance of hydrogen absorption in the dissolution of iron. E. LIEBREICH (Z. physikal. Chem., 1931, **155**, 123—142).—Phenomena quoted by Evans in support of his theory of corrosion are observed also in an atm. of H_2. The flake formation can be explained by the depassifying action of the corrosion product. When a film of hydroxide covers the surface of the Fe the diffusion out of the H_2 is impeded and the pressure of H_2 on the surface is raised. Thus Fe covered with fine glass powder is attacked even more readily than usual by dil. H_2SO_4; also the cathodic over-potential of a corroded Fe surface is lower than that of a fresh one. J. W. SMITH.

Corrosion of iron by steam at high temperatures. I. W. KRAUSS (Korrosion u. Metallschutz, 1931, **7**, 29—34; Chem. Zentr., 1931, i, 2390).—An apparatus for measuring electrically the interaction between metals and gases is described, and the results of its use with Fe and H_2O at 510° and 630° are recorded. The method was compared with the gravimetric method for interaction at 600°, 700°, and 800°. A. A. ELDRIDGE.

Spontaneous inflammability of magnesium powder. LENZE, METZ, and RUBENS (Jahresber. Chem.-tech. Reichsanst., 1930, **8**, 12—14; Chem. Zentr., 1931, i, 2387).—Finely-divided Mg does not ignite more readily when heated in air than coarser powder or filings; the ignition temp. in air is about 550°. Rise of temp. and liberation of H_2 by the action of H_2O do not lead to inflammation. The transport of Mg is discussed. A. A. ELDRIDGE.

Atmospheric corrosion of metals. I. Copper. W. H. J. VERNON.—See B., 1931, 763.

Reaction between benzyl chloride and water. T. TITANI and K. KURANO (Bull. Chem. Soc. Japan, 1931, 152—162).—A layer of distilled water which was stirred vigorously was placed above one of benzyl chloride, and the progress of the reaction was followed by determining the conductivity of the aq. layer. The rate of reaction is largely affected by the speed of stirring, and it is therefore concluded that the HCl formed inhibits further hydrolysis by its adsorption at the benzyl chloride–H_2O interface. F. J. WILKINS.

Variation of the velocity of decomposition of cellulose nitrate with temperature. J. DUCLAUX and J. BARBIÈRE (J. Chim. phys., 1931, **28**, 257—259).—By observation of the change in the viscosity of solutions of cellulose nitrate in $COMe_2$ with the previous history of the nitrate it has been shown that for three stable preps. of cellulose nitrate the change occurring in 17 years at 18° is about the same as that which occurs in 18 hr. at about 110°, indicating a temp. coeff. for the reaction of about 2·7 for a 10° interval. For two less stable nitrates the change in 17 years at 18° is comparable with that occurring in 2·5 hr. at 100°, the temp. coeff. being about 3·8. J. W. SMITH.

Ozonation of aldehydes. Action of ozone on the share of oxygen in the oxidation. E. BRINER, A. DEMOLIS, and H. PAILLARD (Helv. Chim. Acta, 1931, **14**, 794—803; cf. A., 1929, 290, 674).—The oxidation of PhCHO dissolved in hexane to BzOH (with some perbenzoic acid) by O_2 containing 0·9—8·0% O_3 has been studied, the gases being passed for 1 hr. at the rate of 10 litres per hr. The optimum

concentration of O_3 is 1·6%, the wt. of BzOH formed being more than 30 times that equiv. to the wt. of O_3 consumed, which, moreover, is min. in this case. The O_3 therefore acts mainly as a catalyst. Substitution of CCl_4 for hexane causes a marked reduction in the rate of oxidation. The mechanism of the reaction is discussed from the point of view of the theory of chain reactions, the O_3 being regarded as a source of energy of activation for the O_2 mols., but no definite chain is proposed.

N. H. HARTSHORNE.

Ozonation of sulphurous acid and of sulphur dioxide. Action of ozone on the share of oxygen in the reaction. E. BRINER, S. NICOLET, and H. PAILLARD (Helv. Chim. Acta, 1931, **14**, 804—810).—The action of ozonised O_2 on SO_2 solution is similar to its action on PhCHO (see preceding abstract) and its mechanism is probably of a related type. The optimum concentration of O_3 is about 1%, the wt. of SO_3 formed being about twice that equiv. to the O_3 consumed. The action on dry SO_2 is very slow.

N. H. HARTSHORNE.

Esterification in presence of anhydrous salts. F. M. WHITACRE and H. T. BRISCOE (Proc. Indiana Acad. Sci., 1929, **38**, 187—194).—The catalytic effect of anhyd. Cu, Cd, Al, Mn, Fe, Ca, and K Al sulphates on esterification of AcOH with EtOH, and of $CuSO_4$ on that of higher alcohols and acids, was studied. $CuSO_4$ gave the highest yield of EtOAc; $CaSO_4$ retarded esterification, whilst Na_2SO_4 had no effect. The temp. of dehydration is important; the effect is due partly to removal of H_2O and partly to other causes. CHEMICAL ABSTRACTS.

Iron and cerium compounds and insulin as inductors in oxidation reactions; mechanism of induced reactions. N. R. DHAR (J. Physical Chem., 1931, **35**, 2043—2048).—During the induced oxidation of HCO_2Na by air at room temp. in presence of $Fe(OH)_2$ or $Ce(OH)_2$, Fe_2O_5 or Ce_2O_5 is formed as an intermediate compound. The high induction factors sometimes observed are due to the liberation of ions during the primary exothermic oxidation of the inductor. These ions activate further mols. of the reactants, and more ions are then produced; the primary oxidation thus causes the oxidation of a large quantity of the acceptor. When an oxidation is effected by H_2O_2 the intermediate Fe oxide differs from that formed when O_2 is used. When air is passed through a solution of insulin oxidation takes place and CO_2 is formed; dextrose, if added, is also oxidised to CO_2, and the insulin, which then acts as an inductor, is oxidised more slowly. To this type of reaction is due the physiological action of insulin and the disappearance of the material in the body. The induced oxidation of dextrose is accelerated by Na_2HPO_4. H. F. GILLBE.

Positive ion catalysis in the Knoevenagel reaction. K. C. BLANCHARD, D. L. KLEIN, and J. MACDONALD (J. Amer. Chem. Soc., 1931, **53**, 2809—2810).—The velocity of condensation of cinnamaldehyde with malonic acid in 50% EtOH in the presence of NH_2-acids is accelerated by increase of [H˙]. Amines exhibit enhanced catalytic activity in acid solution, and very weak bases, *e.g.*, carbamide, which are inactive in aq. or alcoholic solution, are very active catalysts in AcOH where strong dissociation occurs. This supports the view that the positive ion of the amine is the catalyst.

J. G. A. GRIFFITHS.

Catalysed formation of water from hydrogen and oxygen by platinum as a chain reaction. N. I. KOBOSEV and V. L. ANOCHIN (Z. physikal. Chem., 1931, **B**, **13**, 63—71).—In the catalysed combination of H_2 and O_2 in presence of Pt saturated with O_2 at. H is formed, probably by the reaction $PtO+H_2=PtOH+H$, and sets up a reaction chain, the direct product of which is principally H_2O_2, which is decomposed by the Pt, giving H_2O. As a whole, the reaction is not a genuine catalysis, but is rather a case of induced reaction, the Pt–O complex being the inductor, the H the actor, and the O the acceptor.

R. CUTHILL.

Catalysts for the production of hydrogen by the water-gas reaction. I. Activity of an iron oxide catalyst. R. YOSHIMURA (J. Soc. Chem. Ind. Japan, 1931, **34**, 193—195B).—The efficiency of two Fe_2O_3 catalysts on the reaction between CO and H_2O ($p_{CO} \cdot p_{H_2O} = 1:3{\cdot}0$) at atm. pressure and with a rate of gas flow of 33·3 c.c. per min. has been studied at 360—410°, 510—710°, and 800°. The same results were obtained with the two catalysts, one of which contained Mn, Al, Si, Ca, P, Ni, Cu, Cr, and S (arranged in order of decreasing quantity) as impurities, and the other only Mn and possibly a trace of P. The optimum temp. range was 510—710°. The deposition of free C on the catalyst surface, which was observed only at the lower temp., increased with falling temp., and also with increasing partial pressure of CO in the resultant gases. In these cases the activity of the catalyst varied irregularly during the course of the reaction, and subsequent treatment of the catalyst with HCl usually revealed the presence of Fe carbide, the formation of which is known to occur in the decomp. of CO ($2CO=CO_2+C$) at an Fe catalyst. The appearance and magnetic properties of the catalyst after a run showed that reduction to a lower oxide, probably Fe_3O_4, had occurred. The alteration of the catalyst surface and its dependence on the temp. are discussed.

N. H. HARTSHORNE.

Hydrogenation catalyst. Action of hydrogen on colloidal palladium. M. BOURGUEL, (MLLE.) V. GREDY, and (MLLE.) H. ROUBACH (Bull. Soc. chim., 1931, [iv], **49**, 897—925).—The velocity of hydrogenation of various org. compounds in the presence of colloidal Pd is not proportional to the wt. of the catalyst, but depends on the concentration of Pd in the aq. phase. The variation of velocity with concentration is independent of the H-acceptor. At const. concentration of Pd, the velocity of hydrogenation depends on the pressure of H_2 at the moment it first comes into contact with the Pd, and the variation is again independent of the substance undergoing hydrogenation. These results confirm the view that the first stage of catalysis is the formation of a compound Pd_nH_2, where n depends on the pressure of H_2 and concentration of Pd. This combination is reversible and n is necessarily variable, but its order of magnitude appears to be about 100. E. S. HEDGES.

Kinetics of decomposition of ammonia in the presence of iron. J. ZAWADZKI and B. MODRZEJEWSKI (Rocz. Chem., 1931, **11**, 505—515).—The velocity of the reaction $2NH_3 \quad N_2+3H_2$ in the presence of an Fe wire heated at 470—560°, at 1—5 atm., is independent of the pressure. The catalytic action of Fe wire is at first small, but increases with use; at the same time the wire becomes brittle and spongy. R. TRUSZKOWSKI.

Catalytic reduction of carbon monoxide at atmospheric pressure. IX. K. FUJIMURA (J. Soc. Chem. Ind. Japan, 1931, **34**, 227—229B).—A Co–Cu–MgO (4 : 1 : 1) catalyst was used at 240° with pumice as carrier; the nitrates were heated with sucrose and the oxide mixtures were reduced with H_2. This process gives a very voluminous catalyst; the complete burning out of the C by long heating is detrimental. Otherwise yields of liquid products per unit catalyst volume were nearly uniform with different methods of prep. Excess of H_2 in the gas mixture results in H_2O formation. Great variation in the CO and CO_2 contents of the exit gases occurred. C. IRWIN.

Oxide hydrates and active oxides. XLIV. Relations between solubility of zinc oxide and its previous history. G. F. HUTTIG and B. STEINER (Z. anorg. Chem., 1931, **199**, 149—164; cf. this vol., 1000).—The solubility and rate of dissolution in aq. KOH of ZnO prepared by various methods has been determined with the object of correlating the catalytic activity in the MeOH synthesis, the thermodynamic activity, and the physical uniformity. ZnO obtained by ignition of $ZnCO_3$ below 300° has a relatively high catalytic activity and is physically practically completely uniform; therefore either all the mols. participate equally in the catalysis, or the active mols. are uniformly distributed. Nevertheless, an increase in catalytic activity may often be expected to accompany a decrease in uniformity. R. CUTHILL.

Characteristics of a calcium–vanadium catalyst and a new catalyst for sulphuric acid manufacture. W. W. SCOTT and E. B. LAYFIELD.—See B., 1931, 716.

Suitability of nickel catalysts for the synthesis of benzine. F. FISCHER and K. MEYER.—See B., 1931, 748.

Compound catalysts for synthesis of methyl alcohol. V. A. PLOTNIKOV, K. N. IVANOV, and D. A. POSPECHOV.—See B., 1931, 751.

[Electrolytic] separation of niobium and tantalum. D. D. PEIRCE (J. Amer. Chem. Soc., 1931, **53**, 2810).—Electrolytic reduction of Nb in alkaline solution affords an amalgam at a Hg cathode; Nb alone is deposited, at a current density of 3 amp./sq. dm., on a Cu cathode from a mixture of Nb and Ta oxides in saturated aq. Na_2CO_3 at 103°. J. G. A. GRIFFITHS.

Electrolyses in liquid ammonia. S. GOLDSCHMIDT and F. NAGEL.—See this vol., 1053.

Preparation of metal powders by electrolysis of fused salts. III. Tantalum. F. H. DRIGGS and W. C. LILLIENDAHL.—See B., 1931, 722.

Formation and decomposition of ozone in the electric discharge. L. A. M. HENRY (Bull. Soc. chim. Belg., 1931, **40**, 305—314).—The formation of O_3 from O_2 by the action of the discharge in a Geissler tube depends on the production of ions or of excited atoms or mols. The pressure assumes a steady value due to the establishment of an equilibrium caused by partial decomp. of the O_3 by particles with high kinetic energy. With increase of current the velocity of formation increases at a diminishing rate, and the greatest yield is obtained with a narrow tube. He reduces the velocity to a greater degree than does A. At the temp. of liquid air the O_3 decomposes slowly, probably as a result of catalytic action of the deposit of metal, derived from the cathode, on the walls of the tube. H. F. GILLBE.

Formation of nitrogen oxides in the electric discharge. L. A. M. HENRY (Bull. Soc. chim. Belg., 1931, **40**, 295—304).—At room temp. O_2 and N_2 do not combine when submitted to the silent electric discharge or to the discharge through a Geissler tube, but at about −180° NO_2 is formed in the latter case, the yield being greatest for the mixture N_2+2O_2. O_2 alone exhibits a contraction during the discharge, and a subsequent slow expansion to the initial pressure. The silent electric discharge does not cause reaction at low temp. Combination can occur only in presence of excited or ionised atoms or mols. of N_2 or O_2. H. F. GILLBE.

Kinetics of the formation of hydrogen chloride and carbonyl chloride as a problem of modern photochemistry. G. B. KISTIAKOWSKY (Z. angew. Chem., 1931, **44**, 602—605).—Theoretical. An appreciation principally of the contributions made by Bodenstein to the study of the photochemical formation of HCl and $COCl_2$. H. INGLESON.

Photo-reaction of hydrogen and iodine monochloride. T. IREDALE and D. P. MELLOR (J. Amer. Chem. Soc., 1931, **53**, 2802—2803).—Polemical against Rollefson and Lindquist (A., 1930, 1135; this vol., 578). The reaction occurs in 5461—5791 Å. light with approx. equal pressures of H_2 (about 70 mm.) and ICl (*ibid.*, 180). J. G. A. GRIFFITHS.

Action of light on mixtures of ozone and chlorine. I. Experimental. Results with low ozone concentrations. A. J. ALLMAND and J. W. T. SPINKS (J.C.S., 1931, 1652—1666).—The photosensitisation by Cl_2 of the decomp. of O_3 has been investigated in order to study the relation between the quantum efficiency γ and the wave-length. With a Cl_2 concentration $>$2—3% the rate of decomp. is proportional to the light intensity, but increases less rapidly if the Cl_2 concentration is less than this. For blue light γ is independent of the Cl_2 concentration, but at 365 mμ it rises as the Cl_2 concentration is decreased below 2%. Decrease of wave-length is accompanied by an increase of γ. Change of temp. has no effect on γ. F. J. WILKINS.

"Speed" of photographic emulsions. R. DAVIS and G. K. NEELAND (J. Opt. Soc. Amer., 1931, **21**, 416—419).—Errors caused by deviations from the strict H. & D. speed definition are pointed out. Fog densities should always be subtracted from the total densities. J. LEWKOWITSCH.

Application of oxalic acid–uranyl acetate actinometer to measurement of sunlight intensity in connexion with photochemical changes in gasoline. L. C. Beard, jun., and O. M. Reiff (Ind. Eng. Chem. [Anal.], 1931, **3**, 280—281).—The actinometer consists of a solution containing 6·30 g. of $H_2C_2O_4,2H_2O$ and 0·2121 g. of $UO_2(OAc_2)_2,2H_2O$ per litre and the amount of decomp. after exposure to sunlight is measured by titrating the $H_2C_2O_4$ with 0·1*N*-$KMnO_4$. The amount of change in the actinometer is proportional to the discoloration produced in gasoline exposed under similar conditions. Change of temp. has little influence on the discoloration of gasoline by sunlight. E. S. Hedges.

Photochemical oxidation of organic hydrocarbons. II. Toluene, and the oxidation of benzaldehyde. C. J. Kothari and H. E. Watson (J. Ind. Inst. Sci., 1931, **14A**, 11—30; cf. A., 1925, i, 1136).—The solvent has a marked effect on the oxidation of PhCHO, C_6H_6 and PhMe retarding the reaction in the dark, but accelerating it in light. The general results appear to be rendered inconsistent through the presence of minute amounts of impurity in PhCHO. The similarity of the temp. coeffs. in light and in the dark and the independence of the rate of oxidation and vol. of liquid indicate that reaction is mainly confined to the surface. The oxidation of PhMe takes place slowly or not at all in the absence of a catalyst and appears to be a vol. reaction. PhCHO is not the intermediate product determining the rate of reaction, and the active substance is H_2O_2 or an org. peroxide. E. S. Hedges.

Photochemical oxidation of alcohols by potassium dichromate. III. E. J. Bowen, T. A. Peacock, and E. R. Wellburn (J.C.S., 1931, 1866—1870).—The effect of changes in [H˙] and dichromate concentration on the rate of the photochemical oxidation of MeOH, EtOH, and $Pr^{\beta}OH$ has been studied using light of λ 3660 and 4360 Å. The results can be described quantitatively if it is assumed that the photoactive ion is $HCrO_4'$ and that the CrO_4'' ion which is also present acts as an inner filter. F. J. Wilkins.

Photochemical hydrolysis of sucrose. A. K. Bhattacharya and N. R. Dhar (Z. anorg. Chem., 1931, **199**, 1—6).—The results previously reported (A., 1930, 555) are amplified. R. Cuthill.

Photo-polymerisation of styrene and vinyl acetate. H. S. Taylor and A. A. Vernon (J. Amer. Chem. Soc., 1931, **53**, 2527—2536).—The photo-polymerisation of O_2-free styrene in PhEt and vinyl acetate in EtOAc has been measured by means of the effect of the products on the f. p. of C_6H_6. The temp. coeff. between 30° and 100° is about 1·3 per 10°. The quantum efficiency, γ, at λ 300—400 mμ is about 935 for pure vinyl acetate and 4 for styrene; values of γ between 1 and 8 are recorded for λ 2300 and 2536. The results indicate a chain reaction, which is inhibited by quinol. O_2 accelerates the photo-polymerisation of styrene and retards that of vinyl acetate. J. G. A. Griffiths.

Substitution of water of crystallisation by hydrogen peroxide. F. Munzberg (Lotos, 1928, 76, 351—363; Chem. Zentr., 1931, i, 2302).—$NaNH_4HPO_4$, $MgNH_4PO_4$, $MgNH_4AsO_4$, $NH_4H_2PO_4$, Na_2HAsO_4, K and Na pyroantimonates, NH_4, K, Ca, Sr, and Ba pyrophosphates can combine additively with H_2O_2. Equilibria in the systems Na_2SO_4–H_2O–H_2O_2, $Na_4P_2O_7$–H_2O–H_2O_2, and $Ba_2P_2O_7$–H_2O–H_2O_2 were studied. Theoretical considerations are discussed. A. A. Eldridge.

Action of sodium hypophosphite on aqueous solutions of nickel salts. C. Paal and L. Friederici (Ber., 1931, **64**, [*B*], 1766—1776).—Reduction of aq. $NiSO_4$ by NaH_2PO_2 yields non-homogeneous Ni phosphides containing 13·08—14·17% P. Some of these are scarcely attacked by warm HCl, whereas others are partly sol., leaving a residue containing all the P (approx. Ni_5P_2); the sol. portion is Ni. In presence of NH_3 $NiSO_4$ is reduced more rapidly and with smaller expenditure of NaH_2PO_2, the product (2·7—3·3% P) consisting of much metallic Ni and little Ni phosphides. The presence of minute amounts of Pd (0·0005—0·00001 g. Pd per g. Ni) greatly accelerates the reaction, yielding products with 2·3—3·7% P. In presence of Na K tartrate, $NiSO_4$ is scarcely reduced by NaH_2PO_2 in absence of Pd; in presence of minute amounts of Pd, a little Ni is first formed followed by a greyish-black to a black ppt. containing Ni, P, and O. Reduction of $NiSO_4$ by NaH_2PO_2 in presence of NaOAc occurs only in presence of Pd, giving a mixture of Ni and Ni phosphides containing an oxygenated compound. In alkaline tartrate solution and in presence of NaOAc the separation of Ni is not quant. H. Wren.

Solid silver hydride. E. Pietsch [with F. Seuferling] (Naturwiss., 1931, **19**, 573—574).—Salt-like *Ag hydride* is obtained by the prolonged action of at. H on Ag foil. It is decomposed by H_2O with evolution of heat. AgH is stable in H_2 up to at least 500° and is also stable in air. It is unacted on by light and is unchanged when heated in a Bunsen flame to dull redness. It shows great analogy to alkali hydrides, especially to LiH. J. W. Smith.

Compounds of hexamethylenetetramine with certain salts of silver and other metals and the influence of anionic volume on the capacity for association by the central positive atom. P. R. Ray and J. D. Gupta (Proc. XV Indian Sci. Cong., 1928, 168).—Compounds of various Ag salts (except AgF) with hexamethylenetetramine accord with Ephraim's generalisation that the capacity of a cation to associate with neutral mols. increases with the anionic vol. Compounds with Cu, Cd, and Ag cyanides were also prepared. Ag_2TeO_4, Ag_3PO_4, Ag_3BO_3, $AgIO_3$, Ag_3AsO_3, and Ag_3AsO_4 did not associate with hexamethylenetetramine. Chemical Abstracts.

Stability of magnesium peroxide. A. Wøhlk.—See B., 1931, 756.

Cyanamides of alkaline-earth and earth metals. (Mlle.) G. Bernheim (Compt. rend., 1931, **192**, 1647—1649).—The most favourable reaction temp. and corresponding max. yields of cyanamides formed according to the equation $C_2N_2+MO=CN_2M+CO$ are: M=Ca, 860°, 94·6; Sr 850°, 65·2; Ba 850—900°, 96; Be 550°, 37·5; Mg 900°, 81·1; Zn 1025—1050°, 90; Cd 700°, 93%. C. A. Silberrad.

Hydrothermal synthesis of calcium silicates under pressure. I. S. NAGAI (J. Soc. Chem. Ind. Japan, 1931, **34**, 222—224B).—CaO, quartz powder, and H_2O in various proportions were heated in an autoclave, and the dried samples analysed. In all cases $3CaO,2SiO_2$ was the first product, being formed at 181°; with longer heating CaO,SiO_2 was produced, most readily with mixtures of low CaO content. A 2 : 1 mixture did not give the second product at the temp. studied. C. IRWIN.

Preparation of mercurous iodide. A. AGRESTINI (Boll. Chim. farm., 1931, **70**, 448—450).—$SnCl_2$ in HCl solution is added to a solution of $HgCl_2$ (1 mol.) and KI (2 mols.) in EtOH; yield 52—57·5%. An excess of KI decreases the yield but increases the purity of the product. O. F. LUBATTI.

Deflagration and detonation of mercuric fulminate. P. LAFFITTE and M. PATRY (Compt. rend., 1931, **193**, 171—174).—Hg fulminate arranged in a line not exceeding 1 cm. wide, in the open air, and ignited by a Bickford fuse, only deflagrates; when placed in a tube it invariably detonates, as does Pb azide in either case. When placed on heated Hg the fulminate inflames after 39 min. at 135°, and after decreasing intervals at higher temp., until it does so instantaneously at 277°. Below 135° it decomposes without inflammation. C. A. SILBERRAD.

Aluminium chloride- and bromide-acetates. H. FUNK and J. SCHORMÜLLER (Z. anorg. Chem., 1931, **199**, 93—96).—The following *compounds* have been obtained by reaction of AcOH with $AlCl_3$ or $AlBr_3$: $AlCl_3,2Al(OAc)_3$, $Al(OAc)_3,2AlO(OAc)$, $2Al(OAc)_3,AlBr(OAc)_2,Et_2O$, and $Al(OAc)_3,2AlBr(OAc)_2,1{\cdot}5Et_2O$. R. CUTHILL.

Hydrates and hydrogels. XIII. Dialuminium hydroxide gel and its transformations. H. KRAUT and H. HUMME (Ber., 1931, **64**, [B], 1697—1708).—Addition of aq. $Al_2(SO_4)_3$ at 48° to 15% aq. NH_3 at the same temp. followed by keeping the mixture at 48—50° for ½ hr. and subsequent rapid washing leads to the isolation of *dialuminium hydroxide*, $Al_2O_3,2H_2O$. It is peptised to an almost transparent solution by 0·1—1% HCl, is not appreciably sol. in cold conc. HCl, sol. in warm 5—10% HCl and in 4% NaOH. Under H_2O or dil. HNO_3 it is readily converted into the trihydrate (identified as bayerite by the Röntgen diagram), which, although resembling the dialuminium compound in solubility, is not peptised by very dil. HCl. Separation of the compounds from one another is thus rendered possible. The *B* preps. are mixtures of $Al_2O_3,2H_2O$ and $Al(OH)_3$. It is proposed to designate $Al_2O_3,2H_2O$ as Al hydroxide *B*. Above 60°, ageing of $Al_2O_3,2H_2O$ is accompanied by loss of H_2O. In 2 days under gently boiling aq. NH_3 or more slowly in boiling aq. suspension, products are formed containing chains of 4—8 Al atoms, thus closely resembling the polyhydroxides *A*. They are highly disperse and cannot be separated from $Al_2O_3,2H_2O$ by very dil. HCl but differ from the last-named compound, since their H_2O content does not alter during several years. The limit lies at about 27% H_2O, corresponding with a tetra-aluminium hydroxide. All preps. with lower H_2O content (23—26%) remain unchanged in composition, whereas those with higher content become transformed into bayerite. It is possible that original preps. with 30—35% H_2O contain $3Al(OH)_2-2H_2O$ as well as $2Al(OH)_3-H_2O$ and that the trialuminium compound is also converted into bayerite. $Al_2O_3,2H_2O$ gives the interference lines of böhmite. It is probable that all colloidal Al hydroxides containing Al·O·Al chains in the mol. have a structure analogous to that of böhmite. The ageing of $Al_2O_3,2H_2O$ is readily followed by the changes in the Röntgen diagram; the intermediate products give the superposed interferences of bayerite and böhmite and are separable by dil. HCl into portions giving the homogeneous lines of the two materials. The transformation of $Al_2O_3,2H_2O$ into bayerite is a discontinuous process in which the single mols. of $Al_2O_3,2H_2O$ pass by addition of 1 mol. of H_2O into $Al_2O_3,3H_2O$. H. WREN.

Selenates of neodymium and their solubilities in water and selenic acid solutions. J. A. N. FRIEND (J.C.S., 1931, 1802—1809).—The methods of prep. of the hydrates of $Nd_2(SeO_4)_3$, including a *dodecahydrate*, are described. The solubility of $Nd_2(SeO_4)_3$ in H_2O and aq. H_2SeO_4 solutions of various concentrations has been measured over the temp. range 0—100°. F. J. WILKINS.

Anhydrous acetates and acid acetates of rare-earth metals. A. KOTOVSKI and H. LEHL (Z. anorg. Chem., 1931, **199**, 183—192).—The *acetates* $La(OAc)_3$, $Pr(OAc)_3$, $Nd(OAc)_3$, $Sa(OAc)_3$, $Gd(OAc)_3$, and $Yt(OAc)_3$ have been prepared by the action of Ac_2O on the nitrates. The following intermediate *compounds* have also been isolated: $Pr(OAc)_3,0{\cdot}5Ac_2O$, $Nd(OAc)_3,0{\cdot}5Ac_2O$, $Sa(OAc)_3,0{\cdot}5Ac_2O$, and $Gd(OAc)_3,0{\cdot}5Ac_2O$. The formation of compounds of the type $[Ce_3(OAc)_3](NO_3)_6,5Ac_2O$ (cf. A., 1923, i, 291) has been detected. The *acid acetates*, $La(OAc)_3,3AcOH$, $Ce(OAc)_3,3AcOH$, $Pr(OAc)_3,3AcOH$, $Nd(OAc)_3,AcOH$, $Sa(OAc)_3,AcOH$, and $Yt(OAc)_3,3AcOH$ have been prepared by the action of AcOH on the normal acetates. R. CUTHILL.

Rare earths. I. Preparation of [sulphates and] bromates of cerium group rare earths. J. A. HARRIS (J. Amer. Chem. Soc., 1931, **53**, 2475—2477; cf. A., 1926, 810; 1927, 14).—Conc. neutral solutions of the Ce group rare-earth sulphates are easily prepared by adding gradually the calc. vol. of dil. H_2SO_4 to the moistened oxides, evaporating to dryness, and dissolving in the calc. vol. of H_2O. J. G. A. GRIFFITHS.

Volatile thallium and lead hydrides. E. PIETSCH and F. SEUFERLING (Naturwiss., 1931, **19**, 574).—When at. H acts on a film of TlCl the latter is reduced first to Tl and then a film of Tl is gradually deposited on the glass walls of the reaction tube, moving along gradually with the gas stream. The v. p. of TlCl and of Tl are insufficient to account for this vaporisation, which is attributed to the formation of *Tl hydride*, which is vaporised from the surface of the metal but decomposed again on contact with the glass walls of the vessel. Analogous results are obtained with $PbCl_2$, which must give rise to a volatile *Pb hydride*. J. W. SMITH.

Hydrates and hydrogels. XIV. Simple preparation of monosilicic acid and the course of its condensation. H. KRAUT (Ber., 1931, 64, [*B*], 1709—1713).—Monosilicic acid is prepared from 1 mol. of $Na_2SiO_3,6H_2O$ and 1·8 mols. of HCl with addition of AcOH to supply the required p_H. Only between p_H 3·0 and 3·3 are the solutions sufficiently stable to permit determination of mol. wt. in freezing H_2O. At p_H 3·20 the acid can be preserved for several days. The nature of the org. acid appears to influence the reaction. Citric acid has much the same effect as HCl and AcOH, whereas formic acid gives essentially disilicic acid, and oxalic and tartaric acids yield trisilicic acid. The condensation of monosilicic to polysilicic acid is an auto-catalytic process, greatly accelerated by the polysilicic acid produced. Whilst, however, in the strongly acidic region p_H 1·5, in the feebly acid region p_H 4·3, and at the optimum acidity p_H 3·2 this acceleration is invariably observed, at intermediate ranges of p_H a delay in the condensation or a complete cessation in the alteration of mol. wt. is frequently observed, probably due to intramol. loss of H_2O leading from the ortho- to the meta-forms of silicic acid. In paraffined vessels increase in mol. wt. takes place more rapidly than in those of ordinary glass. H. WREN.

Highly-polymerised compounds. LIII. Polymeric silicic esters and acids. R. SIGNER and H. GROSS (Annalen, 1931, 488, 56—73).—The action of $SiCl_4$ on *cyclo*hexanol affords the *compounds* $SiCl_3(O{\cdot}C_6H_{11})$, b. p. 78°/11 mm., $SiCl_2(O{\cdot}C_6H_{11})_2$, b. p. 156°/11 mm., d_4^{19} 1·1325, and $SiCl(O{\cdot}C_6H_{11})_3$, b. p. 201°/11 mm., d_4^{19} 1·0653. The ester chlorides are hydrolysed by Ag_2CO_3 in anhyd. Et_2O. The trichloride affords polymeric cyclo*hexyl disilicate*, $[Si(O{\cdot}C_6H_{11}),1{\cdot}5O]_{10}$ as a solid mass which decomposes when heated. The dichloride gives the polymeric *metasilicates*, $[Si(O{\cdot}C_6H_{11})_2O]$, m. p. 216°, sublimable in high vac., and $[Si(O{\cdot}C_6H_{11})_2O]_4$, an oil which decomposes when heated. The monochloride yields the *pyrosilicate*, $[Si(O{\cdot}C_6H_{11})_3 0{\cdot}5O]_2$, m. p. 217°, sublimable in high vac. *Tetra*cyclo*hexyl orthosilicate* has b. p. 201°/0·1 mm., m. p. 92°. Hydrolysis of the tetrameric meta-ester and of the pentameric di-ester with HI leads ultimately to silicic acids containing, respectively, 76·93 and 86·96% SiO_2. The analytical data suggest that the acids correspond in mol. wt. and constitution with the esters from which they are derived, but their insolubility in H_2O is not in harmony with this hypothesis and the question of mol. wt. is therefore undecided. Thermal decomp. of the esters takes place with production of *cyclo*hexene accompanied by a little *cyclo*hexanol and di*cyclo*hexyl ether. The disilicic ester at 140° leaves a silicic acid containing 12·86% H_2O; an acid of similar composition is derived from the pyro-ester. H. WREN.

Possibility of partial substitution of lead halide by chromate in lead chloride-phosphate, -vanadate, acid-arsenate (pyromorphite, vanadinite, mimetesite). G. CAROBBI (Atti III Cong. Naz. Chim., 1929, 341—342; Chem. Zentr., 1931, i, 2185—2186).—Fusion of $Pb_3(PO_4)_2$, $PbCl_2$, $PbCrO_4$, and NaCl afforded synthetic pyromorphite, $3Pb_3(PO_4)_2,PbCl_2,PbCrO_4$; synthetic vanadinite and mimetesite were similarly obtained. The max. amount of $PbCrO_4$ is 6%, 6%, and 4%, respectively. A. A. ELDRIDGE.

Mechanism of precipitation processes. VI. Reaction between sodium oxalate and lead halides. Z. KARAOGLANOV and B. SAGORTSCHEV (Z. anorg. Chem., 1931, 199, 7—16; cf. this vol., 926).—If $Na_2C_2O_4$ is added to excess of a solution of $PbCl_2$ or $PbBr_2$ the ppt. of PbC_2O_4 contains Cl or Br, owing to the presence of the *compounds* $PbC_2O_4,PbCl_2$ and $PbC_2O_4,PbBr_2$. If the ppt. is left in contact with the liquid phase the halogen content gradually increases. R. CUTHILL.

Liquid ammonia and sodium nitrate. N. KAMEYAMA (J. Soc. Chem. Ind. Japan, 1931, 34, 173B).—Solid $NaNO_3$ reduces the v. p. of liquid NH_3 to such an extent that the saturated solution obtained can be stored or treated in Fe vessels. A. R. POWELL.

Vanadates of heavy metals. M. B. RANE and K. KONDIAH (J. Indian Chem. Soc., 1931, 8, 289—292).—The following *vanadates* have been prepared by reaction of a salt of the metal with NH_4VO_3 or K_3VO_4 in solution: $2HgO,V_2O_5$, $3HgO,V_2O_5$, $Au_2O_3,(NH_4)_2O,2V_2O_5$, $Au_2O_3,2V_2O_5,H_2O$, ThO_2,V_2O_5,H_2O, and $3CeO_2,V_2O_5,9H_2O$. R. CUTHILL.

Complexes of antimony halides with sulphonium halides. P. C. RAY, N. ADHIKARI, and A. N. RAY (J. Indian Chem. Soc., 1931, 8, 251—255).—The following *compounds* have been prepared by reaction of an Sb halide with a sulphonium halide or an alkyl sulphide and an alkyl halide: SbI_3,Et_3SI, m. p. 169°, SbI_3,Me_3SI, m. p. 194°, $SbBr_3,Et_3SBr$, m. p. 68°, $SbCl_3,Et_3SI$, m. p. 156°, $SbCl_3,Me_3SI$, m. p. 189°, and $SbI_3,3Et_3SBr$, m. p. 182—183°. From conductivity data it appears that these compounds have the constitution $[Et_3S]SbX_4$ (X=halogen). R. CUTHILL.

Purification of protoactinium fixed on tantalum oxide with a view to the determination of protoactinium in radioactive minerals. CHENG DA-CHANG (Compt. rend., 1931, 193, 167—168).—To separate Ra (and Io) from the Ta_2O_5 ppt. carrying the Pa this is melted with 25% (on the wt. of the Ta_2O_5) of $BaSO_4$ and 10% of $KHSO_4$. The mass is treated with H_2O, filtered, washed, and the insol. portion treated with aq. HF, which dissolves only the Ta_2O_5 with the Pa. Subsequent treatment is then as previously described (cf. this vol., 1026). C. A. SILBERRAD.

Action of hydrogen sulphide on potassium chromate solution. H. B. DUNNICLIFF and C. I. SONI (Proc. XV Indian Sci. Cong., 1928, 167).—In solutions containing 2·15% K_2CrO_4 the Cr is recovered as hydroxide and the K as K_2S_5 and $K_2S_2O_3$. CHEMICAL ABSTRACTS.

Interaction of sulphur dioxide and ammonia. G. SAMBAMURTI and M. N. L. NARASIMHAM (Proc. XV Indian Sci. Cong., 1928, 169).—The dry gases form the compounds $NH_2{\cdot}SO{\cdot}ONH_4$ and $NH_2{\cdot}SO_2{\cdot}NH_4$. CHEMICAL ABSTRACTS.

Molybdenum-blue. C. R. ZINZADZÉ (Bull. Soc. chim., 1931, [iv], 49, 872—877).—Mo-blue is prepared

in a pure state by boiling MoO_3 with dil. H_2SO_4 and adding powdered Mo. The Mo-blue may be separated from H_2SO_4 by means of BuOH. The blue colour depends on both the concentration and the acidity of the solution. Dilution causes the solution to become yellow, but the change is reversible, the blue colour reappearing when H_2SO_4 is added or when the solution is evaporated. The blue colour is probably due to the compound $MoO_2,4MoO_3,xH_2O$, which on dilution dissociates into the colourless MoO_2 and MoO_3. E. S. HEDGES.

Oxidations with fluorine. XVIII. Action of fluorine on cerous sulphate and on iodates. F. FICHTER and V. ARNAL (Helv. Chim. Acta, 1931, **14**, 862—867; cf. A., 1930, 1537).—Gaseous F oxidises a solution of $Ce_2(SO_4)_3$, but a large concentration of H_2SO_4 (about 8*N*) is necessary to prevent the precipitation of Ce_2F_3, and this reduces the solubility of the $Ce_2(SO_4)_3$. This limitation and the unavoidable formation of H_2O_2 with its reducing action combine to give poor yields of $Ce(SO_4)_2$. The optimum temp. is 2—4°. The F acts indirectly through the formation of unstable SO_4. No HIO_4 could be obtained by passing F into a solution of either HIO_3 alone, or HIO_3 and H_2SO_4, owing to the formation of H_2O_2; the presence of HIO_3 favours the formation of H_2O_2 (cf. A., 1929, 526). It is supposed that a peroxide I_2O_6, is first formed, which is decomposed by H_2O into HIO_3 and a true peracid, O_2IOOH, the latter in turn reacting with H_2O to give H_2O_2 and HIO_3. In alkaline solution (about 2*N*), KIO_3 may be oxidised to KIO_4, the most favourable yield obtained being 48·5%. N. H. HARTSHORNE.

Polyhalides. I. Methods of preparation. H. W. CREMER and D. R. DUNCAN (J.C.S., 1931, 1857—1866).—Methods of prep. of the polyhalides have been improved. The following new *compounds* are described: KClBrI, m.p. 40°; NH_3Me, m. p. 71°, NH_2Me_2, m. p. 136°, $NHMe_3$, m. p. 67—68°, NH_3Et, m. p. 49°, NH_2Et_2, m. p. 46—47°, $NHEt_3$, NH_3Pr^{α}, NH_3Pr^{β}, m. p. 54°, and NMe_3Et, m. p. 145°, dibromoiodides. NH_4Br_2I has m. p. 198°. Evidence for the existence of the acids $HIBr_2$, HIBrCl, and $HICl_2$ in aq. solution is adduced. F. J. WILKINS.

Working up iodine residues. II. Oxidation of cuprous iodide with chromic acid. III. Conversion of cuprous iodide into potassium iodide. F. T. VAN VOORST (Chem. Weekblad, 1931, **28**, 440—441, 442—443; cf. this vol., 448).—II. No HIO_3 is formed during the oxidation, and losses of I are very low.

III. Cu_2I is treated with sufficient KOH and the filtrate freed from Cu and evaporated. S. I. LEVY.

Action of hydrogen on potassium permanganate. (MLLE.) M. L. DELWAULLE (Compt. rend., 1931, **192**, 1736—1738; cf. A., 1925, ii, 51).—H_2 passed into acid solution of $KMnO_4$ ppts. MnO_2, the velocity increasing with acidity to a limit. In a neutral solution the result is the same save that the MnO_2 remains in colloidal solution. In alkaline solution reduction to K_2MnO_4 first occurs, and finally, after a long time, precipitation of MnO_2. Agitation with H_2 gives the same results except as regards the acid solution, from which there is evolution of O_2, due to the reactions: $2KMnO_4+3H_2=2MnO_2+2KOH+2H_2O$, and $4KMnO_4+2H_2O=4MnO_2+4KOH+3O_2$. C. A. SILBERRAD.

Phosphates of tervalent manganese and of aluminium. A. YAKIMACH (Compt. rend., 1931, **192**, 1652—1653).—On evaporating the solution whence $NH_4Mn^{III}P_2O_7$ (cf. A., 1903, ii, 151) has separated rose lamellæ of $NH_4H_2Mn^{III}(PO_4)_2$ are obtained. $NH_4H_2Al(PO_4)_2$ is prepared by heating 2 parts of $Al(NO_3)_3$ and 1 part of H_3PO_4 until evolution of nitrous fumes ceases, adding more H_3PO_4, and then gradually $(NH_4)_2HPO_4$ with continued heating; the substance which separates differs from Cohen's product (cf. A., 1907, ii, 552), which could not be obtained (cf. A., 1924, ii, 677). Similarly are obtained $KH_2Al(PO_4)_2$ and $Ca[H_2Al(PO_4)_2]_2$, but no corresponding Na compound. C. A. SILBERRAD.

Hydroxy-acid complexes of iron. C. MORTON (Pharm. J., 1931, **127**, 85).—Mixtures of the $FeCl_3$–Na salicylate–$NaHCO_3$ type contain Fe partly as a violet crystalloid complex, $Fe(OH)_2[C_6H_4(OH)CO_2]$, and partly as a red basic hydrosol, in proportions depending on the p_H. Similar complexes, which are hydrolysed to more basic salts in dil. solution, exist in "Fe and NH_4 citrate," viz., $Fe_2(OH)_3C_6H_5O_7$, and "Fe and K tartrate," $Fe_2(OH)_4C_4H_4O_6$. The stability of such mixtures in alkaline solution is due to the peptising and protecting action of the hydroxy-acid anion on the hydrosol. Complexes are formed with glyceric, malic, glycollic, lactic, and mandelic acids, but not with formic, acetic, phthalic, or tricarballylic acid, which contain no OH group. E. HOPKINS.

Arsenides of platinum metals. L. WOHLER and K. F. A. EWALD (Z. anorg. Chem., 1931, **199**, 57—64).—The *arsenides* $IrAs_2$, $RhAs_2$, $RuAs_2$, $PtAs_2$, and $PdAs_2$ have been prepared by heating a mixture of the chloride with excess of As in a current of H_2. R. CUTHILL.

Significance of chemical reactions in chemical analysis. A. SCHLEICHER (Z. anal. Chem., 1931, **84**, 401—406). H. F. GILLBE.

Accurate titration. I. W. PONNDORF (Z. anal. Chem., 1931, **84**, 289—335).—The technique of accurate volumetric analysis as applied to delicate work, such as at. wt. determinations, is discussed in great detail with especial reference to the titration of NaCl and HI with $AgNO_3$. A. R. POWELL.

Identification of solids by means of b.-p. elevation in saturated solutions. J. O. HALFORD (J. Amer. Chem. Soc., 1931, **53**, 2640—2645).—The b. p. of a saturated solution is unaffected by the addition of more of the saturating solute, but is raised by the addition of another solute. This principle has been applied to the identification of substances and the detection of impurities in cases where the m. p. procedure is inapplicable owing to decomp. J. G. A. GRIFFITHS.

Method for increasing sensitivity of certain chemical test reactions. I. STONE (Ind. Eng. Chem. [Anal.], 1931, **3**, 325).—The sensitivity of colour tests may be increased by shaking the aq. solution with an immiscible liquid, whereupon the colour concentrates at the liquid–liquid interface. E. S. HEDGES.

Sources of error in organic elementary analysis VIII. J. LINDNER.—See this vol., 1078.

Use of wide-range indicators for determination of p_H. F. R. McCRUMB (Ind. Eng. Chem. [Anal.], 1931, **3**, 233—235).—An investigation of the errors which may occur in the determination of p_H by wide-range indicators has shown that the so-called universal indicators can be used with safety only on well-buffered solutions or when it is known that the p_H of the indicator is close to that of the sample. In general, the wide-range indicator is useless for H_2O, soil extracts, pure sugar liquors, sewage effluents, evaporator water, laundry rinses, etc. Although fairly accurate results can be secured by using a number of solutions of a wide-range indicator adjusted in steps of 1·0 p_H according to the isohydric method, this procedure has no advantage over the use of several short-range indicators and has the disadvantage that the colour changes are not so distinct.

E. S. HEDGES.

Determination of water by drying. M. DOLCH and K. BUCHE (Pflanzenbau, 1930, **4**, 64—73; Chem. Zentr., 1931, i, 973).—Errors are discussed. Alternatively, the water is extracted by repeated treatment with EtOH, the aq. EtOH being mixed with petroleum and the temp. of separation compared with the curve given by control mixtures. A. A. ELDRIDGE.

Determination of small amounts and traces of water and carbonic acid in silicates. II. E. DITTLER and H. HUEBER (Z. anorg. Chem., 1931, **199**, 17—27).—By means of the method previously described (this vol., 325) determinations of H_2O in various minerals have been made. H_2O and CO_2 may be determined simultaneously by igniting the mineral with powdered quartz and after treatment of the gas evolved with α-naphthyloxychlorophosphine passing it into 0·01*N*-$Ba(OH)_2$, titration of which with standard acid then gives the sum of the amount of CO_2 and the amount of HCl formed by the H_2O. To determine the CO_2, a known excess of standard acid is then added and after boiling to expel CO_2 the solution is titrated with $Ba(OH)_2$. With minerals containing sulphides the SO_3 formed on ignition must be retained with PbO_2 or $PbCrO_4$ to prevent it passing into the $Ba(OH)_2$. The above method is suitable for micro-determinations and has been used for the determination of C and H in diamond. R. CUTHILL.

Application of methyl alcohol in the ebullioscopic method of determination of water. A. BAKOWSKI (Rocz. Chem., 1931, **11**, 490—504).—The ebullioscopic method gives accurate results using MeOH, except in those cases in which the substance examined is sol. in EtOH. The time required for a determination is 30 min., as compared with 62 min. for the xylene method. R. TRUSZKOWSKI.

Determination of moisture by distillation. G. MIDDLETON (Pharm. J., 1931, **127**, 86—87).—A suitable quantity (usually 10 g.) of the substance is boiled with 50 c.c. of tetrachloroethylene or CCl_4 and the vapour condensed in a graduated receiver with a flow-back for the solvent. After 15—20 min. all the H_2O has collected in the receiver, and its vol. may be read to within 0·02 c.c. The method is rapid, and especially suitable for substances containing carbohydrates or volatile oils. E. HOPKINS.

Direct iodine–silver determinations. P. FLEURY and J. COURTOIS (Bull. Soc. chim., 1931, [iv], **49**, 860—872; cf. B., 1931, 630).—An investigation of the conditions under which the reciprocal determination of I and $AgNO_3$ can be carried out in the presence of starch paste. E. S. HEDGES.

Determination of fluorine. P. MOUGNAUD (Compt. rend., 1931, **192**, 1733—1735).—Pure CaF_2 is stable when heated at 800° in a covered crucible; the loss of wt. and production of CaO sometimes observed in determinations by Rose's method are due to decomp. of $Ca(OAc)_2$ not removed (cf. A., 1916, ii, 47). Precipitation of CaF_2 in NH_3 solution (cf. A., 1930, 180) gives on centrifuging the ppt. an excess, on calcination some CaO. The solubility of CaF_2 (precipitated and dried at 100°) at 18° in H_2O is 18·3 mg. per litre (of calcined CaF_2, 15·1); in AcOH 30·8(0·083*N*)—58·6(1·66*N*); NH_4Cl 20·8(0·25*N*)—27·8(1·66*N*); NH_4OAc 20·3 (0·333*N*)—25·5 (1·66*N*); NH_3 17·6 (*N*)—17·5 (1·66*N*). By evaporation in contact with AcOH some HF is evolved.

C. A. SILBERRAD.

Determination of small quantities of oxygen in gases. J. WIERCINSKI.—See B., 1931, 756.

Determination of sulphur [in iron and steel] by the evolution method. F. JUNGBLUT.—See B., 1931, 762.

Standardisation of volumetric sulphuric acid solution. J. L. MAYER (J. Amer. Pharm. Assoc., 1931, **20**, 651—653).—The $BaSO_4$ method is preferred to the Na_2CO_3 and KH tartrate methods (U.S.P.) for the standardisation of H_2SO_4. E. H. SHARPLES.

Potentiometric titration of Caro's acid and hydrogen peroxide. E. MULLER and G. HOLDER (Z. anal.Chem., 1931, **84**, 410—416).—Caro's acid may be determined by potentiometric titration with As_2O_3 solution in presence of $NaHCO_3$. In presence of H_2O_2 the acid may be determined potentiometrically or visually by adding a few drops of KI solution; the I is alternately oxidised by the acid and reduced by the As_2O_3. Potentiometric titration with KI in acid solution is also satisfactory, but the I which separates should be prevented from depositing on the electrode by addition of C_6H_6. The subsequent determination of the H_2O_2 may be effected by potentiometric or visual titration with KBr–Br solution after addition of NaOAc. H. F. GILLBE.

Distillation of free ammonia-nitrogen from buffered solutions. M. S. NICHOLLS and M. E. FOOTE (Ind. Eng. Chem. [Anal.], 1931, **3**, 311—313).—For the quant. recovery of free NH_3 from aq. solutions of NH_4Cl and $(NH_4)_2SO_4$ a const. p_H of 7·4 or above is necessary. A phosphate buffer of p_H 7·4 is recommended. If Na_2CO_3 is used to adjust the p_H, either the recovery is incomplete or an appreciable quantity of org. N is included in the free NH_3 determination.

E. S. HEDGES.

Use of boric acid in micro-Kjeldahl determination of nitrogen. N. M. STOVER and R. B. SANDIN (Ind. Eng. Chem. [Anal.], 1931, 3, 240—242).—Accurate results can be obtained in the determination of N by Pregl's micro-method by the use of H_3BO_3 for absorbing the NH_3. The distillate containing the NH_3 does not require boiling before titrating. A mixed indicator containing Me-red and tetrabromophenol-blue gives good results in H_3BO_3 solution.

E. S. HEDGES.

Micro-Kjeldahl method of nitrogen determination. W. F. ALLEN (Ind. Eng. Chem. [Anal.], 1931, 3, 239—240).—The simple apparatus described gives accurate results rapidly with samples requiring as much as 10 c.c. of conc. H_2SO_4 in the digestion mixture, as well as with samples containing as little as 0·1 mg. N.

E. S. HEDGES.

Modification of Pregl's method of determining nitrogen. J. J. RUTGERS (Compt. rend., 1931, 193, 51—53).—By widening the portion of the combustion tube containing the permanent charge of Cu and CuO from 8 to 20 mm. diameter, and using a larger and more finely divided charge, the period of contact of the gases and surface of contact are increased, and the time of a determination is reduced to 1 hr.

C. A. SILBERRAD.

Bromometric determination of ammonia-nitrogen. I. B. LEVY. II. M. TSCHEPELEVETZKY and S. POSDNIAKOVA [with R. FEIN] (Z. anal. Chem., 1931, 84, 98—106, 106—118).—I. Addition of Br solution to solutions of NH_4 salts containing an excess of $NaHCO_3$ effects complete oxidation of the NH_3 to N without any side-reaction occurring. Excess of Br can then be determined iodometrically.

II. The oxidation is quant. in solutions of p_H 7·5—9·5, but in more alkaline solutions $NaNO_2$ is formed. In the presence of $Fe^{\cdot\cdot\cdot}$ salts NH_4 may be determined bromometrically after addition of a phosphate buffer (see also B., 1931, 756).

A. R. POWELL.

Volumetric determination of nitrites in presence of nitrates. A. WINOGRAD (Chemist-Analyst, 1931, 20, No. 3, 15).—I is liberated from KI and H_2SO_4 by CO_2 which has been passed through the liquid.

CHEMICAL ABSTRACTS.

Use of aluminium and stannous chloride in the Gutzeit test for arsenic. J. P. MAYRAND (J. Amer. Pharm. Assoc., 1931, 20, 637—643).—The U.S.P. Gutzeit method is modified in that 1 g. Al replaces 8—10 g. Zn, 50 c.c. of 5% HCl replaces 25 c.c. of 20% H_2SO_4, 0·8 c.c. of acid $SnCl_2$ is used instead of 0·25 c.c., and a 100-c.c. reduction bottle is employed. "Granular powder" As-free Al (20-mesh) is used and 0·0000004 g. As can be detected.

E. H. SHARPLES.

Elimination of carbon dioxide from pyruvic acid. II. Determination of carbon dioxide in kinetic investigations. U. BOKLUND (Biochem. Z., 1931, 233, 478—483).—An apparatus and method for the determination of CO_2 are described. The process is a modification of that of Westerberg (Svensk Tekn. Tidsk., 1910, 40, 49).

W. MCCARTNEY.

Purification and analysis of alkali cyanides. M. R. THOMPSON (Bur. Stand. J. Res., 1931, 6, 1051—1059).—Work on the purification and analysis of KCN and NaCN is reviewed. Pure (99·32—99·85%) KCN may be prepared by neutralising HCN with alcoholic KOH or KOEt solution, but NaCN so prepared contains Na_2CO_3 and other impurities; the use of NaOEt is preferable to that of NaOH. The salts are more sol. in MeOH than in EtOH, but recrystallisation is not recommended for prep. of the pure salts.

H. F. GILLBE.

Irregularities in sodium determination by sodium sulphate method. G. W. COLLINS (Ind. Eng. Chem. [Anal.], 1931, 3, 291).—The direct sulphate method gives low results in the presence of the side-chain 5-carbon derivatives of barbituric acid. No explanation is given. The method gives accurate results after removing the barbituric acid derivatives by acidification followed by extraction with Et_2O.

E. S. HEDGES.

Rapid volumetric method for determination of potassium. L. CLARKE and J. M. DAVIDSON (Ind. Eng. Chem. [Anal.], 1931, 3, 324—325).—A procedure for determining K in a solution of K_2SO_4 and $MgSO_4$ depends on the precipitation and titration of K H tartrate. A modification is proposed for solutions containing $K^{\cdot}$, $Na^{\cdot}$, Cl', and NO_3'.

E. S. HEDGES.

Determination of free alkali and carbonate in alkaline hypochlorites. KERNY.—See B., 1931, 717.

Determination of calcium by alkalimetric titration. I. C. H. FISKE and E. T. ADAMS (J. Amer. Chem. Soc., 1931, 53, 2498—2501).—0·2 mg. of Ca is determined to 1% by precipitation as oxalate which is transferred to a Pt dish with HNO_3. The nitrate is dried, treated with 0·5 c.c. of 2·5% $H_2C_2O_4$, and ignited. The resultant CaO dissolves easily in excess of 0·02N-HCl, which is titrated back.

J. G. A. GRIFFITHS.

Gravimetric determination of beryllium and its separation from aluminium by means of guanidine carbonate. A. JÍLEK and J. KOŤA (Coll. Czech. Chem. Comm., 1931, 3, 336—353).—In presence of NH_4 tartrate, guanidine carbonate ppts. Be salts in the form of a basic carbonate, whilst Al salts are not precipitated. Be can be determined in the ppt. by igniting and weighing as BeO.

E. S. HEDGES.

Determination of zinc with pyridine and ammonium thiocyanate. C. F. MILLER (Chemist-Analyst, 1931, 20, No. 3, 8—9).—Details are recorded.

CHEMICAL ABSTRACTS.

Determination of a very small quantity of cadmium in a rich zinc ore. J. G. FAIRCHILD (Chemist-Analyst, 1931, 20, No. 3, 5—7).—Precipitation of CdS in 3N-H_2SO_4 is recommended; the ppt. is dissolved and reprecipitated twice, the Cd being weighed as $CdSO_4$.

CHEMICAL ABSTRACTS.

Determination of lead with sodium carbonate. S. KOMARETZKY (Z. anal. Chem., 1931, 84, 407—410).—Pb may be titrated with Na_2CO_3 in neutral solution, using phenolphthalein as indicator. If free acid is present it is determined by titration with Na_2CO_3 and Me-orange, and a second portion of the solution is then

neutralised and heated for 30 min. to remove CO_2 prior to determination of the Pb. The results are satisfactory at the b. p. and at room temp., but at lower temp. are high probably because of diminished hydrolysis. H. F. GILLBE.

Polarographic studies with the dropping mercury cathode. XX. Simultaneous determination of copper, bismuth, lead, and cadmium. K. SUCHY (Coll. Czech. Chem. Comm., 1931, **3**, 354—366).—When a solution of the sulphides of Cu, Bi, Pb, and Cd in HNO_3 is neutralised with NaOH, with the addition of 10% Na K tartrate, and electrolysed with the dropping Hg cathode, the current–potential curves show the presence of these metals by breaks at the following cathodic potentials: Cu −0·14, Bi −0·34, Pb −0·60, Cd −0·80 volt. The tartrate prevents the simultaneous deposition of Cu and Bi. It is advantageous to use the solutions less conc. than 0·001N. Traces of these metals down to 10^{-5} g.-equiv. per litre can be determined, 2 c.c. of the solution being sufficient. If the amounts increase in the series Cu<Bi<Pb<Cd, any proportion may be determined, but if the nobler metals prevail, the less noble can be determined only if they constitute more than 2% of the nobler metals. The accuracy of determination of each component is about 5%. E. S. HEDGES.

Determination of copper in cyanide solutions. E. H. SMITH (Chemist-Analyst, 1931, **20**, No. 3, 10).—CN' is destroyed with HNO_3; the solution is evaporated, acidified with AcOH, treated with KI, and titrated with $Na_2S_2O_3$. CHEMICAL ABSTRACTS.

Quantitative separation of copper and cadmium by reduction of their salts with potassium formate. E. I. FULMER (Ind. Eng. Chem. [Anal.], 1931, **3**, 257—258).—When solutions of Cu salts are treated with HCO_2K, the solution evaporated to dryness and heated at 155—160°, spongy Cu is produced and may be determined as such. If Cd is also present, it is not reduced and may be determined in the filtrate.

E. S. HEDGES.

Determination of very small quantities of mercury and its importance. A. STOCK (Naturwiss., 1931, **19**, 499—502).—The method of Bodnar and Szép (A., 1929, 614) is improved. A. J. MEE.

Inaccuracy in determination of mercury by direct precipitation as mercuric sulphide from acid solution. E. P. FENIMORE and E. C. WAGNER (J. Amer. Chem. Soc., 1931, **53**, 2453—2456).—The ppt. is too heavy, and this effect is increased by the presence of iodides or excess of other salts. Volhard's method is accurate in the absence of iodides or large quantities of other salts. J. G. A. GRIFFITHS.

Anhydrous distillation method for determination of certain metals in organic compounds. I. Mercury. E. P. FENIMORE and E. C. WAGNER (J. Amer. Chem. Soc., 1931, **53**, 2468—2475).—The sample containing 0·15 g. of Hg is decomposed by gently heating with 20 c.c. of conc. H_2SO_4 and 10 g. of NH_4SO_4. The Hg is distilled as $HgCl_2$ by heating in a stream of gaseous HCl. SO_2 is oxidised by Br. 5 c.c. of 6N-HCl are added to the previously diluted and neutralised distillate; $ZnHg(SCN)_4$ is precipitated by adding 25 c.c. of reagent (73 g. of $ZnSO_4,7H_2O$+125 g. of KSCN per litre) and determined by titration with iodate (A., 1919, ii, 248). If I is present, the Hg in the distillate, diluted with aq. KI, is precipitated with Zn dust after oxidation of SO_2 with I_2. The excess of Zn is removed by HCl, the residual amalgam is dissolved, and the Hg is determined (*loc. cit.*). Halogens and S do not interfere.

J. G. A. GRIFFITHS.

Oxide content of aluminium and its determination. H. LOWENSTEIN (Z. anorg. Chem., 1931, **199**, 48—56).—Hahn's results for the amount of Al_2O_3 in samples of Al (B., 1930, 512) are too high owing to the Al being heated in a boat of siliceous material, some of which is volatilised as $SiCl_4$. Using a boat of pure Al_2O_3, however, Hahn's method gives the same results as Jander's method (A., 1928, 860). The Al_2O_3 in Al is formed solely by surface oxidation and its amount does not depend on the origin of the metal.

R. CUTHILL.

Analytical chemistry of rhenium. III. Dry reactions of rhenium. W. GEILMANN and F. W. WRIGGE. **IV. Microchemical reactions of rhenium.** W. GEILMANN and K. BRUNGER. **V. Separation of rhenium by distillation with hydrogen chloride.** W. GEILMANN and F. WEIBKE (Z. anorg. Chem., 1931, **199**, 65—76, 77—90, 120—128; cf. this vol., 328).—III. The results of the usual dry tests when applied to Re compounds are described. By a combination of dry tests and microchemical tests 0·05% Re can be detected in 10 mg. of material.

IV. Re may be detected microchemically by formation of K, Rb, and Cs per-rhenates, this test not being affected by presence of Mo compounds. In pure solutions of Re compounds the formation of the perrhenates of various org. bases may also afford a delicate reaction.

V. If an aq. solution of HCl is distilled into H_2SO_4 containing dissolved $KReO_4$ at 175—200° the Re distils over quantitatively. Separation of Re from Mo in this manner is possible, but not convenient.

R. CUTHILL.

Determination of ferric oxide and magnetic oxide in presence of iron and ferrous oxide. E. W. CHESBROUGH (Chemist-Analyst, 1931, **20**, No. 3, 14—15).—Fe is determined by treating 1 g. with 100 c.c. of 20% $CuSO_4$ solution, filtering, acidifying with H_2SO_4, and titrating with $KMnO_4$. The residue is treated in a stoppered flask with 50 c.c. of 7N-H_2SO_4, filtered, and FeO in the solution determined with $KMnO_4$. Fe_3O_4 is separated magnetically and weighed. CHEMICAL ABSTRACTS.

Potentiometric determination of ferric and dichromate ions. E. H. DUCLOUX (Rev. fac. cienc. quim., La Plata, 1930, **7**, II, 97—139).—$Fe^{\cdots}$ is determined potentiometrically in HCl solution by reduction with 0·05—0·1N-$U(SO_4)_2$ in 3N-H_2SO_4; Al, Cr, Ti, Mn, Zn, Ni, or Co salts may be present. Cr_2O_7'' can be determined accurately and simultaneously. CHEMICAL ABSTRACTS.

Determination of traces of nickel and cobalt in steel without destruction of the sample. R. JIRKOVSKY.—See B., 1931, 762.

Volumetric determination of chromium and nickel in the same solution. L. H. JAMES (Ind. Eng. Chem. [Anal.], 1931, **3**, 258—259).—The procedure is a combination of known methods for the volumetric determination of Cr and Ni, utilising the oxidation of Cr salts by $HClO_4$. The method is suitable for the analysis of stainless steels, but the cyanide titration of Ni cannot be carried out in presence of appreciable quantities of Cu or Co.

E. S. HEDGES.

Volumetric determination of uranium. Potentiometric titration of reduced uranium solutions with ceric sulphate, or with potassium permanganate. Application of differential method. N. H. FURMAN and I. C. SCHOONOVER (J. Amer. Chem. Soc., 1931, **53**, 2561—2571; cf. this vol., 927).—The cold solution of U is reduced and the 25—40% of U^{III} produced is easily oxidised by air to U^{IV} before titration of the hot solution with $Ce(SO_4)_2$ (cf. B., 1925, 1016). Cl′, but not OAc′, interferes. Previous results (A., 1922, ii, 661) with $KMnO_4$ are confirmed. J. G. A. GRIFFITHS.

Potentiometric titration of uranium by potassium permanganate. M. A. LUYCKX (Bull. Soc. chim. Belg., 1931, **40**, 269—283).—The electrolytic reduction of the U^{VI} ion has been studied in detail; fall of temp. or increase of acidity favours the reduction. Both U^{III} and U^{IV} are produced at the commencement of the reduction, and the former is then oxidised by the excess of U^{VI} to U^{IV}; when the U^{VI} is entirely reduced an equilibrium is set up between U^{III} and U^{IV}. In practice the reduction is usually incomplete, and it is recommended that the electrolysis should be prolonged for 12—14 min. at 80°, with a current of 1 amp., for a solution containing, *e.g.*, 0·195 g. UO_2SO_4 and about 2% free acid.

H. F. GILLBE.

New reaction of polonium. M. HAISSINSKY (Compt. rend., 1931, **192**, 1645—1647).—On electrolysing a HNO_3 solution of Po to which pyrogallol has been added some time previously, deposition of Po on the cathode ceases; also the Po can be separated almost completely by centrifuging such a solution. It is inferred that the Po is first reduced to the tervalent condition (cf. this vol., 697), and then forms an insol. compound with pyrogallol similar to the insol. $C_6H_3O_3Bi$ (cf. A., 1893, i, 643; 1925, ii, 442). A similar solution of Te gives no such compound.

C. A. SILBERRAD.

Separation of polonium and protoactinium fixed on tantalum pentoxide. F. REYMOND and CHENG DA-CHANG (Compt. rend., 1931, **192**, 1723—1724).—Ta_2O_5 containing Po and Pa, in a state of jelly (0·1545 g.), is dissolved in 6·3% HF (60 c.c.); 0·1 g. H_2SeO_3 is added with a few drops of H_2SO_4 and 3 c.c. of aq. $NaHSO_3$, *d* 1·332, and the whole boiled. On cooling, a few drops more aq. $NaHSO_3$ are added and the Se carrying all the Po is collected. The Ta_2O_5 with all the Pa is then quantitatively precipitated with NH_3 and $(NH_4)_2SO_4$ (cf. this vol., 1021).

C. A. SILBERRAD.

Determination of precious metals in Transvaal platinum ores and concentrates. H. R. ADAM and R. J. WESTWOOD.—See B., 1931, 763.

Micro-determination of platinum in alloys. R. STREBINGER and H. HOLZER.—See B., 1931, 722.

Calibrating thermocouples for low temperatures. A. J. MONACK (Chem. Met. Eng., 1931, **38** 416).—The m. p. of ice, transition point of $Na_2SO_4,10H_2O$ to Na_2SO_4, b. p. of H_2O and of const.-boiling mixtures of C_6H_6 and MeOH, C_6H_6 and AcOH, amyl alcohol and iodide, butyric acid and PhBr, and dil. HNO_3 may be used for calibration.

D. K. MOORE.

Calibration of the Beckmann thermometer. I. Corrected Eucken's method. M. MATSUI, S. KAMBARA, K. MYAMURA, and A. MIYOSHI. **II. Precise calibration of graduation scale.** M. MATSUI and K. MYAMURA (J. Soc. Chem. Ind. Japan, 1931, **34**, 197—200B, 200—202B).—I. A modification of Eucken's method (" Physikalisch-chemische Praktikumsaufgaben," 1928, 36) of calibrating the bore and fundamental interval of a Beckmann thermometer is described.

II. The methods of Gay-Lussac, Neumann and Thiesen, Eucken, and the least square method of Marck, Broch, and Hansen for calibrating the scale of a Beckmann thermometer are compared.

N. H. HARTSHORNE.

Thermostats. III. Time lag of various thermometers. S. KAMBARA and M. MATSUI (J. Soc. Chem. Ind. Japan, 1931, **34**, 167—172B).—An apparatus for determining the time lags of various thermometers and thermocouples is described. The results obtained varied from zero with a bare Cu-constantan couple to 8·7 sec. with a Beckmann thermometer having a scale graduated to 0·002°.

A. R. POWELL.

Apparatus for rapid drying of solutions. W. W. EWING (Science, 1931, **74**, 74—75).—15 c.c. of 40% aq. $Sr(NO_3)_2$ were evaporated to dryness without loss in 24 hr. L. S. THEOBALD.

Photo-electric polarimetry. I. L. EBERT and G. KORTÜM (Z. physikal. Chem., 1931, **B**, **13**, 105—133).—The construction and manipulation of an apparatus suitable for measurements of absorptive and rotatory power with light of wave-length down to 254 mμ are described. The essential feature of the apparatus is the comparison of light intensities by means of two coupled photo-electric cells.

R. CUTHILL.

Error in spectrophotometric determinations. M. SCHLESINGER (Biochem. Z., 1931, **235**, 70—78).—A systematic error appearing in these determinations with high extinction is critically examined.

P. W. CLUTTERBUCK.

Simple cell for conductometric titrations. J. M. PRESTON (J.C.S., 1931, 1827—1828).—The cell, made from a conical flask, is robust and easy to clean.

F. J. WILKINS.

Nomograph for evaluating electrometric p_H determinations. D. S. DAVIS (Chem. Met. Eng., 1931, **38**, 416). D. K. MOORE.

Electrical drop counter. S. E. OWEN (Science, 1931, **74**, 19—20).—An electrical device for recording drop flow over extended periods of time is described.

L. S. THEOBALD.

Glass colour standards for determination of phosphorus by Deniges' colorimetric method. H. D. CHAPMAN (Ind. Eng. Chem. [Anal.], 1931, **3**, 282—284).—The frequent prep. of new standards is obviated by the use of permanent glass colours. The technique described demands little sacrifice in accuracy. E. S. HEDGES.

All-glass steam-distillation apparatus for analytical purposes. V. E. WELLMAN (Ind. Eng. Chem. [Anal.], 1931, **3**, 281).—The simple apparatus described is useful for distillates which act on cork or rubber, and is adapted for quant. work.
E. S. HEDGES.

Dry method of micro-analysis of gases. F. E. BLACET and P. A. LEIGHTON (Ind. Eng. Chem. [Anal.], 1931, **3**, 266—269).—The apparatus described employs samples of 25—100 cu. mm. No liquid reagents are used, O_2 being removed by yellow P, CO_2 by fused KOH, and H_2O vapour by fused P_2O_5. The accuracy of the method is of the same order as that ordinarily attained in the macro-analysis of gases.
E. S. HEDGES.

Marking chemical glassware. K. H. MORKERT and W. D. HATFIELD (Ind. Eng. Chem. [Anal.], 1931, **3**, 242).—For the permanent lettering or numbering of glass apparatus 30% aq. Na_2SiO_3 is applied by means of a steel pen and allowed to dry. The markings are heated for about 1 min. in a Bunsen or blowpipe flame, when a permanent frosting occurs.
E. S. HEDGES.

Extraction apparatus with two-way tap. E. THIELEPAPE (Chem. Fabr., 1931, 293—294, 302—303). —By fitting a two-way tap between the reaction vessel and the flask the ordinary continuous-flow apparatus may be employed for solvent recovery, recrystallisation, the rapid prep. of dry solvents, dialysis, extraction, and for sampling the extract.
H. F. GILLBE.

Apparatus for the extraction of large volumes of liquids. J. FRIEDRICHS (Chem.-Ztg., 1931, **55**, 519—520).—A 7-litre extraction flask gives best extraction of one liquid by another if provided with a relatively small glass frit for diffusion of the extracting liquid together with a stirrer. Large filter plates are unsuitable, as some pores are inevitably larger than others and unequal distribution follows. Two types of apparatus are given for easy and difficult extractions. C. IRWIN.

Large-scale Soxhlet extraction. S. A. LOUGH (Ind. Eng. Chem. [Anal.], 1931, **3**, 344).—A modified apparatus is described. E. S. HEDGES.

Simple, automatic pressure regulator for filtration. E. LEIFSON (Science, 1931, **73**, 707—709).—An apparatus for filtration under controlled pressures is described. L. S. THEOBALD.

Vitreosil gas ejector pump. B. MOORE (Ind. Chem., 1931, **7**, 282—283).—A fused SiO_2 filter pump, suitable for use with hot and cold corrosive gases, is described. The calculation of its dimensions is discussed. C. W. GIBBY.

Surface leakage of pyrex glass. W. A. YAGER and S. O. MORGAN (J. Physical Chem., 1931, **35**, 2026—2042).—A method of measuring the surface leakage of glass is described; results are given and the nature of the process is discussed. The variation of the surface conductivity with the relative humidity resembles the corresponding variation of the thickness of the adsorbed H_2O film. An observed variation with the frequency of the applied voltage is probably due to electrode polarisation. H. F. GILLBE.

Method of winding helical quartz springs and of constructing glass sorption buckets. A. E. CAMERON (J. Amer. Chem. Soc., 1931, **53**, 2646—2648; cf. A., 1926, 493).—The quartz fibre is attached by wire to a horizontal quartz tube which is rotated while the fibre is heated with a small air–O_2–gas flame. Pyrex buckets 1 cm. diameter and weighing less than 0·1 g. are made from bulbs blown on the end of capillary tubes. J. G. A. GRIFFITHS.

Cellophane covers for Petri dishes for keeping out contaminations and studying the effects of ultra-violet light. F. H. JOHNSON (Science, 1931, **73**, 679—680). L. S. THEOBALD.

Modified Engler distillation flask. W. SWIENTOSŁAWSKI (Rocz. Chem., 1931, **11**, 543—544).—The vapours from the distillation flask enter the middle part of the condenser, instead of at the bottom; in this manner, partial evaporation of the condensate by the hot vapours is avoided. R. TRUSZKOWSKI.

Modified vacuum regulator. A. A. SUNIER and C. M. WHITE (Ind. Eng. Chem. [Anal.], 1931, **3**, 259). —The regulator described permits a set of predetermined pressures to be maintained in rotation in an apparatus. E. S. HEDGES.

Continuously operating diffusion vacuum pump. P. ANSIAU (Bull. Soc. chim. Belg., 1931, **40**, 330—332).—When using the Hg-vapour pump described it is unnecessary to remove corrosive or easily condensible gases from the vessel to be evacuated; the pump need not be dried after cleaning.
H. F. GILLBE.

Diaphragm valve. J. Y. YEE and J. REUTER (J. Amer. Chem. Soc., 1931, **53**, 2645—2646).—The valve is greaseless and specially adapted for regulating low rates of gas flow. The edge of the circular Al diaphragm is held against the flange of a glass cup fitted with an outlet, and the centre of the diaphragm is pressed by means of a screw against the ground surface of the capillary inlet situated axially in the cup. J. G. A. GRIFFITHS.

Bubble counter for measurement of gas evolution. E. A. BUDGE (J. Amer. Chem. Soc., 1931, **53**, 2451—2453).—Bubbles are formed under H_2O in the cup fused to the shallow capillary U-tube which communicates with the source of gas and a capillary U-tube containing Hg and two Pt contacts. Contact is broken as each bubble breaks away and is restored before each bubble develops. J. G. A. GRIFFITHS.

Simple ultra-centrifuge. J. W. BEAMS and A. J. WEED (Science, 1931, **74**, 44—46).
L. S. THEOBALD.

Determination of specific gravity of semi-solids. W. MAASS (Chem. Fabr., 1931, 318).—The *d* of such materials as bitumen is best determined by the Westphal balance using a Sn foil crucible in which the material to be tested is first dried and then main-

tained at 70—100° above its m. p. for 1 hr. to remove air inclusions. C. IRWIN.

Laboratory furnace with low gas consumption. R. HOEVERS (Chem. Weekblad, 1931, 28, 460—461).—The gas–air mixture burns in an annular space surrounding the furnace tube; the temp. of the latter attains 1100° within 10—15 min., and is const. throughout the length of the tube. H. F. GILLBE.

Geochemistry.

Universal presence of oxides of nitrogen. D. VORLANDER and W. GOHDES (Ber., 1931, 64, [B], 1776—1784).—The assumption that the presence of oxides of N in the atm. is due mainly to lightning and other electrical discharges is inadequate. It is shown that the N_2 and O_2 of moist air yield oxides of N under the influence of ultra-violet irradiation. Moist N_2 and ozonised, electrolytically prepared O_2 do not yield oxides of N at 18—20° in the absence of light during 14 days; irradiation of such mixtures causes conversion of NO_2' into NO_3', probably in the gaseous phase. Oxides of N in crude air are therefore formed during irradiation from N_2 and O_2 or O_3, and this is the permanent source. It is uncertain whether the formation of NO or of O_3 is the primary action.

NO_2' is determined colorimetrically by a solution of α-naphthylamine hydrochloride, sulphanilic acid, and tartaric acid. Moist November air at +5° to +8° contains as an average 22×10^{-6} g. N_2O_3 per cu. m. In the depth of winter N_2O_3 is not present in measurable amount and NO_2 can scarcely be detected. H. WREN.

Hydrogen-ion concentration of the lake water in Japan. S. YOSHIMURA (Proc. Imp. Acad. Tokyo, 1931, 7, 195—197).—Types of lake water are classified, data tabulated for 40 lakes, and conclusions reached. N. M. BLIGH.

Radioactivity of Teano water. P. MISCIATTELLI (Atti III Cong. Naz. Chim., 1929, 582—583; Chem. Zentr., 1931, i, 2187).—The activity is due to accompanying radioactive substances; that of most radioactive Italian springs is due to emanation. A. A. ELDRIDGE.

Mbosi meteoric iron, Tanganyika Territory. D. R. GRANTHAM and F. OATES (Min. Mag., 1931, 22, 487—493).—A wedge-shaped mass of meteoric Fe measuring 10×4×3 feet and estimated to weigh 12—15 tons was found in October, 1930, near Mbosi between Lakes Tanganyika and Nyasa. A polished and etched surface shows well-marked Widmanstätten figures, the structure being that of a medium octahedrite. Analysis by F. OATES gave Fe 90·45, Ni 8·69, Co 0·66, Cu trace, S 0·01, P 0·11, insol. 0·03, total 99·95; and a partial analysis by M. H. HEY gave Fe 90·65, Ni 8·53, Co 0·62, Cu trace, total 99·80; *d* 7·64—7·84. A separate determination of C gave 0·073%. L. J. SPENCER.

Formation of diamond. F. STÖBER (Chem. Erde, 1931, 6, 440—452).—In Moissan's experiment (1893) for the production of diamond, the temp. was about 3000°, the pressure very high, and the time very short, whereas in those of Friedländer (1898) and of Hasslinger and Wolf (1903), the temp. was much lower (about 1400°), the pressure normal, and the time long. There thus appears to be a contradiction, which the author attempts to explain by his theory of crystallisation. L. J. SPENCER.

Glauconite in fossil foraminiferal shells. A. L. DRYDEN, jun. (Science, 1931, 74, 17).—Foraminiferal shells in material from the Oligocene Vicksburg group of Mississippi bear glauconite which evidently has been formed in the shell itself. L. S. THEOBALD.

Three minerals new for Langban [Sweden]. G. AMINOFF (K. Svensk. Veten. Handl. Stockholm, 1931, [iii], 9, no. 5, 49—51).—The three new records for this locality are domeykite, native arsenic, and phenakite. Analysis by K. JOHANSSON of the domeykite gave Cu 71·45, As 27·98, insol. 0·28, total 99·71, agreeing with Cu_3As. L. J. SPENCER.

Pyroaurite. G. AMINOFF and B. BROOMÉ (K. Svensk. Veten. Handl. Stockholm, 1931, [iii], 9, no. 5, 23—43).—A new analysis by K. JOHANSSON of pyroaurite from Langban, Sweden, gave Fe_2O_3 23·19, Al_2O_3 0·11, FeO 0·10, MnO 0·28, MgO 35·44, H_2O 33·62, CO_2 7·01, SiO_2 0·41, total 100·16; neglecting the CO_2 as due to secondary alteration, this agrees with the formula $Fe(OH)_3,3Mg(OH)_2,3H_2O$. The crystals are of two types: (1) larger six-sided plates giving hexagonal *X*-ray pattern and cell dimensions *a* 3·097, *c* 15·56 (*c/a* 5·024); (2) smaller rhombohedral crystals with basal plane, giving trigonal *X*-ray patterns, *a* 3·089, *c* 23·23 (*c/a* 7·520). L. J. SPENCER.

Mineral deposit of Langban [Sweden] from a chemical point of view. G. AMINOFF (K. Svensk. Veten. Handl. Stockholm, 1931, [iii], 9, no. 5, 4—13).—The relative abundance of the 30 elements that have been detected from this locality is calc. There is a special concentration of Fe, Mn, Pb, Ba, and As. The 96 recorded minerals are listed with their chemical composition. L. J. SPENCER.

Arsenoklasite, a new arsenate from Langban [Sweden]. G. AMINOFF [with R. BLIX] (K. Svensk. Veten. Handl. Stockholm, 1931, [iii], 9, no. 5, 52—57).—This new mineral occurs as cryst. films with sarkinite (which it resembles in appearance) along fissures in dolomite impregnated with hausmannite. It is orthorhombic with perfect (010) cleavage; *X*-ray analysis gives the cell dimensions *a* 9·19, *b* 18·01, *c* 5·795 ($a:b:c$=0·510 : 1 : 0·313), containing 4 mols. of $Mn_3(AsO_4)_2,2Mn(OH)_2$. Analysis gave As_2O_5 36·96, MnO 55·01, FeO trace, MgO 0·87, BaO 0·11, CaO 0·57, H_2O 5·86, H_2O (hygr.) 0·04, total 99·42; *d* 4·16. L. J. SPENCER.

Origin of tectites of Indo-China. A. LACROIX (Compt. rend., 1931, 192, 1685—1689; cf. this vol., 60).—From an examination of several thousand more specimens the theory of their meteoric origin in the neolithic period is strengthened. C. A. SILBERRAD.

Diffusion of silica in formation of jasper in Corsica. P. JODOT (Compt. rend., 1931, **192**, 1740—1742).—The schists of N. E. Corsica are interstratified with bands of jasper the middle portions of which are original limestone. The SiO_2 is derived from radiolaria in the limestone, and has first, in the form of unstable α-chalcedony, replaced the purest calcite, and then passed into the stable β-form; where the SiO_2 is not pure it is isotropic. Metamorphism of the more impure calcite has occurred more slowly, and has been further retarded where it touches the phyllites of the schists. C. A. SILBERRAD.

Deposits of serpentine and chromite in Togoland. N. KOURIATCHY (Compt. rend., 1931, **192**, 1669—1672).—The gneissic peneplain in French Togoland contains many intrusions of peridotite, gabbro, norite, eclogite, orthoamphibolite containing clinozoisite, parameters III . 4(5) . 4′ . (4)5 . ['2. '4 . 1(2).2′], and massive serpentine. In the last named at Mt. Ajito and Goudéwé occurs chromite associated with kotschubeite. Analyses of the orthoamphibolite, chromite (4), and serpentine show (in this order): SiO_2 39·36, 0·74—5·54, 39·08; Al_2O_3 16·38, 16·04—24·61, 2·10; Fe_2O_3 3·86, 3·77—7·28 6·21; Cr_2O_3 0·05, 39·14—49·88, 0·29; FeO 10·61, 7·37—10·99, 2·99; MnO 0·19, trace—0·05, 0·12; MgO 12·36, 14·70—16·19, 37·23; CaO 11·08, 0·22—0·62, 0; Na_2O 1·71, trace, 0·06; K_2O 0·30, trace, 0·11; TiO_2 1·42, 0·16—0·44, 0·09; P_2O_5 0·08, 0, 0; Cl 0·06, 0, 0; SO_3 0·22, 0, 0; NiO 0, 0, 0·04; H_2O+ 2·18, 0·29—1·50, 11·87; H_2O- 0·17, 0—0·23, 0·12. C. A. SILBERRAD.

Stannite ore from Oonah Mine, Zeehan, Tasmania. F. L. STILWELL (Proc. Austral. Inst. Min. Met., 1931, 1—7).—The ore contains pyrite, mispickel, cassiterite, stannite, chalcopyrite, tetrahedrite, bismuthinite, and galena in a quartz gangue containing some siderite and fluorite. Of these minerals pyrite, mispickel, cassiterite, and quartz belong to an older generation than the others. The mode of occurrence of the individual minerals is described with reference to a number of photographs of polished sections. A. R. POWELL.

Granite of Dhoon, Isle of Man: a study in contamination. S. R. NOCKOLDS (Min. Mag., 1931, **22**, 494—509).—The rock is a biotite-granodiorite-porphyry and is abnormal in containing clots of biotite associated with zoisite, ilmenite, sphene, epidote, and garnet. These clots represent the remnants of a basic igneous rock (greenstone) which has been absorbed by the granitic magma. The original magma was of an alkali-granite type similar to the quartz-porphyry dikes associated with the mass. Chemical analyses of the granite, quartz-porphyry, and greenstone show that there has been an extensive interchange of oxides between the original magma and the basic igneous rock. L. J. SPENCER.

Pink epsomites and fauserite. M. H. HEY (Min. Mag., 1931, **22**, 510—518).—The existence of the fauserite, $(Mn,Mg)SO_4,6H_2O$, of Breithaupt (1865) from Hungary is doubtful. Analyses of seven pink specimens from Hungary (now Slovakia) all show a preponderance of Mg with usually less than 1% MnO (but in one case 14·70%); these are really epsomites, and the colour is largely due to cobalt (CoO to 3·16%). Solubility curves of the system $MnSO_4$–$MgSO_4$–H_2O at 17—19° show that solutions containing up to 25 mol.-% $MgSO_4$ deposit crystals of $(Mn,Mg)SO_4,5H_2O$, isomorphous with chalcanthite, and containing a much smaller proportion of Mg than the solution. Solutions richer in Mg deposit crystals of $(Mg,Mn)SO_4,7H_2O$, isomorphous with epsomite, and containing a much higher proportion of Mg than the solution. L. J. SPENCER.

Detection of pyro-electricity. A. J. P. MARTIN (Min. Mag., 1931, **22**, 519—523).—The crystal, suspended by a glass fibre, is cooled by immersion in liquid air, and if it develops a pyro-electric charge it is attracted to a metal plate. Dioptase, nepheline, thomsonite, etc. become pyro-electric. This is not in agreement with the degree of symmetry usually ascribed to dioptase. L. J. SPENCER.

Clouded felspars and thermal metamorphism. A. G. MACGREGOR (Min. Mag., 1931, **22**, 524—538).—A special type of cloudiness seen in micro-sections of plagioclase is due to the presence of minute inclusions, which have developed as a result of contact thermal metamorphism acting after the consolidation of the igneous rock. Metamorphosed lavas in Scotland and some other rocks showing this effect are described. L. J. SPENCER.

Apatite from China. G. CAROBBI (Atti III Cong. Naz. Chim., 1929, 338—340; Chem. Zentr., 1931, i, 2186).—The apatite, $3Ca_3(PO_4)_2,[CaO,Ca(OH)_2,CaCl_2,CaF_2]$, contains small quantities of La, Sa, Eu, Er, Y, and possibly of Dy, Nd, and Pr; Ba, Sr, Pb, and As are present. A. A. ELDRIDGE.

Vesuvian lithidionite. G. CAROBBI (Rend. Accad. Sci. fis. mat. Napoli, 1930, **36**, 21—31; Chem. Zentr., 1931, i, 2186—2187).—The blue lithidionite is identical with neocyanite. The formula is $RO,3SiO_2$ ($RO=CuO$, CaO, MgO, PbO, $\frac{1}{3}Fe_2O_3$, K_2O, Na_2O). Similar glasses can be obtained artificially. A. A. ELDRIDGE.

Japanese acid clay. VI. *X*-Ray studies. K. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1931, **34**, 244—247B).—*X*-Ray diffraction patterns of Japanese acid clay are similar to those of English fuller's earth and German activated clay and samples from different localities give similar results. No trace of quartz, felspar, mica, etc. can be detected in the clay by *X*-ray examination, but a kaolinite clay from Formosa which is formed by the decomp. of liparite gives identical patterns. Clay which is extracted with dil. NaOH loses SiO_2 but retains its diffraction patterns. It is therefore concluded that the clay is a mixture of a microcryst. Al silicate and amorphous SiO_2. C. IRWIN.

Thermal decomposition of synthetic hydrargillite (=gibbsite). H. ACHENBACH (Chem. Erde, 1931, **6**, 307—356).—Artificially prepared gibbsite ($Al_2O_3,3H_2O$), with α and β 1·577, γ 1·595, commences to lose H_2O at about 170°, and at about 200° (varying slightly with the v. p. and the time) it passes into the orthorhombic "boehmite" (Al_2O_3,H_2O), with *n* 1·624. Most of the H_2O is lost at 350° (but a small amount remains up to 1000°) and

the product is then γ-Al_2O_3, with n 1·693. At 1100° this changes into corundum. X-Ray data are given for each of these products. L. J. SPENCER.

Chamosite from Schmiedefeld, Thuringia. H. JUNG (Chem. Erde, 1931, 6, 275—306).—The oolitic chamosite ore was cleaned in Clerici's solution from admixed chalybite and magnetite, and gave SiO_2 26·65, TiO_2 trace, Al_2O_3 16·14, Fe_2O_3 6·69, FeO 34·43, MgO 4·47, H_2O+ 11·42, H_2O− 0·08= 99·88; formula, $5Al_2O_3$15(Fe,Mg)O,$11SiO_2$,$16H_2O$. d 3·180—3·205, n 1·63, birefringence 0·005. Most of the H_2O is lost at about 400°. These characters, as well as the X-ray patterns, show that chamosite is distinct from, although closely related to, thuringite (A., 1930, 733). L. J. SPENCER.

"Crystallised sandstone." F. STOBER (Chem. Erde, 1931, 6, 357—367).—Crystals of calcite from Fontainebleau enclose 57—83% of sand. This is imitated in $NaNO_3$ by the author's method of growing large single crystals (Z. Krist., 1925, **61**, 299). In the Ni bowl containing 400 g. of $NaNO_3$ a single crystal is produced in 12 hr., but with the addition of 600 g. of fine quartz sand a single crystal of $NaNO_3$ enclosing sand is produced in 18 min. An elaborate explanation, based on the rapid growth of acicular crystals, is given of this remarkable difference in the rate of growth. L. J. SPENCER.

Volcanic ash from Guatemala. E. DEGER (Chem. Erde, 1931, 6, 376—380).—Eight chemical analyses are given of the ash from the 1929 eruption of the Santa Maria volcano. In the ash are nodules of salt crusts containing NaCl 95·50, $CaSO_4$ 3·01, $MgSO_4$ 0·90, SiO_2 0·30%. L. J. SPENCER.

Origin of salt deposits. H. ERLENMEYER (Chem. Erde, 1931, 6, 390—401).—Based on his observations on the "creeping of crystals" (A., 1929, 503), the author's suggestion is that certain types of salt deposits, *e.g.*, $NaNO_3$ and Na_2CO_3, are due to surface efflorescence by capillarity in arid regions. L. J. SPENCER.

Relation between the chemical composition and the optical properties in the chlorite group. G. L. DSCHANG (Chem. Erde, 1931, 6, 416—439).—Eight new analyses with optical and density data are given of chlorites of various types. These and earlier analyses are plotted against the optical data in the following mixed series: I, serpentine $(H_4Mg_3Si_2O)_9$–amesite $(H_4Mg_2Al_2SiO_9)$; serpentine+amesite–ferroamesite $(H_4Fe^{II}_2Al_2SiO_9)$; III, amesite–kammererite $(H_4Mg_2Cr_2SiO_9)$; ferroamesite–cronstedtite $(H_4Fe^{II}_2Fe^{III}_2SiO_9)$. L. J. SPENCER.

Structure of analcite. W. HARTWIG (Z. Krist., 1931, 78, 173—207).—Analcite from the Lipari Is., d 2·267, analysis: SiO_2 53·79, TiO_2 0·03, Al_2O_3 23·31, Fe_2O_3 0·53, CaO 0·77, MgO 0·24, K_2O 0·57, Na_2O 13·14, H_2O (below 115°) 0·16, (above 115°) 8·11, has a body-centred cubic lattice, a 13·684±0·020 Å., and contains 16 mols. of $NaAlSi_2O_6$,H_2O. Its symmetry, although approximating to, must be regarded as a non-cubic sub-group of, O_h^{10} (cf. A., 1930, 1099; this vol., 550). C. A. SILBERRAD.

Red-earth of Mediterranean countries. E. BLANCK and A. MUSIEROWICZ (Chem. Erde, 1931, 6, 381—389).—Further chemical analyses are given of red-earth (terra rossa) (A., 1930, 732, 1398). The samples now described are from the Yugoslavian–Dalmatian coast. L. J. SPENCER.

Limestone bitumen and molasse at Pyrimont (Ain). J. J. PITTARD (Arch. Sci. Phys. Nat., 1931, [v], **13**, 143—152).—Their genesis is discussed. C. W. GIBBY.

Natural Italian gases. II. Higher hydrocarbons. M. G. LEVI, C. PADOVANI, and M. BUSI (Annali Chim. Appl., 1931, **21**, 245—258).—Analyses of natural gases from various parts of Italy and, in some cases, determinations of the content of condensable hydrocarbons (gasoline) have been made. The methods of analysis are described. T. H. POPE.

Base exchange and the formation of coal. II. W. H. A. PENSELER (N.Z. J. Sci. Tech., 1931, **12**, 363—375; cf. this vol., 931).—The work of Taylor is further criticised and his theory of coal formation is regarded as untenable. A. G. POLLARD.

Organic Chemistry.

Direct oxidation of hydrocarbons by air. P. MONDAIN-MONVAL and B. QUANQUIN.—See this vol., 1015.

Peroxidation of hydrocarbons during combustion in air. E. MARDLES (Nature, 1931, **128**, 116—117).—The presence of MeOH in the oxidation products of CH_4 can be explained satisfactorily by the Engler–Bach peroxide theory (cf. this vol., 598). L. S. THEOBALD.

Slow combustion of methane and ethane. W. A. BONE (Nature, 1931, **128**, 188—189).—No evidence of initial "peroxidation" has yet been discovered and initial "hydroxylation" is the best interpretation of known facts. L. S. THEOBALD.

Transformation of methane. I. Pyrogenic decomposition. C. PADOVANI and F. MAGALDI (Atti III Cong. Naz. Chim. pura appl., 1929, 730—739; Chem. Zentr., 1931, i, 1742).—Rise of temp. from 1000° to 1250° increases the rate of decomp. of CH_4 in a SiO_2 tube and (at first) the quantity of unsaturated hydrocarbons produced; the latter value thereafter falls. The decomp. is accelerated by filling the tube with fragments of porous porcelain. When the CH_4 is mixed with H_2 the amount of unsaturated hydrocarbons formed at lower rates is greater than with CH_4 alone, but at higher rates the reverse holds. A. A. ELDRIDGE.

Synthesis of βλ-dimethyldodecane and βτ-dimethyleicosane. S. LANDA and A. KEJVAN (Coll. Czech. Chem. Comm., 1931, 3, 367—376).—Et sebacate and MgMeBr give βλ-dimethyldodecane-βλ-diol, converted by distillation into mainly βλ-*di*-

methyl-$\Delta^{\alpha\lambda}$-dodecadiene (I), b. p. 239—241°/760 mm. (*tetrabromide*) (oxidation products, $COMe_2$ and sebacic acid), which is reduced catalytically (Pt-black) in Et_2O to *βλ-dimethyldodecane* (II), b. p. 117°/13 mm., m. p. —8·5°. Similarly, Et hexadecane-απ-dicarboxylate and MgMeBr afford βτ-dimethyleicosane-βτ-diol, dehydrated to a mixture of *βτ-dimethyleicosadienes* (III), b. p. 239·5—240·5°/21 mm., m. p. 0°, which is reduced to *βτ-dimethyleicosane* (IV), m. p. 41°.

The viscosities of (I) and (II) at 0—99°, of (III) at 10—99°, and of (IV) at 41—90° have been determined.

H. BURTON.

Knowledge of the double linking. E. BERGMANN (J. pr. Chem., 1931, [ii], **131**, 68—70).—Polemical. A reply to Petrenko-Kritschenko (A., 1930, 1017). H. A. PIGGOTT.

Highly-polymerised compounds. LI. Polymerisation and autoxidation. H. STAUDINGER and L. LAUTENSCHLAGER (Annalen, 1931, **488**, 1—8).—The velocity of autoxidation is measured by heating the substance (trimethylethylene, styrene, isoprene, dimethylbutadiene, *cyclo*pentadiene, tetrahydrobenzene, myrcene, limonene, terpinene, pinene, and menthene) with O_2 in sealed flasks at 80° and determination of the O_2 absorbed. The rate of polymerisation is determined by heating 10 g. of the material in a distillation flask in presence of CO_2 or O_2 for one or more days and removal of all matter volatile below 80°/vac. In all cases polymerisation occurs more rapidly in O_2 than in CO_2, but the differences in the rates are small in the case of terpenes. Since all the substances are autoxidisable, it must be admitted that the process of autoxidation accelerates that of polymerisation. Addition of benzoyl peroxide or of the peroxides of *as*-diphenylethylene, *cyclo*hexene, or phellandrene causes polymerisation to occur more rapidly than in CO_2, but not so quickly as in O_2. It is therefore concluded that the isolated peroxides are not the actual catalysts and that primary peroxides with more pronounced accelerating action are formed during autoxidation. A unimol. peroxide has not been isolated. In presence of a little O_2, styrene gives the polymeride accompanied by small amounts of polymeric peroxide. With larger amounts of O_2 a homogeneous polymeric peroxide is never formed, since the action is always accompanied by polymerisation. Inseparable mixtures of polystyrene and its peroxide are invariably produced which yield styrene and PhCHO when heated. With *as*-diphenylethylene polymerisation is so little pronounced that the polymeric peroxide can be isolated.

H. WREN.

Direct reaction between oxygen and ethylene. S. LENHER (J. Amer. Chem. Soc., 1931, **53**, 2420—2421).—At 300—525° the primary reactions between C_2H_4 and O_2 are the formation of ethylene oxide and CH_2O; dihydroxymethyl peroxide is isolated. Above 500° the polymerisation of C_2H_4 becomes marked. The formation of H_2O_2 has been observed.

H. A. PIGGOTT.

Preparation of unsymmetrical dialkylethylene derivatives. C. C. SCHMITT and C. E. BOORD (J. Amer. Chem. Soc., 1931, **53**, 2427—2428).—The preparation of *β-methyl-Δ^{α}-pentene*, b. p. 61·5—62°/760 mm., *γ-methylenepentane*, b. p. 66·2—66·7°/760 mm., and *βγ-dimethyl-Δ^{α}-butene*, b. p. 56·0—56·5°/760 mm., by methods previously described (cf. this vol., 709) is reported. H. A. PIGGOTT.

Dimerisation of isoprene. T. WAGNER-JAUREGG (Annalen, 1931, **488**, 176—186).—The hydrocarbon obtained together with caoutchouc and dipentene by heating isoprene by itself or with AcOH and regarded by Harries as βξ-dimethyl-$\Delta^{\alpha\epsilon\eta}$-octatriene contains only two double linkings and when hydrogenated in presence of PtO_2 affords *m*-menthane. A *m*-menthadiene obtained by auto-polymerisation of isoprene and described by Aschan as diprene is very similar to Harries' hydrocarbon in physical properties and, like it, affords carvestrene dihydrochloride when acted on by HCl in AcOH. The identity of the hydrocarbons is regarded as established. β-Myrcene, obtained by Ostromisslenski by heating isoprene at 80—90° for several days, is identical with diprene and is the sole dimeride of isoprene formed under these conditions. It appears to be a mixture of very similar hydrocarbons. The formation of aliphatic polymerides of low mol. wt. from isoprene is effected in AcOH containing H_2SO_4. Hydrocarbons and acetates are produced from which geranyl acetate has been isolated; the geraniol, obtained by hydrolysis, is identified as the diphenylurethane. H. WREN.

Explosion limit of crude acetylene mixed with oxygen and nitrogen. S. TAGI and K. TAKEOTA.—See this vol., 1015.

Explosibility of acetylene–steam mixtures. REINARSKI and others.—See this vol., 1015.

Addition of hydrogen bromide to vinyl bromide. G. N. BURKHARDT and W. COCKER (Rec. trav. chim., 1931, **50**, 837—847).—Determinations of the proportions of αα- (I) and αβ-dibromoethanes (II) in mixtures formed during the addition of HBr to vinyl bromide are effected by treatment with cold MeOH–KOH; (II) is readily hydrolysed, whilst (I) is stable. (I) is always the major isomeride when aq. HBr is used, but the amount decreases with increase in concentration of the aq. HBr and temp. With conc. solutions of HBr in AcOH at 17° (II) is the main product; at 100°, formation of (I) is favoured. Theoretical considerations are discussed and some of Wibaut's assumptions (this vol., 598) criticised.

Large amounts of C_2H_2 are produced from (I) or (II) and PhSNa in EtOH. *αβ-Dipiperidinoethane* has b. p. 130—132°/15 mm., 140—142°/20 mm.

H. BURTON.

Preparation of *cyclo*propyl cyanide and trimethylene chlorobromide. J. B. CLOKE, R. J. ANDERSON, J. LACHMANN, and G. E. SMITH (J. Amer. Chem. Soc., 1931, **53**, 2791—2796).—Trimethylene chlorobromide, prepared in 94% yield from trimethylene chlorohydrin and PBr_3, is converted into γ-chlorobutyronitrile, which with $NaNH_2$ in liquid NH_3 and Et_2O gives 75—90% yields of *cyclo*propyl cyanide.

H. BURTON.

Dimethyl*iso*butylcarbinol. Preparation and dehydration. H. DE GRAEF (Bull. Soc. chim. Belg., 1931, **40**, 315—329; cf. A., 1924, i, 1025).—Action of $MgBu^{\beta}Br$ (from $Bu^{\beta}Br$ purified with 2% NaOH) on

$COMe_2$ gives dimethyl*iso*butylcarbinol (yield 35—48%), di*iso*butyl, mesityl oxide, phorone, *iso*phorone, diacetone alcohol, βζ-dimethyl-Δ^{ϵ}-hepten-β-ol-δ-one (A., 1928, 396), *βδζ-trimethylheptane-βδ-diol*, b. p. 116—118°/12 mm., 231—234°/760 mm. (also obtained from $MgBu^{\beta}Br$ and diacetone alcohol), and a *decadiene*, b. p. 152—154°/760 mm. (also obtained by dehydration of the above trimethylheptanediol). Et *iso*valerate (from *iso*valeric acid obtained by oxidation of synthetic *iso*amyl alcohol) and MgMeBr give dimethyl*iso*butylcarbinol (yield 86%), which cannot be freed from Et *iso*valerate. Reduction of mesityl oxide and purification through the hydrogen sulphite compound gives dimethyl*iso*butylcarbinol, b. p. 42—44°/12 mm., 133·1°/760 mm. (yield 90—94%) [bromide, b. p. 83—84°/100 mm. (cf. A., 1914, i, 369)], and βδθ-trimethylnonan-δ-ol-ζ-one (A., 1928, 396), dehydrated to βδθ-trimethyl-Δ^{δ}-nonen-ζ-one. Dehydration of dimethyl*iso*butylcarbinol by various methods gives βδ-dimethyl-Δ^{γ}-pentene, b. p. 82·6°, reduced to βδ-dimethylpentane, b. p. 80·6°, and oxidised to $COMe_2$, *iso*butyric acid, and βδ-dimethylpentan-β-ol-γ-one, which readily isomerises to βγ-dimethylpentan-γ-ol-δ-one (cf. A., 1928, 866). A. A. LEVI.

Cetyl alcohol and its derivatives. (MLLE.) Y. DELCOURT (Bull. Soc. chim. Belg., 1931, **40**, 284—294).—The prep., purification, and physical consts. of cetyl alcohol, m. p. 49·10°, cetyl iodide, m. p. 21·15°, and dotriacontane, m. p. 70°, are recorded.

A. A. LEVI.

Highly-polymerised compounds. LII. Polyvinyl acetates and polyvinyl alcohols. H. STAUDINGER and A. SCHWALBACH (Annalen, 1931, **488**, 8—56).—Irradiation of vinyl acetate in $CHCl_3$ yields compounds of the type $Me\cdot CH(OR)\cdot[CH_2\cdot CH(OR)]_x\cdot CH_2\cdot CHCl_2$, the mol. wt. of which in freezing C_6H_6 corresponds with that calc. from the Cl content. The products can be separated into more and less sparingly sol. fractions in which all the mols. have the same terminal groups. Treatment of a product (about 30 units) with P and HI gives a paraffin hydrocarbon containing P, which is removed by distillation in a high vac. over soda-lime, giving a normal paraffin, mol. wt. about 930. Polymerisation of vinyl acetate occurs by union of many individual mols. to a long chain by normal covalencies. The viscosity of polyvinyl acetate ($n>50$) is similar to that of ordinary org. compounds. Polymerisation of vinyl acetate at low temp. leads to more complex compounds the solutions of which do not obey the Hagen–Poiseuille law. Rise of temp. decreases the viscosity of such solutions independently of the concentration; the effect is reversed by cooling. The dissolved particles must therefore undergo a uniform reversible transformation, thus establishing the presence of mols., not micelles. Solvent mols. become attached to reactive positions, *e.g.*, CO groups, of the polyvinyl acetate and the co-ordinative linkings are partly ruptured by rise of temp. The dissolved mols. hence experience a change in diameter which is expressed in alteration of viscosity. The increase of $\eta_{sp.}$ with concentration is ascribed to the mutual interference of the long mols.; with increase in concentration the sphere of activity rapidly becomes greater than the available vol. of the solution. It is concluded that the mol. wt. of the products can be calc. from the viscosity provided that the relationship between the $\eta_{sp.}/c$ values and mol. wt. has been determined at a definite temp. and all observations are made at that temp. Solutions of polyvinyl alcohols behave similarly to those of polyvinyl acetates. The behaviour of polysaccharides and their acetates is analogous.

Polymerisation of heated vinyl acetate is accelerated by O_2, in the absence of which the process does not occur below 180°. In quartz vessels under the influence of light, polymerisation takes place more rapidly in N_2 or CO_2 than in O_2 or air. The degree of polymerisation of vinyl acetate can be controlled by the experimental conditions within the degree $n=20$—900, the most complex products being obtained by cold photopolymerisation in N_2. The impossibility of preparing the longest chains in O_2 is probably due to attachment of the terminal valencies of the element, whereby further growth of the mol. is inhibited. Polymerisation in solution takes place more slowly, but leads to products of lower mol. wt. than those obtained from the undiluted material under similar conditions. The polyvinyl acetates are readily hydrolysed by KOH or HCl in EtOH to polyvinyl alcohols, complex or less complex products being derived from the acetates of differing mean mol. wt. It has not been found possible to convert a given acetate into the alcohol and thence into the acetate with the original properties. The simplest alcohols are readily sol. in H_2O, formamide, ethylene glycol, and glycerol, whereas the most complex dissolve only in the heated solvent, possibly with slight degradation. The relation between mol. wt. and viscosity of the alcohols is based on the assumption that an acetate of known mean mol. wt. can be hydrolysed to the alcohol without alteration of the length of the C chain. The non-cryst. nature of the polyvinyl alcohols and acetates is ascribed to the presence of asymmetric C atoms which render possible the occurrence of diastereoisomerides and hence an unsymmetrical structure of the thread mols. H. WREN.

Derivatives of aliphatic glycols. III. G. M. BENNETT and A. N. MOSSES (J.C.S., 1931, 1697—1701).—Polymethylene chlorohydrins, prepared from the glycols and conc. HCl at 95° in presence of petroleum (b. p. 90—120°) under conditions suitable for continuous removal are converted by PhSNa into the hydroxy-sulphides $OH\cdot[CH_2]_n\cdot SPh$, and thence by $SOCl_2$ in $NPhEt_2$ and CCl_4 into the chloro-sulphides. The following are described: *η-chloroheptyl*, b. p. 150°/20 mm., m. p. 10—11° (*phenylurethane*, m. p. 76°), *θ-chlorooctyl*, b. p. 125—140°/18 mm. (*phenylurethane*, m. p. 77°), *ι-chlorononyl*, b. p. 140—145°/20 mm., m. p. 28° (*phenylurethane*, m. p. 67°), and *κ-chlorodecyl*, m. p. 10—11° (*phenylurethane*, m. p. 72°), *alcohols*; *phenyl η-hydroxyheptyl*, m. p. 49°, *θ-hydroxyoctyl*, m. p. 55°, *ι-hydroxynonyl*, m. p. 60°, and *κ-hydroxydecyl*, m. p. 66·5°, *sulphides*; *phenyl η-chloroheptyl*, *θ-chlorooctyl*, m. p. 16°, *ι-chlorononyl*, m. p. 5°, and *κ-chlorodecyl*, m. p. 27·5°, *sulphides*. Hexamethylene glycol and AcCl at 100° give *ζ-chlorohexyl acetate*, b. p. 113—116°/17 mm., convertible into *phenyl ζ-hydroxyhexyl*,

m. p. 43°, and ζ-*chlorohexyl*, m. p. 7—8°, *sulphides*. Improvements in the prep. of tetra- to deca-methylene glycols are recorded. H. BURTON.

Oxidisability of glycerol. J. KREPELKA and O. TOMIČEK (Casopis Ceskoslov. Lek., 1930, **10**, 266—267; Chem. Zentr., 1931, i, 2034).—Glycerol is oxidised to CH_2O by $NaBO_3$ at 20° in a few days. A. A. ELDRIDGE.

Styracitol. II. Y. ASAHINA and H. TAKIMOTO (Ber., 1931, **64**, [*B*], 1803—1805).—Styracitol [1 : 5-anhydrosorbitol] (isolation from *Styrax Obassia* described) is converted by boiling PhCHO into *dibenzylidenestyracitol*, m. p. 163—165°, $[\alpha]_D^{23}$ — 148·73° in $CHCl_3$, and m. p. 192—193°, $[\alpha]^{25}$ — 80·47° in $CHCl_3$, and by boiling $COMe_2$ containing 1% of HCl into *diisopropylidenestyracitol*, m. p. 96—97°, $[\alpha]_D^{17}$ — 115·24° in EtOH. Successive treatment of styracitol with KOH and $MeSO_4$ and Ag_2O and MeI lead to *styracitol tetramethyl ether*, b. p. 143—144°/16 mm., d_4^{18} 1·1092, $[\alpha]_D^{1}$, — 35·63°, oxidised by HNO_3 (*d* 1·42) to oxalic and *d*-dimethoxysuccinic acids. H. WREN.

Condensations of polyhydric alcohols, sugars, and hydroxy-acids with aldehydes and ketones by means of phosphoric oxide. J. W. PETTE (Ber., 1931, **64**, [*B*], 1567—1568).—Tribenzylidenemannitol, m. p. 224°, is most readily prepared by addition of P_2O_5 to a well-stirred mixture of PhCHO and mannitol. H. WREN.

Preparation and properties of divinyl ether. W. L. RUIGH and R. T. MAJOR (J. Amer. Chem. Soc., 1931, **53**, 2662—2671).—Divinyl ether (I), b. p. 28·3° ± 0·2°/760 mm., is best prepared (yield about 25%) from ββ'-dichlorodiethyl ether and KOH at 200—240° in a slow stream of NH_3; by-products are H_2, C_2H_2, MeCHO, ethylene oxide, dioxan, and β-chloroethyl vinyl ether. Catalytic reduction (Adams) of (I) in BuOH gives 15% of Et_2O. (I) is only partly polymerised by benzoyl peroxide; polymerisation is inhibited by NH_3. Traces of (I) were obtained from ββ'-dichloro- and -di-iodo-diethyl ethers and $NaNH_2$, but (I) could not be prepared from ββ'-dihydroxydiethyl ether and Al_2O_3 or P_2O_5. The quaternary *di-iodide* from ββ'-di-iododiethyl ether and $NPhMe_2$ has m. p. 220—230° (decomp.). H. BURTON.

Ether-like compounds. V. Synthesis of monoethers of higher diprimary glycols. M. H. PALOMAA and R. JANSSON (Ber., 1931, **64**, [*B*], 1606–1610; cf. this vol., 710).—δ-*Methoxy*-n-*butyl alcohol*, b. p. 63—64°/7 mm., d_4^{20} 0·9286, is obtained in 36·5% yield by the action of Me γ-chloropropyl ether on Mg, trioxymethylene, and a little $ZnCl_2$ in Et_2O; with PCl_3 and pyridine it gives δ-*methoxy*-n-*butyl chloride*, b. p. 142·5—142·8°/751 mm., d_4^{20} 0·9875. Et γ-chloropropyl ether and gaseous CH_2O similarly give δ-*ethoxy*-n-*butyl alcohol*, b. p. 72°/8 mm., d_4^{20} 0·9079, whence δ-*ethoxy*-n-*butyl chloride*, b. p. 157—157·5°/760 mm., d_4^{20} 0·9603. ε-*Methoxy*-n-*amyl alcohol*, b. p. 83—84°/9 mm., d_4^{20} 0·9215, ε-*methoxy*-n-*amyl chloride*, b. p. 41°/5 mm., d_4^{20} 0·9714, and ε-*ethoxy*-n-*amyl alcohol*, b. p. 89—91°/9 mm., d_4^{20} 0·9067, are described. H. WREN.

Soya-bean lecithins. Y. YOKOYAMA and B. SUZUKI (Proc. Imp. Acad. Tokyo, 1931, **7**, 226—229; cf. this vol., 401, 600).—Lecithins of the β-series were brominated and fractionated by successive solvents: *palmito-oleo-*, *dioleo-*, *oleolinoleo-*, *palmitolinoleo-* (*bromide*, m. p. 85°), and *palmitolinoleno-* (*bromide*, m. p. 105°) -β-*lecithins* were isolated in the form of their bromo-derivatives. E. LEWKOWITSCH.

Copper mercaptides and their reaction with carbon disulphide. W. E. DUNCAN, E. OTT, and E. E. REID (Ind. Eng. Chem., 1931, **23**, 381—383).—Cu^{I} *Et*, *Bu*, *hexyl*, *nonyl*, Pr^{β}, iso*butyl*, iso*amyl*, iso*hexyl*, and iso*nonyl sulphides* have been prepared from the mercaptans with $Cu(OAc)_2$. Cu^{II} is reduced to Cu^{I} and an equiv. amount of the disulphide is obtained. On treatment with S, CuS and the alkyl disulphide are obtained. Basic mercaptides are not obtained when the compounds are treated with NaOH and no hydrolysis was observed. With CS_2 thiocarbonates more sol. in org. solvents than the original mercaptides are formed. Additive products of Cu mercaptide, alkyl disulphide, and CS_2 have also been obtained. Double compounds of Cu^{I} and Na thiocarbonates can also be obtained. T. A. SMITH.

Action of phenyl methionate [methanedisulphonate] on hydrazine hydrate. H. J. BACKER and P. L. STEDEHOUDER (Rec. trav. chim., 1931, **50**, 931—935).—Ph methionate and aq. N_2H_4 at 130° give PhOH, Ph methanesulphonate (I), the N_2H_4 salt, m. p. 148—149° (decomp.) [corresponding *Na* and *Ba* (+H_2O) salts], of *Ph H methionate* (+H_2O), and N_2H_4 methionate; at 155°, NH_4 *Ph methionate* (II), m. p. 217°, NH_4 *methionamate*, m. p. 230° (corresponding *Ba* salt), and NH_4 *methionate* (III), not melted at 300°, are produced. Ph methionate and N_2H_4 in EtOH give (I), (II), and (III). *Ph Me methionate* has m. p. 63°.

Ph ethane-αα-disulphonate and N_2H_4 at 130° afford the N_2H_4 salt [corresponding *Ba* (+$5H_2O$), *Tl*, m. p. 130·5°, and *brucine*, decomp. about 270°, salts] of Ph H ethane-αα-disulphonate. H. BURTON.

Action of β-bromoethanesulphonyl chloride on amines. E. RIESZ (Ber., 1931, **64**, [*B*], 1895—1896).—Aniline is converted by β-bromoethanesulphonyl chloride in Et_2O into a substance $C_8H_9O_2NS$, m. p. 53°, which dissolves readily in alkali hydroxide and decolorises alkaline $KMnO_4$; it has the constitution

$$NPh{<}{}^{SO_2}_{CH}{>}CH_2 \text{ or } NHPh{\cdot}SO_2{\cdot}CH{:}CH_2.$$

H. WREN.

Energy transformations at surfaces. I. Reduction of carboxylic acids by induced, intramolecular transformation of siloxen-acid derivatives. H. KAUTSKY and A. HIRSCH (Ber., 1931, **64**, [*B*], 1610—1622).—Reaction between siloxen and gaseous HCO_2H follows the course $:SiH + HCO_2H = :Si{\cdot}O{\cdot}CHO + H_2$; it is greatly facilitated by slight rise of temp. or irradiation. The product is hydrolysed to intensely yellow hydroxysiloxens, HCO_2H, and traces of CH_2O. SO_2 acts as acceptor for the liberated H_2 and the product when hydrolysed yields small amounts of $H_2S_2O_4$. Reaction between siloxen and SO_2 in indifferent media containing a little H_2O follows the course $:SiH + H_2SO_3 = :Si{\cdot}SO_3H + H_2$; $H_2 + 2SO_2 = H_2S_2O_4$. Hydroxysiloxens, readily obtained by hydrolysis of the bromosiloxens, are converted by acids into the siloxen-acids; acid chlorides cause

replacement of almost all OH groups. Bromo- and bromoacetato-siloxens are transformed by NH_3 into aminosiloxens, gaseous NH_3 giving intermediate products of the type $Si_6O_3H_5{\cdot}NH_3{\cdot}Br$; in liquid NH_3 the compound passes into aminosiloxen and NH_4Br, which is readily removed by repeated washing. All aminosiloxens react readily with acids according to the scheme $\colon Si{\cdot}NH_2+2HX=\colon SiX+NH_4X$. Tribromosiloxen in EtOH is converted by gaseous NH_3 into triaminosiloxen, converted by CO_2 into the *carbamido*-compound stable in the dark, but slowly yielding HCN if irradiated. Cautious treatment of the product with O_2 causes reduction of the CO_2 with formation of HCN. The O atom of the CO_2 is absorbed by the Si·Si linking. H_2O liberated in the production of HCN hydrolyses the unchanged $Si{\cdot}O{\cdot}CO{\cdot}NH_2$ and the newly-formed Si·CN groups, so that NH_3 is simultaneously produced; extraneous H_2O operates markedly in this direction. *Triformiatosiloxen* under similar conditions affords CH_2O. Quant. experiments with monoformiatosiloxen indicate the production of CH_2O in about 5% yield. AcOH and BzOH are similarly reduced to the corresponding aldehydes, the change being particularly marked with the highly-substituted Bz compounds.

H. WREN.

Catalysis in organic chemistry. IV. Decompositions of esters and acids by anhydrous zinc chloride. H. W. UNDERWOOD, jun., and O. L. BARIL (J. Amer. Chem. Soc., 1931, **53**, 2200—2202).—The decomps. described below were observed when the substance (1 mol.) was heated with anhyd. $ZnCl_2$ (cf. A., 1930, 321). $Cl{\cdot}CO_2Et$ gives C_2H_4, EtCl, and HCl (at room temp.); $Cl{\cdot}CO_2Pr^{\alpha}$ behaves similarly, but less C_3H_6 is formed; $Bu^{\alpha}{}_2CO_3$ gives BuOH (95%) and a little Δ^{α}-butene; $Pr^{\beta}OBz$ gives C_3H_6, C_6H_6, BzOH, and $Pr^{\beta}Cl$; Bu^{α} phthalate gives Δ^{α}-butene, phthalic acid and anhydride, BzOH, and $Bu^{\beta}OH$; *iso*amyl salicylate gives γ-methyl-Δ^{α}-butene and its dimeride, and PhOH; Me and Et anthranilates give *o*-toluidine (75%) and *o*-aminoethylbenzene (66%), respectively; Et methylmalonate gives C_2H_4 and Et propionate; and $CH_2Ph{\cdot}OAc$ gives AcOH and tar; in all cases except the last CO_2 is generated. Et *m*-nitrobenzoate, Et_2CO_3, HCO_2H, AcOH, and propionic and *n*-butyric acids were recovered unchanged. BzOH, salicylic and cinnamic acids are decomposed to the corresponding hydrocarbon and CO_2.

H. A. PIGGOTT.

Formic acid from hydrolysis of cellulose oxalate. J. P. MONTGOMERY (J. Amer. Chem. Soc., 1931, **53**, 2700—2701).—Details are given for the prep. of formic acid from cryst. oxalic acid, absorbent cotton, and conc. HCl.

H. BURTON.

Separation of glycerides. XIX. B. SUZUKI (Proc. Imp. Acad. Tokyo, 1931, **7**, 230—233; cf. A., 1929, 1271; this vol., 602).—Previous results are summarised and discussed. Fatty acids occur in almost all possible combinations as glycerides; these, however, appear to be selectively distributed in the various organisms, few glycerides occurring in more than 1 or 2 different oils.

E. LEWKOWITSCH.

Thermal transformation of olefines. Cracking of oleic acid under high pressure. A. D. PETROV (Ber., 1931, **64**, [*B*], 1827—1834).—The gaseous products obtained when oleic acid is heated with H_2O and Al_2O_3 at 380—400° for 3—4 hr. contain H_2 48%, CO_2 20%, C_nH_{2n+2} 18%, and C_nH_{2n} 0·0%. The aromatic products (PhMe, $C_6H_4Me_2$) in the liquid fractions cannot therefore be formed in accordance with Davidson's scheme and dehydrogenation of naphthenes of the 6-membered type cannot occur under these conditions as shown by experiments with dimethyl*cyclo*hexane. They arise most probably from *cyclo*hexenes derived from diethylenic hydrocarbons formed by pyrolysis of liquid olefines of high mol. wt. The presence of naphthenes of the 3- and 4-membered type in the liquid products is highly probable. The paraffins of the fractions of lower b. p. have preponderatingly the *iso*-structure.

H. WREN.

Migration of the double linking of oleic acid during hydrogenation. K. H. BAUER and M. KRALLIS (Chem. Umschau, 1931, **38**, 201—203).—Oleic acid heated in contact with Al_2O_3 at 250° in a stream of N_2 yielded a semi-solid product containing 9·2% of (Twitchell) "solid" acids; Δ^{ι}-oleic acid m. p. 41—42°, was identified. Thus the migration of the double linking observed during hydrogenation at 180—220° by Hilditch and Vidyarthi (A., 1929, 423) and by Steger and Scheffers (this vol., 711) is a result of the high temp., and the non-formation of it in the low-temp. experiments of Bauer and Ermann (A., 1930, 1271) is explained. When a reduced Ni–Al_2O_3 catalyst was used, some stearic acid was produced, attributed to the presence of adsorbed H_2 not displaceable by N_2.

E. LEWKOWITSCH.

Couepic acid, a new isomeride of elæostearic acid. J. VAN LOON and A. STEGER (Rec. trav. chim., 1931, **50**, 936—942).—Details are given for the isolation of *couepic acid*, $C_{18}H_{30}O_2$, m. p. 74—75°, from the total fatty acids of the oil from *Couepia grandiflora*, Benth. The acid is reduced to stearic acid and oxidised by O_3 to valeric and azelaic acids. Et couepate is oxidised to valeric acid and Et H azelate, indicating that the acid is a geometrical isomeride of α- and β-elæostearic acids.

H. BURTON.

[Composition of linseed oil and the terminology α- and β-linoleic and α- and β-linolenic acids.] H. P. KAUFMANN and M. KELLER (Chem. Umschau, 1931, **38**, 203—205).—Van der Veen's criticism (this vol., 822) of the thiocyanometric determination of linolenic acid is refuted. The abnormally high thiocyanogen val. for linseed oil found by van Loon (Diss., Delft, 1928) might be due to the excessively long reaction period (4 days) used, which may lead to untrustworthy figures.

E. LEWKOWITSCH.

Kolbe's synthesis with β-*iso*amyloxypropionic acid. F. FICHTER and A. SHNIDER (Helv. Chim. Acta, 1931, **14**, 857—861).—The electrolysis of β-*iso*amylpropionic acid is closely paralleled by the thermal decomp. at 300° of its peroxide to *iso*valeraldehyde, iso*amyl* β-iso*amyloxypropionate*, b. p. 122—125°/12 mm., $\alpha\delta$-di*iso*amyloxybutane (73% of theory), and CO_2, the main reaction being $[CHMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}O\text{-}]_2\longrightarrow[CHMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2\text{-}]_2+2CO_2$, affording a confirmation of the peroxide theory of the Kolbe synthesis. β-iso*Amyloxypropionyl chloride*, b. p. 82°/12 mm., pre-

pared from the acid and PCl_5, is converted by H_2O_2 in pyridine into its *peroxide*, which with NH_3 gives the *amide*, m. p. 65°. H. A. PIGGOTT.

Partition principle applied to structures of enolic sodium derivatives of 1 : 3-diketones and β-keto-esters. A. MICHAEL and J. ROSS (J. Amer. Chem. Soc., 1931, 53, 2394—2414).—In presence of 1 equiv. of NaOEt Et malonate reacts more rapidly than the acetoacetate both with MeI and with EtBr in EtOH; with EtBr the abs. velocities are less and the difference is greater, and the acetoacetate reaction then slower instead of faster than that with NaOEt alone. The interaction in EtOH at 0° of equimol. amounts of NaOEt, Et acetoacetate, and Et malonate with MeI results in almost exclusive methylation of the acetoacetate, but with EtBr the malonate alone is ethylated. It is considered that the Na is attached mainly to the acetoacetate, and that during the slow reaction with EtBr transference of the metal to the malonate occurs.

Et γ-ketobutane-ααβ-tricarboxylate, b. p. 147°/5 mm. (*semicarbazone*, m. p. 76°), is obtained, accompanied by Et ethanetetracarboxylate, by the action of Et sodioacetoacetate on Et chloromalonate; it is converted by MeI and NaOEt (1 equiv.) into the *α-Me* derivative, b. p. 144—152°/2 mm., hydrolysed by aq. $Ba(OH)_2$ to α-carboxy-α-methylsuccinic, α-methyllævulic, and 1 : 3-*diketo*-4 : 5-*dimethyl*cyclo*pentane*-4 : 5-*dicarboxylic*, m. p. 295—300°, acids. Bromoacetone and Et sodiomethylmalonate interact in EtOH to give *Et α-carbethoxy-α-methyl-lævulate*, b. p. 133°/5 mm. (*semicarbazone*, m. p. 102°), hydrolysed by $Ba(OH)_2$ to the *acid* (syrup), which on distillation gives α-methyl-lævulic acid. The action of NaOEt, suspended in EtOH–Et_2O, on Et γ-ketobutane-αββ-tricarboxylate gives a mixture of *liquid*, b. p. 149°/2 mm. (with partial conversion into the solid isomeride) [*disemicarbazone*, m. p. 220°; *semicarbazide* derivative (pyrazole ?), $C_{11}H_{14}O_4N_2$, m. p. 76°], and *solid*, m. p. 86°, enolates; as the former, but not the latter, gives a coloration with $FeCl_3$ the respective constitutions of Et 1 : 4-dihydroxy-$\Delta^{1:3}$-*cyclo*pentadiene-2 : 3-dicarboxylate and 1 : 4-dihydroxy-1 : 4-endomethylene-Δ^2-*cyclo*butene-2 : 3-dicarboxylate are assigned. It is considered that enolisation should occur most readily at the keto-group of Et γ-ketobutane-αββ-tricarboxylate, and that the direction of methylation with MeI is a consequence of the greater reactivity of Na attached to the malonic residue in this compound.

Me chloroformate and sodiobenzoylacetone interact in cold Et_2O to give a mixture of *solid*, m. p. 57°, and *liquid*, b. p. 164°/2 mm., O-*carbomethoxy*-derivatives. By treatment with NH_3, K_2CO_3, NH_2OH, or NH_2Ph under various conditions either benzoylacetone or a derivative of it with these reagents is formed. The solid ester forms two *semicarbazones*, CH_3ON_3:CPh·CHAc·CO_2Me, m. p. 166°, and CH_3ON_3:CPh·CH:CMe·O·CO_2Me, m. p. 183°, the former of which alone gives a coloration with $FeCl_3$. The latter is converted into the former by treatment with acids. The final product in dil. aq. AcOH is *Et 5-phenyl-3-methylpyrazole-4-carboxylate*, m. p. 62°; an unidentified substance, m. p. 202°, is also formed. The liquid ester does not give definite products with semicarbazide. Both liquid and solid esters give propiophenone when reduced catalytically, but benzoylacetone under the same conditions gives *α-phenylbutane-αγ-diol*, b. p. 129—131°/2 mm. (*diacetate*, b. p. 140°/2 mm.). They are therefore regarded as geometrical isomerides of the ester CHBz:CMe·O·CO_2Me, and benzoylacetone therefore reacts in the enolic form corresponding with this in accordance with the partition principle. CH_2Bz_2 under similar conditions gives an O-*carbethoxy*-derivative, m. p. 90°, and considerable unidentified liquid material.

Benzoylacetone and semicarbazide acetate in EtOH give the *mono*-, m. p. 127—128°, and *di-semicarbazone*, m. p. 242°; the former is converted into 5-phenyl-3-methylpyrazole-1-carboxylamide by AcOH or HCl in warm EtOH. H. A. PIGGOTT.

Acetoacetic ester condensation. III. Role of sodium in the condensation. J. M. SNELL and S. M. MCELVAIN (J. Amer. Chem. Soc., 1931, 53, 2310—2316).—Interaction of finely-divided Na with an excess of carefully purified AcOEt produces EtOH and Et acetoacetate in the ratio 1·7 : 1 when the EtOH is removed during the reaction, and 2 : 1 where it is not; the yield of H_2 is only about 0·08—0·09 mol. per atom Na. Allowing for the EtOH produced by reduction, its yield (88%) is thus approx. the same as with NaOEt as condensing agent (93%). Also, under comparable conditions, approx. the same yield of ketonic ester is obtained with NaOEt as with Na. Assuming that AcOEt is reduced by direct addition of Na to the C:O linking (otherwise the argument fails), the mechanism of the condensation consists in the reduction of AcOEt by Na with formation of NaOEt, which then brings about the acetoacetic ester condensation. The sum of the proposed reactions is 9AcOEt $+4Na \longrightarrow 4$ONa·CMe:CH·CO_2Et$+6$EtOH, the H_2 observed being produced by secondary interaction of Na and EtOH. H. A. PIGGOTT.

Lævulic acid. I. Preparation from carbohydrates by digestion with hydrochloric acid under pressure. R. W. THOMAS and H. A. SCHUETTE (J. Amer. Chem. Soc., 1931, 53, 2324—2328).—A yield of 42% of lævulic acid is obtained by heating sucrose with 2·4 times its wt. of 6·5% aq. HCl at 162° in an autoclave for 1 hr. Comparable results are obtained with dextrose, lævulose, and starch. H. A. PIGGOTT.

Determination of the hydroxyl content of organic compounds : determination of castor oil. S. MARKS and R. S. MORRELL (Analyst, 1931, 56, 428—429).—The method of Bolsing, as modified by Peterson and West (cf. A., 1927, 1100), gives the most concordant results. Immersion in boiling H_2O for 15 min., as originally suggested by Verley and Bolsing (cf. A., 1902, ii, 54), is rapid and simple, and gives satisfactory results with substances not decomp. at that temp., *e.g.*, castor oil, β naphthol, vanillin, and guaiacol. T. MCLACHLAN.

Structures of the oxalates of sexavalent molybdenum. H. M. SPITTLE and W. WARDLAW (J.C.S., 1931, 1748—1753).—*Salts* of the type $B_2[MoO_2(C_2O_4)_2]$, where B=quinoline, 2-methylquinoline, or strychnine,

are obtained when the bases are added to a solution of MoO_3 (1 mol.) in aq. oxalic acid (2—3 mols.). The salts may occur in 3 forms, 2 of which should be optical isomerides; the strychnine salt could not, however, be resolved. When the ionic concentration of 2-methylquinolinium oxalate is decreased relatively to the Mo concentration, *2-methylquinolinium hydrogen molybdenum trioxymonoxalate*, $(C_{10}H_{10}N)H[MoO_3,C_2O_4,H_2O]$, results. New formulæ are suggested for the salts $MoO_3,R_2C_2O_4,xH_2O$ and $(MoO_3)_2,R_2C_2O_4,xH_2O$.

H. BURTON.

Supposed isomerism of cyclic oxalic esters. W. H. CAROTHERS and F. J. VAN NATTA (Ber., 1931, 64, [B], 1755—1759).—Repetition of the work of Bergmann and Wolff (A., 1930, 912) gives a product, m. p. 100—110°, rising to 125—130° after crystallisation, which is shown to be a polymeric ethylene oxalate by its cryst. form. The monomeric variety, m. p. 143°, has been isolated only after distillation, never as a primary product. Bergmann's product, m. p. 166°, from methoxalyl chloride and ethylene glycol is not *methyl β-hydroxyethyl oxalate*, which is prepared from Me oxalate and ethylene glycol at 160—185°; it has b. p. 103—105°/0·6 mm., m. p. 32—33°, d_{23}^{20} 1·2830.

H. WREN.

Interaction of sulphuryl chloride with substances containing the reactive methylene group. II. K. G. NAIK and N. T. TALATI (J. Indian Chem. Soc., 1931, 8, 203—207; cf. A., 1927, 758).—The reactivity of the CH_2: group increases with increasing negative character of the adjoining groups, *e.g.*, in substances $CH_2(COR)_2$, in the order $R=NH_2<NH\cdot C_6H_4\cdot NO_2<OEt$. The following substances were obtained by treatment of the corresponding unchlorinated compounds with SO_2Cl_2, nuclear chlorination not taking place in these cases: *dichloromalondi*-o-, m-, p-*nitroanilides*, m. p. 152°, 166°, and 178°, respectively; *dichloromalondiethylamide*, m. p. 131°; *dichloromalondi*iso*butylamide*, m. p. 84°; dichloromalondiheptylamide; dichloromalondi-*p*-3-xylidide; dichloromalonamide; monochloromalontetraphenylamide; *monochloromethylmalondiethylamide*, m. p. 108°; *monochloromethylmalondi*iso*butylamide*, m. p. 102°; *monochloromethylmalondibenzylamide*, m. p. 159°. *Malondi*-m- and-p-*nitroanilides*, m. p. 196° and 243°, respectively, were prepared from $CH_2(CO_2Et)_2$ and the nitroanilines, but *o*-nitroaniline did not react even at 200°. The o-*compound*, m. p. 182°, was obtained by condensing the base with $CH_2(CO_2H)_2$ in presence of $POCl_3$. *Methylmalondiethylamide* and -iso*butylamide*, m. p. 151° and 133°, respectively, were obtained from $CHMe(CO_2Me)_2$ and the respective bases.

R. S. CAHN.

Polymorphism of malonic, succinic, and glutaric acids as a function of temperature. F. D. LA TOUR (Compt. rend., 1931, 193, 180—182; cf. A., 1930, 1100).—The above acids are dimorphous, the curve of transition points following a similar course to that of the m. p. *X*-Ray measurements are recorded for some of the substances.

A. A. LEVI.

Rotation and configuration in the Walden inversion. W. D. BANCROFT and H. L. DAVIS (J. Physical Chem., 1931, 35, 1624—1647).—A discussion. Rotations and configurations of optically active compounds can be correlated by means of criteria outlined by van 't Hoff. These show that *l*-(—)-malic, *l*-(—)-chlorosuccinic, *l*-(+)-aspartic, *l*-(+)-lactic, *l*-(+)-alanine, and *l*-(—)-chloropropionic acids are all of the same configuration. (The signs in parentheses indicate actual rotations in H_2O, and *l* indicates that lævorotatory salts and esters are produced.) In the two series thus determined HNO_2, Ag_2O, and NOCl act by replacement, whilst PCl_5, $SOCl_2$, KOH, and NH_3 produce a Walden inversion. The hydroxy-acids can be correlated by this method, which shows that *l*-(+)-lactic, *l*-(—)-mandelic, *l*-(*l*—)-malic, and *l*-(—)-tartaric acid have the same configuration.

L. S. THEOBALD.

Identification of mesaconic acid. H. H. MOTTERN and G. L. KEENAN (J. Amer. Chem. Soc., 1931, 53, 2347—2349).—Micro-crystallographic data are given for the *hydrazide*, m. p. 217—218° (corr.), and *p*-nitrobenzyl ester, m. p. 134° (corr.), of mesaconic acid, and for the acid itself, m. p. 204·5°. The Et_2 ester has b. p. 93—95°/10 mm.

H. A. PIGGOTT.

Cork. V. Phloionic acid. VI. Phloionolic acid. VII. Phellogenic acid. P. ZETZSCHE and M. BAHLER (Helv. Chim. Acta, 1931, 14, 846—849, 849—851, 852—856).—V. Phloionic acid (*Me* ester, m. p. 77—78°), when purified by repeated crystallisation from MeOH, or by means of its Pb salt, has m. p. 124°, is dibasic, and appears to have the formula $C_{18}H_{34}O_6$. It does not form an anhydride.

VI. *Phloionolic acid*, dimorphic, m. p. 104° (stable) and 95° (*Me* ester, m. p. 77°), is isolated from fraction K_6 (this vol., 713), and purified by repeated crystallisation from MeOH, AcOEt, or 80% EtOH. It is monobasic, has the formula $C_{18}H_{26}O_5$, and therefore is probably a trihydroxystearic acid. Its properties closely resemble those of an acid, m. p. 107—108°, isolated from cutin (A., 1925, i, 1025).

VII. The conversion of phellonic acid into phellogenic acid by fusion with KOH at 350° occurs with loss of $1CO_2$, giving nonadecanedicarboxylic acid. The same product is similarly obtained from α-hydroxyarachidic acid, and margaric acid from α-hydroxystearic acid.

H. A. PIGGOTT.

Synthesis of agaric acid. M. PASSERINI and G. BANTI (Atti III Cong. Naz. Chim. pura appl., 1929, 343—346; Chem. Zentr., 1931, i, 1432—1433).—The Na derivative of Et acetonedicarboxylate was heated with cetyl iodide; the cetyl derivative was treated with phenylcarbimide and AcOH in Et_2O during 40 days, the product being hydrolysed with alcoholic KOH. The product afforded Me heptadecyl ketone, m. p. 81—83°, methylcetylmaleic anhydride, m. p. 33°, and *r*-cetylcitric (agaric) acid (+1·5H_2O), m. p. 130—132°.

A. A. ELDRIDGE.

Pyranoid structure of glycuronic acid and of theophyllinearabinoside. J. PRYDE and R. T. WILLIAMS (Nature, 1931, 128, 187).—Methylation, followed by esterification and oxidation with HNO_3, of bornyl-*d*-glycuronide gives a mixture of *d*-dimethoxysuccinic acid and r-*xylotrimethoxyglutaric acid* showing that the glycuronic acid in bornylglycuronide possesses a pyranoid structure. Methylation of *d*-glycurone yields two stereoisomeric cryst. trimethylglycurones. The main oxidation product (with HNO_3)

of the pentose residue of trimethyltheophylline-*l*-arabinoside is d-*arabotrimethoxyglutaric acid*, indicating that theophyllinearabinoside is a pyranoid compound. The purine residue of this arabinoside has been isolated as a yellow cryst. compound, $(C_7H_7N_4O_2{\cdot}NO_2)_2,H_2O$, m. p. 275°, presumably 8-nitrotheophylline. L. S. THEOBALD.

Muconic and hydromuconic acids. V. Ester-addition to ethyl muconate. E. H. FARMER and T. N. MEHTA (J.C.S., 1931, 1762—1764).—*Ethyl* Δ^{α}-*butene-αδ-dicarboxylate-γ-malonate*, b. p. 175—180°/2 mm. (oxidation products, oxalic and tricarballylic acids), and a trace of an isomeric ester are formed when Et muconate is condensed with Et malonate in presence of a little NaOEt; cyclisation and isomerisation are inhibited (cf. J.C.S., 1922, **121**, 2015; 1923, **123**, 3324). H. BURTON.

Synthesis of ethyl thioacetoacetate. P. C. RAY (Nature, 1931, **128**, 189).—Et thioacetoacetate has been synthesised as indicated by $CMeCl{:}CH{\cdot}CO_2Et \xrightarrow[KSH]{alcoholic} SH{\cdot}CMe{:}CH{\cdot}CO_2Et \rightleftharpoons CSMe{\cdot}CH_2{\cdot}CO_2Et$. This ester behaves like Et acetoacetate towards hydrazines, NH_2OH, aromatic amines, etc., undergoes Grignard, Reformatsky, and Michael reactions, and in Knoevenagel's reaction yields thioaldehydes.

L. S. THEOBALD.

Photosynthesis of formaldehyde and carbohydrates. G. G. RAO and N. R. DHAR.—See this vol., 920.

Formose. P. KARRER and E. VON KRAUSS (Helv. Chim. Acta, 1931, **14**, 820—831).—The solution obtained by polymerising aq. CH_2O with $Ca(OH)_2$ contains pentoses, hexoses, and presumably some heptoses, that can be fractionated by distillation of the crude mixture of their *iso*propylidene compounds, by which means fractions corresponding either with pentoses or with hexoses are obtained. Without exception the individual fractions after hydrolysis reduce Fehling's solution only very feebly, but interact with I, and therefore probably contain ·CHO groups. In an attempt to fractionate the *iso*propylidene compounds, b. p. 110—120°/0·6 mm., by means of phenylhydrazine, an *osazone*, m. p. 156—158°, was obtained in small amount. H. A. PIGGOTT.

Reactions of acetaldehyde over zinc chromite under a pressure of 210 atmospheres. H. ADKINS, K. FOLKERS, and M. KINSEY (J. Amer. Chem. Soc., 1931, **53**, 2714—2720).—A more detailed account of work previously reviewed (A., 1930, 1559).

H. BURTON.

Reactions of *ortho*-derivatives of aldehydes and ketones. W. COCKER, A. LAPWORTH, and A. T. PETERS (J.C.S., 1931, 1382—1391).—A generalisation according to electronic theories of the Pinner–Kotz theory regarding the action of KCN on $CCl_3{\cdot}CHO$ (A., 1913, i, 1309) is discussed, being supported by the ready loss of HCl from 2-*chloro*-1-*cyano*cyclo*hexane*, b. p. 138°/15 mm., and the formation of BzOEt from BzCN and cold NaOEt. It explains the conversion of $CCl_3{\cdot}CHO$ in EtOH into Et dichloroacetate. The arguments of Chattaway and Irving (A., 1929, 795) are refuted. Chloral alcoholate and HCN in cold EtOH in the presence of NPr_3 form chloralcyanohydrin exothermally. The generalised theory is applied to the conversion of cyanohydrins into aminonitriles, which proceeds by way of the free aldehyde or ketone, and to the reversible formation of acetals. HCl is removed from 6-nitro-2 : 4-bis(trichloromethyl)-1 : 3-benzdioxin not only by KCN, but also by NaOH. *cyclo*Hexanone in ligroin shaken with KCN in aq. NH_3 gives 1-aminocyano*cyclo*hexane, the *hydrochloride* of which [m. p. 233° (decomp.)] with dil. H_2SO_4 at 115—120° yields 1-*amino*cyclo*hexanecarboxylic acid*, m. p. 350° (decomp.). MeCHO, aq. KCN, and $NHEt_2$ give diethylaminopropiononitrile. R. S. CAHN.

Purported addition of magnesium benzyl chloride to the ethylenic linking in citronellal. H. GILMAN and W. F. SCHULZ (J. Amer. Chem. Soc., 1931, **53**, 2799—2801).—Polemical against Kharasch (Ann. Survey of Amer. Chem., 1930, **5**, 193).

H. BURTON.

Modern chemistry of the sugars. H. PRINGSHEIM (Z. angew. Chem., 1931, **44**, 677—682).—The natural occurrence of individual sugars is discussed.

H. WREN.

Synthesis of *d*-threose. J. R. MENDIVE (Chemia, 1930, **7**, 321—331; Chem. Zentr., 1931, i, 1596—1597).—*d*-Threose (phenylhydrazone, m. p. 164—165°) has been obtained ash-free by degradation of *d*-xylose by Wohl's method; cryst. derivatives were not obtained. Tetra-acetylxylonitrile, m. p. 83°; diacetylamido-*d*-threose, m. p. 166°.

A. A. ELDRIDGE.

Decarboxylation of *d*-galacturonic acid with special reference to the hypothetical formation of *l*-arabinose. C. M. CONRAD (J. Amer. Chem. Soc., 1931, **53**, 2282—2287).—*l*-Arabinose could not be isolated from the syrupy products of decarboxylation of Ba *d*-galacturonate and Ehrlich's tetra-acid "*a*" (A., 1929, 1273) with boiling 4% H_2SO_4. It was, however, obtained by similar treatment of apple and lemon pectins, in the former case in more than twice the yield that could have formed by decarboxylation of galacturonic acid (measured by CO_2 evolution). It is therefore concluded that the hydrolysis of galacturonic acid to furfuraldehyde does not proceed by way of arabinose, and that arabinose units are present in the plant materials in cases where it is isolated by their hydrolysis. H. A. PIGGOTT.

Reactivity of methylated sugars. IV. Action of dilute alkali on trimethylxylose. C. E. GROSS [with W. L. LEWIS] (J. Amer. Chem. Soc., 1931, **53**, 2772—2784).—The equilibrium solution from xylose and dil. $Ca(OH)_2$ contains xylose (52·9%), lyxose (8·3%), and a condensation product (9·8%) derived from 4 mols. of the expected 2-ketoxylose. Evidence of a stable, intermediate enol could not be obtained. Under similar conditions, 2 : 3 : 4-trimethylxylose is transformed partly into trimethyl-lyxose; evidence of a stable enol is obtained. Acidification of the equilibrated solution gives some furfuraldehyde, and the gum isolated contains trimethyl-lyxose (70%), trimethylxylose (26%), and partly demethylated products (4%). The conversion of trimethylxylose into trimethyl-lyxose confirms the identity of their ring structures. H. BURTON.

Oxidation of sugars. I. Electrolytic oxidation of aldoses in presence of a bromide and calcium carbonate. H. S. Isbell and H. L. Frush (Bur. Stand. J. Res., 1931, 6, 1145—1152).—Details are given of the electrolytic oxidation of various aldoses in presence of a bromide as catalyst, whereby the monocarboxylic acids are produced in almost quant. yield; in presence of $CaCO_3$ the Ca salts are readily isolated by crystallisation from the reaction products. The anode efficiency is 80—99%, and the process is economically practicable on a technical scale. H. F. Gillbe.

Determination of small quantities of biologically important sugars with the exclusion of non-carbohydrate reducing substances. O. Lehmann (Planta [Z. wiss. Biol.], 1931, 13, 575—642).—A comprehensive scheme for sugar analysis is based on the method of Hagedorn and Jensen (A., 1923, ii, 673). Lævulose–dextrose mixtures are examined before and after differential decomp. with HCl, and sucrose, maltose, and starch after hydrolysis with acid or fermentation. In pentose–hexose mixtures the total reducing value is obtained by the Hagedorn–Jensen reagent, hexoses are removed by fermentation, and pentoses determined by a modified furfuraldehyde method (A., 1924, ii, 876). A. G. Pollard.

Identity of the saccharals of epimeric sugars. M. Gehrke and F. Obst (Ber., 1931, 64, [B], 1724—1729).—The configurative difference between epimeric sugars is destroyed by the introduction of a double linking between the 1- and 2-C atoms. As predicted, *d*-glucal is found to be identical with *d*-mannal and *d*-xylal with *d*-lyxal. Acetobromoglucose or acetobromolyxose is converted by Zn and 50% AcOH into d(—)-*xylal* (*lyxal*) *diacetate*, b. p. 79—82°/0·2—0·3 mm., m. p. 39—40°, $[\alpha]_D$ —314·2° in $CHCl_3$, hydrolysed by $Ba(OH)_2$ in MeOH to d(—)-*xylal* (*lyxal*), b. p. 91—92°/0·2—0·3 mm., m. p. 49—50°, $[\alpha]_D$ —254·6° in H_2O. The diacetate is hydrogenated in MeOH in presence of Pd-asbestos to d(—)-*dihydroxylal* (*lyxal*) *diacetate*, b. p. 82—83°/0·2—0·3 mm., $[\alpha]_D$ —38·8° in EtOH, which does not add Br or show reducing properties. d(—)-*Dihydroxylal* (*lyxal*), b. p. 97—99°/0·2—0·3 mm., m. p. 67—68°, $[\alpha]_D$ —44·9° in H_2O, is oxidised by perbenzoic acid in AcOEt to *d*(—)-lyxose, identified as the phenylbenzylhydrazone. The prep. of *d*(—)-lyxose from penta-acetylgalactonitrile is described. Acetobromomannose is transformed into *d*(—)-glucal triacetate, m. p. 54—55°, $[\alpha]_D$ —15·5° in EtOH, and thence into *d*(—)-mannal, *d*(+)-dihydromannal triacetate, and *d*(+)-dihydromannal, identical with the series of compounds derived from acetobromoglucose. H. Wren.

Action of sulphite and hydrogen sulphite solutions on sugars at high temperatures. E. Hägglund (Fenno-Chem., 1930, 2, 49—54; Chem. Zentr., 1931, i, 2040).—If dextrose is heated with $NaHSO_3$ solution in a closed vessel at 135°, the cold product treated with H_2SO_4, the Na_2SO_4 removed with EtOH, and the filtrate neutralised with $BaCO_3$, a Ba sulphonate is obtained of which part is hydrolysed by boiling H_2O to $BaSO_3$. A disulphonate (Ba 35·5, S 12·4%) was isolated; prolonged hydrolysis of this gave *d*-gluconic acid. The sulphonic acid contains a CO_2H group and is stable towards boiling dil. acid and alkali. A. A. Eldridge.

Determination of hexoses in the hydrolytic products of polysaccharides. E. Schmidt, M. Atterer, and H. Schnegg (Cellulosechem., 1931, 12, 235—242).—The hexose content of the hydrolytic products (Clark's method, B., 1922, 339A) of pentosan-free polysaccharides, including viscose-silk and mannan, is 84·1—84·5% as determined by fermentation with *Schizosaccharomyces Pombe* or *Sacch. Vordermannii*. The presence of Ba inhibits fermentation. One ClO_2 treatment of the hydrolytic products is more effective than an animal charcoal treatment in converting humin substances into products which do not retard fermentation. Even dil. Cl_2 (0·1%) oxidises dextrose and should not be used for bleaching. The activity of the yeasts decreases quickly during use, but can be restored by growing in wort. *d*-Galactose can be determined by *S. Vordermannii* only in presence of a phosphate-containing nutrient. *S. Pombe* does not ferment *d*-galactose. The agreement between the fermentation values of hemicellulose hydrolytic products (cf. A., 1929, 1113; B., 1929, 937) points to the absence therein of *d*-galactose. A. Renfrew.

Reaction between dextrose and potassium permanganate in acid solution. S. L. Ridgway (J. Physical Chem., 1931, 35, 1985—2004).—Gluconic acid could not be isolated from the products of oxidation of dextrose in acid solution by $KMnO_4$ or by HBr and $KMnO_4$. The velocity of the former reaction increases very slowly with increase of the total concentration, but fairly rapidly with increase of the $KMnO_4$ or the acid concentration. The first stage of the process is very rapid, but the point at which the velocity diminishes is not const.; the $KMnO_4$ is at this point almost entirely reduced to MnO_2, which then oxidises the remaining dextrose relatively slowly. Dextrose cannot be determined by oxidation with $KMnO_4$ in acid solution. H. F. Gillbe.

Compounds of carbohydrates with acetaldehyde; ethylideneglucose. B. Helferich and H. Appel (Ber., 1931, 64, [B], 1841—1847).—Dextrose is converted by paracetaldehyde containing a little conc. H_2SO_4 into a mixture of 4 : 6-*ethylidene*-α- and -β-d-*glucose* from which the homogeneous α-compound, m. p. 179—182° (corr.), $[\alpha]_D^{18}$ +66·4° to $[\alpha]_D^{20}$ —2·36° in H_2O, is obtained by repeated crystallisation from aq. $COMe_2$. It reduces boiling Fehling's solution. The 6-position is occupied, since it fails to react with CPh_3Cl. The *osazone*, $C_{20}H_{24}O_4N_4$, has m. p. 185—186°, $[\alpha]_D^{15}$ —79·57° in $CHCl_3$. β-Methyl-*d*-glucoside is converted similarly into 4 : 6-*ethylidene*-β-*methyl*-d-*glucoside*, m. p. 189—190° (corr.), $[\alpha]_D$ —79·1° in H_2O, transformed by Ac_2O and NaOAc at 100° into 4 : 6-*ethylidene*-β-*methyl*-d-*glucoside* 2 : 3-*diacetate*, m. p. 180·5—182°, $[\alpha]_D^{18.5}$ —65·9° in $CHCl_3$, also obtained by treating ethylideneglucose with Me_2SO_4 and NaOH and subsequently with Ac_2O in pyridine. Methylation of ethylideneglucose or ethylidene-β-methyl-*d*-glucoside affords *ethylidene*-β-*methyl*-d-*glucoside* 2 : 3-*dimethyl ether*, m. p. 109·5—111°, $[\alpha]_D^{18}$ —47·8° in $CHCl_3$, obtained in smaller yield from 3-methylglucose and paracetaldehyde. The substance is converted by PhCHO and $ZnCl_2$ into benzylidene-β-

methyl-*d*-glucoside 2 : 3-dimethyl ether, m. p. 133·5—134°, $[\alpha]_D^{18}$ −60·0° in EtOH. H. WREN.

Condensation products of dextrose and *p*-toluidine. M. AMADORI (Atti R. Accad. Lincei, 1931, [vi], **13**, 72—77).—When heated together in 95% EtOH, *p*-toluidine (7 g.) and dextrose (10 g.) yield the (?)glucosidic compound $C_{13}H_{19}O_5N$, m. p. 115°, moderately stable in alkaline solution, but decomp. into the original components in acid solution. If the toluidine and dextrose, in the above proportions, are heated at 80—90° until molten, they give an isomeric *compound*, m. p. 154°, which is stable in neutral or acid, but decomposes, apparently with formation of dextrose, in alkaline, solution, and is analogous to Schiff's bases. T. H. POPE.

Rotatory dispersion of aldehydo-sugar acetates. M. L. WOLFROM and W. R. BRODE (J. Amer. Chem. Soc., 1931, **53**, 2279—2281).—The values of $1/M[\alpha]\lambda$ in the visible region for the aldehydo-acetates of *d*-galactose and *l*-arabinose in $CHCl_3$ lie on a straight line when plotted against λ^2. In the case of dextrose a slight deviation is observed in the violet region. H. A. PIGGOTT.

Mutarotation of the alcoholate and aldehydrol of aldehydogalactose penta-acetate. M. L. WOLFROM (J. Amer. Chem. Soc., 1931, **53**, 2275—2279).—The rotation of the cryst. alcoholate (A., 1930, 1023) of aldehydogalactose penta-acetate, $[\alpha]_D$ + 1·5° in EtOH-free $CHCl_3$, falls rapidly to a min. and then increases, rather less rapidly, to a value higher than the original. The form of the curve is regarded as pointing to reversible decomp. of the semi-acetal into aldehyde ($[\alpha]_D$ −25°) and EtOH, and formation from these of a semi-acetal with a new configuration, *e.g.*,

$$\mathrm{H{-}\overset{\displaystyle OH}{\underset{\displaystyle R}{C}}{-}OEt} \rightleftharpoons \mathrm{H{-}\underset{\displaystyle R}{C}{=}O + EtOH} \rightleftharpoons \mathrm{H{-}\overset{\displaystyle OEt}{\underset{\displaystyle R}{C}}{-}OH}$$

The aldehydrol, on the other hand, under like conditions, shows only a steady fall in rotation along an exponential curve, indicating a simple unimol. decomp. into free aldehyde and H_2O, and favouring the aldehydrol structure assigned. No mutarotation is shown by the aldehyde itself. H. A. PIGGOTT.

Ring structure of β-methylgalactoside. A. MÜLLER (Ber., 1931, **64**, [*B*], 1820—1826).—β-Galactose penta-acetate is converted by HBr in AcOH into α-acetobromogalactose, m. p. 81—82°, $[\alpha]^{20}$ +235·2° in C_6H_6, transformed by Ag_2CO_3 in MeOH into acetomethylgalactose, m. p. 94°, which is hydrolysed by NaOMe to β-methylgalactoside, m. p. 174°. The last-named compound is transformed by CPh_3Cl in pyridine into *β-methylgalactoside 6-triphenylmethyl ether*, m. p. 167—169° after softening at 80°, $[\alpha]^{20}$ −39·48° in $CHCl_3$ (2 : 3 : 4-*triacetate*, m. p. 138°, $[\alpha]_D^{18}$ −50·29° in $CHCl_3$). The corresponding Bz_3 compound, m. p. 95°, $[\alpha]_D^{20}$ +77·73° in $CHCl_3$, is converted by HBr in AcOH into the non-cryst. *β-methylgalactoside* 2 : 3 : 4-*tribenzoate*, converted by *p*-toluenesulphonyl chloride into 2 : 3 : 4-*tribenzoyl-β-methylgalactoside* 6-p-*toluenesulphonate*, m. p. 194° after softening at 190°, $[\alpha]^{20}$ +148·7° in $CHCl_3$, transformed by NaI in $COMe_2$ at 100° into 2 : 3 : 4-*tribenzoyl-β-methylgalactoside-6-iodohydrin*, m. p. 145°, $[\alpha]_D^{20}$ +169·3° in $CHCl_3$ (also $+COMe_2$, m. p. 140°). With AgF in pyridine the iodohydrin yields 2 : 3 : 4-*tribenzoyl-β-methyl-Δ^5-galactoseenide*, which readily absorbs Br. After hydrolysis with KOH in EtOH it is inactive towards Fehling's solution, which it strongly reduces after acidification of the hydrolysate with HCl. H. WREN.

Colorimetric determination of lævulose and its application to mixtures of various carbohydrates. H. BREDERECK (Ber., 1931, **64**, [*B*], 1730—1732).—1 c.c. of the solution, mixed with 10 c.c. of 4% $(NH_4)_2MoO_4$ and 0·25 c.c. of $4N$-HNO_3, is heated in a closed tube for 2½ min. at 65° and cooled for 3 min. at 0°. The colour is matched against that produced by standard lævulose solutions. Lævulose may be determined quantitatively in presence of 70—80% of dextrose, 80—90% of galactose, 60—70% of mannose, 80—90% of arabinose, and 80% of a mixture of the sugars cited above. Under the experimental conditions the hydrolysis of sucrose is so slight that lævulose can be accurately determined in presence of 80% of sucrose and of 70—80% of a mixture of sucrose and dextrose. H. WREN.

Model experiments based on the theory of alcoholic fermentation. IV. Preparation and oxidation of di-β-di*iso*propylidenefructose-1-phosphoric acid. H. OHLE and F. GARCIA Y GONZALEZ (Ber., 1931, **64**, [*B*], 1759—1765; cf. A., 1930, 70).—β-Di*iso*propylidenefructose does not yield *tri-β-diisopropylidenefructose phosphate*, m. p. 135—136°, $[\alpha]_D^{20}$ −29·5° in $CHCl_3$, under the action of $POCl_3$ in pyridine or in Et_2O or $CHCl_3$ in absence or presence of pyridine; it is obtained in small amount by aid of PCl_5 in Et_2O, readily by means of $POCl_3$ and PCl_5 in Et_2O. Hydrolysis of the ester with NaOH in aq. MeOH affords *diisopropylidenefructose hydrogen* 1-*phosphate* (*Na* salt, $[\alpha]^{20}$ −23·5° in H_2O; non-cryst. *K* salt; *Ag* salt, m. p. 210° (decomp.); *cinchonidine* salt, m. p. 212—213° (decomp.), $[\alpha]_D^{20}$ −66·06° in MeOH; *Me* ester, m. p. 108—109°, $[\alpha]^{20}$ −35·69° in MeOH, from the Ag salt and MeI; *Et* ester, m. p. 113—114°, $[\alpha]^{20}$ −34·77° in MeOH, from the acid and Et orthoformate). The acid is very stable towards alkalis, whereas its hydrolysis with acids involves the $:CMe_2$ groups to a greater or smaller extent. Hydrolysis of the Me or Et ester with NaOH is accompanied by partial re-formation of di-β-di*iso*propylidenefructose hydrogen 1-phosphate. Oxidation of Na di-β-di*iso*propylidenefructose 1-phosphate by $NaMnO_4$ in initially neutral solution follows the same course as that of di*iso*propylidenefructose 1-sulphate (*loc. cit.*), leading through the expected intermediate product to the *salt*,

$$(CO_2Na)_2CH{\cdot}\underset{\llcorner O\cdot CMe_2\cdot O \lrcorner}{CH\text{———}C}(OH){\cdot}CH_2{\cdot}O{\cdot}P(OH)O_2Na,$$

which is decomposed by dil. mineral acids to H_3PO_4, CO_2, $COMe_2$, methylglyoxal, and glycollic acid. The yield of methylglyoxal is considerably less than that obtained from the sulphuric ester, due to partial conversion into acetol and pyruvic acid. H. WREN.

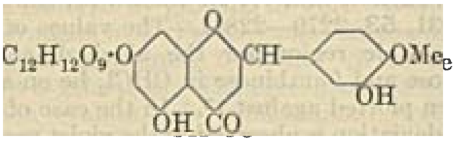
Action of mercury salts on acetohalogeno-sugars. VI. Syntheses of gentiobiose- and

cellobiosido-6-glucose derivatives. G. ZEMPLÉN and A. GERECS [with J. ERDÉLYI] (Ber., 1931, **64**, [*B*], 1545—1554).—Detailed descriptions are given of the conversion of starch successively into β-glucosan and its triacetate. The last-named substance is transformed by $TiCl_4$ in $CHCl_3$ into α-1-chloro-2 : 3 : 4-triacetyl-*d*-glucose, m. p. 124—125°, $[\alpha]_{\rm D}^{19}$ −189·2° in $CHCl_3$, and by $TiBr_4$ into α-1-*bromo*-2 : 3 : 4-*triacetyl*-d-*glucose*, decomp. 126—127°, $[\alpha]_{\rm D}^{19}$ +217·4° in $CHCl_3$ (converted by MeOH and Ag_2CO_3 into β-1-methyl-2 : 3 : 4-triacetyl-*d*-glucose, m. p. 133—134°, $[\alpha]_{\rm D}$ −16 0° in $CHCl_3$). Acetobromoglucose, 1-chloro-2 : 3 : 4-triacetylglucose, and $Hg(OAc)_2$ in C_6H_6 afford *acetochlorogentiobiose*, $C_{26}H_{35}O_{17}Cl$, m. p. 136·5—137°, $[\alpha]_{\rm D}^{18}$ −82·83° in $CHCl_3$, transformed by Ag_2CO_3 in aq. $COMe_2$ and subsequent acetylation into gentiobiose octa-acetate, m. p. 166—167°, +27·39° in $CHCl_3$, which gives gentiobiose when hydrolysed. Acetobromocellobiose, 1-chloro-2 : 3 : 4-triacetylglucose, and $Hg(OAc)_2$ yield 1-*chloro*-6-β-*cellobiosidoglucose decaacetate* $C_{38}H_{51}O_{25}Cl$, decomp. about 223—224°, $[\alpha]_{\rm D}^{18}$ +48·37° in $CHCl_3$, the formation of an intermediate, halogen-free product being indicated. Interaction of 1-chloro-2 : 3 : 4-triacetylglucose, acetobromocellobiose, and $Hg(OAc)_2$ in boiling C_6H_6 gives a mixture of α- and β-6-cellobiosidoglucose hendeca-acetate (identified by hydrolysis to the free sugar), from which 1-chloro-6-β-cellobiosidoglucose deca-acetate is obtained by treatment with $TiCl_4$ in C_6H_6. α-1-*Bromo*-6-β-*cellobiosidoglucose deca-acetate* has decomp. 205°, $[\alpha]_{\rm D}^{20}$ +69·91° in $CHCl_3$. H. WREN.

Action of mercury salts on acetohalogeno-sugars. VII. Synthesis of 1-β-methylgentiobiose and 1-β-methyl-6-α-glucosidoglucose; *iso*maltose question. G. ZEMPLÉN and Z. BRUCKNER (Ber., 1931, **64**, [*B*], 1852—1858).—The action of acetobromoglucose on 2 : 3 : 4-triacetyl-1-β-methylglucose in C_6H_6 in presence of $Hg(OAc)_2$ readily affords 1-β-methylgentiobioside hepta-acetate, m. p. 82°, $[\alpha]_{\rm D}$ −16·99° in $CHCl_3$, when a considerable proportion of $Hg(OAc)_2$ is used, but when less is used the corresponding α-derivative preponderates in the non-crystallisable product. Hydrolysis of the latter by NaOMe followed by treatment with BzCl in pyridine yields the non-cryst. 1-β-*methyl*-6-α-*glucosidoglucose heptabenzoate*, m. p. about 85° after softening at 75°, $[\alpha]_{\rm D}^{18}$ +54·67° in $CHCl_3$, whereas treatment of it with Me_2SO_4 and NaOH gives *heptamethyl*-1-β-*methyl*-6-α-*glucosidoglucose*, $[\alpha]_{\rm D}^{18}$ +95·13° in EtOH, +93·1° in H_2O. 1-β-*Methylgentiobioside heptabenzoate* has m. p. 203°, $[\alpha]_{\rm D}^{19}$ +2·0° in $CHCl_3$.

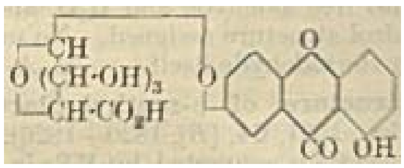
The product of the methylation of Fischer's *iso*maltose is separated by distillation in a high vac. into several fractions; those of lower b. p. are analogous to 1-β-methyl-6-α-glucosidoglucose, whereas those of higher b. p. solidify completely at room temp. *iso*-Maltose octa-acetate after saponification has about 40% of the reducing power of dextrose, rising only to 80% after hydrolysis. It contains therefore considerable amounts of foreign matter of high mol. wt. in addition to the disaccharide or mixture of disaccharides. H. WREN.

Natural glucosides. III. Position of the biose residue in hesperidin. F. E. KING and A. ROBERTSON (J.C.S., 1931, 1704—1709).—The formula assigned to hesperidin ($Ac_{8(\text{or } 9)}$ derivative, m. p. 175—176°) by Asahina and Inubuse (J. Pharm. Soc. Japan, 1929, **49**, 11) is confirmed. Hesperidin with Me_2SO_4 and dil. NaOH or MeI and K_2CO_3 in $COMe_2$, gives products hydrolysed by dil. acid to 4-*hydroxy*-2 : 6-*dimethoxyphenyl* 3 : 4-*dimethoxystyryl ketone* (I), m. p. 194° (*acetate*, m. p. 175°), synthesised from 4-hydroxy-2 : 6-dimethoxyacetophenone and veratraldehyde. Catalytic reduction (Pd) of (I) affords 4-*hydroxy*-2 : 6-*dimethoxyphenyl* β-3 : 4-*dimethoxyphenylethyl ketone*, m. p. 109°, also obtained together with the 2-hydroxy-4 : 6-dimethoxy-isomeride by the Hoesch condensation of β-3 : 4-dimethoxyphenylpropionitrile and phloroglucinol Me_2 ether. By analogy with hesperitin (*ibid.*, 1928, **48**, 207), hesperidin is considered to have the following structure :



H. BURTON.

Natural glucosides. IV. Constitution of euxanthic acid. A. ROBERTSON and R. B. WATERS (J.C.S., 1931, 1709—1714).—Euxanthic acid with MeI and Ag_2O gives *Me* O-*tetramethyleuxanthate*, m. p. 168°, hydrolysed by HCl in aq. MeOH to 7-hydroxy-1-methoxyxanthone, m. p. 235° (lit. 240°), and a trimethylglycuronic acid, apparently identical with that described by Challinor *et al.* (this vol., 465). Oxidation of the glycuronic acid with HNO_3 and esterification of the products formed afford a little Me *d*-dimethoxysuccinate and mainly *Me trimethyl*-δ-*saccharolactonate*, m. p. 106°, also obtained by oxidation of 2 : 3 : 4-trimethyl-α-methylglucoside and subsequent esterification. The last-named compound, b. p. 130°/0·1—0·2 mm., and a small amount of a substance, m. p. 79°, are obtained by hydrolysis of 6-triphenylmethyl-2 : 3 : 4-trimethyl-α-methylglucoside, m. p. 166—167° (cf. A., 1925, i, 9), with HCl in MeOH. Euxanthic acid has the structure :



H. BURTON.

Highly-polymerised compounds. LIII. Constitution of compounds of high mol. wt., particularly cellulose. H. STAUDINGER (Ber., 1931, **64**, [*B*], 1688—1697).—Mainly a reply to Hess and Sakurada (this vol., 828). The validity of applying measurements of viscosity to the determination of the mol. wt. of cellulose and its derivatives is justified by the complete analogy of the behaviour of these substances with that of synthetic highly polymerised compounds. With both synthetic and natural products, deviations from the Hagen–Poiseuille law become more marked with increase in mol. wt. and more noticeable in conc. than in dil. solution. They are not observed in very dil. solution (sol solution) in which the mols. have freedom of movement. Diminution of the viscosity of cellulose

solutions with increasing purification of the preps. is not due to the removal of incrusting matter, but to degradation of the sensitive macromols. The observation that the viscosity of a cellulose acetate solution is more dependent on pressure than that of a solution of the cellulose from which it was prepared is attributed to the greater diameter of the acetate mol. The applicability of the Bergmann–Machemer method to the determination of mol. wt. of materials belonging to the same polymeric homologous series is supported by the results of new measurements of the mol. wt. of highly-degraded cellulose acetates in dioxan. Hess' conception of the cellulose mol. is adversely criticised.

H. WREN.

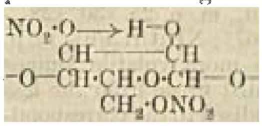
Action of sodium on cellulose in liquid ammonia. P. C. SCHERER, jun., and R. E. HUSSEY (J. Amer. Chem. Soc., 1931, 53, 2344—2347).—Interaction of Na with cellulose in dry liquid NH_3 at its b. p./1 atm. proceeds rapidly to the monosodio-derivative (1Na : $1C_6H_{10}O_5$), the theoretical amount of H_2 being evolved; further reaction is then slow, but yields eventually the Na_3-derivative. The formation of $NaNH_2$ could not be detected. H. A. PIGGOTT.

Treatment of cellulose and oxidised cellulose with acetic–sulphuric acid mixtures. R. H. VAN DYKE, C. J. STAUD, and H. LEB. GRAY (J. Amer. Chem. Soc., 1931, 53, 2725—2732).—Cellulose (cotton linters) is oxidised with CrO_3 (=0·5 and 2O per $C_6H_{10}O_5$ unit) or $KMnO_4$ (=0·5 and 1O) in N-H_3PO_4 (cf. A., 1930, 750). The oxidised and unoxidised celluloses are treated with AcOH and H_2SO_4 at 20—25° during 330—335 hr. and the Ac contents of the various products determined. The most vigorously oxidised celluloses give products with the smallest Ac content. The results indicate that 1 OH group per $C_{24}H_{40}O_{20}$ in cellulose behaves differently from the other 11.

H. BURTON.

Acetylation of cellulose. D. KRUEGER and E. TSCHIRCH (Ber., 1931, 64, [B], 1874—1878).—Under certain conditions $HClO_4$ is much more efficient than H_2SO_4 as catalyst for the acetylation of cellulose. Both acids are effective in concentration so small that the solubility of cellulose does not enter into the question, and the acceleration of the process must be attributed to a sp. property depending on the structure of the acids. The formation of mixed esters, observed on the acetylation of cellulose in presence of H_2SO_4, is not a general property of acid catalysts; primary cellulose acetates obtained in homogeneous or heterogeneous systems in presence of $HClO_4$ are free from this acid. Acetylation of cellulose occurs at a lower temp. and with a rapidity not previously observed when $HClO_4$ is used as catalyst. H. WREN.

Modern organic solvents. I. Development of the solvents industry. New conception of the constitution of cellulose nitrate. Solvent action in dyeing [dry cleaning] and allied processes. E. CLAYTON and C. O. CLARK (J. Soc. Dyers and Col., 1931, 47, 183—191).—Historical review of industrial solvents manufacture. In the esterification of cellulose the primary OH external to the anhydro-glucoside ring is first attacked and the micellar structure is loosened. Entry of a second ester group possibly produces a 5-ring chelated compound, in which all



associating power has been lost. Further nitration breaks down the chelated structure and usually also (by oxidation) the chains themselves. Solubility in $COMe_2$ persists so long as free OH remains, *e.g.*, in all the nitrates, but not in the triacetate. Highly nitrated cellulose may, however, owe its solubility in $COMe_2$ to degradation by oxidation. The highest nitrates and the triacetate, being non-associated, have a natural solubility in the non-associated solvent, $CHCl_3$. The degree of hydrolysis accompanying the esterification of cellulose is a measure of the breakdown of primary valencies of the intramicellar chains, and the increased area exposed to the solvent leads to accelerated solvation. A table is given showing the solvent effects of pyridine, EtOH, MeOH, glycol mono-ethyl and -butyl ethers, diacetone alcohol, and diglycol mono-ethyl and -butyl ethers on 15 acid, direct, and basic dyes. The presence of more than a certain, usually small, proportion of solvent leads to const. partition of dye between fibre and solvent mixture, and prevents exhaustion of the dye-bath unless solvent is removed during dyeing. The use of mixtures of solvents with wetting agents is discussed. The "benzine soap" used in dry-cleaning owes its solubility in the petroleum to the presence of excess of fat or fatty acid. NH_4 oleate, insol. in light petroleum, dissolves instantly on addition of oleic acid, the electrovalent (ionised) form passing into the covalent (co-ordinated) form. C. HOLLINS.

Pine-wood lignin. B. RASSOW and H. GABRIEL (Cellulosechem., 1931, 12, 227—235). Wood cellulose appears to adsorb lignin superficially, since, by repeated extraction with ammoniacal CuO solution, followed by washing with dil. H_2SO_4, the total extract, mostly lignocellulose, increases. Some lignin is also dissolved. The amounts of materials dissolved from wood-meal by glycerol or glycol decrease after repeated extractions. Lignin can be detected in the glycol extract. Extraction for 5—10 min. at 165—175° by glycerol containing about 0·15% of mineral acid gives a viscous solution rich in lignin. If glycol replaces glycerol the separation of lignin from cellulose is complete and takes place with little decomp., giving an easily-filtered solution from which glycol-lignin can be separated by precipitation with H_2O, dissolution in AcOH, and reprecipitation with H_2O. With HCl it gives lignin, OMe val. 17·3. The process is contrasted with that of Hibbert and co-workers (A., 1930, 1275). The OMe val. of a lignin is shown to be an index of its purity. A. RENFREW.

Sulphur derivatives of simple amines. I. Amine hydrogen sulphides. M. ACHTERHOF, R. F. CONAWAY, and C. E. BOORD (J. Amer. Chem. Soc., 1931, 53, 2682—2688).—*Amine hydrogen sulphides* are prepared from the dry amine and an excess of dry H_2S usually in Et_2O below 0° in absence of air; the following are described (the m. p. in parentheses are those in closed tubes): NH_2Me, m. p. 40—44° (90—92°); $NHMe_2$, m. p. 34—40°; NMe_3, m. p. 15—20° (28—30°); NH_2Et, m. p. 50—55° (55—57°); (55—62°); Et_3, m. p. 25—27°; NH_2Pr, m. p. 38—

42° (40—42°); $NHPr_2$, m. p. 58—62° (76—78°); NH_2Bu, m. p. 18—20°; $NHBu_2$, m. p. 25—30° (28—32°); *iso*amylamine, m. p. 62—67°; $NH(CH_2Ph)_2$, m. p. 32—34°. The salts from the more volatile amines decompose in air giving S, whilst those from the less volatile amines are similarly oxidised to the corresponding thiosulphates. H. BURTON.

Influence of poles and polar linkings on tautomerism in the simple three-carbon system. II. Prototropy in bisquaternary αγ-propenylenediammonium salts. C. K. INGOLD and E. ROTHSTEIN (J.C.S., 1931, 1666—1683; cf. A., 1929, 300).—Salts containing the isomeric ions
$[Et_3N\cdot CH\colon CH\cdot CH_2\cdot NMeEt_2]^{++}$ and
$[Et_3N\cdot CH_2\cdot CH\colon CH\cdot NMeEt_2]^{++}$ are synthesised and shown to be interconvertible in presence of $0\cdot1N$-KOH or -$NaOPr^{\beta}$ at 30°. The interconversion is regarded as prototropic and not dependent on primary addition to the double linking, since β-hydroxy- and β-methoxytrimethylenediammonium salts could not be converted into similar unsaturated substances.

Tetraethyl-β-chlorotrimethylenediamine (I), b. p. 109°/10 mm. (*dipicrate*, m. p. 153°), from the β-OH-derivative and $POCl_3$ in $CHCl_3$, is converted through its dimethiodide into NNN-*methyldiethyl*-N'N'N'-*methyldiethyl-β-chlorotrimethylenediammonium dipicrate*, m. p. 215° (decomp.). Successive treatment of the dimethobromide from (I) and MeBr in $MeNO_2$ with EtOH–KOH, dil. HCl, and Na picrate, affords NNN-*methyldiethyl*-N'N'N'-*methyldiethyl-αγ-propenylene-diammonium dipicrate* (II), m. p. 234° (decomp.), reduced catalytically (Pt-black) to NNN-*methyldiethyl*-N'N'N'-*methyldiethyltrimethylenediammoniumdipicrate*, m. p. 282° (decomp.) [in this and similar experiments the original picrate is usually converted into the chloride, reduction (or oxidation etc.) carried out, and the new salt converted into the new picrate]. The last-named picrate is also prepared by way of the dimethiodide of tetraethyltrimethylenediamine, b. p. 81·9°/9 mm. (from trimethylene dibromide and $NHEt_2$ in $MeNO_2$). Oxidation of (II) with aq. 1% $KMnO_4$ gives $NMeEt_2$ (*picrate*, m. p. 185°) and the betaine $\overset{\oplus}{N}MeEt_2\cdot\overset{\ominus}{C}H_2\cdot CO_2$ [picrate, m. p. 146° (lit. 153—154°)]. Methyldiethyl-β-chloro-γ-diethylamino-*n*-propylammonium bromide (corresponding *dipicrate*, m. p. 133°), from (I) and MeBr in $MeNO_2$, eliminates HCl with hot EtOH–KOH forming, after treatment with Na picrate, *methyldiethyl-γ-diethylamino-Δ^α-propenyl-α-ammonium dipicrate*, m. p. 198°. This is converted by Et_2SO_4 into $N^{\alpha}N^{\alpha}N^{\alpha}$-*methyldiethyl*-$N^{\gamma}N^{\gamma}N^{\gamma}$-*triethyl-Δ^α-propenylene-αγ-diammonium dipicrate* (III), m. p. 229—230° (decomp.), reduced catalytically to NNN-*methyldiethyl*-N'N'N'-*triethyltrimethylenediammonium dipicrate*, m. p. 263—264° (decomp.), and oxidised to the betaine $NEt_3\cdot CH_2\cdot CO_2$ (*picrate*, m. p. 193—194°). *Triethyl-β-chloro-γ-diethylamino-n-propylammonium iodide*, m. p. 213—214° (decomp.) (corresponding *picrate*, m. p. 184°), from (I) and EtI, is converted into *triethyl-γ-diethylamino-Δ^α-propenyl-α-ammonium dipicrate*, m. p. 167—168°, which with MeI gives $N^{\alpha}N^{\alpha}N^{\alpha}$-*triethyl*-$N^{\gamma}N^{\gamma}N^{\gamma}$-*methyldiethyl-Δ^α-propenylene-αγ-diammonium dipicrate* (IV), m. p. 230° (decomp.) (oxidation product $NMeEt_2\cdot CH_2\cdot CO_2$). (III) and (IV) are interconvertible in presence of alkalis.

α-Chloro-γ-iodo*iso*propyl alcohol and NMe_3 in EtOH at 75—80° give *trimethyl-γ-chloro-β-hydroxy-n-propylammonium iodide*, m. p. 140—150°, converted by successive treatment with NEt_3 and Na picrate into NNN-*trimethyl*-N'N'N'-*triethyl-β-hydroxytrimethylenediammonium dipicrate*, m. p. 230°. Tetraethyl-β-hydroxytrimethylenediamine (*dipicrate*, m. p. 163°), from epichlorohydrin and $NHEt_2$, when treated successively with MeI and Na picrate affords NNN-*methyldiethyl*-N'N'N'-*methyldiethyl-β-hydroxytrimethylenediammonium dipicrate*, m. p. 259—260° (decomp.). *Methyldiethyl-γ-diethylamino-β-hydroxy-n-propylammonium picrate* has m. p. 205° (decomp.).

αγ-Dichloro-β-methoxypropane and $NHEt_2$ at 100° afford *tetraethyl-β-methoxytrimethylenediamine*, b. p. 98—101°/9 mm. [*dipicrate*, m. p. 110°; *chloroplatinate*, m. p. 215° (decomp.)], also formed from (I) and boiling MeOH–KOH. The following salts are prepared, usually by addition of 1 or 2 mols. of alkyl halide to this ditert. base and subsequent treatment with the requisite reagent: NNN-*methyldiethyl*-N'N'N'-*methyldiethyl-β-methoxytrimethylenediammonium dipicrate*, m. p. 164—167° [corresponding *chloroplatinate*, m. p. 237—238° (decomp.)]; *triethyl-γ-diethylamino-β-methoxy-n-propylammonium picrate*, m. p. 220° [corresponding *chloroplatinate*, m. p. 224—225° (decomp.)]; *methyldiethyl-, benzyldiethyl-, and* p-*bromobenzyldiethyl-γ-diethylamino-β-methoxy-n-propylammonium chloroplatinates*, m. p. 217—218° (decomp.), 201° (decomp.), and 210° (decomp.), respectively; NNN-*triethyl*-N'N'N'-*triethyl*-, NNN-*benzyldiethyl*-N'N'N'-*benzyldiethyl*- and NNN-p-*bromobenzyldiethyl*-N'N'N'-*benzyldiethyl-β-methoxytrimethylenediammonium chloroplatinates*, m. p. 263° (decomp.), 195° (decomp.), and 156—160° (decomp.), respectively. 2 : 4 : 6-*Trinitrophenyl* p-*bromobenzyl ether*, from *p*-bromobenzyl bromide and Ag picrate, has m. p. 125°. H. BURTON.

Oxidation of *N*-methylhydroxylamine by iodine. O. L. BRADY and M. D. PETERS (J.C.S., 1931, 1604—1605; cf. A., 1926, 1142).—CH_2O was isolated from the products of oxidation of *N*-methylhydroxylamine by I. The reactions are formulated: $NHMe\cdot OH + I_2 \longrightarrow 2HI + CH_2\colon N\cdot OH \longrightarrow CH_2O + NH_2OH$. R. S. CAHN.

Preparation of glycine. J. M. ORTEN and R. M. HILL (J. Amer. Chem. Soc., 1931, 53, 2797—2799).—$CH_2Cl\cdot CO_2H$ is treated with a large excess of aq. NH_3 during 48 hr. at room temp., the excess of NH_3 evaporated in a vac., and the glycine precipitated with MeOH. The yield of pure glycine is 60—64%. H. BURTON.

Reactions of alanine. J. A. SANCHEZ (Semena méd., 1931, i, 651—653).—(*a*) Alanine (0·01 g.) is heated at 100° for 1 min. with $KMnO_4$ solution (1%); after cooling, oxalic acid (0·05 g.) is added, followed by EtOH (2 c.c.), *o*-nitrobenzaldehyde (0·02—0·03 g.), and NaOH (30% solution, 10 drops); indigotin is extracted by shaking with $CHCl_3$. (*b*) CHI_3 is formed when alanine is heated with NaOCl, and NaOH and I in KI are added. (*c*) The products of dry distillation of alanine contain NH_2Et, which is detected with Bouchardat's, Dragendorff's, or Sanchez' reagents. CHEMICAL ABSTRACTS.

Aminolysis of alanine. S. MOLINARI.—See this vol., 1015.

α-Cyano-β-methylbutyric acid. F. C. B. MARSHALL (J. Amer. Chem. Soc., 1931, **53**, 2415—2416).—The isolation of α-cyano-β-methylbutyric acid (cf. A., 1913, i, 1038) in a cryst. form, m. p. 31°, is described.

H. A. PIGGOTT.

Rotatory power of ricinoleamide. E. ANDRÉ and C. VERNIER (Compt. rend., 1931, **193**, 178—180).—Repeated treatment of castor oil with NH_3 in EtOH gives fractions of ricinoleamide of gradually increasing dextrorotatory power.

A. A. LEVI.

Hypoglycæmia-producing substances. II. ψ-Thiocarbamide, amidine, and carbamide derivatives. S. KAWAI, T. HOSONO, Y. SHIKINAMI, and S. YONECHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, **16**, 9—16).—Pentamethylene dichloride and thiocarbamide in boiling BuOH yield *pentamethylene -αε-di-ψ-thiocarbamide dihydrochloride* $[CH_2]_5[SC(NH)\cdot NH_2]_2,2HCl$, m. p. 206° ($+H_2O$), 210° (anhyd.), as well as a by-product, m. p. 144°. Decane-ακ-diol (improved prep.) is converted by $SOCl_2$ into *decamethylene dichloride* (I), b. p. 147—148°/11 mm., which does not react with thiocarbamide in boiling BuOH, but in a sealed tube at 175—190° gives NH_4Cl, a colourless solid, m. p. 53—53·5°, containing N but not S or Cl, and a liquid, b. p. 174—179°/14 mm. (I) with NaI in $COMe_2$ gives the crude di-iodide, which with thiocarbamide in boiling *iso*amyl alcohol, followed by treatment with AgCl, leads to *decamethylene-ακ-di-ψ-thiocarbamide dihydrochloride*, m. p. 186° (*picrate*, m. p. 112—112·5°). *Hexane-*, m. p. 230—231° (decomp.), and *octane-*, m. p. 185—186°, *-ωω'-di-ψ-thiocarbamide dihydrochlorides* are similarly prepared. *Hexane-*, decomp. 302—303°, *heptane-*, m. p. 214—215°, *octane-*, decomp. 191—192°, *nonane-*, decomp. 160—161°, and *decane-*, m. p. 175—175·5°, *-ωω'-di-amidine dihydrochlorides* are prepared from the corresponding polymethylene dicyanides through the crude di-imino-ether dihydrochlorides, decomp. 126—127°, 115—116°, 106—107°, 72—75°, and 112°, respectively. The polymethylenedi-ψ-thiocarbamide dihydrochlorides and polymethylenedi-amidine hydrochlorides have $\frac{1}{..}$—$\frac{1}{10}$ the hypoglycæmic action of the corresponding diguanidine dihydrochlorides, but have the same toxicity; the corresponding dicarbamides are, however, less toxic, but not being H_2O-sol., they cannot be administered.

J. D. A. JOHNSON.

Oxycyanogen. I. H. HUNT (J. Amer. Chem. Soc., 1931, **53**, 2111—2115; cf. A., 1925, ii, 568).—CNO cannot be obtained by the methods described by Lidov (A., 1913, i, 252, etc.), and the reactions and equations recorded have not been confirmed.

J. G. A. GRIFFITHS.

Organic gold compounds. II. Preparation and properties of gold–carbon compounds of the type R_2AuX and $RAuX_2$. M. S. KHARASCH and H. S. ISBELL (J. Amer. Chem. Soc., 1931, **53**, 2701—2713).—Compounds of the type AuR_2X cannot be prepared by the Grignard method when R is a strongly electronegative radical, *e.g.*, Ph. The following gold dialkyl halides are prepared and converted into the cyanides by AgCN in Et_2O or C_6H_6 (the decomp. temps. of the compounds are given in parentheses): *Au diethyl chloride*, m. p. 48° (48°), bromide, m. p. 58° (58°), and *cyanide*, m. p. 92° (92—160°); *Au di-n-propyl chloride*, an oil (107—120°), *bromide*, an oil (95°), and *cyanide*, m. p. 84° (128—147°); *Au diisopropyl chloride* (95—120°), *bromide* (100—130°), and *cyanide*, m. p. 88—90° (121—123°); *Au di-n-butyl bromide*, an oil (65°), and *cyanide* (125—130°); *Au diisobutyl bromide* and *cyanide*, m. p. 112—113° (160°); *Au diisoamyl bromide* and *cyanide*, m. p. 70° (135—140°); *Au dicyclohexyl chloride* (180—190°), *bromide* (140—148°), and *cyanide*, m. p. 152° (slight decomp.) (155°); *Au dibenzyl chloride* (70—110°), *bromide* (77°), and *cyanide* (122°); *Au di-β-phenylethyl bromide*, m. p. 112—115° (105—115°), and *sulphate* (105—108°) (from the bromide and Ag_2SO_4). *Au dicyclohexyl thiosalicylate*, decomp. 173—180°, is prepared from the corresponding chloride and thiosalicylic acid in C_6H_6 and alcoholic KOH. The above β-phenylethyl derivatives are disulphonated (*Ca* salts isolated) by oleum in $CHCl_3$. The cyanides are more stable than the halides, and all the above compounds are more stable towards reducing agents than Au^{III} salts. *Au β-phenylethyl*, decomp. 150—160°; *benzyl*, decomp. about 140°, and cyclo*hexyl*, decomp. 150°, *dibromides*, prepared from the appropriate AuR_2Br and Br_2 in $CHCl_3$, are very unstable towards reducing agents. Solutions of these dibromides in $CHCl_3$ are intensely coloured; the colour is discharged by unsaturated substances indicating addition to the double linking. Compounds of the type AuR_3 could not be prepared.

H. BURTON.

Magnesium *cyclo*hexyl chloride and bromide. H. GILMAN and E. A. ZOELLNER (J. Amer. Chem. Soc., 1931, 1945—1948).—Details are given for the prep. of Mg *cyclo*hexyl chloride and bromide in yields of 96·5 and 92%, respectively. Chlorides are preferred to other halides in the prep. of Grignard reagents.

H. BURTON.

Transformation of benzene into methane. A. MAILHE and CREUSOT (Compt. rend., 1931, **193**, 60—63).—A quant. study of the formation of CH_4 on passing C_6H_6 and H_2 over heated Ni showed that the yield (1) depended on the mode of prep. of the catalyst, (2) was highest when the C_6H_6 was free from thiophen, and (3) commenced below 250°, reached a max. at 280°, then falling until 310°, and subsequently rising (sometimes to a max.). The activity of the catalyst decreases with time at 280°, owing to deposition of a yellow substance, sol. in $COMe_2$, but is restored by raising the temp. to 320—330°, the yellow substance then disappearing. The max. yield obtained was 82·3%.

R. S. CAHN.

Conversion of toluene and [*m*-]xylene into methane. A. MAILHE and CREUSOT (Compt. rend., 1931, **193**, 176—178).—Hydrogenation of PhMe and *m*-xylene gives a max. yield of CH_4 at two different temps., between which a waxy substance is also formed.

A. A. LEVI.

Photochemical oxidation of organic hydrocarbons. II. Toluene, and the oxidation of benzaldehyde. C. J. KOTHARI and H. E. WATSON. —See this vol., 1019.

Addition of free radicals to unsaturated compounds. J. B. CONANT and H. W. SCHERP (J. Amer.

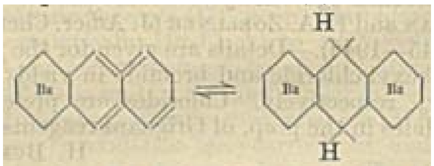
Chem. Soc., 1931, **53**, 1941—1944).—Prolonged interaction of hexaphenylethane and isoprene in N_2 gives 45% of *ααα ζζζ-hexaphenyl-γ-methyl-Δ^γ-hexene*, m. p. 166°, oxidised by O_3 to βββ-triphenylpropionic acid and *βββ-triphenylethyl methyl ketone* (I), m. p. 140·5°; (I) is synthesised from βββ-triphenylpropionyl chloride and ZnMeCl. 1 : 4-Addition of CPh_3 occurs. βγ-Dimethylbutadiene and CPh_3 afford a *hydrocarbon*, $C_{44}H_{40}$, m. p. 240° (decomp.), oxidised by O_3 to (I).

H. Burton.

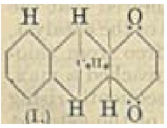
1-Ethylnaphthalene and its hydrogenation products. G. Levy (Compt. rend., 1931, **193**, 174—176; cf. this vol., 949).—Catalytic reduction of 1-acetylnaphthalene (A., 1897, i, 75) at 200° gives 1-ethylnaphthalene, m. p. 15°, b. p. 256·5°/756 mm. (purified through the picrate, m. p. 98·5°), and a little 1-ethyltetrahydronaphthalene. Reduction of 1-ethylnaphthalene with Na in amyl alcohol gives the *dihydro*-derivative, b. p. 246°/758 mm. With H_2 and Ni at 200° it gives the *tetrahydro*-derivative, b. p. 115°/17 mm., 237·5°/764 mm., whilst at 160° *1-ethyldecahydronaphthalene*, b. p. 222°/760 mm., is obtained. Hydrogenation is more difficult than for the 2-isomeride, whilst the exaltation of the mol. refractivity is less for the 1- than for the 2-series.

A. A. Levi.

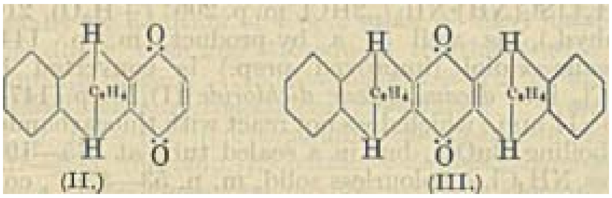
Polynuclear, aromatic hydrocarbons and their derivatives. IX. Constitution of anthracene. E. Clar (Ber., 1931, **64**, [*B*], 1676—1688).—Further evidence is adduced in favour of the view that anthracene is an equilibrium mixture,



Anthracene is converted by *p*-benzoquinone in boiling $C_6H_4Me_2$ into *p*-benzoquinoneanthracene (I), decomp.



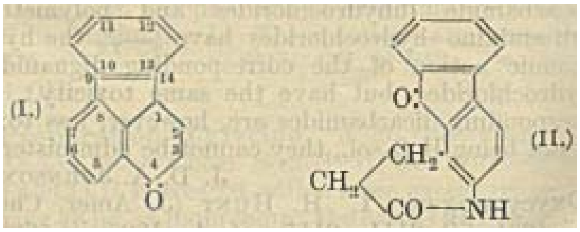
250° after darkening at 207°. It shows no tendency towards dissociation, does not react with picric acid, gives a normal mol. wt. in camphor, and is converted by excess of CrO_3 into anthraquinone. Its absorption spectrum is intermediate between those of anthracene and dihydroanthracene. Continuous oxidation with CrO_3 converts it into endo-9 : 10-o-*phenylene*-9 : 10-*dihydro*-1 : 4-*anthraquinone* (II), m. p. 289—294° (decomp.) according to the rate of heating, which yields an almost black *quinhydrone* with quinol. It is converted by phenylhydrazine or $Na_2S_2O_4$ into 1 : 4-*dihydroxy*-endo-9 : 10-o-*phenylene*-9 : 10-*dihydroanthracene*, m. p. 345° (decomp.) after darkening at 340° (*diacetate*, m. p. 253—254°), transformed by distillation with Zn into anthracene and quinol. It can also be obtained by the action of a trace of HBr on *p*-benzoquinoneanthracene. 2 : 3-*Dichloro*-9 : 10-o-*phenylene*-9 : 10-*dihydroanthraquinone*, m. p. 270° (partial decomp.), is prepared by chlorinating *p*-benzoquinoneanthracene or *endo*-9 : 10-*o*-phenylene-9 : 10-dihydro-1 : 4-anthraquinone in boiling AcOH or from anthracene and chloroanil in boiling AcOH or $C_6H_4Me_2$ or without solvent. With NH_2Ph in AcOH it affords 2-*chloro*-3-*anilino*-endo-9 : 10-o-*phenylene*-9 : 10-*dihydro*-1 : 4-*anthraquinone*, m. p. 235—239° (decomp.) according to the rate of heating. 2 : 3-*Dibromo*-endo-9 : 10-o-*phenylene*-9 : 10-*dihydro*-1 : 4-*anthraquinone*, m. p. 320—325° (decomp.), is described. 9 : 10-Diphenylanthracene and *p*-benzoquinone in boiling $C_6H_4Me_2$ yield the corresponding *quinhydrone*, m. p. 195° after softening at 155°, which readily decomposes into its components. endo-9 : 10-o-*Phenylene*-9 : 10-*dihydro*-1 : 4-*anthraquinoneanthracene*, becoming brown at 265° and blackening without melting at 370°, prepared from its components in boiling $C_6H_4Me_2$, is converted by Br in boiling AcOH into endo-1 : 4 : 5 : 8-*di*-o-*phenylene*-2 : 3 : 6 : 7-*dibenzanthraquinone* (III), not molten below 370°, reduced by phenylhydrazine to endo-1 : 4 : 5 : 8-*di*-o-*phenylene*-2 : 3 : 6 : 7-*dibenzanthraquinol*, darkening without melting at 360—370°.



The products obtained previously from 2 : 3 : 6 : 7-dibenzanthracene-9 : 10-diyl and *p*-benzoquinone or chloroanil are not quinol ethers, but 2 : 3 : 6 : 7-dibenzanthracene-benzoquinone or -chloranil, respectively.

H. Wren.

Fluoranthene and its derivatives. III. J. von Braun and G. Manz (Annalen, 1931, **488**, 111—126).—Under certain conditions mono-substitution in fluoranthene can be effected, the entering group being considered to occupy position 4 for the following reasons. Since the Br atom of bromofluoranthene is readily replaced by H, it is apparently attached to the $C_{10}H_8$ nucleus. 4-Keto-1 : 2 : 3 : 4-tetrahydrofluoranthene (I) is reduced in feebly acid solution to 4-*hydroxy*-



1 : 2 : 3 : 4-*tetrahydrofluoranthene*, m. p. 130—134°, apparently stereoisomeric with the *product* m. p. 136—139°, of the hydrogenation of 4-hydroxyfluoranthene and yielding the same *phenylcarbamide*, m. p. 274—275°. 4-Aminofluoranthene is reduced to 4-*amino*-5 : 6 : 7 : 8-*tetrahydrofluoranthene*, m. p. 114—116°, the *Ac* derivative, m. p. 224—225°, of which is oxidised to a ketocarboxylic acid; the deacetylated acid passes by spontaneous loss of H_2O into the *lactam* (II), m. p. 346—348°.

4-*Bromofluoranthene*, b. p. 205—207°/0·2 mm., m. p. 103°, prepared by adding 1 mol. of Br in CS_2 to a boiling solution of fluoranthene in CS_2 containing a little PBr_3 and irradiated with a quartz lamp, is separated from dibromo-compounds by means of its

picrate, m. p. 129—130°. It is very resistant towards alkali hydroxide, does not react with Mg, and is reduced by Na–Hg to 1 : 2 : 3 : 4-tetrahydrofluoranthene, m. p. 73—74°. It does not react with K phthalimide, but with CuCN at 260° yields 4-*cyanofluoranthene*, m. p. 112°. Treatment of fluoranthene in $CHCl_3$ with $ClSO_3H$ yields a mixture of isomeric monosulphonic acids which by successive treatment with NaCl, $POCl_3$, and NH_2Et in C_6H_6 affords *fluoranthene-4-sulphonethylamide*, m. p. 167—168°, transformed by KCN and NaCN into 4-cyanofluoranthene. The nitrile is hydrolysed by conc. HCl at 130° to *fluoranthene-4-carboxylic acid*, decomp. 264—275° [*Et* ester, b. p. 250—253°/0·5 mm., m. p. 73—75°; corresponding *amide* (from the acid by means of $SOCl_2$ and NH_3), m. p. 271—273°]. 4-*Hydroxyfluoranthene*, m. p. 185—187°, obtained from the sulphonethylamide and KOH at 290—340°, is converted by NH_3 in EtOH at 300° into 4-*aminofluoranthene*, m. p. 111—112° (*hydrochloride*, m. p. 285—288°; *Ac* compound, 241—242°), which cannot be prepared from the sulphomethylamide and $NaNH_2$. Treatment of fluoranthene with HNO_3 (*d* 1·42) in glacial AcOH affords 4-*nitrofluoranthene*, m. p. 159—160°, reduced by $SnCl_2$ and HCl to 4-aminofluoranthene, from which 4-hydroxyfluoranthene is prepared by the action of *N*-HCl at 230°. H. WREN.

Molecular compounds of the perylene series. K. BRASS and E. TENGLER (Ber., 1931, **64**, [*B*], 1650—1653).—Perylene and picric acid in C_6H_6 yield the *compounds* $C_{20}H_{12},C_6H_3O_7N_3$, m. p. 221°, and $C_{20}H_{12},2C_6H_3O_7N_3$, m. p. 154—155°. The following *substances* are described: ($R=C_{20}H_{12}$); $2R,SbCl_5$, $R,2SnCl_4$, $R,FeCl_3$; (R'=perylenequinone) $R',SbCl_5$; $R',SnCl_4$; $2R',FeCl_3$; $2R',AlCl_3$. Dibromo-3 : 10-perylenequinone and bromodi-3 : 10-perylenequinonyl sulphide yield the *compounds* $C_{20}H_8O_2Br_2,SbCl_5$ and $C_{40}H_{17}O_4BrS,2SbCl_5$. H. WREN.

Reduction of benzylideneaniline, benzophenoneanil, and benzilanil by the system $Mg+MgI_2$. W. E. BACHMANN (J. Amer. Chem. Soc., 1931, **53**, 2672—2676).—Benzylideneaniline, Mg, and MgI_2 in $Et_2O–C_6H_6$ give the compound $(\cdot CHPh\cdot NPh\cdot MgI)_2$, hydrolysed by dil. AcOH to dianilinodibenzyl. Similarly, benzophenoneanil gives $IMg\cdot CPh_2\cdot NPh\cdot MgI$ (hydrolysed to benzhydrylaniline), whilst fluorenoneanil yields 9-fluorenylaniline. Benzilanil is converted into (probably) $IMgO\cdot CPh{:}CPh\cdot NPh\cdot MgI$ (I), hydrolysed to desylaniline and converted by I or O_2 into benzilanil. Hydrolysis of the product from (I) and CO_2 gives desylaniline and CO_2. H. BURTON.

α-Phenylethylguanidine and α-phenylethyldiguanide. F. BOBECK (Annalen, 1931, **487**, 294—300).—dl-α-*Phenylethylguanidine* (I), but not dl-α-*phenylethyldiguanide* (II), is resolvable by mandelic acid, and thus constitutes a readily accessible, optically active base, nearly as strong as KOH. *dl*-Phenylethylammonium chloride (III) and cyanamide at 120° gave (I), hygroscopic, cryst. No racemisation occurs with active material if the reaction is carried out at 100°, and the *l*-base has $[\alpha]_D$ −29·3°. The following salts are described: *chloride*, l-, m. p. 177—178°; *sulphate*, dl-, m. p. 242°; *nitrate*, dl-, m. p. 123—124°; *carbonate*, dl-, m. p. 184° (sealed tube); *hydrogen carbonate*, dl-, m. p. 182° (sealed tube); *oxalate*, dl-, m. p. 240°, d- and l-, m. p. 250°; *acetate*, l-, m. p. 160—170°; *picrate*, dl-, m. p. 175·5°, d- and l-, m. p. 150°; *chromioxalate*, $Cr(C_2O_4)_3,(C_9H_{13}N_3)_3,10H_2O$ (no loss of wt. at 105°). Mandelic acid is resolved by the active bases. The $CuSO_4$ *compound* ($+H_2O$) of (II) is obtained (*a*) from α-phenylethylamine, dicyanodiamide, and cryst. $CuSO_4$ kept at room temp. for several months, and (*b*) from (III) and dicyanodiamide at 120—140°, followed by ammoniacal $CuSO_4$. The following derivatives of (II) are also described: $NiSO_4$ *compound* ($+3H_2O$); *hydrogen sulphate*, m. p. 220°. The nitrate of (I) has μ 101·5, whence U_k=30·5. R. S. CAHN.

Quaternary ammonium salts from tertiary amines and benzenesulphonyl chloride. F. SCHLEGEL (Ber., 1931, **64**, [*B*], 1739—1743).—Benzenesulphonyltrialkylammonium salts are formed from the sulphonyl chloride and strong tert. bases in presence of H_2O, but reaction does not take place with weak bases, *e.g.*, pyridine and $NPhMe_2$. The following are described: *benzenesulphonyldimethylethylammonium chloroplatinate*, incipient decomp. 211°, *chloride*, decomp. about 227°, *picrate*, m. p. 120—124°, *chloroaurate*, m. p. 167° after softening at 145°, *perchlorate*, m. p. 123—126° (decomp.); *dimethylethylammonium picrate*, m. p. 195°, and *chloroaurate*, m. p. 206° (decomp.); *benzenesulphonylbenzyldimethylammonium chloroaurate*, m. p. 136—138° (decomp.); *benzyldimethylammonium chloroaurate*, m. p. 142—143°, and *chloroplatinate*, m. p. 192°; *benzyltrimethylammonium benzenesulphonate*, m. p. 137°, or ($+H_2O$), m. p. about 75°, from benzyldimethylamine and Me benzenesulphonate in anhyd. Et_2O, converted into the corresponding *chloroaurate*, m. p. 137—140° (decomp.), *chloroplatinate*, m. p. 233—236° (decomp.), and *perchlorate*, m. p. 126—127°; *benzylammonium benzenesulphonate*, m. p. 190°. H. WREN.

2 : 7-Diaminofluorene as reagent for zinc, cadmium, and copper. J. SCHMIDT and W. HINDERER (Ber., 1931, **64**, [*B*], 1793—1796).—Fluorene is converted by HNO_3 (*d* 1·52) and glacial AcOH into 2 : 7-dinitrofluorene, m. p. 269° (decomp.), reduced by Sn and fuming HCl to 2 : 7-*diaminofluorene hydrochloride* (corresponding *chlorostannate*; 2 : 7-diaminofluorene, m. p. 165°). In about 1% solution in EtOH the base gives an immediate ppt. of the *sulphate* with H_2SO_4 or a sol. sulphate. The chlorides or nitrates must therefore be used in investigating its behaviour towards salts. With $MgCl_2$, $MnCl_2$, $CoCl_2$, $Co(NO_3)_2$, $Ni(NO_3)_2$, $CrCl_3$, $Cd(OAc)_2$, or $Zn(OAc)_2$ ppts. or colorations are not observed. Even in very dil. solutions $ZnCl_2$ and $CdCl_2$ or solutions of Zn or Cd salts in presence of NaCl yield white ppts. of $C_{13}H_{12}N_2,ZnCl_2$ and $C_{13}H_{12}N_2,CdCl_2$, respectively. $CuCl_2$ yields a dark blue *ppt.* $C_{13}H_{12}N_2,CuCl_2$, appearing in very dil. solution as a blue to green colour; the reaction is more sensitive than that with NH_3. As the base is readily precipitated from EtOH by H_2O the aq. solution of the salt should be diluted with twice its vol. of EtOH. H. WREN.

Reduction of aromatic nitro- and nitroso-compounds with sodium alkoxides. II. F. B. DAINS and W. O. KENYON (J. Amer. Chem. Soc., 1931, **53**, 2357—2364).—The reducing action of a series of alkoxides and Na derivatives of ketones and ketonic esters on NO_2-compounds, PhNO, and *p*-nitroso-toluene and -dimethylaniline is described. The reaction is, in the cases tried, catalysed by org. bases. In general, amines and azoxy-compounds are produced, but the polyhydric alcohols tend to give azo-derivatives. *p*-Nitrotoluene and its derivatives form considerable amounts of stilbenes, *m*-nitrobenzaldehyde gives *m*-nitrobenzoic acid almost quantitatively, and 3 : 4-dichloronitrobenzene gives 3 : 4 : 3′ : 4′-*tetrachloroazoxybenzene*, m. p. 137—138°, with no evidence of the formation of 3-chloro-4-nitrophenyl ethers (cf. A., 1929, 54). Glycol and glycerol as reducing agents react more slowly than the monohydric alcohols, and are oxidised to oxalic and volatile org. acids; deoxybenzoin is converted into benzilic acid. Et sodioacetoacetate, in contrast to benzoylacetic and malonic esters, reduces *p*-chloronitrobenzene to NH_2Ph.

The formation of amino-acids appears to be confined to *o*-halogenonitrobenzenes (cf. A., 1928, 1366), and propyl or higher alcohols. The interaction of 2 : 5-dibromonitrobenzene with $NaOPr^a$ gives α-2 : 5-*dibromoanilinopropionic acid*, m. p. 156°, also obtained from 2 : 5-dibromoaniline and α-bromopropionic acid; α-4-*chloro*-m-*toluidinopropionic acid*, m. p. 158°, is similarly prepared. Addition of aq. Br_2 to 2 : 5-dibromoaniline in dil. H_2SO_4 gives 1 : 2 : 3 : 5-*tetrabromoaniline*, m. p. 118°. H. A. PIGGOTT.

Constitution of a bromonitroazoxybenzene. D. BIGIAVI [with C. ALBANESE and I. POGGI] (Gazzetta, 1931, **61**, 392—396).—Bromo-α-*p*-nitroazoxybenzene (I), m. p. 135—137° (A., 1913, i, 1110), by reduction gives NH_2Ph and bromo-*p*-phenylenediamine (*hydrochloride*, blackens without melting at 250°; Bz_2 derivative, m. p. 235°), showing the Br atom to be in the same nucleus as the NO_2 group. *o*-Bromo-*p*-nitroaniline is oxidised by H_2SO_5 to o-*bromo*-p-*nitronitrosobenzene*, m. p. 123°, which, by condensation with NH_2Ph and oxidation with peracetic acid, gives (I), for which the formula $Ph{\cdot}NO{:}N{\cdot}C_6H_3Br{\cdot}NO_2$ is suggested. E. E. J. MARLER.

Diphenyl derivatives. J. FELDMANN (Helv. Chim. Acta, 1931, **14**, 751—778).—Diphenyl-4 : 4′-disulphonic acid (*dichloride*, m. p. 203°) is converted by nitration into the 2 : 2′-dinitro-derivative [*Na* ($+2H_2O$) and *K* salts; *dichloride*, decomp. 151°; *dianilide*, m. p. 104—104·5° (sinters 72—72·5°)], which is reduced by Fe and AcOH to 2 : 2′-*diaminodiphenyl*-4 : 4′-*disulphonic acid* (H_2O) [*anilide dihydrochloride* is obtained by reduction of the nitroanilide with $Fe(OH)_2$], the constitution of which is proved by its conversion into carbazole by 20% HCl at 230°. 2 : 2′-*Di*-p-*nitrobenzamidodiphenyl*-4 : 4′-*disulphonic acid* is reduced by Fe and HCl to the *di*-p-*aminobenzamido*-derivative. The 2 : 2′-*dihydrazine* (*dihydrochloride*) may be prepared by reducing the diazotised diamino-acid with $SnCl_2$ (but not with Na_2SO_3); it combines with Et acetoacetate to form a *bispyrazolone* (+2AcOH). The following new *dyes* are described (shades are on wool): from tetrazotised 2 : 2′-diaminodiphenyl-4 : 4′-disulphonanilide and 2 mols. of: α-naphthol-4-sulphonic acid (brick-red); α-naphthol-3 : 8-disulphonic acid (brownish-red); 8-acetamido-α-naphthol-3 : 6-disulphonic acid (bordeaux); β-naphthol-6 : 8-disulphonic acid (brown to red; acid-coupled); from tetrazotised 2 : 2′-diaminodiphenyl-4 : 4′-disulphonic acid: β-naphthol (orange); 1-phenyl-3-methyl-5-pyrazolone (yellow); 8-acetamido-α-naphthol-3 : 6-disulphonic acid (reddish-violet); salicylic acid (orange-brown); and from tetrazotised 2 : 2′-di-*p*-aminobenzamidodiphenyl-4 : 4′-disulphonic acid and: β-naphthol (orange-brown); phenylmethylpyrazolone (yellow); 1 : 8-aminonaphthol-3 : 6-disulphonic acid (brownish-violet); α-naphthol-3 : 8-disulphonic acid (reddish-orange); 6-phenylamino-α-naphthol-3-sulphonic acid (yellowish-red); salicylic acid (orange); bispyrazolone (above) (yellow). The dye from 2 mols. of diazobenzene and the bispyrazolone is yellow. The majority of these dyes are characterised by poor affinity. H. A. PIGGOTT.

2 : 4 : 6-Trichlorophenylhydrazine. F. D. CHATTAWAY and H. IRVING (J.C.S., 1931, 1740—1743).—2 : 4 : 6-*Trichlorophenylhydrazine*, m. p 143—144° (decomp.) (β-*Ac*, m. p. 157°, β-*Bz*, m. p. 163·5°, and β-*Bz*-α-*Ac*, m. p. 156°, derivatives; *hydrochloride*, m. p. above 350°), is prepared by reduction of 2 : 4 : 6-trichlorobenzenediazonium chloride with $SnCl_2$–HCl. *Citraconyl*-2 : 4 : 6-*trichlorophenylhydrazide*, m. p. 166—167° (decomp.), and *cinnamaldehyde*-, m. p. 104—105°; *benzaldehyde*-, m. p. 91—92°; *salicylaldehyde*-, m. p. 98·5—99·5°; 2 : 4-*dinitrobenzaldehyde*-, m. p. 109—110°; 2 : 4 : 6-*trinitrobenzaldehyde*-, m. p. 145—146°; *acetone*-, m. p. 58—59°; *benzophenone*-, m. p. 106—107°; *mesoxalic acid*-, m. p. 183° (decomp.), and *pyruvic acid*-2 : 4 : 6-*trichlorophenylhydrazone*, m. p. 126—127°, are described. H. A. PIGGOTT.

Isomerism of hydrazones. II. Molecular compounds of stereoisomeric hydrazones. M. BUSCH, L. WESELY, and O. KÜSPERT (Ber., 1931, **64**, [*B*], 1589—1596; cf. A., 1925, i, 40).—The possibility that isomerism of hydrazones $NHR{\cdot}N{:}CPh{\cdot}CH_2{\cdot}NHR$ is due to the existence of a form $R{\cdot}N{:}N{\cdot}CHPh{\cdot}CH_2{\cdot}NHR$ is excluded by the production of isomerides with *as*-dialkylhydrazines. Since the compounds do not react with aldehydes, the possible existence of desmotropes, $NHR{\cdot}NH{\cdot}CPh{:}CH{\cdot}NHR$, is negatived. The hydrazones form mol. compounds of the two isomerides, the relationships resembling somewhat those observed with optically active and racemic compounds. Phenacyl-*p*-toluidine and *as*-phenylbenzylhydrazine in $CHCl_3$–EtOH in presence of AcOH give bimol. *phenacyl*-p-*toluidinephenylbenzylhydrazone*, m. p. 141°. Cautious crystallisation of the substance from $CHCl_3$–EtOH leads to its separation into the unimol. n-*form* (? *anti*-form), m. p. 118°, and *h*-form (? *syn*-variety), m. p. 127°. Boiling AcOH causes partial isomerisation of the *n*- to the *h*-form. Addition of ligroin to a solution of equal amounts of the *n*- and *h*-varieties in C_6H_6 results in separation of the bimol. form. In EtOH the isomerides do not react with PhCHO or CH_2O in presence of AcOH or HCl. n-*Phenacyl*-p-*toluidinephenylmethylhydrazone*, m. p. 155·5°, is the sole product isolated from *as*-phenylmethylhydrazine and phenacyl-*p*-toluidine in $CHCl_3$ containing AcOH,

whereas in EtOH containing AcOH at 60—65° the h-*hydrazone*, m. p. 160—161°, is also produced. Partial isomerisation of the *n*- to the *h*-compound occurs in boiling AcOH. The *dimeride*, m. p. 176°, is obtained from the simpler isomerides in C_6H_6–ligroin. According to conditions, the action of phenacyl-*p*-phenetidine and *as*-phenylbenzylhydrazine affords the separate n-*form*, m. p. 119°, and h-*variety*, m. p. 126°, of *phenacyl*-p-*phenetidinephenylbenzylhydrazone* or the *bimol.* substance, m. p. 134° (existing as its components in C_6H_6); the last-named substance is obtained from its components by the method described above. Partial isomerisation of the *n*-hydrazone occurs in boiling EtOH. The h-*form*, m. p. 121°, and n-*variety*, m. p. 93—94°, of *phenacyl*-N-*methylanilinephenylbenzylhydrazone* are described; the corresponding bimol. product could not be obtained. H. WREN.

Constitution of normal diazotates. A. ANGELI and Z. JOLLES (Gazzetta, 1931, **61**, 397—404; cf. A., 1930, 1428).—A reply to Hantzsch (this vol., 614) refuting that author's arguments in favour of the stereoisomerism of diazohydroxides.

E. E. J. MARLER.

Bromination of 1-diazo-β-naphthol-4-sulphonic acid. P. RUGGLI and M. MICHELS (Helv. Chim. Acta, 1931, **14**, 779—783).—The technical bromo-derivative of diazo-β-naphthol-4-sulphonic acid, prepared by bromination in $ClSO_3H$ or H_2SO_4, is converted by Cu_2O in EtOH into 6-*bromo*-β-*naphthol*-4-*sulphonic acid* (*Na* salt), identified by its conversion by Na–Hg in feebly acidic solution into 6-bromo-β-naphthol and β-naphthol, and by its oxidation with alkaline $KMnO_4$ to 4-bromophthalic acid; it is therefore the 6-bromo-derivative. H. A. PIGGOTT.

Cyclic esters of sulphuric acid. I. Methylene sulphate. W. BAKER (J.C.S., 1931, 1765—1771).—Methylene sulphate (convenient prep. described) reacts with pyrocatechol and protocatechualdehyde (but not the acid) with formation of methylene ethers. With monohydric phenols the ethers $CH_2(OAr)_2$ are formed, of which the following are new: *di*-o-, m. p. 129°, -m-, m. p. 112°, and -p-*nitrophenyl*, m. p. 147°, *dianisyl*, m. p. 54°, and *di*-p-*acetamidophenyl*, m. p. 191—192°, *methylene ethers*; *di*-p-*aminophenyl methylene ether*, m. p. 103°, is prepared by alkaline hydrolysis of the last-named. Resorcinol Me ether did not give a definite product. Glycols give cyclic ethers, *e.g.*, *pinacol methylene ether*, m. p. 12°, b. p. 125°/752 mm.; saligenin gives 1 : 3-benzdioxin and *di*-o-(*hydroxymethylphenoxy*)*methane*, m. p. 118°. H. A. PIGGOTT.

Catalytic reduction of mixtures of *p*-nitro- and -nitroso-phenols with ketones. R. T. MAJOR (J. Amer. Chem. Soc., 1931, **53**, 2803—2804; cf. this vol., 837).—Catalytic reduction of a mixture of *p*-nitrosophenol and $COMe_2$ at room temp. gives *p*-*iso*propylaminophenol, which is not formed under similar conditions from *p*-aminophenol and $COMe_2$. *p*-Hydroxyphenylhydroxylamine is probably an intermediate in the first case (cf. *loc. cit.*).

H. BURTON.

Chlorine derivatives of benzylphenols. I. Dichloro-derivatives of *o*- and *p*-benzylphenols. R. C. HUSTON and E. F. ELDRIDGE (J. Amer. Chem. Soc., 1931, **53**, 2260—2264).—Chlorination of 4-hydroxydiphenylmethane in $CHCl_3$ gives the 3 : 5-*dichloro*-derivative, m. p. 58—58·5° (*benzoate*, m. p. 98—99°; *benzenesulphonate*, m. p. 93—94°; p-*toluenesulphonate*, m. p. 120—121°), also obtained, together with 2 : 6-*dichlorophenyl benzyl ether*, m. p. 39·5—40°, b. p. 194—196°/15 mm., by the Friedel–Crafts reaction with $CH_2Ph{\cdot}OH$ and 2 : 6-dichlorophenol. Chlorination of 2-hydroxydiphenylmethane in $CHCl_3$ yields 3 : 5-*dichloro*-2-*hydroxydiphenylmethane*, m. p. 77—77·5° (*benzoate*, m. p. 66—67°; *benzenesulphonate*, m. p. 110—110·5°; p-*toluenesulphonate*, m. p. 124·5—125°), also obtained, admixed with 2 : 4-dichlorophenyl benzyl ether, by interaction of CH_2PhCl and Na 2 : 4-dichlorophenoxide in PhMe. It was not found possible to chlorinate further these dichlorobenzylphenols. 2 : 4- and 2 : 6-Dichlorophenyl benzyl ethers are also obtained by interaction of the Na phenoxide and CH_2PhCl in MeOH. H. A. PIGGOTT.

Action of aromatic alcohols on aromatic compounds in presence of aluminium chloride. VII. Condensation of benzyl alcohol with *p*-cresol. R. C. HUSTON and W. C. LEWIS (J. Amer. Chem. Soc., 1931, **53**, 2379—2382).—The interaction of $CH_2Ph{\cdot}OH$, *p*-cresol, and $AlCl_3$ in light petroleum below 30° gives 3-benzyl-*p*-cresol, m. p. 35—36° (previously described as a liquid) (*Bz*, m. p. 42—42·5°, b. p. 205—206°/5 mm., and 5-*bromo*-, m. p. 46—47°, derivatives; *benzenesulphonate*, b. p. 190—192°/2 mm., p-*toluenesulphonate*, m. p. 58—59°), and (presumably) 2 : 5-dibenzyl-*p*-cresol (*Bz* derivative, b. p. 243—245°/6 mm.). The same products are obtained from CH_2PhCl and Na *p*-tolyloxide in PhMe (cf. A., 1925, i, 656). The orientation of the bromo-derivative is proved by its prep., together with a little of its *benzyl ether*, m. p. 40—41°, from 6-bromo-*p*-cresol, Na, and CH_2PhCl in PhMe. H. A. PIGGOTT.

Bromination of *m*-cresol. G. DARZENS and A. LÉVY (Compt. rend., 1931, **193**, 292—294).—*m*-Cresol and Br in AcOH give 6-bromo-*m*-cresol, b. p. 135—137°/18 mm., m. p. 63° (Ac, b. p. 135—136°/17 mm., m. p. 10·5°, and Bz, m. p. 83°, derivatives; Me ether, b. p. 112°/14 mm., m. p. 9·5°, converted by the Grignard method into 5-methoxy-*o*-toluic acid). 5-Bromo-*m*-cresol could not be prepared by brominating either *m*-cresol or its acetate (cf. A., 1889, 389).

H. BURTON.

α-Naphtholsulphonic acids and derivatives. II. E. GEBAUER-FULNEGG and E. HAEMMERLE (J. Amer. Chem. Soc., 1931, **53**, 2648—2653).—α-Naphthol-2 : 4 : 7-trisulphonyl chloride (A., 1929, 1440) is obtained from $ClSO_3H$ and α-naphthol-2 : 4- or -4 : 7-disulphonic acid. Similarly, α-naphthol-4 : 6- and -6 : 8-disulphonic acids yield *α-naphthol*-4 : 6 : 8-*trisulphonyl chloride*, m. p. 217° (cf. *loc. cit.*), whilst the 3 : 8- and 4 : 8-disulphonic acids afford *naphthsultone*-3-, m. p. 190—191°, and -4-*sulphonyl chlorides*, m. p. 195°, respectively. The α-naphtholtrisulphonyl chlorides, m. p. 203° and 140° (*loc. cit.*), are probably the 2 : 3 : 6- and 3 (or 2) : 5 : 7-derivatives, respectively. O-*Carbethoxy*-*α*-*naphthol*-3 : 8-, m. p. 180—181°, -4 : 8-, m. p. 177—179°, -3 : 6-, m. p. 95°, and -4 : 7-, m. p. 120°, -*disulphonyl chlorides* are prepared from the corresponding carbethoxynaphtholdisulphonic acids and PCl_5. H. BURTON.

Preparation of β-orcinol. A. SONN [with C. RIESZ and H. FISCHER] (Ber., 1931, 64, [*B*], 1847—1850).—2 : 5-*Dimethyldihydroresorcinol*, m. p. 175—176° after slight softening, is obtained by treatment of 5-methyldihydroresorcinol with MeI and 20% aq. KOH at 60—70°. Alternatively, *p*-xylidine is transformed, in 70% yield, by $Na_2Cr_2O_7$ and H_2SO_4 followed by PbO_2 into *p*-xyloquinone, which with Ac_2O and conc. H_2SO_4 affords the *triacetate* of *hydroxy*-p-*xyloquinol*, m. p. 109—110°; this is partly hydrolysed to the *diacetate*, m. p. 190—192°, from which 2 : 5-dimethyldihydroresorcinol is derived by reduction with Na–Hg. 2 : 5-Dimethyldihydroresorcinol is transformed by Br in $CHCl_3$ into *dibromo-β-orcinol*, m. p. 154—155°, dihalogenated by H_2 in presence of Pd–$CaCO_3$, EtOH, and piperidine to β-orcinol. The last-named is converted by $AlCl_3$, HCN, and HCl in C_6H_6 and subsequent hydrolysis of the imine hydrochloride into the corresponding aldehyde, m. p. 166°. H. WREN.

Substituted di-β-phenylethylamines and benzyl-β-phenylethylamines. J. S. BUCK (J. Amer. Chem. Soc., 1931, 53, 2192—2200).—The following Schiff bases are prepared by interaction of their components at 100° under reduced pressure until no more H_2O is evolved: *veratrylidene-*, m. p. 69°, and *anisylidene-homoanisylamine*, m. p. 74°; *piperonylidene-*, m. p. 101°, *anisylidene-*, m. p. 63°, and *veratrylidene-homoveratrylamine*, m. p. 83°; *veratrylidene-β-phenylethylamine*, m. p. 60°; and *piperonylidene-homopiperonylamine*, m. p. 114°. By reduction with PtO and H_2 these are converted into *veratrylhomoanisylamine*, b. p. 197°/0·48 mm. (*hydrochloride*, m. p. 223°; *hydrobromide*, m. p. 233°); *anisylhomoanisylamine*, m. p. 44° (*hydrochloride*, m. p. 271°; *hydrobromide*, m. p. 254°); *piperonyl-*, m. p. 34°, b. p. 203°/0·44 mm. (slight decomp.?) (*hydrochloride*, m. p. 219°; *hydrobromide*, m. p. 204°; *hydriodide*, m. p. 198°), *anisyl-*, m. p. 47° (*hydrochloride*, m. p. 234°; *perchlorate*, m. p. 198°), and *veratryl-homoveratrylamine*, m. p. 79° (*hydrobromide*, m. p. 187°; *hydrogen oxalate*, m. p. 230°); *veratryl-β-phenylethylamine*, b. p. 182°/0·35 mm. (*perchlorate*, m. p. 177°; *hydriodide*, m. p. 170°); and piperonylhomopiperonylamine (A., 1927, 1199; *hydrochloride*, m. p. 243°; *hydrogen sulphate*, m. p. indef.): *benzylhomoveratrylamine*, b. p. 178°/0·75 mm. (*hydrochloride*, m. p. 200°; *picrate*, m. p. 160°), is prepared similarly. The following were prepared by interaction of the appropriate phenylethyl halide and primary amine: *β-phenylethylhomoveratrylamine*, b. p. 178°/0·48 mm. (*hydrochloride*, m. p. 183°; *hydrobromide*, m. p. 172°); *dihomoveratrylamine*, b. p. about 240°/1·0 mm., m. p. 51° [*hydrochloride*, m. p. 196°; *hydriodide*, m. p. 182° (softens 175°)]; and di-β-phenylethylamine [hydrochloride, m. p. 233° (lit. 260°, 265°); *hydrobromide*, m. p. 193°].

The following were prepared by demethylation with aq. HI (colourless; *d* 1·7), conversion into the hydrochlorides being effected by AgCl: benzyl-3 : 4-dihydroxy- [*hydrochloride*, m. p. 87° (resolidifies 120° and re-melts 180°); *dipicrate*, $C_{15}H_{17}O_2N,2C_6H_3O_7N_3$, m. p. 131°], piperonyl-3 : 4-dihydroxy- (*hydriodide*, m. p. 237°; *hydrochloride*, m. p. 219°), *4-hydroxybenzyl-4′-hydroxy-* (this base alone is stable), m. p. 118° (decomp.) (*hydriodide*, m. p. 192°; *hydrochloride*, m. p. 234°), 4-hydroxybenzyl-3′ : 4′-dihydroxy- [*hydrochloride*, m. p. 200—205°; *dipicrate*, m. p. 97° (solidifies and re-melts about 140°)], 3 : 4-dihydroxybenzyl-4′-hydroxy- (*hydriodide*, m. p. about 163°; *hydrochloride*, m. p. 180°), and 3 : 4-dihydroxybenzyl-3′ : 4′-dihydroxy-β-phenylethylamine [*hydrochloride* (+$1H_2O$), m. p. 182°, anhyd.; *dipicrate*, m. p. 173°]; 3 : 4 : 3′ : 4′-tetrahydroxydi-β-phenylethylamine [*hydriodide*, m. p. 187°; *hydrochloride* (+$2·5H_2O$), m. p. 230°].

3 : 4-*Dimethoxy-β-phenylethyl alcohol*, b. p. 166—168°/8 mm., d_{20}^{20} 1·1426 (p-*nitrobenzoate*, m. p. 81°; *phenylcarbamate*, m. p. 98—99°), was prepared by action of HNO_2 on homoveratrylamine, and converted into the *chloride* (not purified) by PCl_5 in CCl_4. H. A. PIGGOTT.

3 : 3′ : 5 : 5′-Tetranitro-2 : 2′-dimethoxydiphenyl. J. VAN ALPHEN (Ber., 1931, 64, [*B*], 1819—1820).—The compound exists in dimorphous forms, m. p. 179° and 191°, respectively. The variety of higher m. p. is obtained by inoculating the molten product at 185° or its boiling saturated solution in AcOH which is immediately diluted with H_2O. Inoculation with the variety, m. p. 191°, of solutions of the form, m. p. 179°, in boiling $COMe_2$, AcOH, or EtOH and subsequent slow cooling leads to separation of the form of lower m. p. H. WREN.

Stereoisomerism of disulphoxides and related substances. VII. Further pairs of isomeric dioxides. VIII. Isomeric tetrabromides of a disulphide. G. M. BENNETT and F. S. STATHAM (J.C.S., 1931, 1684—1689, 1690—1692).—VII. The same dioxide, m. p. 150° (decomp.) (cf. A., 1879, 37), is obtained by oxidation of diethyldithiolethane with either H_2O_2 or HNO_3. Oxidation of ethylenedithioldiacetic acid with H_2O_2 in AcOH gives the α-, m. p. 147° (decomp.), and β-*dioxides*, m. p. 133° (decomp.) (cf. A., 1914, i, 384). *pp′*-Dinitrodiphenyldithiolethane with HNO_3 (*d* 1·2) gives a mixture of α-, m. p. 195—197° (decomp.) (*monohydrochloride*), and β-*disulphoxide*, m. p. 174° (decomp.) (*diacetate*; *dihydrochloride*), and with an excess of CrO_3 in AcOH gives the *disulphone*, m. p. 303° (decomp.). From the corresponding *oo′*-dinitro-compound are obtained the α-, m. p. 174° (decomp.), and β-*disulphoxide*, m. p. 160·5° (decomp.), and a *disulphone*, m. p. 265° (lit. 164°). p-*Nitrodiphenyldithiolethane*, m. p. 79—80°, prepared by interaction of PhSK with *p*-nitrophenyl β-chloroethyl sulphide in EtOH, is oxidised by H_2O_2 in AcOH to α-, m. p. 173°, and β-, m. p. 155°, *-disulphoxides*, and by CrO_3 to the *disulphone*, m. p. 238°. 1 : 4-*Diethyldithiolbenzene*, m. p. 46·5°, the product of ethylation of dithioquinol with EtI and KOH in EtOH, similarly gives α-, m. p. 155°, and β-, m. p. 134°, *-disulphoxides*. Oxidation of 1 : 3-dithiolan with H_2O_2 in AcOH under varying conditions gives an amorphous, m. p. 128° (decomp.), and a cryst. *dioxide*, m. p. 157—158·5° (decomp.), and a *trioxide*, m. p. 128° (decomp.).

VIII. The "dimorphous" tetrabromides, m. p. 105—110° and 86—90°, of *p*-dimethyldithiolbenzene (A., 1909, i, 643) are shown by mixed-f. p. depressions in C_6H_6 to be stereoisomerides. They are converted by Ag_2O in H_2O into α- and a mixture of α- and β-di-

oxides, respectively; conversely, dry HBr in $CHCl_3$ converts the α-dioxide into a mixture of both tetrabromides, and the β-dioxide into the latter only: they are therefore regarded as the α- and β-forms, respectively. On crystallisation from $CHCl_3$ the latter is converted into the former. With Br in C_6H_6 *p*-diethyldithiolbenzene and dibenzyldithiolethane give single *tetrabromides*, m. p. 73—78° (decomp.) and 80—85° (decomp.), respectively. H. A. PIGGOTT.

Stereochemistry of diphenylbenzenes. *cis*- and *trans*-1 : 3 : 4 : 6-Tetrahydroxydi-3′-bromomesitylbenzenes and corresponding acylates. XV. P. R. SHILDNECK and R. ADAMS (J. Amer. Chem. Soc., 1931, **53**, 2203—2214).—α-3 : 6-*Dihydroxy-2 : 5-di-3′-bromomesityl*-p-*benzoquinone*, decomp. 397—400° (block) [*Na_2 salt*; *Ac_2*, m. p. 272—273° (corr.), and *dibutyryl*, m. p. 167°, derivatives], is prepared from the corresponding 3 : 6-dibromo-compound (α) and NaOH in aq. EtOH. It is reduced by $SnCl_2$ and HCl in EtOH to α-1 : 3 : 4 : 6-*tetrahydroxy-2 : 5-di-3′-bromomesitylbenzene*, m. p. 360—362° (decomp., block) [*Ac_4*, m. p. 294—295° (corr.), and *tetrabutyryl*, m. p. 124° (corr.), derivatives], from which it is regenerated by oxidation with *p*-benzoquinone. Similar reduction of its Ac_2 derivative gives α-3 : 6-*diacetoxy-2 : 5-di-3′-bromomesitylquinol*, m. p. 251—252° (corr.), which is readily hydrolysed to the $(OH)_4$ compound or acetylated to its Ac_4 derivative. All the above acyl derivatives are prepared by means of the anhydride and pyridine. An exactly similar series of reactions has been carried out in the β-series without any evidence of conversion into α-derivatives. The following are described: β-3 : 6-*dihydroxy-2 : 5-di-3′-bromomesityl*-p-*benzoquinone*, m. p. 387—390° (decomp., block) [*Na_2 salt*; *Ac_2*, m. p. 272—273° (corr.), and *dibutyryl*, m. p. 147° (corr.), derivatives]; β-1 : 3 : 4 : 6-*tetrahydroxy-2 : 5-di-3′-bromomesitylbenzene*, m. p. 355—357° (block) [*Ac_4*, m. p. 269—270° (corr.), *tetrabutyryl*, m. p. 103° (corr.), and 3 : 6-*diacetyl*, m. p. 240—241° (corr.), derivatives]. On account of their higher m. p. the α- are regarded as the *trans*-forms. Confirmation of this is afforded by conversion of the β-dihydroxyquinone and its Ac_2 and dibutyryl derivatives into the α-forms by heating with mesitylene or glacial AcOH, or, in the case of the last, alone above its m. p. The Br_2-, $(OH)_4$-, and tetra-acyloxy-derivatives, however, appeared to be stable under these conditions. The isomerism, in accordance with theory, disappears when the mesityl nuclei become symmetrically substituted; bromination of both α- and β-forms of the $(OAc)_4$-compound gives a single 1 : 3 : 4 : 6-*tetra-acetoxy-2 : 5-di-3′ : 5′-dibromomesitylbenzene*, m. p. 347—348° (corr.).

H. A. PIGGOTT.

1-Trichloromethyl*cyclo*pentanol. C. E. GARLAND and W. A. WELCH (J. Amer. Chem. Soc., 1931, **53**, 2414—2415).—*cyclo*Pentanol, $CHCl_3$, and solid KOH are allowed to interact for 6 days at 0—10°, and the 1-*trichloromethyl*cyclo*pentanol*, b. p. 102—102·5°/10 mm., formed is separated from unsaturated by-products by bromination followed by fractional distillation. The corresponding product from *cyclo*hexanone appeared to be formed in small amount, but could not be isolated. H. A. PIGGOTT.

Oxidation of benzyl alcohol by chloronitrobenzenes. R. E. LYONS and G. H. STEMPEL, jun. (Proc. Indiana Acad. Sci., 1929, **38**, 197—200).—$CH_2Ph\cdot OH$ with *p*-$C_6H_4Cl\cdot NO_2$ gave BzOH and *pp′*-dichloroazoxybenzene, a little $(ClC_6H_4\cdot N:)_2$ also being formed when a xylene solution of $C_6H_4Cl\cdot NO_2$ was employed instead of the solid. *m*-$C_6H_4Cl\cdot NO_2$ and $CH_2Ph\cdot OH$ gave $(m\text{-}C_6H_4Cl)_2N_2O$; the *o*-derivative gave unidentified products.

CHEMICAL ABSTRACTS.

Variations in sweetening power of saccharin and its derivatives. II. B. ODDO and Q. MINGOIA (Gazzetta, 1931, **61**, 435—446; cf. A., 1927, 878).—Mg saccharinate (I) reacts as follows with *N*-magnesyl derivatives, $R\cdot NH\cdot MgBr$:—

$$\text{(I.)}\quad C_6H_4{<}\begin{matrix}CO-\\SO_2\end{matrix}{>}N\cdot Mg\cdot N{<}\begin{matrix}CO-\\SO_2\end{matrix}{>}C_6H_4 \longrightarrow$$

$$[(NHR)_2{:}C(OMgBr)\cdot C_6H_4\cdot SO_2N(MgBr)]_2Mg \longrightarrow NH_2\cdot SO_2\cdot C_6H_4\cdot C(OH)(NHR)_2 \quad \text{(II.)}$$

On boiling with Ac_2O and NaOAc the sulphonamide (II) gives instead of the Ac derivative the internal ester, $C_6H_4{<}\begin{matrix}C(NHR)_2\\SO_2\end{matrix}{>}O$, analogous in structure to saccharin, but tasteless, which is hydrolysed by alkali (but much less easily than saccharin) to a carbinol-sulphonic acid, $OH\cdot SO_2\cdot C_6H_4\cdot C(OH)(NHR)_2$. The following are described: o-*sulphonamido-ωω-dianilinobenzyl alcohol*, m. p. 195° (corresponding *sulphonic acid*, m. p. 285°; internal *ester*, m. p. 315°); o-*sulphonamido-ωω-di-*o*-toluidinobenzyl alcohol*, m. p. 183° (*acid*, m. p. 280°; *ester*, m. p. 278°); o-*sulphonamido-ωω-diethylaminobenzyl alcohol*, m. p. 159° (*acid*, m. p. 186—188°; *ester*, m. p. 276°). All these compounds are tasteless. Attempts to combine $NH_2\cdot MgX$ with Mg saccharinate were unsuccessful.

E. E. J. MARLER.

Optical activity and the Walden inversion. I. E. OTT [with E. ZINNIUS, R. WEGLER, D. BEISCHER, and K. PACKENDORFF] (Annalen, 1931, **488**, 186—202).—Assuming that the differing action of bases in the replacement of Cl by OH in the Walden inversion is due to the differing rates of reaction, it is possible to reconcile the results with those obtained during the study of additive reactions and to explain both on common principles of energy. From this point of view observations have been made of the effect of varying the rate of reaction by alterations of temp. and concentration without change of reactants. Diazotisation of the NH_2 group consists in the reversible change $R\cdot NH_2 + HNO_2 \rightleftharpoons R\cdot N_2\cdot OH\ (R\cdot NH\cdot NO) + H_2O$ and the irreversible reaction $R\cdot N_2\cdot OH = N_2 + R\cdot OH$. In aq. solution the action of HNO_2 on α-phenylethylamine is accompanied by inversion, whereas in AcOH the alcohol has the same sign as the amine. Gradual addition of H_2O to the solution of the amine in AcOH causes the sign of rotation of the alcohol to pass from + through 0 to −. Addition of NaOAc, which functions as a retarding agent to solutions of const. H_2O, amine, AcOH, and $NaNO_2$ concentration, causes reversal of the sign of rotation which does not occur in absence of this addition.

The replacement of OH in phenylmethylcarbinol by Cl is effected by $SOCl_2$, the disturbing effect of the HCl thereby formed being nullified by operating in

CCl_4 in which HCl is insol.; the action of the $SOCl_2$ is not greatly retarded and the effect can be compensated by increasing its amount. The rotatory power of the chloride increases with increasing rate of substitution; the latter is controlled by raising the temp. or varying the vol. of the solution. The presence of pyridine retards the reaction, since the additive product of the base and $SOCl_2$ is less active than $SOCl_2$.

Further data are accumulated in favour of the view that racemic compounds exist in the liquid or dissolved condition without complete decomp. into the optical antipodes. α-Phenylethylamine is resolved by its H malate into the active forms, $[\alpha]^{15}_{Hg\ yellow}$ $\pm 42{\cdot}63°$, which appear to represent the limit of efficiency of the method. If (+)-phenylethylamine is partly diazotised, a "residual amine" (10% of the material) remains with appreciably higher activity than that given by Pasteur's method. With the (—)-amine a residual product of slightly lower sp. rotation remains. The b. p. and n of the residual (+)-amine agree with those of the initial active material. A (+)-amine, $[\alpha]^{1}_{Hg\ yellow}+52°$, is obtained from a prep. $[\alpha]^{15}_{Hg\ yellow}+42{\cdot}63°$ by partial treatment with $ClCO_2Et$ (Schotten–Baumann). The bulk of the amine gives the corresponding *urethane*, m. p. 35°, $[\alpha]^{1}_{Hg\ yellow}+92{\cdot}5°$, from which the amine can be regenerated without undue racemisation by distillation with solid KOH. By similar means the (—)-amine gives a residual amine of the slightly enhanced activity, $[\alpha]^{20}_{Hg\ yellow}$ $-44°$. Fractional precipitation of the active amine by addition of alkali hydroxide to the acid solution yields a "residual amine," $[\alpha]^{30}_{Hg}$ 44·3° or $[\alpha]^{18\cdot5}_{Hg\ yellow}$ $+48{\cdot}83°$. H. WREN.

Pharmacodynamic researches on derivatives of chloral–benzene condensation products. FLORENCE (Bull. Soc. chim., 1931, [iv], **49**, 925—929).—Condensation of $CCl_3{\cdot}CHO$ with C_6H_6 in presence of $AlCl_3$ affords phenyltrichloromethylcarbinol, b. p. 160°/23 mm., oxidised to *ααα-trichloroacetophenone*, b. p. 128—132°/14 mm. Neither the carbinol, nor its p-*nitrobenzoate*, m. p. 109°, p-*aminobenzoate*, m. p. 131° (*hydrochloride*, m. p. 118°), m-*nitrobenzoate*, m. p. 90°, m-*aminobenzoate* (*hydrochloride*), o-*nitrobenzoate*, m. p. 119°, or o-*aminobenzoate*, m. p. 141°, possesses any pharmacodynamic action on rabbits and guinea-pigs, and in contrast to acetophenone and chloroacetophenone, the trichloroacetophenone has no hypnotic or lachrymatory properties. R. BRIGHTMAN.

[New reaction of the aliphatic double linking.] Z. FOLDI (Ber. 1931, **64**, [*B*], 1911; cf. A., 1930, 1423).—α-Methylamino-β-hydroxy-α-phenylpropane has been described by Emde and Runne (A., 1911, i, 714). H. WREN.

***iso*Phenylvinyl acetate, CHPh:CH·OAc, product of the oxidation of styryl methyl ketone by peracids.** J. BOESEKEN and A. KREMER (Rec. trav. chim., 1931, **50**, 827—832).—Oxidation of CHPh:CHAc with perbenzoic acid in $CHCl_3$ or peracetic acid in AcOH gives a *β-phenylvinyl acetate*, b. p. 128—129°/15 mm., 68°/0 mm., which is hydrolysed by H_2O at 108° (to AcOH and $CH_2Ph{\cdot}CHO$) to about the same extent as the isomeric acetate of Semmler (A., 1909, i, 239). H. BURTON.

Action of formic acid on δ-phenyl-β-ethinylbutan-β-ol (the acetylene-carbinol from β-phenylethyl methyl ketone). H. RUPE and H. HIRSCHMANN (Helv. Chim. Acta, 1931, **14**, 687—701).—*δ-Phenyl-β-ethinylbutan-β-ol*, b. p. 125—128°/10 mm., prepared from sodiobenzylacetone and C_2H_2 in Et_2O, is converted by boiling 86% HCO_2H into a mixture of carbonyl compounds, the main constituent of which, $C_{12}H_{14}O$, b. p. 140—141·5° (*semicarbazone*, m. p. 182°), does not combine with $NaHSO_3$, is reduced to a *dihydro*-derivative, b. p. 123—124·5° (*oxime*, b. p. 158—162°/9 mm.; *semicarbazone*, m. p. 71—73·5°), and is oxidised to BzOH by alkaline $KMnO_4$; a hydrocarbon, $C_{12}H_{12}$, b. p. 98°/10 mm., and *semicarbazones*, m. p. 191—192° (*carbonyl* compound, b. p. 138—139°/9 mm.), 146—147°, and 148°, were also isolated.

The following were prepared for comparison with the substance, b. p. 140—141·5°, but all were different: *γ-phenyl-α-methyl*-n-*propyl methyl ketone*, b. p. 127—128°/8 mm. [*semicarbazone*, m. p. 180° (sinters 162°); *oxime*, b. p. 154—158°/7 mm., m. p. 95—96°], by interaction of $ZnMe_2$ and *γ-phenyl-α-methylbutyryl chloride*, b. p. 128—129°/8 mm.; β-*phenylethyl* n-*propyl ketone*, b. p. 133—135°/8 mm. [*semicarbazone*, m. p. 79° (sinters 71°); *oxime*, b. p. 162—165°/8 mm., m. p. 43° (sinters 30°)], by reduction with H_2 and Ni of the *benzylidene* derivative, b. p. 135—140°/10 mm., of $COMePr^{\alpha}$; β-*phenylethyl* iso*propyl ketone*, b. p. 126—127°/8 mm. (*semicarbazone*, m. p. 93—94°; *oxime*, b. p. 156—158°/8 mm.), by a similar hydrogenation of the *benzylidene* derivative, b. p. 139—141°/8 mm., of $COMePr^{\beta}$; and *γ-phenylpropyl ethyl ketone*, b. p. 137—140°/10 mm. (*semicarbazone*, m. p. 149°), by condensation of γ-phenylbutyryl chloride with $ZnEt_2$. H. A. PIGGOTT.

Condensations by sodium instead of by the Grignard reaction. I. Tertiary carbinols. A. A. MORTON and J. R. STEVENS (J. Amer. Chem. Soc., 1931, **53**, 2244—2247).—Interaction of PhCl (2 mols.) with BzOEt (1 mol.) and Na (4 atoms) in Et_2O gives triphenylcarbinol in 98% yield. Other halogenobenzenes, with Me or Bz benzoates, Et_2CO_3, or $Et_2C_2O_4$ as examples of carbonyl compounds, and hydrocarbon solvents may also be used. The method is extended to the prep. of phenyldiethylcarbinol from PhBr and $COEt_2$, triethylcarbinol from EtBr and $COEt_2$ or $Et{\cdot}CO_2Et$, and di(?)phenylethylcarbinol from EtBr and PhCHO. H. A. PIGGOTT.

Character of triarylcarbinol derivatives. I. S. KAWAI and K. TAMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, **16**, 17—19).—The tautomerism of *p*-hydroxydiphenyl-α-naphthylcarbinol (A., 1920, 735) is illustrated by the partial conversion of p-*dimethylaminodiphenyl-α-naphthylcarbinol*, m. p. 183°, into phenyl-α-naphthylquinomethane on heating with conc. HCl in AcOH, or by the action of $AlCl_3$ in C_6H_6 at room temp. J. D. A. JOHNSON.

Derivatives of optically active triarylcarbinols and their halochromic salts. E. S. WALLIS (J. Amer. Chem. Soc., 1931, **53**, 2253—2260).—*l*-Phenyldiphenylyl-α-naphthylmethylthioglycollic acid (A.,

1930, 773) is slowly racemised in AcOH. It forms halochromic compounds with H_2SO_4, $HClO_4$, $HgCl_2$, and $TiCl_4$, the first three of which give *dl*-phenyldiphenylyl-α-naphthylmethylcarbinol, and the last regenerates the glycollic acid in an inactive form when decomp. with ice. The halochromic compounds with $FeCl_3$ and $ZnCl_2$, however, regenerate the original compound without any trace of racemisation. The regeneration of an optically active compound cannot be reconciled with the quinonoid theory of halochromism (cf. A., 1902, i, 89), but supports rather the "carbonium" theory (A., 1922, i, 24; 1925, i, 650) if the racemisation that occurs in some cases be explained by the inherent instability of this ion (cf. A., 1930, 1177). H. A. PIGGOTT.

Isomerisation of ergosterol and its derivatives. A. WINDAUS, K. DITHMAR, H. MURKE, and F. SUCKFULL (Annalen, 1931, **488**, 91—110).—The action of HCl on ergosteryl acetate in $CHCl_3$ yields *ergosteryl*-B_1 *acetate*, m. p. 142°, $[\alpha]_D^{15}$ —53·6°, hydrolysed by KOH in MeOH to *ergosterol*-B_1, m. p. 148°, $[\alpha]_D^{15}$ —40·3° in $CHCl_3$. Treatment of the mother-liquors with maleic anhydride yields a sparingly sol. *ergosteryl*-B_3 *acetate-maleic anhydride*, m. p. 207° (*ergosteryl*-B_3 *acetate*, m. p. 132°, $[\alpha]_D$ —182·9° in $CHCl_3$; *ergosterol*-B_3, m. p. 136°, $[\alpha]^{12}$ —190° in $CHCl_3$), after removal of which *ergosteryl*-B_2 *acetate*, m. p. 100°, $[\alpha]^{12}$ —80·4° in $CHCl_3$ (*ergosterol*-B_2, m. p. 126°, $[\alpha]_D$ —88·4° in $CHCl_3$), is isolated. If treatment of ergosteryl acetate is effected at 0°, ergosteryl-B_3 acetate gradually accumulates in the product owing to the slow conversion of the B_1 and B_2 esters into the B_3 product. In boiling $CHCl_3$–HCl solution the B_3 acetate is extensively converted into the B_1 and B_2 substances. Contrary to Reindel, the $CHCl_3$ solution must not be warmed above 0° while HCl is present if ready isolation of the B_3 ester is desired. Ergosterols B_1, B_2, and B_3 have approx. the same absorption spectrum with max. at 248 mμ. B_1 and B_2 do not react with maleic anhydride, with which B_3 readily combines. The sterols are not hydrogenated by Na and EtOH. The literature is critically reviewed. Ergosteryl-*D* acetate behaves similarly to ergosteryl acetate towards HCl.

The action of NaOEt on sterols at about 200° causes (1) a more or less complete transformation at the *sec.* OH group leading to an equilibrium mixture of two alcohols differing only in arrangement of the H and OH groups and therefore yielding the same ketone. The new *epi*-derivatives, unlike the parent compounds, are not precipitated by digitonin. This property is shared by the irradiated products of ergosterol, which do not belong to the *epi*-series, since all the latter are transformed by NaOEt to a smaller or greater extent into the precipitable isomerides, whereas this is invariably not the case with irradiated products (dihydroergosterol I, ergosterol B_1, B_2, and *D*); (2) hydrogenation at the double linking combined with epimerisation (ergosterol, dehydroergosterol, and cholesterol); (3) steric transformation in the C skeleton combined with epimerisation and hydrogenation. The following transformations are recorded: ergosterol-B_1 into epi*ergosterol*-B_1, m. p. 182—183° (*acetate*, m. p. 136°); ergosterol-B_2 into epi*ergosterol*-B_2, m. p. 163° (*acetate*, m. p. 127°); ergosterol-*D* into epi*ergosterol*-D, m. p. 203—204°, $[\alpha]_D^{19}$ +36·2° in $CHCl_3$ (*acetate*, m. p. 150°, $[\alpha]_D$ +40·6° in $CHCl_3$); dihydroergosterol I into epi*dihydroergosterol* I, m. p. 156°, $[\alpha]_D$ +4·01° in $CHCl_3$ (*acetate*, m. p. 215—216°, $[\alpha]_D$ —4·4° in $CHCl_3$), dehydrogenated by $Hg(OAc)_2$ to *epi*ergosterol-*D* and a *substance*, m. p. 160—161°, $[\alpha]_D$ —34·4° (*acetate*, m. p. 123—124°, and its additive *product* with maleic anhydride, m. p. 212°, $[\alpha]_D$ —56·7°); ergosterol to dihydroergosterol II, m. p. 163°, $[\alpha]_D^{20}$ —8·8° in $CHCl_3$ (acetate, m. p. 164—165°, $[\alpha]_D^{21}$ —16·2° in $CHCl_3$), and epi*dihydroergosterol* II, m. p. 216°, $[\alpha]_D^{20}$ —4·92° in $CHCl_3$ (*acetate*, m. p. 155—156°, $[\alpha]_D^{18}$ +3·88° in $CHCl_3$); dihydroergosterol II to *epi*dihydroergosterol II; dehydroergosterol to ergosterol *D*, m. p. 170°, $[\alpha]_D$ +17·8° (acetate, m. p. 173—174°, $[\alpha]_D$ +20·7°), and *epi*ergosterol *D*. H. WREN.

Constitution of colourless and coloured triphenylmethane derivatives. A. HANTZSCH and A. BURAWOY (Ber., 1931, **64**, [*B*], 1622—1635).—Aminated and non-aminated CPh_3 derivatives do not differ fundamentally. Colourless ψ-salts (homopolar compounds such as CPh_3Cl, triaminophenylacetonitrile) exist as well as coloured, true salts (heteropolar compounds such as CPh_3ClO_4, triaminophenylmethyl chloride) of quinonoid or quinolide structure. Their colour is not dependent on the quinonoid structure of a single C_6H_6 ring, but on a consequent conjugated system, *e.g.*, $[H_2N\cdot C_6H_4\cdot CR{:}C_6H_4{:}\overset{+}{N}H_2]$ (R = $C_6H_4\cdot NH_2$), $[MeO\cdot C_6H_4\cdot CR{:}C_6H_4{:}\overset{+}{O}Me]$ (R = $C_6H_4\cdot OMe$) and

Colourless and coloured compounds are related to one another as "valency isomerides." They differ in that a certain linking in the colourless isomerides is ester-like (covalent), whereas in the coloured derivatives it is ionogenic (electrovalent). The solid compounds are either colourless ψ-salts or coloured true salts. A compound CAr_3X has not been isolated in the two forms. The occurrence of a compound as colourless ψ-salt or coloured true salt depends on the positive character of the triarylmethyl group or the negative nature of the acidic residue. The tendency towards the formation of coloured, true salts increases with increasingly positive character of the triarylmethyl residue caused mainly by the introduction of NH_2 and OR groups (CPh_3Cl is a colourless ψ-salt, whereas triaminotriphenylmethyl chloride is a coloured, true salt) and with increasingly negative nature of the acidic residue (CPh_3ClO_4 is coloured and triaminotriphenylacetonitrile is colourless). The ability of inorg. ψ-salts, such as $SnCl_4$, $HgCl_2$, and of acid mols. to convert colourless triarylmethyl derivatives by addition into coloured salts is probably attributable to enhancement of the negative character of the acidic residue. In the absence of solvolysis, equilibrium usually exists between the true and ψ-salts in the solutions of the (solid) colourless and coloured triarylmethyl derivatives; the position of the equilibrium is displaced in the direction of the coloured salt with increasingly positive nature of the triarylmethyl

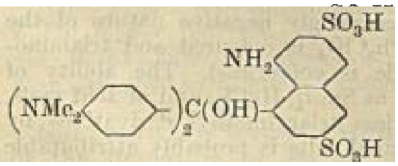
residue and increasingly negative character of the acidic radical. Rise in temp. and irradiation with ultra-violet light operate in the same sense. The position of the equilibrium is also influenced by the solvent. Colourless and coloured derivatives are solvatised in solution, but the nature and position of union with the solvent mols. remain undetermined.
H. WREN.

Absorption of light and constitution. III. Coloured triarylmethyl salts. A. BURAWOY (Ber., 1931, **64**, [*B*], 1635—1646; cf. preceding abstract).—The constitution of triarylmethyl salts or their cations can be decided only by their optical behaviour and not on a chemical or an electrochemical basis. All are quinonoid or quinolide. Absorption of light is due to conjugated systems. Optical investigation of positively substituted triarylmethyl salts shows that the first positive groups are positively charged, since their bathochromic action increases in the sequence $NR_2<OR<SR$; the atoms N^+, O^+, S^+ are negative auxochromic atoms. The atoms O, S, N of the second positive groups which have increasingly bathochromic action in the sequence $OR<SR<NR_2$ are positive auxochromic atoms. The third positive groups are in branchings of the chromophoric conjugated systems, since they exert a feeble hypsochromic effect. The formulae

$$\left[NR_2\cdot C_6H_4\cdot C\begin{array}{l}\nearrow C_6H_4{:}NR_2\\ \searrow C_6H_4\cdot NH_2\end{array}\right]\quad\left[OR\cdot C_6H_4\cdot C\begin{array}{l}\nearrow C_6H_4{:}OR\\ \searrow C_6H_4\cdot OR\end{array}\right]$$

and $\left[SR\cdot C_6H_4\cdot C\begin{array}{l}\nearrow C_6H_4{:}SR\\ \searrow C_6H_4\cdot SR\end{array}\right]$ are advanced. Substitution of the first and second C_6H_6 residue of the CPh_3 ion by the $Ph\cdot C_6H_4$ residue displaces the absorption bands appreciably towards the red end, whereas replacement of the third C_6H_6 groups does not appreciably alter the position of the max. of the bands. Phenyldibiphenylylmethyl sulphate has two bands in the visible portion of the spectrum. The non-positively substituted triarylmethyl ions have the quinolide constitution, and the absorption of light depends on the presence of conjugated systems.
H. WREN.

Naphthalene-green-V. F. FRISCH (Helv. Chim. Acta, 1931, **14**, 669—671).—Interaction of tetramethyldiaminobenzhydrol with α-naphthylamine-3 : 6-disulphonic acid in 15% H_2SO_4 at its b. p. for several days gives a leuco-compound in 3% yield, oxidised by PbO_2 to a pure blue dye (annexed formula) characterised by its fastness to alkalis. The



given structure is assigned on account of its conversion by elimination of the NH_2-group into the Me_4 analogue of naphthalene-green-V in place of the desired analogue of the dye having the structure formerly assigned to the latter (cf. A., 1930, 1430). H. A. PIGGOTT.

Alkamines in the tetrahydronaphthalene series. E. MOSETTIG and A. BURGER (J. Amer. Chem. Soc., 1931, **53**, 2295—2300).—The action of diazomethane on 2-ketotetrahydronaphthalene in Et_2O–MeOH gives 2-*methylenetetrahydronaphthalene oxide*, $\begin{array}{l}C_6H_4\cdot CH_2\\ CH_2-CH_2\end{array}\!\!>C<\!\!\begin{array}{l}O\\ CH_2\end{array}$ (I), b. p. 137—138°/1 mm., which on interaction with the appropriate *sec.*-amines gives 2-*dimethylaminomethyl*-, b. p. 116—118°/1 mm. [*hydrochloride*, m. p. 175—176°; *perchlorate*, m. p. 158—159°; *chloroplatinate*, m. p. 197—198° (decomp.)] [accompanied by a homologue (?) isolated as *perchlorate*, m. p. 184°; *hydrochloride*, m. p. 196—198°, *chloroplatinate*, m. p. 197—198°]; 2-*diethylaminomethyl*-, b. p. 135—137°/1 mm. [*hydrochloride*, m. p. 125—126° ($+1H_2O$, lost at 92°); *perchlorate*, m. p. 155—156°; *chloroplatinate*, m. p. 190° (decomp.)]; and 2-*piperidinomethyl*-2-*hydroxytetrahydronaphthalene*, b. p. 146—148°/1 mm. [*hydrochloride*, m. p. 200—200·5°; *perchlorate*, m. p. 147·5—148°; *chloroplatinate*, m. p. 214—216° (decomp., rapid heating)]. The oxide (I) is accompanied by a yellow oil of the same b. p., but inactive towards *sec.*-amines. Diazoethane reacts vigorously with 2-ketotetrahydronaphthalene, but no definite products were isolated on treatment with amines. The formation of an unstable additive compound of this ketone with piperidine is reported. H. A. PIGGOTT.

Dissociable organic oxides. A fourth oxidation stage of rubrene: dihydroxydihydrorubrene. C. DUFRAISSE and M. BADOCHE (Compt. rend., 1931, **193**, 63—65).—*Dihydroxydihydrorubrene* (I), m. p. 307—308° (Maquenne block), $C_{42}H_{28}(OH)_2$, is one of the products formed by the action of Grignard reagents (or, in small yield, of MgI_2) on *iso*rubrene oxide (A., 1930, 1173). On heating it yields rubrene monoxide, and on dehydration readily loses $2H_2O$ to yield a *substance*, $C_{42}H_{26}$, m. p. 455°, with a violet fluorescence, and apparently identical with the adulterant of rubrene previously reported (A., 1926, 945). (I) is not dissociable, but is reduced by Fe powder to rubrene. On the basis of these reactions (I) is assigned the formula $\left(C_6H_4<\!\begin{array}{c}CPh\\ CPh(OH)\end{array}\!>C-\right)_2$. The capacity of rubrene to form dissociable, as well as non-dissociable but reducible, oxides by addition of O_2 indicates predisposition to attack by oxidising agents, and is shared by methæmoglobin. Methæmoglobin may, therefore, possibly form several oxides, one or other predominating according to the method of prep., which explains the discordant results in this field.
R. S. CAHN.

Syntheses of cyclic compounds. IX. Reduction of ethyl 3-methyl*cyclo*pentylidene-1-cyanoacetate with moist aluminium amalgam and its bearing on the configuration of the 3-methyl*cyclo*pentane ring. A. I. VOGEL (J.C.S., 1931, 1795—1801).—The condensation of 3-methyl*cyclo*pentanone with Et cyanoacetate in presence of piperidine gives α- (cf. this vol., 843) and β *Et* 3-*methyl*cyclo*pentylidene*-1-*cyanoacetate*, b. p. 155—156°/12 mm., both of which are oxidised by cold aq. $KMnO_4$ to 3-methyl*cyclo*pentanone, and reduced by Al–Hg in moist Et_2O to Et *r*-3-methyl*cyclo*pentyl-1-cyanoacetate (*loc. cit.*) and a mixture of bimol. esters, m. p. 69—70°, the last-named being produced in a yield of 16% from the α-form and 13% from the β-form, indicating that the

3-methyl*cyclo*pentane ring is strainless, a result in agreement with parachor measurements. Both α- and β-forms condense with Et cyanoacetate and NH_3 in EtOH to give the dicyanoimide (this vol., 727), and with KCN in EtOH to give a nitrile, converted by acid hydrolysis into 1-carboxy-3-methyl*cyclo*pentane-1-acetic acid, m. p. 117° (cf. this vol., 843; *anhydride*, b. p. 156—158°/11 mm.), and, in the case of the α-form, an isomeric (?) acid. H. A. PIGGOTT.

Equilibrium $C_6H_6+CO_2 \rightleftharpoons C_6H_5{\cdot}CO_2H$. C. R. KINNEY and D. P. LANGLOIS (J. Amer. Chem. Soc., 1931, **53**, 2189—2192).—The decarboxylation of BzOH is reversible in presence of Zn–Cu–Cr oxide catalysts (cf. B., 1930, 49). Decomp. of the acid begins at 240—250°, but equilibrium is not reached at the end of 5 days at 300°. At 300°/35 atm. 0·08% of BzOH, calc. on C_6H_6, is obtained by the reverse reaction. H. A. PIGGOTT.

***N*-Acylsulphamic acids.** P. BAUMGARTEN and I. MARGGRAFF (Ber., 1931, **64**, [*B*], 1582—1588).—Acetamide and *N*-pyridiniumsulphonic acid at 100° yield *pyridinium acetamidosulphonate*, m. p. 123—124°, converted by 1 mol. of KOH into the *salt*, $NHAc{\cdot}SO_3K$, also obtained by heating NH_2Ac with trimethylsulphamic acid at 150° and treatment of the product with K_2CO_3, $KHCO_3$, or KOH. It is rapidly decomposed by acids but converted by KOH into the K_2 salt, $NKAc{\cdot}SO_3K,2H_2O$, hydrolysed in boiling aq. solution to KOAc and $NH_2{\cdot}SO_3K$. *K benzamidosulphonate* (also $+1H_2O$) yields NH_2Bz in boiling PhCN; the last-named compound is obtained in 90% yield when NH_2Bz and *N*-pyridiniumsulphonic acid are heated at 220°. The K_2 salt is described. *K_2 benzenesulphonamidosulphonate* is transformed by $HClO_4$ in H_2O into *K benzenesulphonamidosulphonate*. H. WREN.

Molecular rearrangements involving optically active radicals. II. Hofmann rearrangement of optically active acid amides. E. S. WALLIS and S. C. NAGEL (J. Amer. Chem. Soc., 1931, **53**, 2787—2791).—d-α-*Benzylpropionamide*, m. p. 104·5°, from the corresponding chloride and NH_3 in Et_2O, is converted by the Hofmann method into *d*-α-benzylethylamine, having a sp. rotation identical with that of the compound obtained previously (A., 1926, 279) by rearrangement of *d*-benzylmethylacetazide. The results are discussed briefly with reference to the Walden inversion. H. BURTON.

Oxidation by permanganate of cinnamic acid. E. M. STODDART (J.C.S., 1931, 1874—1875).—Oxidation of boiling 1% aq. Na cinnamate with $KMnO_4$ gave, with absorption of 3·5 O_2 per mol. of acid, PhCHO (70% of theory) and phenylglyceric acid (about 10%), about 20% remaining unchanged. No oxalate was formed. H. A. PIGGOTT.

Hydroxy-complexes of iron. C. MORTON.—See this vol., 1022.

Electrolyses in liquid ammonia; reactive forms of free radicals. S. GOLDSCHMIDT and F. NAGEL (Ber., 1931, **64**, [*B*], 1744—1755).—Electrolysis of a variety of org. compounds, mainly phenols and carboxylic acids, in liquid NH_3 shows that the effect of the current, if passing, consists essentially in the transport from the cathode to the anode of the org. substance, which can be recovered almost quantitatively. H_2 and N_2 are liberated at the cathode and anode in the vol. ratio 3 : 1. The formation of N_2H_4 cannot be detected. The possibility of intermediate radical formation is examined with 9-chloro-10-hydroxyphenanthrene. The compound is dehydrogenated by $K_3Fe(CN)_6$ in liquid NH_3 at −40° to the peroxide, which can be determined by titration with hydrazobenzene; evolution of N_2 and H_2 during electrolysis is not observed. If salicylic acid is substituted for the phenanthrol and electrolysis is effected in presence of NHPhMe or hydrazobenzene, *s*-diphenyldimethylhydrazine and azobenzene respectively are produced in modest amount. It is therefore concluded that the electrolysis of org. acids, largely independent of their constitution, leads to the production of discharged anions richer in energy than the radicals produced by chemical means and differing sharply from them in their reactions. They are incapable of forming stable, dimeric mols. with loss of energy. Their great chemical reactivity is shown by their reaction with NH_3 and other mols. and with the Pt electrodes, which are invariably corroded; in the case of salicylic acid an insol. loose deposit of a complex Pt salt is formed on the anode. If the new radicals lack opportunity to discharge their energy by chemical reaction, they decompose as, *e.g.*, in the electrolysis of carboxylic acids in H_2O, either according to the Kolbe synthesis of hydrocarbons or to more complicated changes. H. WREN.

Mercury salicylate. P. BRENANS and B. RAPILLY (Compt. rend., 1931, **193**, 55—58).—Hg salicylate, prepared by the older methods (A., 1902, i, 851; 1903, i, 246, 392), consists mainly of anhydro-5-hydroxymercurisalicylic acid, $OH{\cdot}C_6H_3{<}\genfrac{}{}{0pt}{}{CO}{Hg}{>}O$, since on treatment with I it gives 5-iodosalicylic acid (I) and 3 : 5-di-iodosalicylic acid (separated by its less sol. Ba salt), and on treatment with KCN followed by I in KI yields (I). The less sol. K cyanomercurisalicylate is the 5-cyanomercuri-derivative, since it yields (I) (contrast A., 1925, i, 1107). The salt obtained by treating salicylic acid or its Na salt with $HgSO_4$ (A., 1927, 685) contains a large amount of a dimeric compound, $HO{\cdot}C_6H_4{\cdot}CO_2{\cdot}Hg(5\text{-}){\cdot}C_6H_2(OH){<}\genfrac{}{}{0pt}{}{(3\text{-})Hg}{\text{---}CO}$ since on treatment with hot aq. KCN it yields *K* 3 : 5-*dicyanomercurisalicylate*, which with I in KI gives 3 : 5-di-iodosalicylic acid. A volumetric and a gravimetric method of determining Hg in these compounds are given. R. S. CAHN.

Condensation of chloral with *m*-cresotic acid. N. M. SHAH and R. L. ALIMCHANDANI (J. Indian Chem. Soc., 1931, **8**, 261—270; cf. J.C.S., 1921, **119**, 201; A., 1925, i, 1272).—Condensation of chloral with *m*-cresotic acid by keeping in conc. or 90% H_2SO_4 for 1 or 3 days occurs in the *p*-position (cf. A., 1925, i, 111), as with the Me ether of the acid (A., 1929, 813), the products being α : 5-*dihydroxy*-2-βββ-*trichloroethyl*-p-*toluic acid* (I), $C_6H_2Me(OH)(CO_2H){\cdot}CH(OH){\cdot}CCl_3$, efflorescent, m. p. 218° (*Ac* derivative, m. p. 160°) (gives an intense violet colour with $FeCl_3$), the *lactone* of (I), m. p. 340° (decomp.), and 5-*hydroxy*-2-(α-

hydroxy-ββ-dichlorovinyl)-p-*toluic acid* (II), $C_6H_2Me(OH)(CO_2H)\cdot C(OH)\vdots CCl_2$, m. p. 165° (decomp.). Some sulpho-*m*-cresotic acid was also formed. The constitution of (I) is proved by the following reactions. Hydrolysis of (I) with aq. NaOH gave *4-hydroxy-5-carboxy-2-methylmandelic acid* (III), m. p. 227° (decomp.) [*Ba* salt, $+4H_2O$, of which $2H_2O$ are lost at 115—120°; *Ac* derivative, $+1H_2O$, m. p. 168—170° (decomp.)], which on oxidation by $KMnO_4$ yielded α-coccinic acid, also obtained from (I) without isolation of (III). Reduction of (I) by Zn dust and AcOH afforded *4-hydroxy-2-ββ-dichloroethyl*-p-*toluic acid* (IV), m. p. 206° [*Ac* derivative, m. p. 160°; Me ester of MeO-derivative (by Me_2SO_4 and NaOH below 45°) identical with that previously described], which yielded *4-hydroxy-5-carboxy*-o-*tolylacetic acid*, m. p. 251° (*Ba* salt, $+2H_2O$, of which $1H_2O$ is lost at 115—120°; Me derivative identical with that previously obtained). On methylation of (IV) above 45°, or on heating its Me derivative with NaOH, HCl was lost, and *5-methoxy-2-β-chlorovinyl*-p-*toluic acid*, m. p. 163° (gives no colour with $FeCl_3$), obtained.

The structure of an internal β-lactone is assigned to the lactone of (I), because the substance does not give a colour with $FeCl_3$, dissolves slowly in hot NaOH, is obtained by heating (I) at 220—223°, forms an *Ac* derivative, m. p. 315° [which with Zn dust and AcOH yields (IV)], and gives (III) on hydrolysis with NaOH and (IV) on treatment with Zn dust and AcOH.

The structure of (II) is assigned, since the substance gives a violet colour with $FeCl_3$, yields an *Ac* derivative, m. p. 216—217° (decomp.), but does not react with semicarbazide or phenylhydrazine, and is reduced by Zn dust and AcOH to *5-hydroxy-2-ethyl*-p-*toluic acid*, m. p. 315° (decomp.). It thus reacts only in the enolic form (contrast A., 1927, 458).

When dry HCl is passed into *m*-cresotic acid and chloral hydrate in conc. H_2SO_4, *4-hydroxy-2-αβββ-tetrachloroethyl*-p-*toluic acid*, m. p. 227—228° (decomp.) (*Ac* derivative, m. p. 197°), is obtained. This yields (III) on hydrolysis by KOH, and (IV) on reduction by Zn dust and AcOH. R. S. CAHN.

Relation between chemical constitution and action on micro-organisms. X. Glycerol and dihalogenohydrin esters of benzoic and simple or substituted hydroxybenzoic acids. T. SABALITSCHKA and H. JEGLINSKI (Arch. Pharm.. 1931, **269**, 228—246; cf. A., 1930, 71; B., 1930, 530).—The phenol coefficients of the following esters (where sufficiently H_2O-sol.) are determined; glycerol α-monobenzoate, 0·5; α-salicylate, m. p. 76°, 0·3 (iso*propylidene ether*, m. p. 49·5°); α-p-*hydroxybenzoate*, m. p. 154° (iso*propylidene ether*, m. p. 124·5°); *α-3-hydroxy*-p-*toluate*, m. p. 98·5°, 1·6 (iso*propylidene ether*, m. p. 48·5°); *α-4-hydroxy*-m-*toluate*, m. p. 82°; *α-5-hydroxy*-o-*toluate*, m. p. 125°, 0·3; *α-6-chloro-3-hydroxy*-p-*toluate*, m. p. 91°, 60; *α-3-chloro-4-hydroxybenzoate*, m. p. 113°, 4·1; *5-iodosalicylate*, m. p. 105°, 9·0; *ββ'-dichloro*iso*propyl benzoate*, b. p. 157—160°/12 mm.; *salicylate*, m. p. 49°; p-*hydroxybenzoate*, m. p. 101·5°, 61; *3-hydroxy*-p-*toluate*, b. p. 192—194°/11 mm.; *4-hydroxy*-m-*toluate*, m. p. 44°; *5-hydroxy*-o-*toluate*, m. p. 104°; *6-chloro-3-hydroxy*-p-*toluate*, m. p. 76°; *β-chloro-β'-iodo*iso*propyl salicylate*, m. p. 57°; glyceryl tri-*p*-hydroxybenzoate, m. p. 190°, 48; *tri-3-hydroxy*-p-*toluate*, m. p. 115°. Staphylococci are killed in 15 min. by ββ'-dichloro*iso*propyl *p*-hydroxybenzoate alone at 0·07% concentration, or in admixture with glycerol α-salicylate in 5 min. at 0·10 concentration (mixture). C. HOLLINS.

Condensation of dichloroacetaldehyde with anisic acid and *p*-nitroanisole. F. D. CHATTAWAY and L. H. FARINHOLT (J.C.S., 1931, 1828—1834).—Condensation of anisic acid with dichloroacetaldehyde alcoholate in presence of H_2SO_4 and HCl gives *2-methoxy-5-carboxy-1-αββ-trichloroethylbenzene*, m. p. 189—190° (*Et* ester, m. p. 69°; *chloride*, m. p. 94°; *amide*, m. p. 156°), the orientation of which depends on its oxidation by alkaline $KMnO_4$ to 4-methoxy*iso*phthalic acid and *ββ-dichloro-αα-di-(5-carboxy-2-methoxyphenyl)ethane*, m. p. 315° (*Me*, m. p. 154°, and *Et*, m. p. 117°, esters; *chloride*, m. p. 134°; *amide*, m. p. 257°; *anilide*, m. p. 209°); the latter is the sole product in absence of HCl. The action of KOH in EtOH on the former gives *αβ-dichloro-5-carboxy-2-methoxystyrene*, m. p. 227—228°. Similarly from *p*-nitroanisole are prepared *5-nitro-2-methoxy-1-αββ-trichloroethylbenzene*, m. p. 140°, and *ββ-dichloro-αα-di-(5-nitro-2-methoxyphenyl)ethane*, m. p. 237°. The former is converted by EtOH–KOH into *αβ-dichloro-5-nitro-2-methoxystyrene*, m. p. 66° (*dichloride*, m. p. 165°, converted by EtOH–KOH into αββ-trichloro-5-nitro-2-methoxystyrene), by oxidation with $KMnO_4$ in $COMe_2$ into 5-nitro-2-methoxybenzoic acid, and by further condensation with *p*-nitroanisole in conc. H_2SO_4 into the above ethane derivative, m. p. 237°. H. A. PIGGOTT.

Preparation and properties of chloromandelic acids, methyl esters, and amides. S. S. JENKINS (J. Amer. Chem. Soc., 1931, **53**, 2341—2343).—The prep. of *o*-chloromandelic acid (*Me* ester, b. p. 134—136°/6 mm.; *amide*, m. p. 87·5°), m-*chloromandelic acid*, m. p. 115—115·5° (*Me* ester, m. p. 84°; *amide*, m. p. 126·5°), and *p*-chloromandelic acid (*Me* ester, m. p. 55·6°) from the corresponding benzaldehyde through the cyanohydrin is described. H. A. PIGGOTT.

Benzylidene- and furfurylidene-pyruvic acids. E. FRIEDMANN (Helv. Chim. Acta, 1931, **14**, 783—793).—KOH is a better condensing agent than NaOH in the prep. of benzylidenepyruvic acid, the *K* salt being obtained in 81—91% yield. Furfurylidenepyruvic acid, m. p. 112° ($+1H_2O$, lost below m. p.) [*phenylhydrazone*, m. p. 164—165°; *Na* salt ($+2H_2O$, lost at 100°)], is similarly prepared by condensation of the components in dil. aq. NaOH (cf. A., 1898, i, 300). It is oxidised by aq. H_2O_2 to β-furfurylacrylic acid. H. A. PIGGOTT.

Resolution of *spiro*heptanedicarboxylic acid. H. J. BACKER and H. B. J. SCHURINK (Rec. trav. chim., 1931, **50**, 921—930).—Improved methods of prep. of pentaerythritol, its tetra-bromide and -iodide, and *spiro*heptanedicarboxylic acid, m. p. 212° (cf. A., 1907, i, 906) [*brucine* ($+6H_2O$), m. p. (anhyd.) 133°, and *strychnine*, m. p. about 238° (decomp.), salts; *dianilide*, m. p. 228], are recorded. The acid is resolved by brucine (cf. A., 1925, i, 359) into the *d*-form, $[M]_D$ +1·9° in Et_2O. *spiro*Heptane-

tetracarboxylic acid [*Ba* (+$7H_2O$) salt] has m. p. 219° (decomp.) (cf. J.C.S., 1912, **101**, 476).

H. BURTON.

Strainless monocyclic rings. I. Isomerism of 1-carboxy-4-methyl*cyclo*hexane-1-acetic acid. Evidence of strainless *cyclo*hexane ring. M. QUDRAT-I-KHUDA (J. Indian Chem. Soc., 1931, **8**, 277—287).—1 - *Carboxy*-4 - *methyl*cyclo*hexane*-1 - *acetic acid* (I; R=OH) $(I)\ CHMe<^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}>C<^{CO_2H}_{CH_2\cdot COR}$ has been isolated in four modifications, each giving different anhydrides and anilic acids (I; R=NHPh). These are considered to be the two pairs of *cis–trans* isomerides derivable from the boat- and chair-shaped *cyclo*hexane rings, which are stabilised by the bulky substituents. Modified directions are given for the prep. of Et 4-methyl*cyclo*hexylidenecyanoacetate, b. p. 165°/12 mm., which on condensation with KCN (cf. A., 1928, 1243) yields *Et* 1-*cyano*-4-*methyl*cyclo*hexane*-1-α-*cyanoacetate*. This on hydrolysis by boiling conc. HCl gives a mixture of isomerides of (I) (R=OH), separable into *acid A*, m. p. 137° (*anhydride*, m. p. 77°; *anilic acid*, m. p. 195°; *anil*, m. p. 130°; *imide*, m. p. 119—120°; p-*toluidinamic acid*, m. p. 199°; p-*toluidinimide*, m. p. 210—215°; β-*naphthylamic acid*, m. p. 200°; β-*naphthylimide*, m. p. 162°), *acid B*, m. 129° (*anhydride*, m. p. 59°; *anilic acid*, m. p. 183°; *anil*, m. p. 142—143°; *imide*, m. p .130°; p-*toluidinamic acid*, m. p. 174°; p-*toluidinimide*, m. p. 134°; β-*naphthylamic acid*, m. p. 192°; β-*naphthylimide*, m. p. 144°), *acid C*, m. p. 174° (*anhydride*, m. p. 104°; *anilic acid*, m. p. 185°; *anil*, m. p. 185°), *acid D*, m. p. 146° (*anhydride*, an oil; *anilic acid*, m. p. 184°), and a little oily residue.

R. S. CAHN.

Lichen substances. IX. Synthesis of divaricatic acid. H. SONN (Ber., 1931, **64**, [*B*], 1851—1852).—*Et* n-*propyldihydroresorcinolcarboxylate*, m. p. 87°, obtained from *n*-Δ^{α}-hexene-α-carboxylic acid, is converted by Br in AcOH into *Et dibromo*-n-*propylresorcinolcarboxylate*, dehydrogenated by H_2 and Pd–$CaCO_3$ to *Et divarate*, m. p. 96—98°. Treatment of the ester with diazomethane in Et_2O affords Et divaricatate [Et 2-hydroxy-4-methoxy-6-*n*-propylbenzoate], m. p. 44°, hydrolysed to divaricatic acid, decomp. 150—160°, identical with the products isolated from *Evernia divaricata* or *illyrica*.

H. WREN.

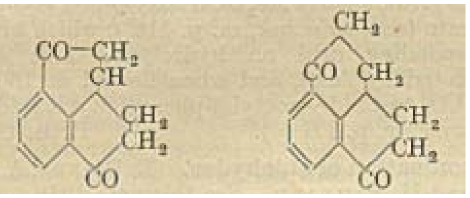
1 : 2-Diketohydrindene-3-acetic acid, a further carbon analogue of isatin. J. VON BRAUN and F. FISCHER (Ber., 1931, **64**, [*B*], 1790—1793).—*Et* 1-*ketohydrindene*-3-*acetate*, b. p. 200—202°/18 mm., is converted by amyl nitrite and conc. HCl in EtOH into *Et* 1-*keto*-2-*oximino*-1-*hydrindene*-3-*acetate*, m. p. 132—133°, hydrolysed to 1-*keto*-2-*oximinohydrindene*-3-*acetic acid*, decomp. about 170° [*Bz* compound, m. p. 137° (decomp.)]; the corresponding *dioxime* and *oximesemicarbazone*, gradual decomp. above 190°, are described. The oximino-acid is transformed by conc. HCl and CH_2O into 1 : 2-*diketohydrindene*-3-*acetic acid*, m. p. 128—130°, the dark blue solutions of which in an excess of aq. KOH are slowly decolorised with formation of o-β-*carboxyethylbenzoylformic acid*, gradual decomp. above 230°. With thiophen and H_2SO_4 the diketo-acid gives the indophenin reaction with scarcely less intensity than does isatin. The *phenylosazone*, $C_{32}H_{20}O_2N_4$, m. p. 184°, and *quinoxaline* derivative, $C_{17}H_{12}O_2N_2$, m. p. 198—200° (decomp.), are described.

H. WREN.

Sulphonation of phthalic anhydride. H. WALDMANN and E. SCHWENK (Annalen, 1931, **487**, 287—294).—Passage of SO_3 in an all-glass apparatus into phthalic anhydride at 190—210° for 66 hr. gives 4-sulphophthalic anhydride (K H_2 and Na H_2 salts of the corresponding acid lose H_2O at 220—230° in vac.), containing only 2·5% of H_2SO_4, and yielding with HCl and $NaClO_3$ 4-chlorophthalic acid. Addition of Hg_2SO_4 to the anhydride causes disulphonation to occur (contrast B., 1930, 941), 3 : 5-*disulphophthalic anhydride* (K_2 H_2 salt of the corresponding acid loses $2H_2O$ of crystallisation at 150°, and passes into the anhydride at 220—230° in vac.) being formed. This with $SOCl_2$ at 180° gives 3 : 5-dichlorophthalic anhydride, passing on boiling in H_2O into 3 : 5-dichlorophthalic acid.

R. S. CAHN.

Benzopolymethylene compounds. XVI. J. VON BRAUN and K. WEISSBACH (Ber., 1931, **64**, [*B*], 1785—1790).—β-Phenylglutaric acid, m. p. 140°, is converted by PCl_5 but not by $SOCl_2$ into the corresponding *chloride*, b. p. 178—180°/18 mm., m. p. 46°, transformed by $AlCl_3$ in CS_2 into 3-ketohydrindyl-1-acetic acid in 80% yield; ill-defined compounds containing S and Cl are also produced. 4-Hydroxydiphenyl is partly hydrogenated in presence of Ni to 4-*cyclo*hexyl*cyclo*hexanol and 4-phenyl*cyclo*hexanol, oxidised by CrO_3 in AcOH to 4-*cyclo*hexyl*cyclo*hexanone and 4-*phenyl*cyclo*hexanone*, m. p. 78° [*$NaHSO_3$* compound; *semicarbazone*, m. p. 229° (decomp.)]. Oxidation of the last-named ketone with alkaline $KMnO_4$ leads to β-phenyladipic acid, m. p. 148° (*Et* ester, b. p. 197—200°/10 mm.), converted into the chloride and thence by $AlCl_3$ in CS_2 into almost equal amounts of the diketone (I), m. p. 149° (*semi-*

(I)  (II)

carbazone, decomp. 395°), and (?)4-*keto*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-1-*acetic acid*, m. p. 60—63° [*semicarbazone*, m. p. 228—230° (decomp.)] (cf. Manske, this vol., 620). γ-Phenylpentane-αε-diol is converted into the corresponding dibromide and thence into αε-dicyano-γ-phenylpentane, b. p. 184—186°/0·15 mm., m. p. 50—51°, transformed into γ-phenylpimelic acid, m. p. 85°. The corresponding chloride is converted by $AlCl_3$ in CS_2 mainly into the diketone (II), m. p. 182—185°/0·3 mm., with smaller quantities of β-4-keto-1 : 2 : 3 : 4-tetrahydronaphthalene-1-propionic acid. The diketone is converted by Reformatsky's reaction into the *substance* $C_{21}H_{24}O_4$, b. p. about 240°/0·1 mm.

H. WREN.

Positive ion catalysis in the Knoevenagel reaction. K. C. BLANCHARD, D. L. KLEIN, and J. MACDONALD.—See this vol., 1017.

Condensation of acetonedicarboxylic acid with phenols and phenolic ethers. I. Formation

of β-substituted glutaconic acids. D. B. LIMAYE and V. M. BHAVE (J. Indian Chem. Soc., 1931, **8**, 137—141).—PhOMe condenses with acetonedicarboxylic acid to give β-*p-anisylglutaconic acid*, m. p. 176° (decomp.) [*Et H* ester, m. p. 126—127°; *monoanilide*, m. p. 190° (decomp.); *anil*, m. p. 204—205°], converted at 180° or by boiling Ac_2O into its *anhydride*, m. p. 160°, and decarboxylated to *p*-*iso*propenylanisole (A., 1901, i, 272). The anhydride reacts with semicarbazide to give a *compound*, m. p. 208·9° (decomp.), a similar *compound*, m. p. 193°, being obtained from β-phenylglutaconic anhydride.

J. W. BAKER.

Constitution of some δ-ketocarboxylic acids. M. QUDRAT-I-KHUDA (J. Indian Chem. Soc., 1931, **8**, 215—221; cf. A., 1929, 1273).—In accordance with expectations from the modified strain theory, but contrary to the statements of Barat (A., 1930, 925), acids of the type $R\cdot CO\cdot CH_2\cdot CHR'\cdot CH(CO_2H)_2$ and the corresponding monocarboxylic acids exist in the open-chain and not the lactol forms, as evidenced by the following reactions. α-Carboxy-γ-benzoyl-β-phenylbutyric acid (I), when heated alone, or with AcCl, yields only the monobasic acid, and not the dilactone; (I) on esterification gives the normal Me_2 ester, and not the OMe-ester of the lactol acid. The constitutions assigned to the anhydride of (I) (A., 1929, 443) and to γ-acetyl-β-phenylbutyric acid (II) (A., 1897, i, 285) are proved correct by reactions described in the literature. (II) and, contrary to the statements of Barat, (I) are sol. in $NaHCO_3$, if finely divided. The Me_2 ester of (I) (*semicarbazone*, m. p. 143°) is conveniently prepared by condensation of $CH_2(CO_2Me)_2$ with Ph styryl ketone in MeOH in the presence of NaOMe, and with KOH in aq. EtOH yields a little Ph styryl ketone and (I) [semicarbazone, m. p. 220°, not 215° (Barat)]. $CH_2(CO_2Me)_2$ and styryl Me ketone give similarly Me_2 α-carboxy-γ-acetyl-β-phenylbutyrate (*semicarbazone*, m. p. 118°), which gives the corresponding acid on hydrolysis. This acid is unaffected by AcCl, and when heated at 160—165° loses CO_2 to yield γ-acetyl-β-phenylbutyric acid (*semicarbazone*, m. p. 171·5°).

R. S. CAHN.

Ozonisation of aldehydes. E. BRINER, A. DEMOLIS, and H. PAILLARD.—See this vol., 1016.

Aldehydes. IV. Catalytic reduction of simple and substituted cinnamaldehydes. M. T. BOGERT and G. POWELL (J. Amer. Chem. Soc., 1931, **53**, 2747—2755).—Reduction of various substituted cinnamaldehydes with H_2 and colloidal Pd in aq. EtOH gives mixtures of the corresponding saturated aldehyde, saturated alcohol, and alkylbenzene. Unsaturated alcohols and alkenylbenzenes were not produced. Thus, 3 : 4-methylenedioxycinnamaldehyde gives dihydrosafrole and γ-3 : *4-methylenedioxyphenylpropyl alcohol*, b. p. 149—150°/6 mm. (*acetate*, b. p. 145°/4 mm.); 3 : 4-methylenedioxy-α-methylcinnamaldehyde affords 3 : *4-methylenedioxy*iso*butylbenzene*, b. p. 238—240°/760 mm., and β-3 : *4-methylenedioxybenzylpropyl alcohol*, b. p. 147—148°/4 mm.; 3 : 4-methylenedioxy-α-ethylcinnamaldehyde yields α-3 : *4-methylenedioxybenzylbutaldehyde*, b. p. 136°/3 mm., β-3 : *4-methylenedioxybenzylbutyl alcohol*, b. p. 148—150°/2 mm., and 3 : *4-methylenedioxy*-1-β-*methylbutylbenzene*, b. p. 255—260°/760 mm.; α-ethylcinnamaldehyde furnishes *α-benzylbutaldehyde*, b. p. 115—116°/12·5 mm., *β-benzylbutyl alcohol*, b. p. 105—107°/4 mm., and β-methylbutylbenzene; α-*n*-amylcinnamaldehyde gives *β-benzylheptyl alcohol*, b. p. 134—135°/3·5 mm. (*acetate*, b. p. 119—120°/2·5 mm.; 3 : 5-*dinitrobenzoate*), and *β-methylheptylbenzene*, b. p. 128—130°/16 mm.; *o*-methoxy-α-methylcinnamaldehyde affords *α-o-methoxybenzylpropaldehyde*, b. p. 113—114°/5·25 mm., *β-o-methoxybenzylpropyl alcohol*, b. p. 131·5—132·5° (corr.)/8·75 mm., and *o*-iso*butylanisole*, b. p. 111—112° (corr.)/31·25 mm.; *o*- and *p*-methoxy-α-ethylcinnamaldehydes yield α-*o*-, b. p. 144—145°/16 mm., and *α-p-methoxybenzylbutaldehydes*, b. p. 116—117°/3 mm., β-*o*-, b. p. 132—134° (corr.)/5·5 mm., and *β-p-methoxybenzylbutyl alcohols*, b. p. 129—130°/2·5 mm., and *o*-, b. p. 100·5—102·5° (corr.)/9 mm., and *p-β-methylbutylanisoles*, b. p. 135—136°/29 mm., respectively. The odours of the above compounds are recorded.

H. BURTON.

Derivatives of veratrole and methylvanillin. III. 4 : 5-Dimethoxy-2-carboxybenzoylformic acid. B. L. VANZETTI and A. OLIVERIO (Gazzetta, 1931, **61**, 479—483).—A new method of preparing this acid is given by oxidation of 5 : 6-dimethoxy-2-oximino-1-hydrindone with cold $KMnO_4$. It forms a dihydrate, m. p. 84—85°, with loss of $2H_2O$ giving the acid, m. p. 151—152°. The aniline (m. p. 179—180°) and *p*-toluidine [m. p. 162—163° (decomp.)] derivatives indicate that it is identical with the acid of Fargher and Perkin (J.C.S., 1921, **119**, 1724).

E. E. J. MARLER.

4 : 4′-Dihydroxydiphenyl-3 : 3′-dialdehyde and its derivatives. R. N. SEN and S. DUTT (J. Indian Chem. Soc., 1931, **8**, 223—229).—Addition of EtOH–$CHCl_3$ (4 : 1) to *pp′*-dihydroxydiphenyl in aq. NaOH at 40—50° and subsequent boiling for 12 hr. gives 4 : *4′-dihydroxydiphenyl*-3 : *3′-dialdehyde* (I) (sol. in NaOH and Na_2CO_3 to give a red solution), yellow, m. p. 185° (*diphenylhydrazone*, m. p. 215°; *disemicarbazone* and *dioxime*, m. p. above 300°; *Bz_2* derivative, m. p. 100°). Condensation with CCl_4 gives 4 : 4′-dihydroxydiphenyl-3 : 3′-dicarboxylic acid. (I) undergoes the benzoin condensation to yield the *substance*

$$\begin{matrix} HO\cdot C_6H_3\cdot CH(OH)\cdot CO\cdot C_6H_3\cdot OH \\ HO\cdot C_6H_3\cdot CH(OH)\cdot CO\cdot C_6H_3\cdot OH \end{matrix} \quad \text{(II), m. p.}$$

above 303° (sol. in NaOH and Na_2CO_3, and reduces Fehling's solution), and condenses with 2 mols. of $COMe_2$ in 40% NaOH solution to yield 4 : *4′-dihydroxy*-3 : *3′-di(β-acetylvinyl)diphenyl*, deep red, m. p. above 300°. On heating with Ac_2O, NaOAc, pyridine, and a little I, (I) yields 6 : *6′-dicoumaryl*, yellowish-brown, decomp. above 200°, precipitated by CO_2 from its solution in NaOH. Azomethine *dyes*, prepared from (I) and the components stated below in hot EtOH, had the following m. p.: NH_2Ph (2 mols.) and NaOAc, reddish-brown, m. p. above 300°; *p*-toluidine (2 mols.) and NaOAc, red, softens at 175°; aminoazobenzene (2 mols.), red, m. p. 260°; benzidine (1 mol.), and *p*-phenylenediamine (1 mol.), reddish-brown, m. p. above 300°; the dye from *m*-phenylenediamine (2 mols.), m. p. above 300°, diazotises and, therefore, has free NH_2 groups. The following pyronine *dyes*, m. p. above 300° in all cases, were pre-

pared from (I) and the phenols stated below in conc. H_2SO_4 at the temp. given, the dye shades being for wool and silk: diethyl-*m*-aminophenol, 120—130°, violet, dyes violet; resorcinol, water-bath, red, dyes orange (K_4 salt; Br_6-derivative, deep red, dyes brilliant red); pyrogallol, water-bath, greyish-black, dyes black with an Fe and green with a Cr mordant salt). (I) with $NPhMe_2$ and HCl on the water-bath, and with *o*-cresotic acid and cold H_2SO_4 gives *leuco-bases*, oxidised by PbO_2 and nitrosyl sulphate, respectively, to triphenylmethane *dyes*. The former, m. p. above 300°, dyes wool and silk bluish-green; the latter, brown, decomp. 225°, dyes wool and silk yellowish-red with Fe, Al, or Cr mordants. R. S. CAHN.

Cyclic ketones. R. POGGI and V. GUASTALLA (Gazzetta, 1931, **61**, 405—432).—Monobenzylidene-*cyclo*hexanone (I) (A., 1908, i, 424) gives an oxime, m. p. 126·5°; a *hydroxylamino-oxime* (with excess of NH_2OH), $OH{\cdot}N{:}(C_6H_9){\cdot}CHPh{\cdot}NH{\cdot}OH$ (1 : 2), m. p. 190° (decomp.), and a *semicarbazone*, m. p. 199° (decomp.). Bromination of (I) gives a *compound*, m. p. 135° (decomp.), which reacts with pyridine giving a *compound*, m. p. 105—107°. Bromination of the *oxime* of (I) gives a *dibromo-oxime*, $OH{\cdot}N{:}(C_6H_8Br){\cdot}CHBrPh$, m. p. 106° (decomp.). Treatment of (I) with $EtNO_3$ (cf. A., 1928, 641) gives an indefinite product. *cyclo*Hexanone condenses with *p*-anisaldehyde giving *mono*-p-*anisylidene*cyclo*hexanone* (II), m. p. 72·5—74° (*oxime*, m. p. 135°). Condensation of (II) with PhCHO or of (I) with *p*-anisaldehyde gives 2-*benzylidene*-6-p-*anisylidene*cyclo-*hexanone*, m. p. 104·5°, disproving Wallach's conclusion that *o*-substituted *cyclo*ketones do not undergo further condensation. On oxidation with peracetic acid *cyclo*hexanone gives a *peroxide*, m. p. 88—91°; (I) gives a mixture of BzOH and adipic acid and dibenzylidene*cyclo*hexanone gives BzOH and an *acid*, $C_{13}H_{14}O_4$, m. p. 174·5°, the results of further oxidation of which suggest that it is α-*benzylideneadipic acid*. Attempts to prepare the oxime and semicarbazone of dibenzylidene*cyclo*hexanone were unsuccessful. Exaltone, $(CH_2)_{14}CO$, does not react with PhCHO or $EtNO_3$. E. E. J. MARLER.

4-Methyl-1-ethinyl*cyclo*hexanol and its rearrangement into 4-methyl*cyclo*hexenyl methyl ketone. H. RUPE and F. KUENZY (Helv. Chim. Acta, 1931, **14**, 701—708).—The Na derivative of 4-methyl*cyclo*hexanone, prepared by action of $NaNH_2$ in dry Et_2O, combines with C_2H_2 with formation of 4-*methyl*-1-*ethinyl*cyclo*hexanol* (I), b. p. 73—75°/10 mm., m. p. 20° (*Ag* salt; *acetate*, b. p. 100—101°/13 mm.; *benzoate*, b. p. 175—176°/11 mm., m. p. 77°), and 1 : 1′-*dihydroxydi*cyclo*hexylacetylene*, m. p. 155°, b. p. 185—190°/11 mm. (*diacetate*, b. p. 186—187°/11 mm., m. p. 57°). The former isomerises in warm 71% HCO_2H into 4-methyl*cyclo*hexenyl Me ketone (II) (A., 1908, i, 402), reduced by Ni and H_2 in EtOH to α-4-methyl*cyclo*hexylethyl alcohol (A., 1911, i, 472) (*acetate*, b. p. 90°/11 mm.). Ozonisation of (I) in CCl_4 and hydrolysis of the product gives β-methyladipic acid, and oxidation with NaOBr gives Δ^1-tetrahydro-*p*-toluic acid (A., 1894, i, 522); (II) with NaOBr gives hexahydro-*p*-toluic acid. MgEtBr adds to (I) in the 1 : 4-positions with formation of β-4-*methyl*cyclo*hexenylbutan*-β-*ol*, b. p. 76—77°/11 mm. (*acetate*, b. p. 84—85°/11 mm.). H. A. PIGGOTT.

Palladium catalyst. II. Effect of hydrogen chloride in hydrogenation of oximinoketones. W. H. HARTUNG (J. Amer. Chem. Soc., 1931, **53**, 2248—2253).—The substance, m. p. 108—110°, obtained by hydrogenation of oximinopropiophenone in EtOH in presence of Pd–charcoal (A., 1929, 1066) is identified by direct comparison as acetylphenylcarbinoloxime, m. p. 113° (corr.; cf. A., 1930, 935). In addition (in two experiments) phenylpropanolamine, two unidentified bases isolated as Bz, m. p. 164° (corr.), and benzenesulphonyl, m. p. 110°, derivatives, respectively, and a *tert.*-amine (?), m. p. 88° (corr.; sinters, 82°), were formed. The oximes of propionylphenyl- and valerylphenyl-carbinols are similarly obtained from oximino-butyro- and -hexophenones. The effect of HCl on the catalytic hydrogenation of α-oximinoketones (cf. A., 1929, 1066; 1930, 1286) is discussed. H. A. PIGGOTT.

Isomerism of phenacylamine oximes. M. BUSCH [with K. KÜSPERT] (Ber., 1931, **64**, [*B*], 1816—1818; cf. A., 1930, 603).—If the evidence of the optical behaviour of phenacyl-*p*-toluidine-*n*-oxime is accepted as conclusive (cf. following abstract), its chemical reactions indicate that it can assume the ψ-oxime structure under certain conditions. Hydroxydiphenyl-*p*-tolyldihydroiminazole (*loc. cit.*) is reduced by Zn dust and AcOH to *diphenyl*-p-*tolyldihydroiminazole*, m. p. 152—153°, dehydrogenated by $FeCl_3$ in EtOH to diphenyl-*p*-tolyliminazole, m. p. 148°. H. WREN.

Structure and isomerism of oximes. K. VON AUWERS and H. WUNDERLING (Ber., 1931, **64**, [*B*], 1806—1816).—The probability suggested by Raikowa (A., 1929, 1276) that under certain conditions isomerisation of the type $R{\cdot}C({:}NOH){\cdot}CH_2R' \longrightarrow R{\cdot}C(NH{\cdot}OH){:}CHR'$ may be impossible is fulfilled by the oximes of mesityl oxide, hexahydrobenzophenone, ω-bromoacetophenone, γ-keto-Δ^α-pentenoic acid and its acetate, ketosuccinic acid and its Et ester, β-benzoylpropionic acid, and other compounds. The many exceptions are held to invalidate the rule. The formation of a red coloration with $FeCl_3$ is not valid evidence of the presence of the ·NH·OH group. Aldoximes generally give the reaction, but frequently only after some hrs. The oximes of $COMe_2$, Ph Pr^β and *tert.*-Bu ketones, and PhCOMe are indifferent, as are those of dibenzyl ketone and hydrindone. Ph Et ketoxime and Me CH_2Ph ketoxime give immediate colorations. Styryl Me ketoxime gives an immediate red colour which is not observed with its α-chloro- and α-bromo-derivatives. Ph styryl ketoxime reacts with $FeCl_3$, whereas its α-halogeno-derivatives do not. It appears probable that the red coloration with $FeCl_3$ given by many oximes does not depend simply on the formation of a complex Fe compound, but that the chloride reacts chemically with the oximes. The (fully described) spectrochemical behaviour of the oximes of MeCHO, *iso*butaldehyde, Me Et ketone, Pr^α Pr^α ketone, Pr^β Pr^β ketone, PhCOMe, Ph Et ketone, Ph Pr^α ketone, Ph Pr^β ketone, and Ph *tert.*-Bu ketone does not distinguish sharply between the suggested structures, but observations with the oximes of

CH_2Ph Me ketone, CH_2Ph Pr^{β} ketone, dibenzyl ketone, *n*-cinnamaldehyde, styryl Me ketone, Ph styryl ketone, and its α-bromo-derivative are more decisive. The optical behaviour of certain simple oximes is not incompatible with Raikowa's hypothesis, which is definitely contradicted by that of other oximes. Since there is no chemical evidence for the assumption of the existence of groups of oximes of differing constitution, the customary uniform conception must be maintained.

The spectrochemical behaviour of the compounds obtained by the action of NH_2OH on phenacyl-*p*-toluidine contradicts the hypothesis that they are isomerides $OH{\cdot}N{:}CPh{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4Me$ and $OH{\cdot}NH{\cdot}CPh{:}CH{\cdot}NH{\cdot}C_6H_4Me$ (cf. A., 1930, 603).

Benzyl isopropyl ketoxime has m. p. 60—61°.

H. WREN.

Condensations by sodium instead of by the Grignard reaction. II. Reaction with benzonitrile. Preparation of diphenylketazine. A. A. MORTON and J. R. STEVENS (J. Amer. Chem. Soc., 1931, **53**, 2769—2772).—PhCN, PhCl, and Na in Et_2O and N_2 afford a red solution of sodiodiphenylmethyleneimine, converted by H_2O, O_2, and I into $COPh_2$, benzophenoneoxime, and diphenylketazine, respectively. PhCN and MgPhBr give the compound $CPh_2{:}N{\cdot}MgBr$, converted by I into diphenylketazine.

H. BURTON.

Benzophenone diazide. S. GOTZKY (Ber., 1931, **64**, [*B*], 1555—1560).—*Benzophenonediazide*, $C_{13}H_{10}N_6$, m. p. 42°, prepared in 88% yield by the action of AgN_3 on benzophenone chloride in Et_2O, is stable at room temp. and little more sensitive than picric acid to shock. It passes in boiling amyl ether, or when distilled under diminished pressure, into N_2 and diphenyltetrazole, m. p. 146°. With MeOH it affords benzophenonedimethylacetal, m. p. 107°. With 70% H_2SO_4 it gives N_2, N_3H, and benzanilide. The last-named product is also obtained when H_2SO_4 or HNO_3 is added to the diazide in C_6H_6. The parachor indicates a cyclic structure of the N_3 group.

H. WREN.

Reduction of aromatic ketones and benzils by magnesium triphenylmethyl bromide. W. E. BACHMANN (J. Amer. Chem. Soc., 1931, **53**, 2758—2763).—Xanthone, fluorenone, $COPh_2$, and 4-chloro-, 4-phenyl-, and 4 : 4′-diphenyl-benzophenones are reduced by $MgCPh_3Br$ to the corresponding pinacols. The initial reaction $COR_2+MgCPh_3Br \longrightarrow CR_2{\cdot}OMgBr+CPh_3$, is followed by association of the free radicals. Benzil, 4 : 4′-dichloro-, and 4 : 4′-dimethyl-benzils are reduced by $MgCPh_3Br$ to the corresponding benzoins; reaction occurs by way of the stilbenediol derivative $(CPh{\cdot}OMgBr)_2$. MgPhI (2 mols.) in Et_2O added to PhCHO (1 mol.) in warm C_6H_6 gives a product containing $CH_2Ph{\cdot}OH$ (25%), $CHPh_2{\cdot}OH$, and $CPh_3{\cdot}OH$ (16%) (cf. Marshall, A., 1925, i, 1428).

H. BURTON.

Preparation of fluorenone from fluorene and from diphenic acid. E. H. HUNTRESS, E. B. HERSHBERG, and I. S. CLIFF (J. Amer. Chem. Soc., 1931, **53**, 2720—2724).—Almost quant. yields of fluorenone are obtained when diphenic acid or anhydride or fluorenone-4-carboxylic acid is heated at 360°. An improved process for the prep. of fluorenone from fluorene is given.

H. BURTON.

Anthracene derivatives. V. E. DE B. BARNETT, J. A. LOW, and F. C. MARRISON. **VI.** E. DE B. BARNETT and C. L. HEWETT (Ber., 1931, **64**, [*B*], 1568—1571, 1572—1581).—V. Me groups in the 2- and 3-position have a similar influence on the properties of 10-bromoanthrone, but the effect is more marked with the 2-compound. When the substituents are present in both positions, an enhanced action is observed. 2-Methylanthrone is converted by Br in CS_2 into 10-*bromo-2-methylanthrone*, decomp. 130°, transformed into 10-p-*dimethylaminophenyl-2-methylanthrone*, m. p. 170° (decomp.) after darkening, and 10-*piperidino-2-methylanthrone*, m. p. 108° (decomp.). 10-*Bromo-3-methylanthrone*, decomp. 118°, yields 10-p-*dimethylaminophenyl-3-methylanthrone*, m. p. 184° (decomp.) after softening, and 10-*anilino-3-methylanthrone*, decomp. about 180°, but is transformed by piperidine in $CHCl_3$ into 10-*bromo-3 : 3′-dimethyldianthrone*, decomp. about 175°. 2-Phenylanthrone is transformed by Ac_2O in pyridine into 2-*phenylanthranyl acetate*, m. p. 158°, and by Br in CS_2 into 10-*bromo-2-phenylanthrone*, decomp. 127°, which yields 2-*phenyl*-10-p-*dimethylaminophenylanthrone*, m. p. 183° (decomp.).

VI. The majority of the abnormalities found in the behaviour of 1 : 4-dimethylanthrone are not observed with the 1 : 3- or 2 : 4-Me_2 compounds. Investigation of the 2- and 3-Me and the 2 : 3-Me_2 derivatives indicates that this effect is not due to a hindering influence of the Me group in the β-position.

1 : 3-Dimethylanthrone, m. p. 119—120°, is obtained in 50% yield by condensation of phthalic anhydride with *m*-xylene followed by dehydration of the product with conc. H_2SO_4 at 100° and reduction with Al powder; 1 : 3-*dimethylanthranyl acetate* has m. p. 153°. *o*-2 : 4-Dimethylbenzoylbenzoic acid is reduced by activated Zn dust to *o*-2 : 4-dimethylbenzylbenzoic acid, converted by 80% H_2SO_4 into 2 : 4-*dimethylanthrone*, m. p. 157° (2 : 4-*dimethylanthranyl acetate*, m. p. 118°). 1 : 3-Dimethylanthrone and Mg benzyl chloride yield 9-*benzyl*-1 : 3-*dimethylanthracene*, m. p. 126°, converted into 10-*bromo*-9-*benzylidene*-1 : 3-*dimethyl*-9 : 10-*dihydroanthracene*, m. p. 139° (decomp.), which with $CaCO_3$ and MeOH yields 10-*methoxy*-9-*benzylidene*-1 : 3-*dimethyl*-9 : 10-*dihydroanthracene*. 2 : 4-Dimethylanthrone and MgMeI afford 2 : 4 : 9-*trimethylanthracene*, m. p. 100°. 9-*Benzyl*-2 : 4-*dimethylanthracene*, m. p. 149°, yields 10-*bromo*-9-*benzylidene*-2 : 4-*dimethyl*-9 : 10-*dihydroanthracene* (or 9-α-*bromobenzyl*-2 : 4-*dimethylanthracene*), m. p. 130°, transformed into 9-α-*methoxybenzyl*-2 : 4-*dimethylanthracene*, m. p. 153°, and the corresponding α-*ethoxy*-compound, m. p. 128°. 10-*Bromo*-1 : 3-*dimethylanthrone*, m. p. about 132° (decomp.), gives the corresponding 10-*piperidino*-, m. p. 122° (decomp.), 10-*anilino*-, m. p. 194° (decomp.) after softening, 10-p-*dimethylaminophenyl*-, m. p. 162° (decomp.), and 10-*methoxy*-, m. p. 79°, derivatives (10-*methoxy*-1 : 3-*dimethylanthranyl acetate*, m. p. 128°). Similarly, 10-*bromo*-2 : 4-*dimethylanthrone*, m. p. 151° (decomp.), gives the corresponding 10-*piperidino*-, m. p. 123°, 10-*anilino*-, m. p. 196° (decomp.), 10-p-*dimethylaminophenyl*-, m. p. 186° (decomp.), and 10-*methoxy*-, m. p.

86°, compounds (2 : 4-*dimethoxyanthranyl acetate*, m. p. 93°). 10-*Phenyl*-1 : 3-*dimethylanthrone*, m. p. 161°, from the 10-bromo-compound, $AlCl_3$ and C_6H_6 (10-*phenyl*-1 : 3-*dimethylanthranyl acetate*, m. p. 149°), is converted by MgMeI into 10-*phenyl*-1 : 3 : 9-*trimethylanthracene*, m. p. 165°. 10-*Phenyl*-2 : 4-*dimethylanthrone*, m. p. 154° (10-*phenyl*-2 : 4-*dimethylanthranyl acetate*, m. p. 203°), gives 10-*phenyl*-2 : 4 : 9-*trimethylanthracene*, m. p. 121°. 10-*Phenyl*-9-*benzyl*-2 : 4-*dimethylanthracene* has m. p. 137°. Reduction of 1 : 3- or 2 : 4-dimethylanthrone with activated Zn, NH_3, and NaOH yields dihydroanthranols converted by HCl in MeOH into 1 : 3-dimethylanthracene, m. p. 82°.
H. WREN.

Mixed benzoins. V. Reversibility of benzoin condensation and preparation of mixed from simple benzoins. J. S. BUCK and W. S. IDE (J. Amer. Chem. Soc., 1931, **53**, 2350—2353).—The reversibility of the reaction of benzoin formation is proved by the formation of mixed benzoins from a simple benzoin (*e.g.*, benzoin, piperoin, or furfuroin) and a suitable aldehyde in aq.-alcoholic KCN. p-*Dimethylaminobenzpiperoin*, m. p. 132° (turbid, clear at 136°), is obtained either from the appropriate aldehydes in the usual way, or from piperoin and *p*-dimethylaminobenzaldehyde as described above.
H. A. PIGGOTT.

Mixed benzoins. VI. Further examples of reversibility. Formation of additive compounds. J. S. BUCK and W. S. IDE (J. Amer. Chem. Soc., 1931, **53**, 2784—2787).—*o*-Chloroanisoin and *p*-NMe_2·C_6H_4·CHO in aq.-alcoholic KCN give *o*-chloro-*p'*-dimethylaminobenzoin; benzanisoin or benzpiperoin with the same aldehyde give *p*-dimethylaminobenzoin. Similarly, benzpiperoin and *o*-Cl·C_6H_4·CHO afford *o*-chlorobenzpiperoin, whilst benzoin with piperoin and furoin yields benzpiperoin and benzfuroin, respectively.

Cryst. additive compounds of 1 mol. of benzoin and 1 mol. of benzpiperoin, anisoin, or piperoin, and of 1 mol. of piperoin with 1 mol. of anisoin or *p*-NMe_2·C_6H_4·CHO, are readily obtained; they do not persist in solution.
H. BURTON.

Pinacol–pinacolin [transformation]. E. BERGMANN and W. SCHUCHARDT (Annalen, 1931, **487**, 225—263).—The synthesis of pinacols from a ketone, Mg, and I (A., 1929, 1067) is considered to proceed by way of $(R_2\dot{C}\cdot O\cdot)_2Mg$ and $\begin{matrix}CR_2\cdot O\\ |\\ CR_2\cdot O\end{matrix}\!>\!Mg$ rather than by formation of "MgI," partly from known facts, and partly because, using Ph α-naphthyl ketone, gradual addition of dioxan causes a ppt. with a varying Mg : I ratio. The I functions by activating the Mg. The Tiffeneau–Meerwein theory of the pinacol–pinacolin transformation is considered too narrow, partly from known facts, and partly for the following reasons.

(*a*) 9-α-Hydroxybenzhydrylfluorenol (I), which with conc. H_2SO_4 or $POCl_3$ gives 9 : 9-diphenylphenanthrone (II) (A., 1913, i, 485), with AcCl or $SOCl_2$ gives 9-benzoyl-9-phenylfluorene (III) [accompanied by (II) in one experiment with $SOCl_2$]. (III) with cold conc. H_2SO_4 gives (II), and is, therefore, the primary product of the transformation, contrary to the above theory. Different results, however, were obtained with the corresponding *p*-anisyl- and *p*-tolyl-pinacols. Me fluorenol-9-carboxylate, Mg, and *p*-bromoanisole gave 9-(*hydroxydi*-p-*anisylmethyl*)*fluorenol* (IV), m. p. 134—137° (variable), which with AcCl or $SOCl_2$ gave 9 : 9-*di*-p-*anisylphenanthrone* (V), m. p. 150°, but tars with $POCl_3$ or conc. H_2SO_4. (V) was synthesised from 9 : 9-dichlorophenanthrone, PhOMe, and $AlCl_3$ in CS_2. 9-*Hydroxy*-9-p-*anisylfluorene*, an oil (from fluorenone and Mg *p*-anisyl bromide), AcCl, and HCl in C_6H_6 gave 9-*chloro*-9-p-*anisylfluorene*, m. p. 147°; transformed by hot MeOH into 9-*methoxy*-9-p-*anisylfluorene* (VI), m. p. 173—174°, which with Na in Et_2O and *p*-anisoyl chloride gave 9-p-*anisoyl*-9-p-*anisylfluorene*, m. p. 137°. This was unchanged by hot AcCl. (VI) with Na in Et_2O, followed by EtOH, yielded 9-p-*anisylfluorene*, m. p. 121°. 9-(*Hydroxydi*-p-*tolylmethyl*)*fluorenol* (VII), m. p. variable (163° to 174—175°) (similarly prepared), with AcCl, $SOCl_2$, or conc. H_2SO_4 gave 9 : 9-*di*-p-*tolylphenanthrone*, m. p. 158°, which with KOH in MeOH gave an acid, probably 2-*di*-p-*methylbenzhydryldiphenyl*-2′-*carboxylic acid*. The fact that this acid was not *p*-toluic acid proves the constitution of the phenanthrone.

(*b*) The diastereomeric forms of phenylnaphthyl- and phenyl-*p*-chlorophenyl-pinacols behave differently on rearrangement. Reduction of Ph α-naphthyl ketone by Zn and AcOH gave the pinacol (*A*), m. p. 159°, or, if air was excluded, a *substance*, $C_{68}H_{50}O_5$, m. p. 234°, which liberates I from KI in AcOH, and yields BzOH on oxidation with CrO_3. A form, m. p. 220°, could not be obtained (cf. A., 1929, 316). Prep. of the pinacol by Gomberg's method gave, under certain conditions, a *substance*, m. p. 215°. The isomeride, m. p. 199° (A., 1929, 1175) (best prepared from Et α-naphthoate and MgPhBr), gave with AcCl, $SOCl_2$, or AcOH and I an amorphous substance, which liberated I from KI in AcOH, whereas isomeride *A* with $SOCl_2$ gave α-naphthyl diphenyl-α-naphthylmethyl ketone (cf. *loc. cit.*), which was synthesised by treatment of diphenyl-α-naphthylmethyl chloride (from the carbinol, AcCl, and HCl in C_6H_6) with Na in Et_2O, followed by α-naphthoyl chloride. No substance, m. p. 180—183°, could be isolated on reduction of *o*-chlorobenzophenone (contrast *loc cit.*). The pinacol, m. p. 164°, from *o*-chlorobenzophenone was unchanged by $SOCl_2$, but with AcCl, or AcOH and 70% H_2SO_4 gave p-*chlorophenyl diphenyl*-p-*chlorophenylmethyl ketone*, m. p. 139°, the constitution of which is proved by hydrolysis with KOH in MeOH to *o*-chlorotriphenylmethane and *o*-chlorobenzoic acid. The isomeric pinacol, m. p. 186°, was unchanged by AcCl, but with AcOH and 70% H_2SO_4, AcOH and I, or $SOCl_2$ gave the above ketone, m. p. 139°.

(*c*) PhNCO and (I) at 120—130°, or at 90° yield diphenylcarbamide, 9-diphenylenephenanthrone, and benzophenone. The following mechanism, involving free radicals, is assumed: (I) $\longrightarrow C_6H_4\cdot\dot{C}(OH)\cdot C_6H_4$ (A) + $\dot{C}Ph_2\cdot OH$ (B): $2A \longrightarrow H_2O + \left[\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\ \ \end{matrix}\right]_2$ (C); $C \rightarrow \begin{matrix}C_6H_4\text{—}CO\quad C_6H_4\\ C_6H_4\text{—}C\text{——}C_6H_4\end{matrix}$; $B \rightarrow Ph_2CO + H$. (VII) similarly gives diphenylcarbamide, 9-diphenylenephenanthrone, and di-*p*-tolyl ketone, but (IV) gives the normal product of pinacolin transformation (V).

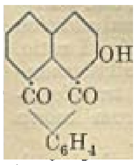
Similar rupture of the ethane C·C linking was observed with xanthonepinacol. This pinacol (H_2O must be excluded during its prep.) with AcCl gives xanthone, dixanthylene, and (probably) *dixanthyl peroxide*, $\left[O{<}{C_6H_4 \atop C_6H_4}{>}CH{\cdot}O{\cdot}\right]_2$, decomp. 237° (liberates I from KI in AcOH). This is interpreted as dehydration to $O{<}{C_6H_4 \atop C_6H_4}{>}C{-}O{-}C{<}{C_6H_4 \atop C_6H_4}{>}O$, which dissociates to xanthone and $O{<}{C_6H_4 \atop C_6H_4}{>}C{:}$, two free radicals then combining to yield dixanthylene. Simultaneously some of the pinacol dissociates to $2O{<}{C_6H_4 \atop C_6H_4}{>}\dot{C}(OH)$, which isomerise to $2O{<}{C_6H_4 \atop C_6H_4}{>}CH{\cdot}O{\cdot}$, and these unite to form the peroxide. Xanthonepinacol and PhNCO yield xanthone and a little dixanthylene. A possible mechanism, involving free radicals, for this reaction is discussed. The velocity of the disproportionation of tetra-arylpinacols, on heating in indifferent solvents, into ketones and secondary alcohols was studied ebullioscopically (1 mol.⟶2 mols.) with xanthopinacol in PhMe, the pinacols of *o*-chlorobenzophenone (m. p. 186° form) and Ph α-naphthyl ketone in *m*-xylene, and benzpinacol in *m*-xylene and PhCl. The reactions are unimol. The heat of activation of benzpinacol and the relative values of the velocity coeff. are in harmony with the assumption that disproportionation is a very rapid reaction, preceded by dissociation into free radicals. This view is supported by the change of the low-melting pinacol of *o*-chlorobenzophenone into the high-melting isomeride on heating in indifferent solvents. The ebullioscopic consts. (determined by fluorene) for PhMe, PhCl, and *m*-xylene are 3·16, 4·42, and 4·09, respectively.

Anthrapinacol with AcCl gave α-anthrapinacolin, m. p. 215°, and in one experiment also a little 9 : 9′-dianthryl, m. p. 300—302°, which was always formed with AcOH and H_2SO_4 (whereas methods of prep. hitherto described often fail). Dianthryl, m. p. 360° (J.C.S., 1923, **123**, 380), could not be obtained. The compound, m. p. 298—300° (A., 1926, 295), described as dihydroantnryl is the above dianthryl, the constitution being proved because, on treatment with Na in Et_2O, followed by CH_2PhCl and H_2O, the ratio of ionic Cl to recovered dianthryl was 3·1 : 1, showing that 4 Na atoms had reacted. The pinacolin has the α-structure because, like α-benzpinacolin, it does not react with MgPhBr, which, contrary to statements in the literature, reacts with β-benzpinacolin in the cold to give pentaphenylethyl alcohol. R. S. Cahn.

Cleavage of β-diketones. I. Cleavage by organic magnesium compounds. E. P. Kohler and J. L. E. Erickson (J. Amer. Chem. Soc., 1931, **53**, 2301—2309).—Highly-enolised β-diketones react with organomagnesium compounds in the monoenolic form; thus dibenzoylmethane reacts with 2 equivs. of MgPhBr, with decomp. of 1 equiv. and addition of the other, to give phenacyldiphenylcarbinol, and acetylacetone with MgMeI gives diacetone alcohol. In the case of mono- and di-substituted derivatives of these ketones, which do not normally exhibit enolic properties, 2 equivs. of Grignard reagent are added, and fission of the primary Mg derivative occurs; *e.g.*, dibenzoylphenylmethane gives deoxybenzoin and triphenylcarbinol on account of fission of the primary additive product: $COPh{\cdot}CHPh{\cdot}CPh_2{\cdot}OMgBr \longrightarrow CPh(OMgBr){:}CHPh + COPh_2$. A slight tendency to fission of this character occurs in the case of the mono-Mg derivative from CH_2Bz_2; consequently PhCOMe and $COPh_2$ are usually found among the reaction products. It is also characteristic of the Mg-enolate of phenacyldiphenylcarbinol, which with MgPhBr gives triphenylcarbinol and ααγγ-tetraphenylpropane-αγ-diol. In some cases it can be avoided; *e.g.*, addition of MgPhBr to dibenzoylphenylmethane at −10° followed immediately by acidification gives tetraphenylpropenone in 67% yield. The interaction of diphenylpropanetrione with MgPhBr gives triphenylcarbinol and benzoin on account of primary attack of the central CO group and subsequent behaviour of the reaction product as a typical β-diketone. The inverse reaction with 1 equiv. only of MgPhBr gives, not the expected carbinol, but its isomeride, *benzoin benzoate*, m. p. 123—124°. Further examples are afforded by the reaction with MgPhBr of αα-dibenzoylethane, which gives propiophenone and triphenylcarbinol, ββ-dibenzoylpropane, which gives $PhCOPr^{\beta}$ and triphenylcarbinol, and dimethylacetylacetone, which gives $MeCOPr^{\beta}$ and αα-diphenylethyl alcohol; dimethylacetylacetone also reacts with Mg mesityl bromide (or iodide?) to give $MeCOPr^{\beta}$ and acetomesitylene (m-*nitrobenzylidene* derivative, m. p. 82°). Mono- and di-bromodibenzoylmethanes interact in an essentially different manner and yield CH_2Bz_2 and β-bromo-ααγ-triphenylpropan-α-ol-γ-one (cf. A., 1905, i, 215) respectively. H. A. Piggott.

Supposed chalkone from phloracetophenone and piperonal. A. Sonn and H. Fischer (Ber., 1931, **64**, [*B*], 1909—1910).—Contrary to Shriner and Kleiderer (A., 1929, 701), the compound $C_{16}H_{12}O_6$ is formed only in very small amount by the condensation of phloracetophenone or pyrogallol with piperonal in alkaline solution. The product appears to be formed when the solution is acidified. It is suggested that it is due to the loss of $1H_2O$ from 2 mols. of phloroglucinol and 1 mol. of piperonal and further loss of $1H_2O$ during desiccation. H. Wren.

Phthalyl-β-naphthol, an instance of *peri*-condensation of phthalic anhydride. A. Rieche and E. Fruhwald (Ber., 1931, **64**, [*B*], 1603—1606).—β-Naphthol and phthalic anhydride in conc. H_2SO_4 containing H_3BO_3 at 160—165° yield 1 : 8-*phthalyl*-β-*naphthol* (I), m. p. 196°, identical with the "hydroxynaphthanthraquinone" of G.P. 298345. It is not reduced by Zn and NaOH and does not react with Br or $NHPh{\cdot}NH_2$ in AcOH. The corresponding *Ac*, m. p. 216°, and *Bz*, m. p. 213°, derivatives are described. It is converted by NaOH at 240—280° into 7-hydroxynaphthoic acid, m. p. 252—253° (Ac derivative, m. p. 222—223°). H. Wren.



(I.)

Isomerism of the compounds $C_5HO_3Br_3$, the so-called tribromotriketopentamethylene and xanthogallic acid. A. Hantzsch and E. Strasser

(Annalen, 1931, **488**, 203—210).—Xanthogallic acid (cf. A., 1888, 1084; 1917, i, 460) and the "tribromotriketopentamethylene" of Hantzsch (A., 1888, 1190; cf. Henle, A., 1907, i, 222) are represented as

$$CO{<}{\begin{matrix}CHBr\cdot CO\\ CBr_2-CO\end{matrix}}\ \text{(I.)}\quad\text{and}\quad CO{<}{\begin{matrix}CBr_2\cdot CO\\ CBr{=}C\cdot OH\end{matrix}}\ \text{(II.)}\quad \text{(II.)}$$

respectively. (I) reacts very slowly with Et diazoacetate, whereas (II) reacts violently. (I) and CH_2N_2 in Et_2O give a *Me ether*, m. p. 109—111°, also formed from the Ag salt of (I) and MeI; an isomeric *Me ether*, m. p. 88°, is obtained from (II) and CH_2N_2. (I) and Br in AcOH afford 1 : 1 : 3 : 3-*tetrabromo*-2 : 4 : 5-*tri-keto*cyclo*pentane*, m. p. 149° (decomp.), whilst (I) and (II) are converted by aq. HBr into penta- and hexabromoacetone, respectively. Xanthogallol (*loc. cit.*) and PCl_5 at 260—290° give octachlorocyclopentene. The non-identity of the above Me ethers suggests that (I) and (II) are stable isomerides; the unusual stability is due to the negative groups in the mol.

H. Burton.

Constitution of embelin. K. S. Nargund and B. W. Bhide (J. Indian Chem. Soc., 1931, **8**, 237—240).—Oxidation of embelin (I) with $KMnO_4$ in $COMe_2$ or aq. NaOH gives *n*-lauric acid (cf. A., 1900, i, 498; 1929, 1306). Hydrolysis of (I) with aq. KOH yields *α-ketomyristic acid*, m. p. 63·8° (*Na* salt; *oxime*, m. p. 94—95°; *semicarbazone*, decomp. above 170°), the constitution of which is proved by oxidation with boiling HNO_3 or alkaline $KMnO_4$ to tridecoic acid. The constitution (I) assigned to embelin (A., 1900, i, 498) is thus confirmed, hydrolysis taking place according to the scheme $C_{11}H_{23}\cdot C{<}{\begin{matrix}CO\cdot C(OH)\\ C(OH)\ CO\end{matrix}}{>}CMe$ (I) $\longrightarrow$ $C_{11}H_{23}\cdot CH{<}{\begin{matrix}CO\cdot CO\\ CO\cdot CO\end{matrix}}{>}CHMe \longrightarrow C_{11}H_{23}\cdot CH_2\cdot CO\cdot CO_2H$ $+Et\cdot CO\cdot CO_2H$ (II) (cf. A., 1908, i, 658). α-Ketomyristic acid could not, however, be isolated.

R. S. Cahn.

Constitution of the active principle of *Embelia ribes*. II. R. Kaul, A. C. Ray, and S. Dutt (J. Indian Chem. Soc., 1931, **8**, 231—235; cf. A., 1929, 1306).—Embelin contains two reactive CH_2 groups, since it condenses with one or two mols. of aldehydes or NO-compounds. It also reacts with HCO_2Et, but the product could not be purified. With HNO_2 it yields a yellow cryst. compound, unstable above 0°. Boiling with dil. HNO_3 oxidises embelin to *n*-lauric acid, and a small quantity of an acid, m. p. 34—35°, which may be impure *n*-lauric acid, or *iso*lauric acid. *n*-Lauric, and not *iso*lauric acid (*loc. cit.*), together with $(CO_2H)_2$ and $CH_2(CO_2H)_2$ are obtained on oxidation with $KMnO_4$. The formula

$C_{11}H_{23}\cdot CO\cdot CH{<}{\begin{matrix}CO\cdot CH_2\\ CO\cdot CH\end{matrix}}{>}CO^*$ is assigned to embelin, the CO groups marked * being considered truly ketonic, and the others capable of keto–enol tautomerism.

The following embelin derivatives were prepared by the method indicated by the letter in parentheses, viz., condensation in (A) H_2SO_4 in EtOH under reflux, (B) dry HCl in abs. EtOH at room temp., or (C) EtOH–AcOH (1 : 1) on the water-bath. *Benzylidene*-, $-H_2O$, (A) (isol. in NaOH; gives a red colour with conc. H_2SO_4 and chars), m. p. 112°; *dibenzylidene*-, $+H_2O$, (B), m. p. 142° (insol. in NaOH, and with conc. H_2SO_4 gives a reddish-violet colour); *disalicylidene*-, $+H_2O$, (A), m. p. 152°; *dianisylidene*-, $+H_2O$, (A), m. p. 167°; *divanillylidene*-, $+H_2O$, (A), m. p. 230°; *di*-p-*toluylidene*-, $+H_2O$, (B), m. p. 244°; *diethylidene*-, $+H_2O$, (B), m. p. 123° (from paraldehyde); *dibutylidene*-, $+H_2O$, (B), m. p. 120°; *bis-phenylimino*-, (C), m. p. 195° (decomp.); *bis*-p-*hydroxyphenylimino*-, (C), m. p. 207°; *bis*-p-*dimethylaminophenylimino*-, (C), m. p. above 290°; p-*dimethylaminophenylimino*-, (B), m. p. above 290°; *bis*-2 : 4-*dihydroxyphenylimino*-, (C), m. p. 230°; *bis*-2-*hydroxynaphthylimino-embelin*, (C), m. p. above 290°. The compounds with aldehydes lose the H_2O of crystallisation with partial decomp. at 120°, or without decomp. at 70° in vac., are yellow to orange-red, form dibromides, and with dil. $KMnO_4$ regenerate the ketone with destruction of the embelin mol. The imino-compounds, which are buff to dark brown, are readily reduced, *e.g.*, by Zn dust and AcOH, to embelin and the aromatic amine; with stronger reducing agents, dihydroembelin is formed.

R. S. Cahn.

Alteration of the additive capacity of quinones by the introduction of substituents. K. Brass and E. Tengler (Ber., 1931, **64**, [*B*], 1654—1664).—Introduction of halogen, NH_2, or OH into quinones generally diminishes their power of forming additive compounds with metallic salts. Particularly in the $SbCl_5$ series, this generalisation is not in harmony with the view that the metallic atom is united with the carbonyl O in the molecular compounds of quinones with metallic salts. It is more probable that the total amount of free valency of the substituted quinone is responsible for the saturation of the metallic atom. The compounds of $SnCl_4$ with dihalogenated anthraquinones appear exceptional. The compounds are prepared from the components in $CHCl_3$, C_6H_6, PhMe, $C_6H_4Me_2$, or $PhNO_2$ at room temp. or (max.) 100°. *Adducts* from the following are described: $2C_{14}H_8O_2$, $SnCl_4$; di-1-chloroanthraquinone, $SbCl_5$; 2-iodoanthraquinone, $SbCl_5$; 2-aminoanthraquinone, $SbCl_5$; 1-aminoanthraquinone, $SbCl_5$; 1 : 2-dibromoanthraquinone, $SbCl_5$ (also $+CHCl_3$); 1 : 2-dibromoanthraquinone, $SnCl_4$; 2 : 3-dibromoanthraquinone, $SbCl_5$, $CHCl_3$; 2 : 3-dibromoanthraquinone, $SnCl_4$; di-2 : 3-dibromoanthraquinone, $AlCl_3$; di-2 : 3-dibromoanthraquinone, $FeCl_3$; di-2 : 3-dibromoquinizarin, $SbCl_5$; di-2 : 3-dibromoquinizarin, $SnCl_4$; di-2 : 3-dibromoalizarin, $SnCl_4$, and the complex salt, $C_{28}H_8O_6(OH)_2Br_4,SnCl_2$; α-naphthaquinone, $SnCl_4$; 2 : 3-dibromo-α-naphthaquinone, $SbCl_5$; 2 : 3-dibromo-α-naphthaquinone, $SnCl_4$; di-β-naphthaquinone, $SbCl_5$; dichloro-β-naphthaquinone, $SnCl_4$; bisdichloro-β-naphthaquinone, $SbCl_5$; 2-bromophenanthraquinone, $SbCl_5$; di-2-bromophenanthraquinone, $SnCl_4$.

H. Wren.

Direct formation of quinones from 2 : 6-disubstituted derivatives of 4-nitrophenol. E. C. S. Jones and J. Kenner (J.C.S., 1931, 1842—1857).—4-Nitro-2 : 6-diphenylphenol decomposes spontaneously in AcOH solution into 2 : 6-diphenyl-1 : 4-benzoquinone, NO, H_2O, and a *substance*, $C_{108}H_{72}O_8$, which is readily oxidised to the quinone by aq. $H_2Cr_2O_7$. The reaction, which is also brought about by heat in absence of a solvent, appears to depend on the pre-

sence of *op*-directing groups in the 2 : 6-positions, and is not undergone by 2-nitro-*s*-xylenol, nor apparently by the 2-Ph or 2-Et derivatives of *p*-nitrophenol. Except in the cases of 4-nitro-2 : 6-diphenyl- and -2 : 6-di-*m*-tolyl-phenols, the evolution of NO is far from quant., and the decomp. is not undergone at all by the 2 : 6-di-*o*-tolyl derivative. The nature of the second org. product also seems to vary with the substituents. In every case, however (with the exception of the 2 : 6-dihalogeno-derivatives, which on thermal decomp. evolve nitrosyl halides in addition to NO), smooth oxidation to quinone is brought about by $Pb(OAc)_4$. The reaction, the mechanism of which is discussed at length, is similar to the thermal decomp. of the quinitrols (A., 1899, i, 30); 3 : 5-dichloro-4-methylquinitrol, when heated with AcOH, gives NO, NOCl, and a little N_2.

s-*Di*-o-, m. p. 50—52°, b. p. 201°/16 mm. (*semicarbazone*, m. p. 142—143°), and s-*di*-m-*tolylacetone*, b. p. 204°/16 mm. (*semicarbazone*, m. p. 92—93°), are obtained by distillation of the Ca tolylacetates. *Di*-p-*tolylacetonesemicarbazone* has m. p. 84—85°. The following are obtained by interaction of the appropriately substituted $COMe_2$ with Na nitromalonaldehyde : 4-nitro-2 : 6-diphenylphenol; 4-*nitro*-2 : 6-*di*-o-*tolyl*-, m. p. 192—193°, -2 : 6-*di*-m-*tolyl*-, m. p. 145°, -2 : 6-*di*-p-*tolyl*-, m. p. 137°, -2 : 6-*diethyl*-, m. p. 130—131°, -2 : 6-*dicarbethoxy*-, m. p. 61°, -2-methyl-6-ethyl-, m. p. 135—136°, and -2-*ethyl-phenol*, m. p. 79—80°; 5-nitro-*m*-2-xylenol, also prepared, together with 2 : 6-xyloquinone, by nitration of *m*-2-xylenol. The following quinones are formed by heating the corresponding nitrophenols with $Pb(OAc)_4$ in glacial AcOH : 2 : 6-diphenyl-1 : 4-benzoquinone; 2 : 6-xyloquinone; 3 : 5-dibromo-2 : 6-xyloquinone; 2 : 6-*di*-o-*tolyl*-, m. p. 124°, 2 : 6-*di*-p-*tolyl*-, m. p. 161° (*quinol*, m. p. 105°), 2-*methyl*-6-*ethyl*-, m. p. 40—41° (*quinol*, m. p. 99—100°), 2 : 6-diethyl- (*quinol*, m. p. 102—103°), and 2 : 6-*di*-m-*tolyl*-1 : 4-*benzoquinone*, m. p. 103—104°.

4-*Amino*-2 : 6-*di*-o-*tolylphenol*, m. p. 215°, obtained by reduction of the corresponding nitrophenol with $SnCl_2$–HCl in AcOH, is converted into 2 : 6-di-o-tolyl-1 : 4-benzoquinone by oxidation with $Na_2Cr_2O_7$ and H_2SO_4 in the usual way. H. A. PIGGOTT.

Synthesis of polyporic acid and atromentin dimethyl ether. P. R. SHILDNECK and R. ADAMS (J. Amer. Chem. Soc., 1931, **53**, 2373—2379; cf. A., 1926, 407).—The prep. of 2 : 5-diphenylquinol (cf. A., 1922, i, 1164) in 65% yield is described. Its 3 : 6-Br_2-derivative, m. p. 237°, is oxidised by benzoquinone in 95% EtOH to 3 : 6-*dibromo*-2 : 5-*diphenylbenzoquinone*, m. p. 224° (uncorr.), which is hydrolysed by NaOH in aq. MeOH to 3 : 6-dihydroxy-2 : 5-diphenylbenzoquinone (polyporic acid : Ac_2 derivative, m. p. 215°), yields of 90% or more being obtained at every stage. Reduction of diacetylpolyporic acid with $SnCl_2$ in $COMe_2$ gives 3 : 6-*diacetoxy*-2 : 5-*diphenylquinol*, m. p. 246° (Ac_2 derivative, m. p. 267—268°).

2 : 5-Dianisylquinol (A., 1922, i, 1164) is converted by bromination in AcOH into 3 : 6-*dibromo*-2 : 5-*dianisylbenzoquinone*, m. p. 282—283°, which is hydrolysed as above to 3 : 6-dihydroxy-2 : 5-dianisylbenzoquinone, m. p. 297—298° (atromentin Me_2 ether). Interaction of benzoquinone and $PhOBu^a$ with $AlCl_3$ in CS_2 gives 2 : 5-*di*-(p-n-*butoxyphenyl*)*benzoquinone*, m. p. 173°. H. A. PIGGOTT.

Action of organomagnesium compounds on halogenated quinones. E. CLAR and J. ENGLER (Ber., 1931, **64**, [*B*], 1597—1602).—Bromoanil is converted by MgMeI into 2 : 3 : 5 : 6-*tetrabromo*-1 : 4-*dihydroxy*-1 : 4-*dimethyl*-1 : 4-*dihydrobenzene*, m. p. 229—230° (decomp.), from which the Br atoms are not removed by KOH in EtOH. 2 : 3-Dichloro-1 : 4-naphthaquinone affords 3-*chloro*-1 : 4-*dihydroxy*-1 : 2 : 4-*trimethyl*-1 : 4-*dihydronaphthalene*, m. p. 115—117°. Chloranil and MgPhBr afford a mixture of 6-*chloro*-1 : 4-*dihydroxy*-1 : 2 : 3 : 4 : 5-*pentaphenyl*-1 : 4-*dihydrobenzene*, m. p. 264—266°, and 3 : 6-*dichloro*-1 : 4-*dihydroxy*-1 : 2 : 4 : 5-*tetraphenyl*-1 : 4-*dihydrobenzene*, m. p. 242° (decomp.). Bromoanil gives 6-*bromo*-1 : 4-*dihydroxy*-1 : 2 : 3 : 4 : 5-*pentaphenyl*-1 : 4-*dihydrobenzene*, m. p. 206° (decomp.), converted by KOH in boiling EtOH into 1 : 4 : 6-*trihydroxy*-1 : 2 : 3 : 4 : 5-*pentaphenyl*-1 : 4-*dihydrobenzene*, m. p. 208—210°. 2 : 4-Dichloro-1 : 4-naphthaquinone is converted by MgPhBr into 1 : 4-*dihydroxy*-1 : 2 : 3 : 4-*tetraphenyl*-1 : 4-*dihydronaphthalene*, m. p. 241·5°, and by $MgC_{10}H_7{}^{\alpha}Br$ into 2 : 3-*dichloro*-1 : 4-*dihydroxy*-1 : 4-*di*-α-*naphthyl*-1 : 4-*dihydronaphthalene*, m. p. 261° (decomp.) after darkening at 249°. H. WREN.

Synthesis and orientation of trichloroanthraquinones and amino-disulphonates of anthraquinone. I. A. A. GOLDBERG (J.C.S., 1931, 1771—1794).—Sulphonation of 1-chloroanthraquinone with 20% oleum at 160° gives the -6-*sulphonate* [*Na* salt; *chloride*, m. p. 207—208° (decomp.)] and -7-*sulphonate* [*Na* salt; *chloride*, m. p. 200—201° (decomp.)], converted by HCl and $KClO_3$ into 1 : 6, and 1 : 7-dichloroanthraquinones, respectively; these are reduced by Zn and aq. NH_3 to 1 : 6-*dichloro*-, m. p. 149—150°, and 1 : 7-*dichloro-anthracene*, m. p. 160—161°. In presence of $HgSO_4$ the sulphonation gives 1-*chloroanthraquinone*-5-*sulphonic acid* [*Na* salt; *chloride*, m. p. 243—244° (decomp.)] and -4 : 5-*disulphonic acid* (*Na* salt), converted by chlorination as above into 1 : 5-dichloro- and 1 : 4 : 5-*trichloro-anthraquinone*, m. p. 254°. By the action of NH_3 on the corresponding chloro-derivative, 1-*aminoanthraquinone*-6-*sulphonic acid* [*Na* salt (+0·5H_2O)] is obtained; *Na* 1-*diethylaminoanthraquinone*-6- (+0·5H_2O) and -7-*sulphonates*, *Na* 1-*aminoanthraquinone*-7-*sulphonate*, and 1-*piperidinoanthraquinone*-6-*sulphonic acid* were similarly prepared. Sulphonation of Na 1-chloroanthraquinone-6-sulphonate gives the -4 : 6- (*Na_2* and *Na H* salts) and -2 : 6-*disulphonic acids* (*Na_2* salt), from which 1 : 4 : 6-*trichloro-anthraquinone*, m. p. 236°, and -*anthracene*, m. p. 158—159°, 1 : 2 : 6-*trichloroanthraquinone*, m. p. 222—223°, *Na* 1-*aminoanthraquinone*-4 : 6- (+2·5H_2O) and -2 : 6-*disulphonates*, and 1-*diethylaminoanthraquinone*-4 : 6-*disulphonic acid* are prepared. Na 1-chloroanthraquinone-5-sulphonic acid gives on further sulphonation the -2 : 5-*disulphonic acid* (*Na_2* salt), converted by chlorination into 1 : 2 : 5-*trichloroanthraquinone*, m. p. 228—230°. 1 : 2-Dichloroanthraquinone is conveniently prepared from 1-chloro-2-aminoanthraquinone by Sandmeyer's reaction, and is converted by sulphonation into its -6- (*Na* salt) and -7-*sulphonic acids* (*Na* salt), from which

1 : 2 : 6- (above) and 1 : 2 : 7-*trichloroanthraquinone*, m. p. 225—226°, are obtained by Ullmann's method. The last-named is similarly prepared from 1-*chloroanthraquinone*-2 : 7-*disulphonic acid* (*Na* salt; *Na* 1-*aminoanthraquinone*-2 : 7-*disulphonate*), obtained from the -7-sulphonic acid, and is converted by reduction into 1 : 2 : 7-*trichloroanthracene*, m. p. 208—209°. 1 : 3-Dichloro- and 1 : 2 : 3-*trichloro-anthraquinone*, m. p. 194—195°, are obtained by diazo-reactions from 1 : 3-dichloro-2-aminoanthraquinone. The former gives on sulphonation 1 : 3-*dichloro*-6- (*Na* salt) and -7-*sulphonic acids* (*Na* salt), converted as usual into 1 : 3 : 6-*trichloro*-, m. p. 212—213°, and 1 : 3 : 7-*trichloro-anthraquinone*, m. p. 216—217°. Similarly, from 1 : 4-dichloroanthraquinone the -6-*sulphonic acid* (*Na* salt) and 1 : 4 : 6-trichloroanthraquinone, from 1 : 8-dichloroanthraquinone the -4-*sulphonic acid* (*Na* salt), 1 : 4 : 5-trichloro- and (by use of a large excess of HCl and $KClO_3$) 1 : 4 : 5 : 8-*tetrachloro-anthraquinone*, m. p. 341—342° (block), and from 1 : 5-dichloroanthraquinone the -2- (*Na* salt; 1 : 2 : 5-*trichloroanthraquinone*, m. p. 235—236°) and -4-*sulphonic acids* (*Na* salt; 1 : 4 : 5-trichloroanthraquinone), the -2 : 8-*disulphonic acid* (crude Na_2 salt), and, in presence of Hg, the -4-*sulphonic acid* and -4 : 8-*disulphonic acid* (isolated as *Na* salts, and identified by conversion into the corresponding chloroanthraquinones) are obtained.

The action of gaseous Cl_2 on Na anthraquinone-1 : 5-disulphonate in conc. H_2SO_4 with I as catalyst at 160° gives 1 : 5-dichloroanthraquinone only. Attempts at nitration of the 1 : 5-, 1 : 8-, 2 : 6-, and 2 : 7-disulphonic acids in conc. H_2SO_4 or oleum at 100° failed. The slow addition of aq. $NaClO_3$ to anthraquinone-1 : 5-disulphonic acid and HCl at 100° gives a small amount of 1-chloroanthraquinone-5-sulphonic acid. The interaction of phthalic anhydride, *o*-chlorophenol, and $AlCl_3$ in tetrachloroethane gives 3′-*chloro*-4′-*hydroxybenzoylbenzoic acid*, m. p. 224—225°, cyclised by H_2SO_4 to 2-*chloro*-3-*hydroxyanthraquinone*, identified by its conversion by PCl_5 in xylene into 2 : 3-dichloroanthraquinone (cf. A., 1930, 1183). H. A. Piggott.

Stereochemistry of diphenyls. Preparation and properties of 1 : 1′-dianthraquinonyl-4 : 4′-dicarboxylic acid. XVII. W. M. Stanley and R. Adams (J. Amer. Chem. Soc., 1931, **53**, 2364—2368).—1-*Chloro-4-cyanoanthraquinone*, m. p. 271—272°, is prepared from the corresponding aminoanthraquinone, and hydrolysed by 86% H_2SO_4 at its b. p. to 1-chloroanthraquinone-4-carboxylic acid; the *Me* ester, m. p. 187·5—188·5°, of this is heated with Cu powder at 265—300° (exothermic reaction), and the product hydrolysed by EtOH–KOH to give 1 : 1′-*dianthraquinonyl*-4 : 4′-*dicarboxylic acid*, m. p. 448° (block, corr.). According to *X*-ray data this should be resolvable, but attempts at this by fractionation of its *di*-l-*menthyl* ester, m. p. 298—299°, or of its quinine salts failed. H. A. Piggott.

Constitution of alkannin. H. Raudnitz, L. Redlich, and F. Fiedler (Ber., 1931, **64**, [*B*], 1835—1841).—The spectroscopic behaviour of alkannin in KOH and H_3BO_3–AcOH solutions differs so widely from that of quinizarin, 5 : 6 : 7 : 8-tetrahydroquinizarin, and naphthazarin that Liebermann and Romer's conception of it as an anthraquinone derivative cannot be maintained. 1 : 4-*Dihydroxy*-5 : 6 : 7 : 8-*tetrahydroanthraquinone*, m. p. 155°, is obtained from 1 : 4-dihydroxy-5 : 6 : 7 : 8-tetrahydronaphthalene and maleic anhydride in presence of NaCl and $AlCl_3$ at 180°. Technical alkannin is purified by dissolution in aq. KOH and precipitation with acid, followed by protracted distillation with steam; repeated dissolution in C_6H_6 and precipitation with ligroin are necessary to remove a previously undetected nitrogenous impurity. When purified through *leucoalkannin acetate*, $C_{24}H_{24}O_8$, in which the presence of two ethylenic linkings is shown by catalytic hydrogenation, it has the composition $C_{15}H_{14}O_4$. When sublimed in vac. at 300° it yields quinizarin in small amount. Oxidation with dil. HNO_3 affords oxalic acid. The close relationship to naphthazarin and the formation of anthracene and 2-methylanthracene on distillation with Zn dust indicate that the substance is 5 : 8-dihydroxy-2-β-methyl-$\Delta^{\alpha\gamma}$-pentadienyl-1 : 4-naphthaquinone. Short action of $SOCl_2$ on alkannin leads to the formation of the *substance* $C_{16}H_{13}O_3Cl$, converted by aq. alkali into alkannin, whereas prolonged action affords the *compound* $C_{16}H_{12}O_3Cl_2$. H. Wren.

Benzanthraquinones. H. Waldmann (J. pr. Chem., 1931, [ii], **131**, 71—81).—The interaction of naphthalene-1 : 2-dicarboxylic anhydride with C_6H_6 and $AlCl_3$ (cf. A., 1930, 1292) gives, in addition to 1-benzoyl-2-naphthoic acid (*Me* ester, m. p. 113—114°), 2-benzoyl-1-naphthoic acid (*Me* ester, m. p. 153—154°). The anhydride also condenses with quinol in presence of $AlCl_3$–NaCl to give 5 : 8-*dihydroxy*-1 : 2-*benzanthraquinone*, m. p. 222° (*Ac* derivative, m. p. 212—214°; Me_2 *ether*, m. p. 185—186°), reduced by Sn and HCl to 5 : 8-*dihydroxy*-1 : 2-*benzoxanthrone*, m. p. 206°, and converted by *p*-toluidine and H_3BO_3 into 5 : 8-*di-p-toluidino*-1 : 2-*benzanthraquinone*, m. p. 310°. By similar condensations of naphthalene-1 : 2-dicarboxylic anhydride with appropriate substances the following are obtained: 6(or 7)-*methyl*-5 : 8-*dihydroxy*-, m. p. 245—246°; 6(or 7)-*chloro*-5 : 8-*dihydroxy*-, m. p. 233—235°; 5 : 6(or 7) : 8-*trihydroxy*-, m. p. 250—251°; 5(or 8)-*chloro*-8(or 5)-*hydroxy*-, m. p. 204—205° (accompanied by the intermediate ketonic *acid*, m. p. 261—262°); and 8(or 5)-*hydroxy*-5(or 8)-*methyl*-1 : 2-*benzanthraquinone*, m. p. 173—175°; 5 : 8-*dihydroxy*-, m. p. 246°, and 5(or 8)-*hydroxy*-1 : 2 : 6 : 7-*dibenzanthraquinone*, m. p. 261—263°. The condensation of 4 : 5-dichlorophthalic anhydride and $C_{10}H_8$ by the Friedel–Crafts method gives 4 : 5-*dichloro-2-naphthoylbenzoic acid*, m. p. 207·5° (*Me* ester, m. p. 151°), dehydrated by conc. H_2SO_4 to 6 : 7-*dichloro*-1 : 2-*benzanthraquinone*, m. p. 227°. Phthalic anhydride and 1 : 4-dichloronaphthalene yield a mixture of acids, cyclised as before to a mixture of three *dichlorobenzanthraquinones, ang.*-, m. p. 248°, and *lin.*-, m. p. 296° and 310°, neither of the two last being identical with the known *lin.*-dichlorobenzanthraquinone; consequently a change in position of a Cl atom is believed to occur during condensation. H. A. Piggott.

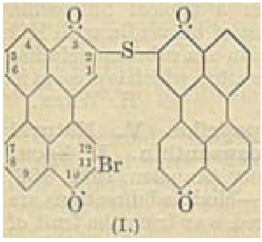
Reduction products of naphthacenequinone. L. F. Fieser (J. Amer. Chem. Soc., 1931, **53**, 2329—2341).—Improvements in the prep. of *o*-tetrahydro-β-naphthoylbenzoic acid and derived tetrahydronaphthanthraquinones (cf. A., 1921, i, 861) are described. Naphthacenequinone is obtained in 81% yield by action of Br in AcOH on 2 : 3-tetrahydronaphthanthraquinone. It is reduced by Sn and glacial AcOH, or by strongly alkaline $Na_2S_2O_4$, to 2 : 3-*benz*-9-*anthrone*, m. p. about 196°, from which it is regenerated by air-oxidation in EtOH–NaOH. Reductive acetylation with Sn, Ac_2O, and NaOAc gives *naphthacenequinol diacetate*, m. p. 269°; Zn gives poor results owing to over-reduction. The quinone is reduced by $Na_2S_2O_4$ in a weakly alkaline EtOH suspension to 10-*hydroxy*-2 : 3-*benz*-9-*anthrone*, m. p. 230°, which enolises readily in boiling pyridine, the solution rapidly acquiring the characteristic deep red colour of naphthacenequinol, which disappears on account of oxidation to quinone on shaking with air; enolisation also occurs with Ac_2O and pyridine, naphthacenequinol diacetate being formed. 9 : 10-*Dihydro*-2 : 3-*benz*-9-*anthranol* is the first product of reduction of the -9-anthrone with Zn and alcoholic alkali, but is best prepared, together with a little dihydronaphthacene, by reduction of naphthacenequinone with Zn and aq. EtOH–NaOH for 1 hr. (more dihydronaphthacene is formed on prolonged reduction); it is dehydrated by gentle heating alone or in EtOH, very rapidly in presence of a trace of HCl, to naphthacene. Naphthacene is also obtained by distillation of 2 : 3-tetrahydronaphthanthraquinone with Zn dust. 10 : 10′-*Di*-(2 : 3-*benz*-9-*anthronyl*) *ether*, m. p. 295°, is obtained in small amount during reduction of the quinone with alkaline $Na_2S_2O_4$, and in good yield by action of S in EtOH in presence of a little alkali on 2 : 3-benz-9-anthrone; it contains no active H (Zerevitinov), but rapidly adds more than 1 mol. of Grignard reagent. It is oxidised by CrO_3, reduced to the anthrone by Sn and AcOH, and converted into the hydroxyanthrone by a drop of H_2SO_4 in Ac_2O. Naphthacenequinol is produced by hydrolysis of its diacetate in an atm. of N_2, a series of colour changes leading finally to a bright red solution which in the course of a few days at the b. p. becomes purple. Acidification at the purple stage results immediately, and at the red stage after about 15 min., in a pale yellow solution containing naphthacenequinone and the anthrone, the products of disproportionation of the quinol. The quinol is also produced, but very slowly, by enolisation of the hydroxyanthrone by alcoholic alkali. The marked tendency of completely aromatic derivatives of naphthacene to pass into dihydro-compounds, and their strong colours, are regarded as evidence in favour of an *o*-quinonoid structure for the hydrocarbon (annexed formula).

H. A. Piggott.

***lin*-Benzanthraquinone series.** H. Waldmann and H. Mathiowetz (Ber., 1931, **64**, [*B*], 1713—1724).—2-Amino-3-naphthoic acid is diazotised and converted into 2-cyano-3-naphthoic acid hydrolysed by H_2SO_4 in AcOH to naphthalene-2 : 3-dicarboxylic anhydride, m. p. 246°. This condenses with $AlCl_3$ in C_6H_6 to 2-*benzoyl*-3-*naphthoic acid*, m. p. 209·5° (*Me* ester, m. p. 119—120°), converted by $AlCl_3$ and NaCl at 130—140° into 2 : 3-benzanthraquinone, m. p. 294°. With PhMe the anhydride affords 2-p-*toluoyl*-3-*naphthoic acid*, m. p. 214°, transformed by the successive action of $SOCl_2$ and $AlCl_3$ in CS_2 into 2-*methyl*-6 : 7-*benzanthraquinone*, m. p. 240—242°. PhCl yields successively 2-p-*chlorobenzoyl*-3-*naphthoic acid*, m. p. 232° (*Me* ester, m. p. 113°), and 2-*chloro*-6 : 7-*benzanthraquinone*, m. p. 245°, converted by conc. NH_3 solution and $CuCl_2$ at 230° into 2-*amino*-6 : 7-*benzanthraquinone*, not molten below 310°. *p*-Chlorophenol smoothly affords 1-*chloro*-4-*hydroxy*-6 : 7-*benzanthraquinone*, m. p. 289°, converted by PCl_5 at 160° into 1 : 4-*dichloro*-6 : 7-*benzanthraquinone*, which with NH_2Ph or *p*-toluidine in presence of KOAc and Cu powder at 185° gives 1 : 4-*dianilino*-, m. p. above 310°, and 1 : 4-*di*-p-*toluidino*-6 : 7-*benzanthraquinone*, not molten below 310°, respectively. 1 : 4-*Di*-p-*toluenesulphonamido*-6 : 7-*benzanthraquinone*, m. p. 290—291°, from the dichloro-compound, *p*-toluenesulphonamide, KOAc, and $Cu(OAc)_2$ in $PhNO_2$ at 200—210°, is transformed by conc. H_2SO_4 at 100° into 1 : 4-*diamino*-6 : 7-*benzanthraquinone*, not molten below 310°. 1-p-*Sulphonamido*-4-*hydroxy*-6 : 7-*benzanthraquinone*, m. p. 281°, from the 1-chloro-compound, yields 1-*amino*-4-*hydroxy*-6 : 7-*benzanthraquinone*, m. p. 295°. Naphthalene-2 : 3-dicarboxylic anhydride with the requisite quinol or substituted quinol in presence of $AlCl_3$ and NaCl affords the following compounds: 1 : 4-*dihydroxy*-6 : 7-*benzanthraquinone*, m. p. 304°, converted by Me *p*-toluenesulphonate and K_2CO_3 in trichlorobenzene at 170—180° into 1 : 4-*dimethoxy*-6 : 7-*benzanthraquinone*, m. p. above 310°, and reduced by Sn and conc. HCl to 1 : 4-*dihydroxy*-6 : 7-*benzoxanthrone*, m. p. 229°; 2-*chloro*-1 : 4-*dihydroxy*-6 : 7-*benzanthraquinone*, m. p. 295—296°; 1 : 4-*dihydroxy*-2-*methyl*-6 : 7-*benzanthraquinone*, m. p. 274—275°; 1 : 2 : 4-*trihydroxy*-6 : 7-*benzanthraquinone*, not molten below 310°. 1 : 4-*Dihydroxy*-2 : 3 : 6 : 7-*dibenzanthraquinone*, m. p. above 310°, is derived from 1 : 4-dihydroxynaphthalene and 4-*hydroxy*-1-*methyl*-6 : 7-*benzanthraquinone*, m. p. 270°, from *p*-cresol. Since phthalic anhydride and α-naphthol yield α-hydroxynaphthacenequinone, the analogous product from naphthalene-2 : 3-dicarboxylic anhydride is regarded as 1-*hydroxy*-2 : 3 : 6 : 7-*dibenzanthraquinone*, not molten below 310°. $C_{10}H_8$ in presence of $AlCl_3$ and CS_2 gives a mixture of 2 : 1′- and 2 : 2′-naphthoylnaphthalene-3-carboxylic acid converted by ring closure into 2 : 3 : 6 : 7-dibenzanthraquinone, m. p. 371—372°, and 1 : 2 : 6 : 7-*dibenzanthraquinone*, m. p. 229°, separable from one another by crystallisation from C_6H_6. 2-*p*-Chlorobenzoyl-3-naphthoic acid is converted by Na_2CO_3, Na_2SO_3, and $CuSO_4$ in H_2O at 180° into *Na* 2-p-*sulphobenzoylnaphthalene*-3-*naphthoate*, transformed by 5% oleum at 150° into 2 : 3-*benzanthraquinone*-2 : 2-*disulphonic acid*. H. Wren.

Action of sodium sulphide on dibromo-3 : 10-perylenequinone. K. Brass and E. Tengler (Ber., 1931, **64**, [*B*], 1646—1649).—Perylene (improved prep. given) is transformed successively into 3 : 10-perylenequinone, decomp. 350°, and dibromo-3 : 10-perylenequinone, decomp. above 400°, which when

reduced and benzoylated affords the Bz_2 derivative of *dibromoperylene*-3 : 10-*quinol*, m. p. 238°. Dibromoperylenequinone is converted by Na_2S at 210—250° into *bromodi*-3 : 10-*perylenequinonyl sulphide* (I), reduced and benzoylated to the Bz_4 derivative of *bromodi*-3 : 10-*perylenequinyl sulphide*, darkening at 240° but not molten below 300°. H. WREN.



Crystalline solvates of rotenone. H. A. JONES (J. Amer. Chem. Soc., 1931, **53**, 2738—2741).—Cryst. solvates of 1 mol. of rotenone and 1 mol. of C_6H_6, CCl_4, and $CHCl_3$, and of 2 mols. of rotenone and 1 mol. of AcOH are prepared. These compounds, when heated, lose the solvents of crystallisation and then melt at 171—179°. Solvates were not formed with $COMe_2$, PhCl, AcOEt, EtOH, and ethylene dichloride. H. BURTON.

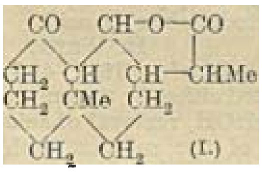
"Yellow compounds" from decomposition of rotenone in solution. H. A. JONES and H. L. HALLER (J. Amer. Chem. Soc., 1931, **53**, 2320—2324).—On exposure to air a pyridine solution of rotenone deposits a mixture of dehydrorotenone and rotenonone; the same changes are undergone more slowly in other solvents, *e.g.*, $COMe_2$, $CHCl_3$, diacetone alcohol, and amylene dichloride. Similar changes are observed with dihydro- and *iso*-rotenones in pyridine. H. A. PIGGOTT.

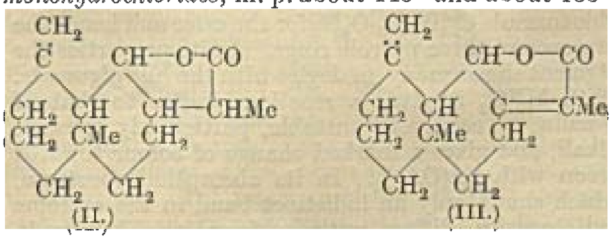
Rotenone. XII. Derivatives of rotenol. H. L. HALLER and F. B. LAFORGE (J. Amer. Chem. Soc., 1931, **53**, 2271—2275).—*Dehydrodihydrorotenol*, m. p. 171°, is produced from dihydrorotenol by action of alkaline $K_3Fe(CN)_6$, and is reconverted into it by Zn and KOH; it does not give an oxime, and is unaffected by boiling Ac_2O and NaOAc. *Dehydrorotenol*, m. p. 124°, is similarly prepared from and reconverted into rotenol, but with H_2 and PtO_2 gives dehydrodihydrorotenol and *dehydrodihydrorotenolic acid*, m. p. 206° [*Ac* derivative (mixed anhydride), m. p. 136°]; the last-named is also the product of reduction of dihydrorotenonic acid with Zn and aq. KOH. Rotenol is converted into *iso*rotenol by H_2SO_4–AcOH at 100°, and this is reduced (Clemmensen) to *deoxyisorotenol*, m. p. 149°, and consequently rotenol and *iso*rotenol are regarded as having ketonic structures; the optical inactivity of *iso*rotenol is also at variance with the alternative alcoholic structure. H. A. PIGGOTT.

Deguelin. II. Relationships between deguelin and rotenone. E. P. CLARK (J. Amer. Chem. Soc., 1931, **53**, 2369—2373).—The oxidation of deguelic acid with alkaline H_2O_2 gives derric acid, and with alkaline $KMnO_4$, risic acid; these are therefore obtained from deguelin by methods similar to those by which they are derived from rotenone (cf. A., 1930, 967; this vol., 491). Dihydrodeguelic acid, obtained by reduction with H_2 and Pt, is identical with "dehydrodihydroxy-β-dihydrorotenonic acid" (this vol., 491), and is oxidised by alkaline H_2O_2 to derric acid. Catalytic reduction (Pt and H_2 in AcOH) of dehydrodeguelin gives a dihydro-derivative identical with dehydro-β-dihydrorotenone (this vol., 491), and converted by oxidation with $Na_2Cr_2O_7$ in aq. AcOH into *oxydehydrodeguelin*, $C_{23}H_{20}O_8$, m. p. 303°, and by Zn and aq.-EtOH–KOH into dihydrodeguelic acid. A non-phenolic mono-*Ac* derivative of deguelic acid, m. p. 128—129°, is obtained by action of a large excess of Ac_2O in pyridine. H. A. PIGGOTT.

Toxicarol. II. Acetyl derivatives. E. P. CLARK (J. Amer. Chem. Soc., 1931, **53**, 2264—2271; cf. A., 1930, 1223).—With Ac_2O and anhyd. NaOAc toxicarol gives a Ac_2 derivative, m. p. 233—236°, reduced by H_2 and Pt in AcOH to *diacetyldihydro*-, m. p. 238—240°, and *monoacetyldihydrodeoxy-toxicarol*, m. p. 156°; the last-named gives *dihydrodeoxytoxicarol*, m. p. 188°, with NaOMe–MeOH. Toxicarol itself is reduced catalytically to *dihydro*-, m. p. 206—209° [*Ac*, m. p. 207° (sinters 200°) and Ac_2 derivatives], and oxidised by alkaline $K_3Fe(CN)_6$ to *dehydro-toxicarol*, m. p. 223° (*Ac* derivative, m. p. 231—232°). Dehydrotoxicarol and its Ac derivative on hydrogenation give dihydro- and acetyldihydro-toxicarol. The action of I in EtOH–KOAc converts toxicarol into an *iododehydro*-derivative, (highest) m. p. 225°, reduced by Zn and AcOH to dehydrotoxicarol. Oxidation of dihydrotoxicarol with alkaline $K_3Fe(CN)_6$ gives *dehydrodihydrotoxicarol*, m. p. 260°. The interrelations of the above products are regarded as indicating the presence of only one true OH group in toxicarol. H. A. PIGGOTT.

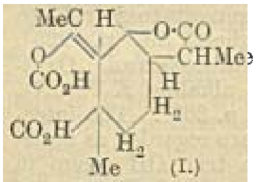
Bitter substances. III. Constitution of *iso*-alantolactone. K. F. W. HANSEN (Ber., 1931, **64**, [*B*], 1904—1908).—The proportion of alanto- to *iso*alanto-lactone is determined by treating the mixture with a small excess of diazomethane in Et_2O, removing the precipitated adduct of diazomethane and the *iso*lactone, and isolation of the adduct of diazomethane and alantolactose from the filtrate. Dihydro-*iso*alantolactone is ozonised in $CHCl_3$ and the ozonide is decomposed with H_2O, thus yielding CH_2O, HCO_2H, and the keto-lactone (I), m. p. 204—205° [*semicarbazone*, m. p. 232—233° (decomp.)], reduced by Zn–Hg and conc. HCl and subsequently dehydrogenated by Se to 2-ethylnaphthalene (picrate, m. p. 69—70°). Dihydro*iso*alantolactone is therefore (II). The expected displaceability of the double linking in the substance is achieved by the action of HCl in Et_2O, whereby a difficultly separable mixture of two *monohydrochlorides*, m. p. about 145° and about 135°, respectively, is obtained. When heated above their m. p. the hydrochlorides lose HCl quantitatively; that of m. p. 145° regenerates the original bitter





substance, whereas that of lower m. p. affords an isomeric *compound*, m. p. 90—91°. Treatment of the *ozonide* from *iso*alantolactone with boiling H_2O is accompanied by complete resinification; CH_2O and HCO_2H are identified in the aq. distillate. Addition of $K_2Cr_2O_7$ and H_2SO_4 and subsequent distillation gives AcOH derived from pyruvic acid. *iso*Alantolactone is therefore (III). H. WREN.

Santonin series. XVI. Constitution and oxidative degradation of santonin. E. WEDEKIND and K. TETTWEILER (Ber., 1931, 64, [B], 1796—1802; cf. this vol., 490).—Santonin chlorohydrin does not react with Br in $CHCl_3$ and α-santonin oxide is stable towards perbenzoic acid. The last-named substance transforms santonin in $CHCl_3$ into α-santonin oxide, m. p. 214° (formerly designated santonin oxide), and *β-santonin oxide*, m. p. 157°. Hydrogenation of the β-compound in presence of Pt-black and MeOH leads to *α-dihydro-β-santonin oxide*, m. p. 146°, and *β-dihydro-β-santonin oxide*, m. p. 117°. O_3 in $CHCl_3$ affects the oxide ring of α-santonin oxide, giving an



ozonide, $C_{15}H_{18}O_6$, m. p. 189°, converted by boiling H_2O into H_2O_2 and santoninketodicarboxylic acid (I) (formerly santononic acid), m. p. 207—208°, which titrates as a monobasic or tribasic acid in cold and hot solution respectively; the *oxime*, decomp., 228° and *quinoxaline* derivative, $C_{21}H_{22}O_5N_2$, m. p. 289° (decomp.), are described. Hydrogenation in presence of Pt-black affords *dihydrosantoninketodicarboxylic acid*, m. p. 174°, whereas oxidation with alkaline $KMnO_4$ gives heptane-ββεζ-tetracarboxylic acid, m. p. 165—166° (decomp.). α-Dihydro-α-santonin oxide is converted by O_3 in $CHCl_3$ into dihydrosantoninketodicarboxylic acid. Santonin and alkaline $KMnO_4$ yield heptanetetracarboxylic and santoninketodicarboxylic acid. H. WREN.

Oocyan. I. R. LEMBERG (Annalen, 1931, 488, 74—90).—The pigment is isolated either by treatment of the egg-shells with HCl in MeOH, removal of acid and porphyrin by agitation of the solution with anhyd. Na_2CO_3, and transference of the pigment to Et_2O or by adsorbing the pigment on the albumin coagulate from aq. HCl, esterifying the MeOH extract, and, after transference to Et_2O, removing porphyrin ester and other impurities by Willstätter's method. *Oocyan Me* ester, m. p. 233—234°, is hydrolysed by Na_2CO_3 in MeOH to *oocyan*. Analytical data combined with determinations of OMe indicate the probable formula $C_{28}H_{31-33}O_6N_3$ for the ester and hence the presence of three pyrrole rings. In its properties the pigment shows many analogies with the bile pigments. With HNO_3 it gives a reaction similar to that of Gmelin, is relatively unstable, particularly towards alkali, and gives a marked change of colour towards green with $Zn(OAc)_2$. In its absorption spectrum, which shows only an indistinct band in the extreme red, oocyan differs entirely from the bilicyanin class, and the Zn salt does not exhibit the typical fluorescence or the absorption in the red. If the solution of the Zn salt is rendered feebly alkaline with NH_3 and preserved, fluorescence bands are developed and HCl liberates a typical bilicyanin. Treatment of different samples of biliverdin with HCl and MeOH leads to the isolation of a substance similar to or identical with oocyan Me ester, which is present in very small proportion. H. WREN.

Colouring matter of paprika. V. Natural and synthetic esters of capsanthin. L. ZECHMEISTER and L. VON CHOLNOKY (Annalen, 1931, 487, 197—213; cf. A., 1930, 479).—Modified directions are given for isolating the coloured wax from the fruit of *Capsicum annuum*. On hydrolysis with KOH in MeOH, this yields capsanthin, m. p. 177—178°, $C_{35}H_{50}O_3$ (or $C_{36}H_{50}O_3$) (not $C_{34}H_{48}O_3$, as hitherto), a yellow cryst. dye, and oleic, myristic, palmitic, carnaubic, and some stearic and unidentified unsaturated acids. Carotene was also isolated. Capsanthin, therefore, occurs as mixed esters. The same acids are obtained from the colourless waxes. Esterification of capsanthin by acyl chlorides in pyridine solution (*diacetate*, m. p. 145—146°; *dipropionate*, m. p. 140°; *dihexoate*, m. p. 102°; *dimyristate*, m. p. 88°; *dipalmitate*, m. p. 85°; *distearate*, m. p. 84°; *dioleate*, m. p. below room temp.; *dibenzoate*, m. p. 121—122°) shows the presence of 2 OH groups, the third O atom forming part of a ring or CO group. The synthetic esters, like the natural products, crystallise in several forms, and mixtures resemble the natural wax in having varying properties, and in being difficult to separate. The diacetate, dihexoate, dipalmitate, and distearate were perhydrogenated, and then yielded perhydrocapsanthin on hydrolysis. Capsanthin is possibly a mixture. All m. p. were taken on a Berl block. R. S. CAHN.

Vegetable dyes. XXXI. Constitution of second form of carotene (α-carotene). P. KARRER and R. MORF. **XXXII. Composition of physalien.** P. KARRER and B. PIEPER. **XXXIII. Constitution of the xanthophylls.** R. NILSSON and P. KARRER. **XXXIV. Dihydrolycopene.** P. KARRER and R. MORF (Helv. Chim. Acta, 1931, 14, 833—838, 838, 843—845, 845—846).—XXXI. Dihydro-α-carotene on complete hydrogenation absorbs 10 H_2 in accordance with its constitution; oxidation with alkaline $KMnO_4$ gives αα-dimethylglutaric acid, pointing to $CH_2{<}\genfrac{}{}{0pt}{}{CH_2\cdot CMe_2}{CH{=}CMe}{>}C{:}[CH\cdot CH{:}CMe\cdot CH]_2{:}CH\cdot CH{:}[CH\cdot CMe{:}CH\cdot CH]_2{:}C{<}\genfrac{}{}{0pt}{}{CMe_2-CH_2}{CHMe\cdot CH_2}{>}CH_2$ as the formula for α-carotene. Hydrolysis of its ozonide gives geronic acid.

XXXII. A small amount of azelaic acid is obtained by ozonisation of cryst. physalien, but not of zeaxanthin, and therefore the dye is not homogeneous, but contains the zeaxanthin ester of an acid, $CHR{:}CH\cdot[CH_2]_7\cdot CO_2H$, probably oleic acid.

XXXIII. The xanthophyll, m. p. 188°, from nettles on catalytic hydrogenation followed by 30% HBr–AcOH at 150° gives an unstable dibromo-derivative, which at 100° passes into a mixture of mono(?)bromo-derivatives; this mixture, when reduced with the Zn–Cu couple and AcOH–H_2O–Et_2O, gives a *hydrocarbon*, $C_{40}H_{78}$, b. p. 244—250°/0·16 mm., $[\alpha]_D$ +0·51° in Et_2O (of the same order as perhydrocarotene).

From the value of $[\alpha]_D$ it is considered that the xanthophyll contains a considerable amount of the α-form, corresponding with α-carotene.

XXXIV. Lycopene when reduced with Al–Hg in moist Et_2O passes into a cherry-red, unstable *dihydro*derivative, m. p. 70° (sinters above 60°).

H. A. PIGGOTT.

Conjugated double linkings. XVIII. Constitution of safran dye. R. KUHN and F. L'ORSA (Ber., 1931, **64**, [*B*], 1732—1736).—Oxidation of crocetin with CrO_3 yields AcOH in amount indicating the presence of 4 Me groups. This result is not in harmony with the crocetin formula $C_{19}H_{22}O_4$, but agrees with $C_{20}H_{24}O_4$. This view is confirmed by fresh elementary analyses, determination of the equiv. of tetradecahydrocrocetin and of the sap. val. of its Me_2 ester, and by the rontgenographic determination of the mol. wt. of crocetin Me_2 ester. Crocin is therefore $C_{44}H_{64}O_{26}$, whilst crocetin is probably $CO_2H\cdot[CMe{:}CH\cdot CH{:}CH]_3\cdot CMe{:}CH\cdot CO_2\cdot H$. *Crocetin Me*$_2$ ester, m. p. 222·5° (corr.), *perhydrocrocetin Me*$_2$ ester, $C_{22}H_{42}O_3$, m. p. 27°, and *perhydrocrocetin* are incidentally described. H. WREN.

Polyterpenoids. IV. Elemic acid. L. RUZICKA, J. R. HOSKING, and A. WICK (Helv. Chim. Acta, 1931, **14**, 811—820).—The method of isolation of elemic acid has been improved, and the previous analyses have been confirmed (cf. A., 1924, i, 1132). It gives with Se at 340° 1 : 2 : 7-trimethylnaphthalene and a hydrocarbon, C_nH_n, m. p. 136—137°, b. p. about 350°, and on dry-distillation a dehydration *product*, $C_{27}H_{40}O_2$, m. p. 200° (not quite pure); it forms additive *compounds*, m. p. 222—223° and 158°, respectively, with $H\cdot CO_2H$ and Ac_2O; these give the acid on long heating with EtOH. Its *Me*, m. p. about 80°, b. p. 250—253°/0·2 mm., and *Et*, m. p. 115—117°, b. p. 268—270°/0·4 mm., esters show an optical exaltation corresponding with two double linkings; hydrogenation of the acid in presence of PtO_2 gives a mixture from which a *dihydro*-derivative, m. p. 246—247° (*Et* ester, m. p. 90°), is isolated. Reduction of the Me ester with Na and amyl alcohol gives a *substance*, $C_{27}H_{44}O_2$, b. p. 255°/0·5 mm. Elemonic acid (*loc. cit.*) contains 2 active H atoms (Zerevitinov), and its *Me* ester, m. p. 146·5—147°, unlike the acid itself, forms an *oxime*, m. p. 184°. On treatment with O_3 in CCl_4 elemic acid absorbs 6 O, but no definite products were isolated.

H. A. PIGGOTT.

Isoprene and caoutchouc. XXXIV. Molecules or micelles in a caoutchouc solution. XXXV. Soluble and insoluble caoutchouc and fractionation of caoutchouc. H. STAUDINGER and H. F. BONDY [with, in part, J. JOSEPH and E. O. LEUPOLD] (Annalen, 1931, **488**, 127—153, 153—175).—XXXIV. A distinction is drawn between depolymerisation, the rupture of larger to smaller mols. of the same polymeric homologous series and ultimately to the monomerides, and disaggregation, the rupture of complexes to ready-formed colloidal particles. The viscosity of caoutchouc solutions exhibits greater alterations in the ϕ values than does that of polystyrene solutions, but it is considered improbable that two complex, colloidal hydrocarbons should have a completely different structure, and the difference is attributed to the greater sensitiveness of caoutchouc in consequence of the presence of double linkings. In dil. solution in tetrahydronaphthalene, caoutchouc exhibits only slight deviations from the Hagen–Poiseuille law; in gel solutions the deviations are more pronounced and increase with increasing concentration. For the determination of the mol. wt. of the most complex caoutchouc fractions by measurements of viscosity, it is necessary to use very dil. solutions; with products of mean mol. wt. 40,000 or less, the deviations from the Hagen–Poiseuille law are so slight that they may be neglected. Decrease in the viscosity of caoutchouc solutions in tetrahydronaphthalene by agitation is not observed in the absence of O_2. Caoutchouc of all degrees of complexity suffers marked degradation when heated at 60° in tetrahydronaphthalene. The presence of traces of O_2 causes caoutchouc to dissolve much more rapidly in tetrahydronaphthalene and to yield sols of much lower viscosity than in the presence of N_2. The stability of solutions of crude caoutchouc in contrast to those of purified or synthetic caoutchouc is due to the presence of anticatalysts which inhibit oxidation. Precipitation of aged and fresh *Hevea* latex and examination of the viscosity of solutions of the ppts. shows that these are much more mobile than solutions of caoutchouc in C_6H_6, probably because of the nearly spherical form of the latex droplets.

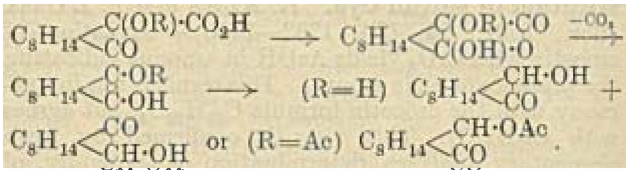
XXXV. Fractionation of caoutchouc in the complete absence of light and O_2 leads to the conclusion that two types must be distinguished. "Sol. caoutchouc," built of thread mols., has the same structure as polystyrene and constitutes a mixture of polymeric homologues (n=500—3000) separable by solvents into fractions. The simplest members have mean mol. wt. < about 100,000 and are sol. in Et_2O, whereas the higher members swell in Et_2O but dissolve in C_6H_6. The most complex products have mol. wt. about 225,000 and the mols. are about 1·5 μ long and about 3·0 Å. in diameter. Pummerer's "gel caoutchouc," sol. in C_6H_6, is a higher fraction of this sol. caoutchouc and consists of thread mols. The second variety, "insol. caoutchouc," swells strongly in C_6H_6 or $CHCl_3$ and is regarded as a three-dimensional macromol. Pummerer's "total caoutchouc" obtained by purifying latex with NaOH consists of varying mixtures of sol. and insol. caoutchouc. Fresh latex contains little insol. caoutchouc, which constitutes aged latex almost exclusively. The transition from the sol. to the insol. variety occurs very readily on contact with air and most rapidly with the fractions of high mol. wt. The change takes place by conversion of the thread mols. into three-dimensional macromols. by O atoms which cannot be detected analytically, since a single O atom suffices for the union of 2 chains of mol. wt. 150,000. The insol. variety can be rendered sol. by chloroacetic and other acids or air; the product is of low viscosity and the action is not therefore a reversal but a rupture of the three-dimensional mols. into short pieces, which again are thread mols., and therefore sol. The majority of the chemical changes of caoutchouc take place with marked degradation of the chains; the products are in the main derivatives of hemicolloidal material. As a consequence of the profound degradation, the same products are derived

from sol. and insol. caoutchouc. The few points of union at which the long chains of sol. caoutchouc are joined in the three-dimensional macromols. of insol. caoutchouc cannot be detected analytically. The union of long thread to three-dimensional mols. influences the physical properties, particularly the solubility, in a very marked degree, but not the chemical properties, since the majority of the isoprene residues remain intact after union. Polystyrene (n= about 3000) with the same length of chain as a non-degraded, sol. caoutchouc (n=1500), behaves similarly with regard to swelling and viscosity, but differs in not exhibiting ageing phenomena. This is explained, since by reason of the saturated C chains it is not autoxidisable and formation of three-dimensional mols. cannot occur. H. WREN.

Rearrangement of acetylenecarbinols from fenchone and tetrahydrocarvone to aldehydes. H. RUPE and F. KUENZY (Helv. Chim. Acta, 1931, **14**, 708—718; cf. A., 1926, 821).—The action of Na and C_2H_2 on fenchone gives in small yield *ethinylfenchyl alcohol*, b. p. 89°/12 mm. (*Ag* salt), which when heated with 86% HCO_2H undergoes rearrangement into *fenchylideneacetaldehyde*, b. p. 121—123°/30 mm. [*semicarbazone*, m. p. 214° (decomp.); *oxime*, resinous].

Interaction of tetrahydrocarvone with C_2H_2 and $NaNH_2$ in C_6H_6 similarly gives 2-*methyl*-5-isopropyl-1-*ethinyl*cyclo*hexanol*, b. p. 104°/9 mm. (*Ac* derivative, b. p. 112—113°/9 mm.), converted by 70% HCO_2H into 2-*methyl*-5-iso*propyl*cyclo*hexylidene*-1-*acetaldehyde* (I) [*semicarbazone*, m. p. 139—140° (decomp.); *oxime*, b. p. 150—153°/10 mm.]. Hydrolysis of the oxime with aq. oxalic acid gives tetrahydrocarvone, but the semicarbazone, in contrast, regenerates the aldehyde. With MgEtBr (2 equivs.) (I) gives γ-*hydroxy*-δ-2-*methyl*-5-iso*propyl*cyclo*hexylidenebutane*, b. p. 112°/12 mm. with partial decomp. into H_2O and a *hydrocarbon*, $C_{14}H_{24}$, b. p. 108—109°/12 mm. Hydrogenation of (I) in presence of Ni gives 2-*methyl*-5-iso*propyl*cyclo*hexyl*-1-*acetaldehyde*, b. p. 103—104°/9 mm. [*semicarbazone*, m. p. 178—179°; *oxime*, m. p. 87° (decomp.)]. Oxidation of (I) with alkaline $KMnO_4$ gives isopropylsuccinic and (probably) β-iso-propyladipic acids. H. A. PIGGOTT.

Hydroxycamphor. IV. 3-Hydroxycamphor and 2-hydroxyepicamphor, and 3-hydroxycamphor-3-carboxylic acid and 2-hydroxy-2 : 3-oxidocamphane-3-carboxylic acid. J. BREDT [with M. FISCHER] (J. pr. Chem., 1931, [ii], **131**, 49—67).—2-Hydroxyepicamphor is converted into an equilibrium mixture with 3-hydroxycamphor by heating with conc. aq. KOH, but not by heating alone at 200—210°, or with pyridine or quinoline. The formation from camphorquinone by the cyanohydrin reaction of two apparently stereoisomeric hydroxycamphorcarboxylic acids, m. p. 184° and 206—207° (cf. J.C.S., 1901, 79, 377), is confirmed. Both give the same *acetate*, m. p. 90—91°, but in the case of the acid of m. p. 184° it is accompanied by an oil that slowly solidifies on keeping and is then identical with the acetate of m. p. 90—91°. This acetate gives on hydrolysis the higher-melting acid, and is slowly decarboxylated at 115—120° to 3-acetoxycamphor, unaccompanied by any epicamphor derivative. This behaviour, and the formation of both 3-hydroxycamphor and 2-hydroxyepicamphor from either of the hydroxycarboxylic acids by decarboxylation (*loc. cit.*) is explained by lactonisation followed by decomp. to the dienolic form, which can rearrange in two ways in the case of the hydroxy-acids, but not in that of the acetoxy-acid :



The acid, m. p. 208—209°, obtained by oxidation of bornylene-3-carboxylic acid with $KMnO_4$ (A., 1909, ii, 499), is not identical, but isomeric, with 3-hydroxycamphor-3-carboxylic acid, differing in cryst. form, and in the m. p. (110—112°) of its *monoacetate* (+$2H_2O$), m. p. 81—82°. It is regarded as 2-hydroxy-2 : 3-oxidocamphane-3-carboxylic acid. H. A. PIGGOTT.

Transformations of camphorquinone. II. Camphorquinone diethylacetal and its rearrangement into 2-hydroxyepicamphor. M. BREDT-SAVELSBERG and E. BUND (J. pr. Chem., 1931, [ii], **131**, 29—48).—Camphorquinone diethylacetal does not react with the usual ketone reagents, but with MgMeI gives β-*hydroxyhomocamphor diethylacetal*, b. p. 130—135°/11 mm., which possesses a single active H atom (Zerevitinov), and on keeping gradually passes into β-*hydroxyhomocamphor*, m. p. 199°. The presence of a CO group in the original substance is also proved by its reduction by Na and EtOH to β-*hydroxycamphor diethylacetal*, b. p. 126—130°/12 mm., which is oxidised by $KMnO_4$ to camphoric acid, and hydrolysed by aq. H_2SO_4 to β-hydroxycamphor, and by MeOH–HCl to its bimol. Me ether and a small amount of a *substance*, $C_{23}H_{15}O_4Cl_2$, m. p. 255—257°; with 65% H_2SO_4 as hydrolysing agent the by-products are epiborneol (*dinitrobenzoate*, m. p. 103°) and an *isomeride* (*dinitrobenzoate*, m. p. 152°). The following *dinitrobenzoates* are also described : α-*hydroxycamphor*, m. p. 129° (additive *compound* with α-naphthylamine, m. p. 184°); β-*hydroxycamphor*, m. p. 151—152° (—α-*naphthylamine*, m. p. 154°); *borneol*, m. p. 154°, $[\alpha]_D^{20}$ +13·38° in toluene (+α-*naphthylamine*, m. p. 140·5°); iso*borneol*, m. p. 133°, $[\alpha]_D^{20}$ +7·19° (+α-*naphthylamine*, m. p. 148°); epiborneol (+α-*naphthylamine*, m. p. 164°). An improved method of prep. of epicamphor is described in which bornylenecarbonyl chloride is heated with NaN_3 at 90° until the calc. vol. of N_2 is evolved, and the resulting product hydrolysed with conc. HCl until the calc. vol. of CO_2 is evolved. H. A. PIGGOTT.

Cedrenene, $C_{15}H_{22}$, and its transformation into cedrene. A. BLUMANN and L. SCHULZ (Ber., 1931, **64**, [*B*], 1540—1545; cf. A., 1929, 1076).—Cedrenol, m. p. 103—104°, obtained by autoxidation of cedarwood oil, is converted by NaOAc and Ac_2O at 130° into cedrenene, d^{15} 0·944, α_D +148° 20′. When in contact with Ac_2O or when distilled under ordinary pressure, the hydrocarbon is partly converted into a

solid *polymeride*, from which it is smoothly regenerated when heated. *Cedrenene dibromide* has m. p. 93—95° (decomp.), $[\alpha]_D$ −375·4° in C_6H_6. The hydrocarbon is also obtained by reduction of cedrenone by Ponndorf's method or by treatment of cedrol with 100% HCO_2H and oxidation of the *l*-cedrene thus produced with O_2 in presence of a Co drier. It is reduced by EtOH and Na to cedrene, identified as cedrenonesemicarbazone. The purest *l*-cedrene, d^{15} 0·9340, α_D −85° 00′, is obtained by treatment of cedrol, $C_{15}H_{26}O$, with HCO_2H. Conversion of cedrene into cedrenone and treatment of the ketonesemicarbazone according to Wolff–Kishner yields a less highly optically active product. H. WREN.

Synthesis of furyl ketones with sodamide. N. MAXIM (Bull. Soc. chim., 1931, [iv], **49**, 891—897).—When treated with $NaNH_2$ in C_6H_6, 2-furyl ketones, $C_4H_3O{\cdot}CHR{\cdot}CH_2{\cdot}COPh$, yield Na derivatives which on alkylation give the ketones, $C_4H_3O{\cdot}CHR{\cdot}CHR'{\cdot}COPh$. The latter with $NaNH_2$ in PhMe are similarly converted, although with greater difficulty, into ketones, $C_4H_3O{\cdot}CHR{\cdot}CR'R''{\cdot}COPh$, the yields being very small when R is an aromatic radical. Cryst. oximes, semicarbazones, and phenylhydrazones were not obtained. Thus β-2-furyl-β-ethylpropiophenone affords β-2-*furyl-α-methyl-β-ethyl-*, b. p. 178°/19 mm.; β-2-*furyl-αα-dimethyl-β-ethyl-*, b. p. 182°/23 mm.; β-2-*furyl-αβ-diethyl-*, b. p. 182°/18 mm., and β-2-*furyl-ααβ-triethyl-propiophenone*, b. p. 176°/12 mm. β-2-*Furyl-β-propylpropiophenone*, b. p. 190°/18 mm. (*semicarbazone*, m. p. 94°), from MgPrBr and furfurylideneacetophenone in Et_2O (yield 70%), similarly gives β-2-*furyl-α-methyl-*, b. p. 198°/28 mm., and β-2-*furyl-αα-dimethyl-β-propylpropiophenone*, b. p. 205°/50 mm., and β-2-*furyl-β-phenylpropiophenone* affords β-2-*furyl-β-phenyl-α-methyl-*, b. p. 222°/22 mm., β-2-*furyl-β-phenyl-αα-dimethyl-*, b. p. 226°/22 mm., and β-2-*furyl-β-phenyl-α-ethyl-propiophenone*, b. p. 275 / 78 mm. (yield 60%, together with an indefinite fraction of higher b. p.). R. BRIGHTMAN.

Action of mixed magnesium organo-compounds on furylideneacetone. N. MAXIM (Bull. Soc. chim., 1931, [iv], **49**, 887—891).—MgMeI, $MgBu^{\beta}I$, Mg *iso*amyl bromide, and MgPhBr with furylideneacetone yield almost exclusively resinous products. MgEtBr in Et_2O gives *γ-2-furylhexan-ε-one*, b. p. 120°/20 mm. (*semicarbazone*, m. p. 112°) (yield, 50%). *γ-2-Furyl-β-methylhexan-ε-one* (61%), b. p. 135°/55 mm. (*semicarbazone*, m. p. 148°), *δ-2-furylheptan-β-one* (50%), b. p. 115°/18 mm. (*semicarbazone*, m. p. 90°), and *δ-2-furylmethylheptan-β-one*, b. p. 116°/18 mm. (*semicarbazone*, m. p. 100°), are similarly obtained from $MgPr^{\beta}Br$, $MgPr^{\alpha}Br$, and $MgBu^{\beta}Br$, respectively. R. BRIGHTMAN.

Derivatives of 4-phenylchroman. P. C. MITTER and P. K. PAUL (J. Indian Chem. Soc., 1931, **8**, 271—276).—2 : 4-Dimethoxybenzophenone, Et bromoacetate, and Zn in C_6H_6 give *Et β-hydroxy-2 : 4-dimethoxy-ββ-diphenylpropionate*, m. p. 79—80°, which could not be dehydrated by Ac_2O and NaOAc, or by AcCl, but passed on distillation in vac. into *Et 2 : 4-dimethoxy-ββ-diphenylacrylate* (I), b. p. 228—232°/11 mm. This is hydrolysed to the corresponding *acid*, m. p. 169—170°, which with AcCl and AcOH gives *7-methoxy-4-phenylcoumarin*, m. p. 114—115° (also obtained by methylation of the condensation product of *Et* benzoylacetate with resorcinol). This with Na and dry EtOH yields *2-hydroxy-4-methoxy-ββ-diphenylpropyl alcohol*, b. p. 253—254°/10 mm., which is converted by dry HCl in EtOH into *7-methoxy-4-phenylchroman*, b. p. 203—204°/10 mm. Reduction of (I) by Na–Hg gave *2 : 4-dimethoxy-ββ-diphenylpropionic acid*, m. p. 129—130° (*Et* ester, m. p. 54°). Resorcinol Me_2 ether, veratroyl chloride, and $AlCl_3$ give *2 : 4 : 3′ : 4′-tetramethoxybenzophenone*, m. p. 126°, which with Et bromoacetate and Zn in C_6H_6, followed by hydrolysis with alcoholic alkali, yields *2 : 4 : 3′ : 4′-tetramethoxy-ββ-diphenylacrylic acid*, m. p. 157°, reduced by Na–Hg to *2 : 4 : 3′ : 4′-tetramethoxy-ββ-diphenylpropionic acid*, m. p. 121°, and converted by AcCl and AcOH into *7-methoxy-4-(3′ : 4′-dimethoxy)-phenylcoumarin*, m. p. 163°. The same coumarin derivative is obtained in better yield when veratroyl chloride is condensed with Et sodioacetoacetate in Et_2O, the product hydrolysed with 10% aq. NH_3 at 40—50°, and the resulting veratroylacetic ester (which decomposes on distillation in vac.) treated with resorcinol Me_2 ether and conc. H_2SO_4 at 0°. It is also formed by methylating *7-hydroxy-4-(3′ : 4′-dimethoxy)-phenylcoumarin*, m. p. 236°, prepared from Et veratroylacetate, resorcinol, and H_2SO_4. On reduction with Na and EtOH it yields *7-methoxy-4-(3′ : 4′-dimethoxy)phenylchroman*, b. p. 263—266°/4 mm., uncrystallisable. R. S. CAHN.

Conversion of 7-hydroxy-3 : 4-dimethylcoumarin into 2 : 4-dimethoxy-αβ-dimethylcinnamic acid. F. W. CANTER and A. ROBERTSON (J.C.S., 1931, 1875—1876).—The product of interaction of resorcinol and Me α-methylacetoacetate in presence of P_2O_5 is 7-hydroxy-3 : 4-dimethylcoumarin (cf. this vol., 963), because on methylation and subsequent hydrolysis it yields *2 : 4-dimethoxy-αβ-dimethylcinnamic acid*, m. p. 133°, oxidised by $KMnO_4$ to 2 : 4-dimethoxyacetophenone. R. S. CAHN.

Reactivity of the methylene group in coumarin-4-acetic acids. III. Condensation of 7-methylcoumarin-4-acetic acid with *m*- and *p*-hydroxybenzaldehydes. B. B. DEY and T. R. SESHADRI (J. Indian Chem. Soc., 1931, **8**, 247—249; cf. A., 1925, i, 953).—The theory previously advanced to explain the colour changes of 7-methyl-4-(4′-hydroxy-3′-methoxystyryl)coumarin (I) in NaOH is supported by the absence of similar changes with the 3′ : 4′-dimethoxy-, 4′-acetoxy-3′-methoxy-, and 3′-hydroxy-compounds, and by their presence with the 4′-hydroxy-compound. (I) with Me_2SO_4 and NaOH gives the *3′ : 4′-(OMe)₂-derivative*, m. p. 188° [sol. in dil. aq. KOH on boiling (by rupture of the pyrone ring) to a faintly yellow solution, from which it is precipitated unchanged by acids], and with Ac_2O and a drop of pyridine the *4′-acetoxy-3′-methoxy-derivative*, m. p. 172°, which is slowly deacetylated by dil. NaOH. Condensation of *p*-hydroxybenzaldehyde and 7-methylcoumarin-4-acetic acid by Knoevenagel's method afforded *7-methyl-4-(4′-hydroxystyryl)coumarin*, m. p. 218°, giving colours with aq. NaOH and conc. H_2SO_4 similar to those given by (I). The *4′-OMe-derivative*, m. p. 180°, dissolves slowly in boiling aq. KOH to a

nearly colourless solution; the 4′-*Ac* derivative, m. p. 209°, dissolves slowly in cold KOH. Both derivatives are precipitated unchanged on acidification of the KOH solutions. *m*-Hydroxybenzaldehyde gave similarly 7-*methyl*-4-(3′-*hydroxystyryl*)*coumarin*, m. p. 207°, sol. in cold dil. NaOH with a pale yellow colour, which fades slowly on keeping and quickly on warming; the yellow solution rapidly, and the colourless solution slowly deposited the substance on acidification. The 3′-*OMe*- and 3′-*OAc*-derivatives, m. p. 146° and 159°, respectively, slowly dissolved in aq. alkalis. R. S. CAHN.

Coumarin series. II. Conversion of substituted coumarins into benzopyrylium salts. I. M. HEILBRON, D. W. HILL, and H. N. WALLS (J.C.S., 1931, 1701—1704; cf. A., 1927, 1082).—MgPhBr converts 3-substituted coumarins into 2-phenylbenzopyrylium salts, but with 4-substituted coumarins the yield is poor, or nil. Chromens result from the use of conc. solutions, or elevated temp. in the latter series. 3-*Methoxycoumarin*, m. p. 162° (from OMe·CH_2·CO_2Na, salicylaldehyde, and Ac_2O at 160°), and MgPhBr in cold Et_2O–C_6H_6 gave 3-*methoxy*-2-*phenylbenzopyrylium chloride* (*ferrichloride*, yellow), but under reflux a mixture of 3-methoxy-2 : 4-diphenylchroman-2-ol and 3-*methoxy*-2 : 4-*diphenyl*-Δ^2-*chromen*, m. p. 172°. 2-Phenyl-3-methylbenzopyrylium chloride (*ferrichloride*, m. p. 132°) and 2 : 3-*diphenylbenzopyrylium chloride*, unstable in air (*ferrichloride*), were similarly prepared. 4-Methylcoumarin gave a poor yield of 2-phenyl-4-methylbenzopyrylium chloride (*ferrichloride*); the yield was the same in conc. solution, but 2 : 2-diphenyl-4-methyl-Δ^3-chromen was the main product. β-*o*-Anisylcinnamic acid and AcCl gave, in the first experiment only, a *modification* of 4-phenylcoumarin, m. p. 92°, passing on melting into the normal form, m. p. 104—105°. This with cold MgPhBr gave a poor yield of 2 : 4-diphenylbenzopyrylium chloride (*ferrichloride*), but in boiling Et_2O gave 2 : 2 : 4-*triphenyl*-Δ^3-*chromen*, m. p. 130°, which was unchanged by boiling AcOH, and on refluxing with aq. or amyl-alcoholic KOH gave a *stereoisomeride*, m. p. 162—163°. 4-Methoxy- and 4 : 7-dimethoxy-coumarin gave no benzopyrylium salt. R. S. CAHN.

Pyryleninium compounds. XVIII. Oxidation products of pyryleninium salts. W. DILTHEY and F. QUINT (J. pr. Chem., 1931, [ii], 131, 1—28).—Pyryleninium salts are readily oxidised by H_2O_2 in AcOH, fission of the ring occurring at the 2 : 3-position with formation of *o*-hydroxybenzoin derivatives, thus indicating a 4-carbonium rather than an oxonium structure; an exception is afforded by the weakly-basic or non-basic NO_2-derivatives, however, which oxidise to coumarins. The condensation of dibenzyl ketone with salicylaldehyde in presence of piperidine gives a mixture of the colourless ψ-*base*, m. p. 166—167° (*Na* salt, red), and the corresponding anhydro-base, 3-*phenyl*-2-*benzylidenebenzopyran* (I), m. p. 112° (*perchlorate*, m. p. 182°). Use of salicylaldehyde Me ether in place of the aldehyde gives a *compound*, m. p. 140—142°, of o-*methoxybenzylidenedibenzyl ketone*, m. p. 138—139°, with piperidine, readily decomposed into its constituents by warming with AcOH, the former of which is demethylated by $AlBr_3$ in boiling C_6H_6 to (I). Oxidation of (I) with H_2O_2 in AcOH gives o-*hydroxydeoxybenzoin phenylacetate*, m. p. 103—104°, and an unidentified substance, m. p. 195—196°; the oxidation is accelerated by acid, and occurs only very slowly in MeOH or EtOH. Hydrolysis of the former with MeOH–KOH gives 2-phenylcoumarone and phenylacetic acid; NH_2OH,HCl and KOH give o-*hydroxydeoxybenzoin oxime*, m. p. 138—139°, hydrolysed by alcoholic HCl to 2-phenylcoumarone. 6-*Nitro*-3-*phenyl*-2-*benzylidenebenzopyran*, m. p. 195—196°, exists in yellow and orange forms, the latter being unstable in solvents and above 165°; it is prepared by use of 5-nitrosalicylaldehyde in the above condensation, and does not form a stable perchlorate. It is oxidised by H_2O_2 in presence or absence of $HClO_4$ to BzOH and 6-*nitro*-3-*phenylcoumarin*, m. p. 252—253°, synthesised for comparison from phenylacetic acid, 4-nitrosalicylaldehyde, and piperidine. 8-*Nitro*-3-*phenyl*-2-*benzylidenebenzopyran*, m. p. 145·5°, similarly prepared, does not form a perchlorate, and is oxidised to 3-*nitro*-3-*phenylcoumarin*, m. p. 238·5—240°. Oxidation of 2 : 3-*diphenylbenzopyryleninium perchlorate*, m. p. 245° (decomp.) (cf. A., 1909, i, 116), gives o-*hydroxydeoxybenzoin benzoate*, m. p. 106—107°, converted as before into 2-phenylcoumarin.

Condensation of deoxybenzoin with *p*-nitrosalicylaldehyde in alcoholic HCl, and addition of $HClO_4$ gives 6-*nitro*-2 : 3-*diphenylbenzopyryleninium perchlorate*, m. p. 245° (decomp.), readily hydrolysed by addition of H_2O to its solution in glacial AcOH to the ψ-*base*, m. p. 162° (*Na* salt), and converted by EtOH and MeOH into the corresponding *Et*, m. p. 126·5—127·5°, and *Me ethers*, m. p. 136—137°. The perchlorate is oxidised by H_2O_2 in AcOH to 3-*nitro*-6-*hydroxydeoxybenzoin benzoate*, m. p. 111—112°, which is hydrolysed to 3-*nitro*-6-*hydroxydeoxybenzoin*, m. p. 182—183°, by dil. NaOH, and regenerated from it by BzCl and pyridine. The same product is obtained from the ethers in EtOH in presence of AcOH, but in its absence they are completely unattacked. Both the benzoin and its Bz derivative are dehydrated by AcOH containing a little H_2SO_4 to ɔ-*nitro*-2-*phenylcoumarone*, m. p. 159—160°; the same product is obtained with P_2O_5 in C_6H_6 in the case of the former. The oxidation product of 2 : 3-dimethylnaphthopyryleninium perchlorate (A., 1926, 1254) is 2-acetoxy-1-naphthylacetone, and is converted by hot 10% NaOH into 2-*methylnaphthocoumarone*, m. p. 57—58°, and by NH_2OH,HCl and KOH in EtOH into 2-*hydroxy*-1-*naphthylacetoneoxime*, m. p. 186°, which gives the coumarone with 70% H_2SO_4. The product from 2-methyl-3-naphthopyryleninium perchlorate (*loc. cit.*) is similarly 2-acetoxy-1-phenacylnaphthalene, and is likewise converted into 2-*phenylnaphthocoumarone*, m. p. 143—144°. The oxidation of 3-phenyl-2-benzylidenenaphthopyran (A., 1928, 767; also obtained with piperidine as condensing agent) gives 1-*phenacyl*-β-*naphthyl phenylacetate*, m. p. 126—127°, converted as before into the coumarone. 2 : 4 : 6-Triphenylpyryleninium perchlorate gives the *O*-Bz derivative of CH_2Bz_2. H. A. PIGGOTT.

Indicators. III. Iodoeosin. I. V. KULIKOV and A. G. PUKIREV (Trans. Inst. Pure Chem. Reag.,

1931, **10**, 46—52).—A diminution of the I content of iodoeosin does not influence its indicator properties. The I content of iodoeosin can be determined by fusion with Na_2CO_3 and $NaNO_3$, followed by reduction with SO_2. E. S. HEDGES.

Oxidative fission of thioindigo-red. E. RIESZ (Ber., 1931, **64**, [*B*], 1893—1894).—*o*-Sulphobenzoic acid is obtained by the oxidation of thioindigo-red with fuming and conc. HNO_3 at 80°. H. WREN.

Supposed isomeride of 1 : 3 : 5-trithian. F. D. CHATTAWAY and E. G. KELLETT (J. Amer. Chem. Soc., 1931, **53**, 2187—2188).—The supposed isomeride, m. p. 247° (decomp.), of 1 : 3 : 5-trithian (Hinsberg, A., 1912, i, 546) is obtained by interaction of H_2S, CH_2O, and aq. HCl; on crystallisation or dissolution, or on exposure to air, by heating at 100°, or by shaking with cold dil. aq. H_2O_2, it is converted into pure 1 : 3 : 5-trithian, m. p. 216°. In the last case reduction of the H_2O_2 is observed. The conversion of 1 : 3 : 5-trithian into this substance is brought about, not only by aq. HI (Hinsberg), but also by other reducing agents, *e.g.*, $SnCl_2$, which do not normally cause inversion in the trithioacetaldehydes. The existence of a stereoisomeride is irreconcilable with the accepted formula of 1 : 3 : 5-trithian, and it is concluded that the supposed isomeride is an unstable reduction product. H. A. PIGGOTT.

Oxidation of dithioparachoral. F. D. CHATTAWAY and E. G. KELLETT (J. Amer. Chem. Soc., 1931, **53**, 2182—2187).—2 : 6 - Bistrichloromethyl - 4-dichloromethylene-1 : 3 : 5-oxadithian is oxidised by an excess of H_2O_2 in cold AcOH to the *dioxide*, m. p. 166—167°, which is unaffected by Cl_2 or Br in the cold or by Sn in boiling HCl–AcOH. Dithioparachloral (α- or β-) is oxidised only with difficulty, and then with elimination of HCl from two $\cdot CH\cdot CCl_3$ groups and complete loss of one of them; thus by CrO_3 in AcOH it is converted into 2 : 6-*bisdichloromethylene*-1 : 3 : 5-*oxadithian* 3 : 3 : 5 : 5-*tetroxide*, m. p. 185° (4 : 4-*dichloro*-derivative, m. p. 143°), a little of the above dioxide, and decomp. products. With warm 10% aq. NaOH, or KOAc in EtOH, or Cl_2 in warm AcOH the dioxide gives 6-*trichloromethyl*-2 : 4-*bisdichloromethylene* - 1 : 3 : 5 - *oxadithian* 3 : 3 - *dioxide*, m. p. 148°, but with aq.-EtOH–NaOH *Et* 2 : 6-*bisdichloromethyl* - 1 : 3 : 5 - *oxadithian* 3 : 3 - *dioxide* - 4-*carboxylate*, m. p. 112·5°, is formed; the corresponding *Me* ester, m. p. 126°, is similarly prepared. These esters could not be hydrolysed to acids. By Cl_2 in AcOH the Et ester is converted successively into *Et* 6-*chloro*-, m. p. 151—152°, and 4 : 6-*dichloro*-6 - *trichloromethyl* - 2-*dichloromethylene* - 1 : 3 : 5 - *oxadithian* 3 : 3-*dioxide*-4-*carboxylate*, m. p. 161·5°.
H. A. PIGGOTT.

Compounds of tungsten and molybdenum sulphides with sulphides of organic [bases]. L. DEBUCQUET and L. YELLUZ (Compt. rend., 1931, **193**, 58—60).—Prolonged passage of H_2S into solutions of MoO_3 or WO_3 (freshly precipitated from Na_2WO_4, and dialysed) in piperidine or piperazine hydrate gives double *salts*, of which the following are described: $(WS_3,C_4H_{10}N_2)_2,H_2S$, lemon-yellow, decomp. on heating, passing on crystallisation from piperazine hydrate into $WS_3,(C_4H_{10}N_2)_2,H_2S$, ochre-yellow; $MoS_3,(C_5H_{11}N)_2,H_2S$, ruby-red; $MoS_3,C_4H_{10}N_2,H_2S$, brick-red, unchanged by crystallisation from piperazine hydrate. The formulæ are confirmed by hydrolysis by dil. HCl to metallic sulphide, hydrochloride of the base, and H_2S. R. S. CAHN.

Piperidine derivatives. XI. Ethyl 4-piperidone-3-carboxylate and 4-piperidone hydrochloride. G. M. KUETTEL and S. M. MCELVAIN (J. Amer. Chem. Soc., 1931, **53**, 2692—2696).—ββ'-Dicarbethoxydiethylamine (*hydrochloride*, m. p. 79·5—80·5°) (improved method of prep. given) and Na in xylene at 85° give 11% of Et 4-piperidone-3-carboxylate [*hydrochloride*, m. p. 168—169° (decomp.)], hydrolysed by 20% HCl to 4-piperidone [*hydrochloride* (+1·5EtOH), m. p. 139—141° (decomp.), (+H_2O), m. p. 92—94°]. H. BURTON.

Pyridine derivatives. XII. Mercaptans and sulphonic acids of pyridine. C. RATH. **XIII. 2-Pyridine-3-arsinic acid.** A. BINZ and H. MAIER-BODE. **XIV. Derivatives of 3-cyanopyridine.** C. RATH and F. SCHIFFMANN (Annalen, 1931, **487**, 105—119, 119—126, 127—134).—XII. The following are prepared by interaction of the corresponding chloro-derivatives with KSH in MeOH: 5-*nitro*-2-*thiolpyridine*, m. p. 168° (decomp.) (*disulphide*, m. p. 150—151°); 5-*chloro*-, m. p. 198° (*disulphide*, m. p. 80°), 5-*bromo*-, m. p. 203—204° (*disulphide*, m. p. 102°), 5-*iodo*-, m. p. 210—211° (in poor yield: *disulphide*, m. p. 155°), 3-*chloro*-5-*nitro*-, m. p. 193—194° (*disulphide*, m. p. 203—204°), 3-*bromo*-5-*nitro*-, m. p. 189° (decomp.), and 3-*iodo*-5-*nitro*-2-*thiolpyridine*, m. p. 195° (decomp.); 2-*thiolpyridine*-5-*carboxylic acid*, m. p. 272° (decomp.) (*Au* salt, m. p. 253°), and 3-*chloro*-2-*thiolpyridine*-5-*carboxylic acid*, m. p. 235°. The above disulphides are prepared by means of aq. H_2O_2 or I in MeOH. Interaction of 2-chloro-5-iodopyridine with KSH (1 equiv.) in MeOH at 130° gives 2-thiolpyridine and the disulphide; the former is also produced from 5-iodo-2-hydroxypyridine and P_2S_5. 5-*Amino*-2-*thiolpyridine*, m. p. 170—171°, is prepared by reduction of the 5-nitro-derivative with $SnCl_2$ and HCl.

Chlorocyanopyridines are converted by NaSH in MeOH into thioamides of the corresponding thiolpyridinecarboxylic acids from which the acids themselves are produced by hydrolysis with conc. HCl at 120°. 2-*Thiolpyridine*-3-*thiocarboxylamide*, m. p. 252° (decomp.), 3-*chloro*-, m. p. 193° (decomp.), 3-*bromo*-, m. p. 195° (decomp.) (*carboxylic acid*, m. p. 230°), and 3-*iodo*-2-*thiolpyridine*-5-*thiocarboxylamide*, m. p. 194° (decomp.) [*carboxylic acid*, m. p. 232° (decomp.)], are described.

3-*Nitro*-, decomp. 260°, and 3-*bromo*-2-*amino*-*pyridine*-5-*sulphonic acid*, m. p. above 300°, are produced by nitration and bromination, respectively, of the aminosulphonic acid. The *chloride*, m. p. 51°, of 2-*chloropyridine*-5-*sulphonic acid*, m. p. 265° (*amide*, m. p. 159°), is prepared by heating 2-hydroxypyridine-5-sulphonic acid with PCl_5 and a drop of $POCl_3$ to 130—140°. The *chloride*, m. p. 72°, of 2-*chloro*-3-*bromopyridine*-5-*sulphonic acid*, m. p. above 280° (*amide*, m. p. 150°), is similarly prepared from the crude residue obtained by evaporating a diazotised solution of 3-bromo-2-aminopyridine-5-sulphonic acid.

XIII. 2-*Pyridone-3-arsinic acid*, m. p. 219—220° (*NaH* and Na_2 salts; N-*Me* derivative, m. p. 255—257°), is prepared in the usual way from 3-amino-2-hydroxypyridine, and is more stable to hydrolysis than is the corresponding -5-arsinic acid. It is converted into 2-*pyridone-3-arsenious oxide*, m. p. 244—247°, and 3 : 3′-*arseno*-2 : 2′-*pyridone* by reduction with H_2S and a little HI, and HPO_2, respectively: the former interacts with PhSH at 130° with formation of 2-*pyridone-3-diphenylthiolarsine*, m. p. 132°, the N-*Me* derivative, m. p. 122°, of which is similarly obtained from 1-*methyl-2-pyridone-3-arsinic acid*, decomp. 255—257° itself obtained by methylation. The product of fusion of 2-pyridone with arsenic acid (A., 1930, 486) is separated by fractional precipitation with MeOH of the aq. NaH salts into 2-pyridone-3- and -5-arsinic acids. 1-Methyl-2-pyridone under similar conditions gives the -3-arsinic acid only.

XIV. The presence of substituents, reactive or otherwise, in the 2-position, does not inhibit the formation of nitrile through the diazo-compound from 3- or 5-aminopyridines. The following are described: 5-*cyano-2-methylpyridine*, m. p. 84—85°, b. p. 216—217°/750 mm. (*hydrochloride*, m. p. 210°), hydrolysed by 50% H_2SO_4 to the -5-carboxylic acid; 5-*cyano-2-hydroxypyridine*, m. p. 252—253° (also prepared by diazotising 5-cyano-2-aminopyridine); 2-*chloro-5-cyanopyridine*, m. p. 115°, hydrolysed by aq. HCl at 150° to 2-hydroxy- [*Et* ester, m. p. 150° (N-*Me* derivative, m. p. 74°, b. p. 190—200°/15 mm.)], and by HCl and Et_2O (A., 1898, i, 196) to 2-chloropyridine-5-carboxylic acid and *amide*, m. p. 205°; 2 : 3-*dichloro-5-cyanopyridine*, m. p. 150°, hydrolysed by HCl and Et_2O to the -5-*carboxylic acid*, m. p. 168°; 2-*chloro-3-bromo-5-cyano-*, m. p. 160°, 2-*chloro-3-iodo-5-cyano-*, m. p. 148°, 5-*iodo-3-cyano-2-hydroxy-*, and 2 : 5-*dichloro-3-cyano-pyridine*, m. p. 118—119°. 2-*Aminopyridine-5-carboxylic acid*, decomp. 310—312°, is obtained by heating the nitrile with conc. HCl to 150—170°. Interaction of 2-chloro-5-cyanopyridine with MgMeI gives 2-*chloro-5-pyridyl methyl ketone*, m. p. 104° (*phenylhydrazone*, m. p. 164°), and the -5-carboxylamide. H. A. PIGGOTT.

Benzyl derivatives of pyridine. J. VON BRAUN and W. PINKERNELLE (Ber., 1931, 64, [*B*], 1871—1874).—Pyridine is readily converted by CH_2PhCl and Cu into a mixture of mono- and di-benzylpyridine, roughly separable by fractional distillation; from the fraction of lower b. p. 2-benzylpyridine, b. p. 275°, is readily isolated as the *picrate*, m. p. 139°. It is reduced, preferably by Na and EtOH, to 2-*benzylpiperidine*, b. p. 268° (*picrate*, m. p. 157°; *Ac* derivative, b. p. 197—200°/16 mm.; *nitroso*-compound). It is converted by Et bromoacetate into *Et 2-benzylpiperidine-1-acetate*, b. p. 192—196°/15 mm., hydrolysed to a non-cryst. *hydrochloride*. With methylal and conc. HCl, α-benzylpiperidine yields small amounts of 2 : 3-*tetramethylene*-1 : 2 : 3 : 4-*tetrahydroisoquinoline*, b. p. about 160°/15 mm. (*picrate*, m. p. 177°). The fractions of higher b. p. from CH_2PhCl and pyridine contain a mixture of dibenzylpyridines from which the 2 : 4-*derivative*, b. p. 220—222°/12 mm., is isolated through the *picrate*, m. p. 161°; the hygroscopic *hydrochloride*, m. p. 156°, and *methiodide*, m. p. 149°, are described. The constitution of the base follows from its formation from CH_2PhCl, 4-benzylpyridine, and Cu powder. 2 : 6-*Dibenzylpyridine*, m. p. 73—75°, gives a *picrate*, m. p. 177°, hygroscopic *hydrochloride*, m. p. 162°, and *methiodide*, m. p. 142°. H. WREN.

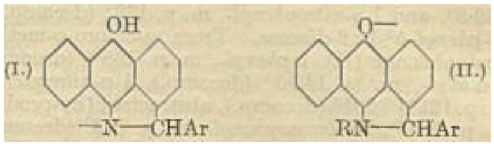
Substituted aromatic aldehydes in Hantzsch's pyridine condensation. II. Methyl- and nitrobenzaldehydes. L. E. HINKEL, E. E. AYLING, and W. H. MORGAN (J.C.S., 1931, 1835—1841; cf. A., 1929, 704).—Hantzsch's pyridine synthesis, applied under standard conditions (which give usually concordant results) to benzaldehydes substituted by the Me, NO_2, Cl, OMe, and OH groups, gives yields in accordance with anticipations from current electronic theories, with the possible exception of the OH group. The following are the mean yields, the radicals named being the substituents R in the Et 4-R-2 : 6-dimethyl-1 : 4-dihydropyridine-3 : 5-dicarboxylates obtained. *Tolyl-*, o-, m. p. 114°, 8·6%; m-, m. p. 138°, 56·5%; p-, m. p. 140°, 36·8%. Nitrophenyl-, *o-* (I), m. p. 125°, not 119—120° (A., 1887, 845), phototropic, 61·7% (a small amount of a *compound*, m. p. 171°, was also formed); *m-*, m. p. 164°, not 161° (*loc. cit.*), 87·7%; *p-*, m. p. 136°, not 118—122° (*loc. cit.*), 63·6% (a small amount of a *compound*, m. p. 140°, was also formed). Chlorophenyl-, *o-*, 61·6%; *m-*, 75·6%; *p-*, 72·6%. Anisyl-, *o-*, 57·3%; *m-*, 75·2%; *p-*, 63·8%. Hydroxyphenyl-, *m-*, 66·7%; *p-*, 67·5%; *o*-hydroxybenzaldehyde gave a small quantity of mixed products. Phenyl-, 74·2%. *Xylyl-*, o-4-, m. p. 114°, 34·6%; m-4-, m. p. 157°, 33·1%; p-3-, m. p. 140°, 43·6%. 3′ : 5′-*Dinitro-p-tolyl-*, m. p. 166°, 67·9%. 2′ : 4′ : 6-Trimethylphenyl-, and 3′ : 5′-dinitro-2′ : 4′ : 6′-trimethylphenyl-, nil; instead of the latter, <1% of a *compound*, m. p. 273°, was obtained. *Et 4-o-nitrophenyl-2 : 6-dimethylpyridine-3 : 5-dicarboxylate*, obtained by oxidation of (I) with boiling N-HNO_3, has m. p. 75°. R. S. CAHN.

Indolenines. IV. Indolenines from as-dibenzyl- and tribenzyl-acetone. H. LEUCHS and H. S. OVERBERG (Ber., 1931, 64, [*B*], 1896—1904).—*as*-Dibenzylacetone is reduced by Zn-Hg and 5*N*-HCl to α-*phenyl*-β-*benzyl*-n-*butane*, b. p. 166°/12 mm. The ketone condenses with PhCHO in presence of NaOH in aq. EtOH forming β-phenyl-α-benzylethyl styryl ketone, m. p. 64—65° (*dibromide*, m. p. 124°), transformed by phenylhydrazine in AcOH into 1 : 5-*diphenyl-3-dibenzylmethylpyrazoline*, m. p. 88° (*monobromo*-derivative, m. p. 114—115°). The unsaturated ketone is reduced by Na–Hg and EtOH to α-ε-*diphenyl*-β-*benzylpentan*-γ-*one*, m. p. 61—62°. The corresponding *phenylhydrazone*, m. p. 87—88°, is converted by $ZnCl_2$ in EtOH at 110—120° into a *compound*, $C_{30}H_{27}N$, m. p. 123—124°, which does not give a picrate or perchlorate, is unaffected by Ac_2O, and is not smoothly hydrogenated. 2-Methyl-3 : 3-dibenzylindolenine is transformed by PhCHO in H_2 at 140—150° into 3 : 3-*dibenzyl-2-styrylindolenine*, m. p. 88—89°, readily oxidised by $KMnO_4$ (*hydrochloride*, m. p. 145°; *perchlorate*), and the *compound*, $C_{37}H_{16}N_2$, m. p. 245—246° (vac.). Hydrogenation of the base in presence of PtO_2 and AcOH affords 3 : 3-*dibenzyl*-2-β-*phenylethylindolenine*, isolated as the

hydrochloride, m. p. 251—253° (vac.), and *perchlorate*, decomp. above 255—260° after blackening. 3 : 3-Dibenzyl-2-methylindolenine and *m*-nitrobenzaldehyde at 120° yield 3 : 3-*dibenzyl*-2-m-*nitrostyrylindolenine*, m. p. 187—188° [*tetrahydrochloride*, m. p. 174—176° (decomp.)], and β-m-*nitrophenyl*-αγ-*di*-3 : 3-*dibenzyl*-2-*indolenylpropane*, m. p. 182—185° (decomp.) after softening. The nitrostyryl compound is oxidised by $KMnO_4$ in $COMe_2$ to *m*-nitrobenzoic acid and 3 : 3-*dibenzylindolenine-2-carboxylic acid*, m. p. 147—149°. 3 : 3-Dibenzyl-2-methylindolenine is converted by $NaNO_2$ in AcOH into 3 : 3-*dibenzylindolenine-2-formoxime*, m. p. 225—227° (decomp.) [also $+\frac{1}{2}$EtOH; *Bz* derivative, m. p. 160°], transformed by boiling Ac_2O into 3 : 3-*dibenzylindolenine-2-nitrile*, m. p. 122—123°, which is hydrolysed by KOH in EtOH to 3 : 3-*dibenzylindolin-2-one*, m. p. 197—199° (*bromo*-derivative, m. p. 235—237°), and 3 : 3-dibenzylindolenine-2-carboxylic acid, m. p. 147—149° (decomp.) (see above). 3 : 3-*Dibenzyl-2-methylindolenine methiodide*, m. p. 152—153° (slight decomp.), is transformed by NH_3 and Et_2O into 3 : 3-*dibenzyl*-1-*methyl*-2-*methylene-indoline*, m. p. 118—119°. 3 : 3-Dibenzyl-2-methylindolenine is reduced by Zn–Hg and 12*N*-HCl to 3 : 3-*dibenzyl-2-methylindoline*, which regenerates the indolenine when attempts are made to isolate it as the picrate. The indoline is identified with certainty by reduction of the indolenine in presence of PbO_2 and immediate conversion of the product into the *Ac* derivative, m. p. 102—103° and 119°, respectively. The dimorphous acetate is obtained less smoothly by hydrogenation of 1-acetyl-3 : 3-dibenzyl-2-methylene-indoline. H. WREN.

Quinoline derivatives. XXV. Synthesis of 4′-hydroxy-2′-methyl-5′-*iso*propyl-2-phenyl-quinolines. H. JOHN and E. ANDRASCHKO (J. pr. Chem., 1931, [ii], **131**, 90—96).—Condensation of isatin with 4-hydroxy-2-methyl-5-*iso*propylacetophenone in presence of 33% KOH gives 2-(4-*hydroxy*-2-*methyl*-5-iso*propylphenyl*)*quinoline*-4-*carboxylic acid*, m. p. 282° (*Et* ester, m. p. 131°), converted by distillation into 2-(4-*hydroxy*-2-*methyl*-5-iso*propylphenyl*)-*quinoline*, m. p. 121°. Similarly from 5-iodoisatin 6-*iodo*-2-(4-*hydroxy*-2-*methyl*-5-iso*propylphenyl*)*quinoline-4-carboxylic acid*, m. p. 142°, is prepared. Interaction of *o*-aminoacetophenone and 4-hydroxy-2-methyl-5-*iso*propylacetophenone in presence of 10% NaOH gives 2-(4-*hydroxy*-2-*methyl*-5-iso*propylphenyl*)-4-*methylquinoline*, m. p. 121°. Various salts of these compounds are described. H. A. PIGGOTT.

Free organic radicals. X. "Aryl*peri*pyrrolinoanthranolazyls" as novel, nitrogenous, homogeneously-crystallised, free radicals, with univalent oxygen and as components of molecular compounds with methane hydrocarbons. R. SCHOLL and O. BÖTTGER [with O. BENNDORF] (Ber., 1931, **64**, [*B*], 1878—1893).—*m*-Xylyl 1-anthraquinonyl ketone, m. p. 196—197° (improved method of prep. substituting $FeCl_3$ for $AlCl_3$ given), is converted by NH_2Me in EtOH in presence of $ZnCl_2$ at 120—125° into two radicals, one of which is identical with the compound regarded previously as the azyl (I) (Ar=*m*-$C_6H_3Me_2$), whereas the other (isolated through its additive *compound* with *n*-heptane) is identical with the product considered to be its *O*-Me ether. The new synthesis, combined with the observation



that the Me is attached to N, has caused a revision of the formulation of the complete group, since the absorption curves of the parent substance and its Me derivatives are nearly identical. The parent substance is therefore regarded as py-m-*xylyl*peri*pyrrolino-anthroxyl* (R=H) and the Me compound is formulated according to II (R=Me). This harmonises with its production from 1-*m*-xyloylanthraquinoneoxime, with the stability of the radical in solution, and its indifference towards NO. With the aryloxy*peri*hydrofuranoanthroxyls they comprise the only known homogeneous radicals with univalent O. These can be readily purified, *e.g.*, by crystallisation from aq. EtOH. They have no tendency towards dimerisation. They form dark violet-blue crystals giving blue or violet to red solutions respectively in more and less highly solvatising media; the last-named solutions generally exhibit vivid fluorescence. The solutions are rapidly decolorised by strong sunlight; in the dark they are very resistant to O_2 and not sensitive to NO. The radicals have feebly basic properties accompanied by weakly acidic nature if an alkyl or acyl group is not attached to the N atom; the radical nature does not disappear in the salts. Readily in dil. aq. NH_3, more difficultly in dil. NaOH, they dissolve to blue solutions of salts which probably conform to the anthroxyl type. Similar salts are derived from the radicals and Ph diphenylyl ketone. Whilst unaffected by hot $Na_2S_2O_4$, the blue solutions in hot EtOH are decolorised by Zn dust and NH_3 in N_2, probably with formation of pyrrolinoanthranols which immediately revert to the radicals in presence of air. They are oxidised by $K_3Fe(CN)_6$ in presence of NH_3 with loss of the H atom attached to N to pyrroleninoanthrones which readily pass back into the radicals by autoreduction. Like the hydrofuranoanthroxyls they consume 3Br or 3OH respectively when titrated with Br or $KMnO_4$ and H_2SO_4, corresponding with the three points of attraction (at the univalent O and the two *meso*-C atoms). The main product of the $KMnO_4$ titration is the 1-aroylanthraquinone. When titrated with CrO_3 they absorb 2 equiv. of O with the probable formation of dimeric peroxides. The violet-red *N*-Me derivative is prepared by means of Me_2SO_4 and NaOH. Apart from the absence of acidic properties, it is distinguished from the non-methylated radical by the consumption of 5OH when titrated with $KMnO_4$. Red Bz derivatives are formed with BzCl and pyridine. The radical nature persists in both types of derivatives, thus demonstrating the unusual stability of these radicals. H. WREN.

Reactions of ω-chloroacetophenone and ω-chloro-*p*-methylacetophenone with phenylhydrazine and its substituted derivatives. A. P. J. HOOGEVEEN (Rec. trav. chim., 1931, **50**, 669—678).—Phenacyl chloride (I) and the appropriate phenyl-

hydrazine give 1 : 3-diphenyl-Δ^2-1 : 2-diazene (A., 1920, i, 96), 1-o-*tolyl*-, m. p. 147·2°, 1-p-*tolyl*-, m. p. 159·8°, and 1-p-*nitrophenyl*-, m. p. 173° (decomp. ?), -3-*phenyl*-Δ^2-1 : 2-*diazene*. From ω-chloro-*p*-methylacetophenone (II), 1-*phenyl*-, m. p. 158·8 (decomp.), 1-o-*tolyl*-, m. p. 143·5° (decomp.), 1-p-*nitrophenyl*-, m. p. 121° [? 201° (decomp.), abstractor] [by-product, m. p. 287°], 1-p-*bromophenyl*-, m. p. 173° (decomp.), -3-p-*tolyl*-Δ^2-1 : 2-*diazene* and 1 : 3-*di*-p-*tolyl*-Δ^2-1 : 2-*diazene*, m. p. 177° (decomp.), are similarly prepared. (I) may be determined by titration of the ionised halogen formed by treating it at 60° with aq.-alcoholic Na_2S. *Di*-p-*tolylacyl sulphide*, from (II) and Na_2S, has m. p. 88°. J. D. A. JOHNSON.

Labile nature of the halogen atom in organic compounds. XIV. Reactivity of halogen derivatives of 5-alkylbarbituric acids. A. B. COX, A. K. MACBETH, and S. W. PENNYCUICK (J.C.S., 1931, 1870—1874; cf. A., 1927, 575).—The halogen atom in 5-bromo-5-alkylbarbituric acids is reactive, as the compound cannot exist in an enolic form, and interaction with N_2H_4 to form the alkylbarbituric acid, HBr, and N_2 is quant. These bromo-compounds are reduced catalytically by the Pt electrodes of a conductivity cell, but only very slowly with polished electrodes. Modified directions are given for the prep. of 5-alkylbarbituric acids, and the following derivatives are obtained from them by adding Br to their aq. solutions: 5-bromo-5-methyl- (I), m. p. 190°, K $1{\cdot}08\times10^{-7}$; 5-*bromo*-5-*ethyl*-, m. p. 202°, K $2{\cdot}25\times10^{-7}$; 5-*bromo*-5-n-*propyl*-, m. p. 163·5°, K $2{\cdot}51\times10^{-7}$; 5-*bromo*-5-iso*propyl*-, m. p. 163°, K $1{\cdot}96\times10^{-7}$; 5-bromo-5-*n*-butyl-, m. p. 109°, K $2{\cdot}76\times10^{-7}$; 5-*bromo*-5-iso*amyl*-, m. p. 175°, K $2{\cdot}98\times10^{-7}$; 5-*bromo*-1 : 3-*diphenyl*-5-*benzyl*-*barbituric acid*, prep. in AcOH, m. p. 195°. (I) and N_2H_4 form 5-*methylbarbiturhydrazide*, m. p. 240°. R. S. CAHN.

Oxygen ethers of barbital [5 : 5-diethylbarbituric acid]. A. W. DOX (J. Amer. Chem. Soc., 1931, 53, 2741—2744).—2 : 4 : 6 - Trichloro - 5 - *sec*.-butylpyrimidine is converted by the requisite NaOAlk into 2 : 4 : 6-*trimethoxy*-, b. p. 245—250°, -*triethoxy*-, b. p. 260—264°, -*tripropoxy*-, b. p. 285—290°, and -*tributoxy*-, b. p. 310—315°, -5-sec.-*butylpyrimidine*. 2 : 2 : 4 : 6-*Tetrabutoxy*-, b. p. 180—183°/3 mm., and 2 : 2 : 4 : 6 - *tetraethoxy*-5 : 5-*diethyldihydropyrimidine*, b. p. 122—123°/3 mm. (hydrolysed by conc. HCl at 140—150° to α-ethylbutyric acid and NH_4Cl), are prepared similarly from the 2 : 2 : 4 : 6-tetrachloro-derivative (this vol., 742). H. BURTON.

Stereochemistry of *NN*′-dipyrryls. Resolution of 2 : 5 : 2′ : 5′-tetramethyl-1 : 1′-dipyrryl-3 : 3′-dicarboxylic acid. XVI. C. CHANG and R. ADAMS (J. Amer. Chem. Soc., 1931, 53, 2353—2357).—Condensation of Et 1-amino-2 : 5-dimethylpyrrole-3 : 3′-dicarboxylate with Et hexane-βε-dione-γ-carboxylate in boiling MeOH gives *Et* 2 : 5 : 2′ : 5′-*tetramethyl*-1 : 1′-*dipyrryl*-3 : 3′-*dicarboxylate*, hydrolysed by 10% EtOH–KOH to the corresponding acid (cf. A., 1904, i, 614). This was resolved by means of its *brucine* salts [d-, m. p. 153—157°, $[\alpha]_D^{20}$ −73·2° in pyridine; l-, m. p. 293—304° (optically impure)] into d-, m. p. 218—219°, $[\alpha]^{20}$ +27·5° in pyridine, and l-2 : 5 : 2′ : 5′-*tetramethyl*-1 : 1′-*dipyrryl*-3 : 3′-*dicarboxylic acid*, m. p. 220—221°. These are very resistant to racemisation, the *d*-form being unchanged by boiling with pyridine for 24 hr., and only partly racemised by boiling with 0·1*N*-NaOH for 84 hr. H. A. PIGGOTT.

Rearrangement of quinazolones into triazole derivatives. III. G. HELLER with R. MECKE (J. pr. Chem., 1931, [ii], 131, 82—89).—The presence of a triazole ring in the product of rearrangement of 3-benzamido-2-phenyl-4-quinazolone (A., 1928, 1381) is proved by its decarboxylation at 350° to 1 : 2 : 3-triphenyl-1 : 3 : 4-triazole. Reduction of this quinazolone with Zn and 90% AcOH removes the NHBz group, and gives 4-hydroxy-2-phenylquinazoline. 3-*Acetamido*-4-*quinazolone*, m. p. 206°, is obtained by action of 95% HCO_2H on *o*-aminobenzacethydrazide at 100°, or by direct acetylation; it is stable to 2*N*-NaOH at 100°, as also is 3-acetamido-2-methyl-4-quinazolone. The *Bz*, m. p. 194°, and Bz_2, m. p. 205°, derivatives of 3-aminoquinazolone, prepared by benzoylation in AcOH and pyridine, respectively, and in the case of the former, by action of HCO_2H on the appropriate hydrazide, are completely hydrolysed by 2*N*-NaOH and acids. *o*-Aminobenzhydrazide gives with MeCHO an *ethylidene* derivative, m. p. 150° (*Bz* derivative, m. p. 207°), which cannot be further condensed to a quinazoline, but its Bz derivative (from the benzoylated hydrazide) readily yields 3-*benzamido*-4-*keto*-2-*methyltetrahydroquinazoline*, m. p. 193°, stable to acids, but hydrolysed by dil. alkalis. 3-*Ethylidene*-*amino*-2-*phenyl*-4-*quinazolone* has m. p. 137°. H. A. PIGGOTT.

Reaction between 2 : 4 : 6-trichloropyrimidine and dimethylaniline. S. KAWAI and T. MIYOSHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 16, 20—23).—2 : 4 : 6-Trichloropyrimidine reacts with boiling $NPhMe_2$ to give MeCl and 2 : 4 : 6-*trismethylanilino*-*pyrimidine*, m. p. 133—134°, also formed using NHPhMe. J. D. A. JOHNSON.

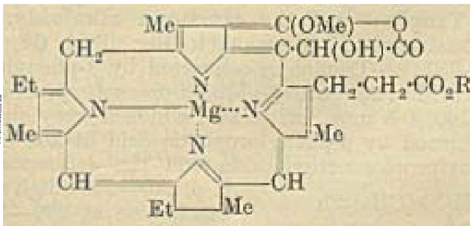
Condensation of β-hydroxyethylguanidine and acetoacetic ester. S. KAWAI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, 16, 25—28).—The product of the interaction of β-hydroxyethylguanidine and Et acetoacetate is proved to be 4-*keto*-6-*methyl*-2 : 3-cyclo*ethyleneiminotetrahydropyrimidine*, $CH_2<\begin{matrix}N{=\!=}C{\cdot}NH{\cdot}CMe\\CH_2{\cdot}N{\cdot}CO{-}CH\end{matrix}$, decomp. 310° (*picrate*, m. p. 234°), since it is obtained together with 6-methyluracil and β-chloroethylamine on heating 2-β-*hydroxyethylimino*-4-*keto*-6-*methyltetrahydropyrimidine*, $OH{\cdot}C_2H_4{\cdot}N{:}C\begin{matrix}{-}NH{-}CMe\\NH{\cdot}CO{\cdot}CH\end{matrix}$, m. p. 204—205° (*picrate*, m. p. 198—199°; *hydrochloride*, m. p. 165—166°), with conc. HCl at 140—148°. J. D. A. JOHNSON.

Ring closure of *o*-aminophenylsemicarbazides to benztriazines. P. C. GUHA and F. ARNDT [with H. SKZYPCZIK and P. S. MAYURANATHAN] (J. Indian Chem. Soc., 1931, 8, 199—202).—Dihydro-1 : 2 : 4-benztriazines are unstable, passing rapidly by atm. oxidation into benzotriazines (cf. A., 1928, 158), contrary to previous statements (A., 1925, i, 1461; 1928, 1263). Reduction of *o*-nitrophenylsemicarbazide (I) and *o*-nitrophenylthiosemicarbazide by the

method previously described gives o-phenylenediamine, and not 3-amino-1 : 2-dihydro-1 : 2 : 4-benztriazine. With a slight excess of $SnCl_2$ and HCl, (I) yields 3-amino-1 : 2 : 4-benztriazine. R. S. CAHN.

Decomposition of uric acid by various charcoal preparations. S. ZYLBERTAL (Biochem. Z., 1931, **236**, 131—137).—The samples of charcoal may be divided into those which, although adsorbing uric acid, scarcely oxidise it at all, those which contain metal (Fe) the oxidation by which is inhibited by CN′, and those samples which are free from metal oxidation by which is not inhibited by CN′. The oxidation proceeds in presence both of O_2 and of methylene-blue but in the latter case is considerably inhibited by CN′. P. W. CLUTTERBUCK.

Chlorophyll series. V. Structure of chlorophyll-*A*. J. B. CONANT, E. M. DIETZ, C. F. BAILEY, and S. E. KAMERLING (J. Amer. Chem. Soc., 1931, **53**, 2382—2393; cf. this vol., 745).—The participation of an external oxidising agent in the allomerisation of chlorophyll necessitates correction of the formula of chlorin *f* (cf. this vol., 368) to that of a dihydrorhodoporphyrin. Oxidation of Me phæophorbide *a* with $K_3Mo(CN)_8$ in $COMe_2$ gives *Me dehydrophæophorbide* a, sinters 260—265°, and some phæopurpurin 7. Hot, rapid hydrolysis of the former gives unstable chlorins, converted by diazomethane into Me_2 phæopurpurin 7; further hydrolysis gives chlorin *f* and oxalic acid. Chlorin *f* is more conveniently prepared by bubbling O_2 through a solution of Me phæophorbide *a* in conc. MeOH–KOH at 0°, and heating the product to boiling in a stream of N_2. Oxidation of chlorin *e* with $K_3Mo(CN)_8$ gives *chlorin* k [*monoMe* ester (diazomethane), m. p. 146—147° (decomp.)]; chlorin *e* Me_3 ester is not oxidised by this reagent. The formula:



is suggested for chlorophyll *a* (R=phytyl) and phæophorbide *a* (R=H; 2H in place of Mg). The absorption of dehydrochlorophyll *a* in the visible spectrum differs slightly according to its mode of prep. [O_2 or $K_3Mo(CN)_8$], and the same differences are found in the phæophytins. H. A. PIGGOTT.

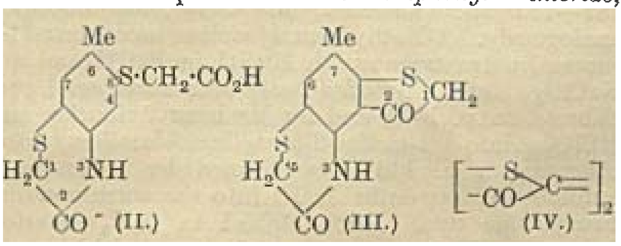
Phylloporphyrin. L. MARCHLEWSKI (Rocz. Chem., 1931, **11**, 529—531).—Polemical against Willstatter. R. TRUSZKOWSKI.

Hæmins and the relationship between hæmins and chlorophyll. H. FISCHER (Z. angew. Chem., 1931, **44**, 617—623).—A lecture.

Local anæsthetics containing the morpholine ring. J. H. GARDNER and E. O. HAENNI (J. Amer. Chem. Soc., 1931, **53**, 2763—2769).—Tri(hydroxyethyl)amine hydrochloride is heated at 200—205°/40 mm., and the resultant product (after removal of unchanged material) hydrolysed by KOH in EtOH to N-β-*hydroxyethylmorpholine*, b. p. 118—120°/24 mm. (*benzoate hydrochloride*, m. p. 204·6—205·8°; p-*nitrobenzoate hydrochloride*, m. p. 214·6—215·4°; p-*aminobenzoate hydrochloride*, m. p. 225·8—226·2°). γ-Aminopropyl alcohol, ββ′-dichlorodiethyl ether, and K_2CO_3 at 120—170° give N-γ-*hydroxypropylmorpholine*, b. p. 134—136°/24 mm. (*benzoate hydrochloride*, m. p. 190·1—190·5°; p-*nitrobenzoate hydrochloride*, m. p. 232·8—233·2°; p-*aminobenzoate hydrochloride*, m. p. 193·3—193·7°). The benzoates and *p*-aminobenzoates possess considerable local anæsthetic activity and low toxicity. H. BURTON.

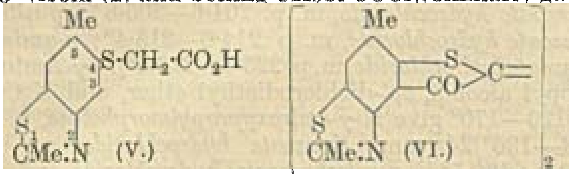
Condensation of aldehydes with *o*-aminothiophenols, benzthiazolines, and benzthiazoles. H. P. LANKELMA and P. X. SHARNOFF (J. Amer. Chem. Soc., 1931, **53**, 2654—2657).—Substituted 5-chlorobenzthiazolines, obtained in 70—90% yield from 4-chloro-2-aminothiophenol and the appropriate aldehyde in pyridine, are oxidised by $FeCl_3$ in EtOH to the corresponding benzthiazoles. The following are new: 5-*chlorobenzthiazoline*, m. p. 168—169° (2-*Me*, m. p. 61°; 2-*Et*, m. p. 60°; 2-*hexyl*, m. p. 51—52°; 2-*Ph*, m. p. 127°, and 2-o-*chlorophenyl*, m. p. 81°, derivatives); 5-*chlorobenzthiazole*, m. p. 106° (2-*Et*, m. p. 56—57°, and 2-o-*chlorophenyl*, m. p. 136—137°, derivatives). H. BURTON.

Condensed thiazine- and thiazole-thionaphthen derivatives. E. RIESZ, R. POLLAK, and A. WITTELS (Annalen, 1931, **487**, 264—269).—Methods of prep. are described for compounds containing the thionaphthen ring system condensed with a thiazole or thiazine ring. The colour of the thioindigoid dyes prepared is deepened by the presence of the extra ring. *p*-Toluidine-2 : 5-disulphonyl chloride (I) is reduced by Zn dust and HCl in AcOH to the corresponding *Zn dimercaptide*, which with NaOH and $CH_2Cl·CO_2Na$ gives 5-*carboxymethylthiol*-2-*keto*-6-*methylbenzdihydrothiazine* (II), m. p. 228°. This with $ClSO_3H$ at 0—10° gave the *thiazine-thionaphthen* derivative (III), characterised by its p-*dimethylaminoanil*, bluish-green (prepared by condensation with *p*-nitrosodimethylaniline in aq.-alcoholic KOH at 45°). (II) with $ClSO_3H$ at 30—40° gives the *thiazine-thioindigo* derivative (IV), bluish-green, which gives a green vat and dyes therefrom in bluish-grey tones. *Aceto*-p-*toluidide*-2 : 5-*disulphonyl chloride*,



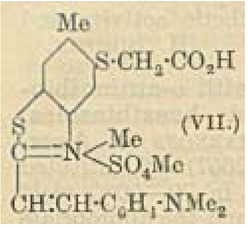
m. p. 125° [from (I) by prolonged boiling with AcCl], with Zn dust and HCl in AcOH yields the corresponding *Zn dimercaptide*, which with NaOH and $CH_2Cl·CO_2Na$ gives 4-*carboxymethylthiol*-1 : 5-*dimethylbenzthiazole* (V), m. p. 146°, which with $ClSO_3H$ at 30° gives the *thiazole-thioindigo* derivative (VI). This dyes bluish-green shades, not fast to acids. *Chloroaceto*-p-*toluidide*-2 : 5-*disulphonyl chloride*, m. p.

118° [from (I) and boiling $CH_2Cl \cdot COCl$], similarly gave



(V.) (VI.)

(V). On treating (V) with Me_2SO_4, and then boiling for 10 min. with Ac_2O and *p*-dimethylaminobenzaldehyde, 4-*carboxymethylthiol*-2 - p - *dimethylaminostyryl methylbenzthiazole* - 2 - *methosulphate* (VII), violet, m. p. 204°, was obtained, which dyes reddish-violet shades, not fast to acids. Treatment of (V) with Et_2SO_4, and subsequent boiling with anisaldehyde and a drop of piperidine in EtOH, and addition of aq. KI gave similarly 4 - *carboxymethylthiol* - 2 - p - *methoxystyryl* - 5 - *methylbenzthiazole*-2-*ethiodide*, m. p. 201°, bright red, which dyes wool and cotton mordanted with tannin orange-yellow tones. R. S. CAHN.



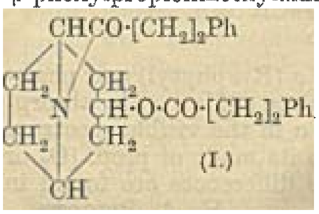
(VII.)

Unusual mode of formation of the simplest thiocyanins. W. KÖNIG, W. KLEIST, and J. GÖTZE (Ber., 1931, 64, [*B*], 1664—1675).—*as*-*p*-Tolylethylthiocarbamide is converted by Br in $CHCl_3$ into 2-*imino*-5-*methyl*-1-*ethylbenzthiazolin*, $C_6H_3Me{<}^{S}_{NEt}{>}C{:}NH$, m. p. 104° [*hydrobromide*, m. p. 291—292° (decomp.) after darkening. 2-*Imino*-1-*ethyl*-β′-*naphththiazolin*, m. p. 130°, and 2-*imino*-1 : 7-*trimethylenebenzthiazolin* [*hydrobromide*, m. p. 328° (decomp.)], are similarly prepared, whereas *N*-thiocarbamyl-1-methylindolin yields only resinous matter. 2-Imino-5-methyl-1-ethylbenzthiazolin is transformed by $NaNO_2$ in AcOH into 2-*nitrosoimino*-5-*methyl*-1-*ethylbenzthiazolin*, m. p. 141° (decomp.) when rapidly heated, which passes in boiling $C_6H_4Me_2$ into N_2 and 5-*methyl*-1-*ethylbenzthiazolone*, $C_6H_3Me{<}^{S}_{NEt}{>}CO$, m. p. 58°. 2-*Nitrosoimino*-1-*ethyl*-β-*naphththiazolin*, m. p. 158° (decomp.), 2-*nitrosoimino*-1 : 7-*trimethylenebenzthiazolin*, m. p. 149° (decomp.), 1-*ethyl*-β-*naphththiazolone*, b. p. 200°/5 mm., m. p. 124°, and 1 : 7-*trimethylenebenzthiazolone*, b. p. 182—185°/about 3 mm., m. p. 77°, are obtained analogously. 1-Methylbenzthiazolone is converted by successive treatment with MgEtI in EtOH and aq. $NaClO_4$ into 1-*methyl*-2-*ethylbenzthiazolium perchlorate*, m. p. 137°, and by Mg benzyl chloride and $HClO_4$ into 1-*methyl*-2-*benzylbenzthiazolium perchlorate*, m. p. 146°, transformed by *p*-dimethylaminobenzaldehyde in AcOH into the corresponding benzylidene dye. With MgMeI in C_6H_6 reaction follows a different course, 1 : 1′-dimethylthiocyanin iodide, m. p. 293° when rapidly heated, being produced, accompanied apparently by evolution of CH_4; the corresponding *perchlorate*, m. p. 310—311°, is described. The dye can also be prepared by treating benzthiazolone with MgMeI and subsequently with Fischer's base. 5 : 5′-*Dimethyl*-1 : 1′-*diethylthiocyanin iodide*, m. p. 290° [corresponding *perchlorate*, m. p. 317° (decomp.) after darkening at 290°], is analogously obtained. 2 : 5-*Dimethyl*-1-*ethylbenzthiazolium perchlorate*, identified as 5 : 5′-dimethyl-1 : 1′-diethylcarbothiocyanin iodide, is isolated from the product of the incomplete action of MgMeI on 5-methyl-1-ethylbenzthiazole in Et_2O. 1 : 1′-*Diethyl*-4 : 5 : 4′ : ɔ -*dibenz*-2 : 2-′*thiocyanin iodide*, m. p. 310°, and 1 : 7 : 1′ : 7′-*ditrimethylenethiocyanin iodide*, darkening at 300°, but not molten below 360° (corresponding *perchlorate*, m. p. above 360°), are prepared similarly. 5-*Methoxy*-1 : 1′-*dimethylthiocyanin iodide* appears to be formed in small amount by treating the methylene base from 5-methoxy-1 : 2-dimethylbenzthiazolium iodide with MgMeI in C_6H_6 and subsequently with 1-methylbenzthiazolone. 5-Chloro-1-methyl-2-methylenebenzthiazoline with MgMeI and subsequently with benzthiazolone affords ɔ-*chloro*-1 : 1′-*dimethyl*-2 : 2′-*thiocyanin iodide*, m. p. 288—289°. 1 : 1′ : 8 : 10 - *Tetramethyl* - 2 : 2′ - strepto*monovinylenethiocyanin perchlorate* is derived from 1-methyl-2-ethylbenzthiazolium iodide and Et orthoformate in AcOH.

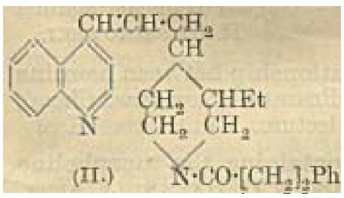
as-p-*Tolylethylthiocarbamide*, m. p. 99°, is prepared from *N*-ethyl-*p*-toluidine hydrochloride and aq. KCNS. as-β-*Naphthylethylthiocarbamide*, m. p. 155°, N-*thiocarbamyl*-1-*methyliodolin*, m. p. 104°, and 2-*thiocarbamyltetrahydroquinoline*, m. p. 141°, are analogously derived. H. WREN.

Sparteine *iso*valerate. F. MERCIER and L. J. MERCIER (Compt. rend., 1931, 192, 1590—1593).—*Sparteine* iso*valerate*, $[CH_2Pr^{\beta} \cdot CO_2H]_2, C_{15}H_{26}N_2, 2H_2O$, m. p. 45·5—46°, from *iso*valeric acid and sparteine in Et_2O solution, is feebly lævorotatory and possesses the physiological properties of the free base. F. R. SHAW.

Action of organic acids on tertiary amines. III. Tropine and the cinchona alkaloids. J. VON BRAUN and K. WEISSBACH (Ber., 1931, 64, [*B*], 1864—1871).—Tropine is converted by β-phenylpropionic acid at 200° into β-*phenylpropionyltropine*, b. p. 158—160°/0·8 mm., m. p. 20°, which is very slowly transformed by β-phenylpropionic acid at 200° into β-phenylpropionmethylamide and the *substance* (I), b. p. 240—242°/high vac Cinchonine at 200—210 is transformed into its β-*phenylpropionate*, b. p. 352—355°/0·15 mm., very extensively decomposed by further heating with the acid. Deoxydihydrocinchonine reacts readily with β-phenylpropionic acid at 200° giving lepidine and the *product* (II), b. p. 300—303°/0·15 mm. (*dihydro*-compound, b. p. 300—303°/0·15 mm.), slowly hydrolysed by 20% H_2SO_4 at 100° into β-phenylpropionic acid and the *base* $C_{19}H_{21}N_2$, m. p. 202—204°/0 1 mm. (*chloroplatinate*, decomp. 300—310° after darkening at 250°); the *dihydro*-base, $C_{19}H_{26}N_2$, b. p. 202—204°/0·1 mm. (*chloroplatinate*, decomp. 275—290°), and the *hexahydro*-base are described.



(I.)



(II.)

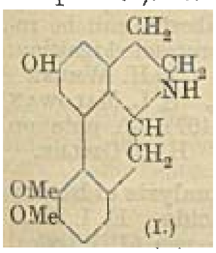
Deoxycinchonine behaves similarly to its dihydro-compound towards β-phenylpropionic acid giving a little lepidene and a *product*, $C_{28}H_{30}ON_2$, b. p. 318—325°/0·2 mm., which is saturated and yields a saturated *base*, $C_{19}H_{22}N_2$, b. p. 215—220°/0·2 mm., m. p. 174—177° after softening at about 167°, $[\alpha]^{21}$ +99·24° [*Ac* compound, m. p. 194—196° after softening at 185°; *methiodide*, decomp. 230°; *Bz* and p-*nitrobenzoyl* derivatives; it is reduced by Na and EtOH to the di-sec. *base*, $C_{19}H_{26}N_2$, b. p. 210—212°/0·2 mm. [Ac_2 derivative, b. p. 250—260°/0·3 mm. (slight decomp.)]. Cinchene is scarcely affected by β-phenylpropionic acid. Deoxyquinine reacts less completely than deoxycinchonine, giving methoxylepidine and the *substance* $C_{29}H_{32}O_2N_2$, b. p. about 340°/0·3 mm., which is saturated and yields a non-cryst. sec.-tert. diamine.

H. WREN.

Hydrocupreidine derivatives. I. S. GHOSH and N. R. CHATTERJEE (J. Indian Chem. Soc., 1931, 8, 257—260).—The following ethers of dihydrocupreidine were prepared by addition of the appropriate alkyl iodide to a solution of the alkaloid and the calc. amount of KOH in EtOH and either keeping for 1 month, or boiling for 3 hr. with a little Cu: *Pr^β ether*, m. p. 181°, giving a blue fluorescence in dil. H_2SO_4 (*dihydrochloride*, m. p. 249° to a brown liquid); *Bu^β ether*, an oil [*dihydrochloride*, m. p. 211° (decomp.)]; iso*amyl ether*, m. p. 168°, fluorrescent in dil. H_2SO_4 (*dihydrochloride*, m. p. 229°); sec. *octyl ether*, an oil [*dihydrochloride*, m. p. 227° (decomp.)].

R. S. CAHN.

Synthesis of aporphine alkaloids. I. H. KONDO and S. ISHIWATA (Ber., 1931, 64, [*B*], 1533—1540).—β-Phenylethylamine is converted by homoanisoyl chloride in C_6H_6 into N-p-*methoxyphenylacetyl*-β-*phenylethylamine*, m. p. 95°, converted by $POCl_3$ in boiling PhMe into the non-cryst. 1-p-*anisylmethyl*-3 : 4-*dihydro*iso*quinoline*, reduced by Zn and HCl in EtOH to 1-*p*-anisylmethyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline isolated as the *hydrochloride*, m. p. 215°. Benzyloxybenzaldehyde, m. p. 53°, and $MeNO_2$ in presence of NaOMe in MeOH afford β-*nitro*-α-3-*benzyloxyphenylethylene*, m. p. 93°, electrolytically reduced to β-3-*benzyloxyphenylethylamine* (*hydrochloride*, m. p. 180°; *hydrobromide*, m. p. 183°). With 2-nitrohomoveratroyl chloride the base yields the non-cryst. amide, transformed by PCl_5 in $CHCl_3$ into 6-*benzyloxy*-1-2′-*nitro*-3′ : 4′-*dimethoxybenzyl*-3 : 4-*dihydro*iso*quinoline*, m. p. 130° [*hydrochloride*, m. p. 210° (decomp.); *methiodide*, m. p. 142—143°; *sulphate*, m. p. 63°], electrolytically reduced to 6-*benzyloxy*-1-2′-*amino*-3′ : 4′-*dimethoxybenzyl*-3 : 4-*dihydro*iso*quinoline* (*hydrochloride*, m. p. 223°). Treatment of the dehydro-base with $NaNO_2$ in 2*N*-H_2SO_4 followed by Cu powder and reduction of the product with Zn and HCl yields 6-*hydroxy*-3 : 4-*dimethoxy*nor*aporphine* (I), m. p. 125° (*hydrochloride*, m. p. 265°). The synthesis is preferably effected through β-*nitro*-α-3-*carbethoxyphenylethylene*, m. p. 83°, obtained from *m*-carbethoxyphenylbenzaldehyde and $MeNO_2$.

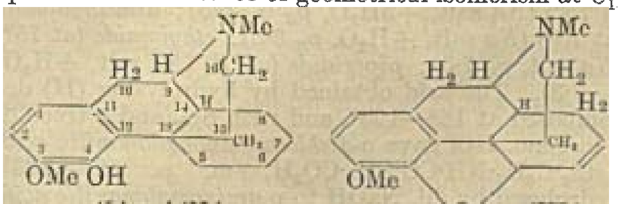


(I.)

β-3-Benzyloxyphenylethylamine and *p*-methoxyphenylacetyl chloride give N-p-*methoxyphenylacetyl*-β-3-*benzyloxyphenylethylamine*, m. p. 96°, converted by PCl_5 in $CHCl_3$ into 6-*benzyloxy*-1-p-*anisylmethyl*-3 : 4-*dihydro*iso*quinoline*, m. p. 97° (*hydrochloride*, m. p. 135°), catalytically reduced in 10% AcOH in presence of $PdCl_2$ to 6-*hydroxy*-1-p-*anisylmethyl*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline* (*hydrochloride*, m. p. 223°). The following compounds are incidentally described: β-*nitro*-α-m-*bromophenylethylene*, m. p. 59—60°, electrolytically reduced to β-m-*bromophenylethylamine* (*hydrochloride*, m. p. 225°; *hydrobromide*, m. p. 235—236°); with 2-nitrohomoveratryl chloride the base gives N-2-*nitrohomoveratryl*-β-m-*bromophenylethylamine*, m. p. 78°, converted by $POCl_3$ in boiling PhMe into β-m-*bromophenylethylimino*-α-2-*nitro*-3 : 4-*dimethoxyphenylethylene*, m. p. 134—135°, which is catalytically reduced to β-m-*bromophenylethylamino*-α-2-*nitro*-3 : 4-*dimethoxyphenylethane*, m. p. 110—111°. 3-Bromo-4-methoxybenzaldehyde and $MeNO_2$ yield β-*nitro*-α-3-*bromo*-4-*methoxyphenylethylene*, m. p. 108—109°, and thence β-3-*bromo*-4-*methoxyphenylethylamine* (*hydrochloride*, m. p. 215—216°; *hydrobromide*, m. p. 213°). N-2-*Nitrohomoveratryl*-β-3-*bromo*-4-*methoxyphenylethylamine*, m. p. 104—105°, is converted by $POCl_3$ in boiling PhMe into β-[β-3-*bromo*-4-*methoxyphenylethylimino*]-α-2-*nitro*-3 : 4-*dimethoxyphenylethylene*, m. p. 147—148°.

H. WREN.

Deoxycodeine. I. II. Dihydrodeoxycodeines. L. F. SMALL and F. L. COHEN (J. Amer. Chem. Soc., 1931, 53, 2214—2226, 2227—2244).—Interaction of α-chlorocodide with MgMeI or MgEtI in Et_2O gives deoxycodeine *A* (I: the identifying letters are assigned by the authors), also obtained from α-chlorocodide (*hydrogen* d-*tartrate*, $[\alpha]_D^{27.5}$ −219·3° in H_2O) by reduction with Zn and EtOH (cf. A., 1920, i, 757), and a little iodocodide [*hydrochloride* (+2 or 2·5H_2O), m. p. 190—191°; *methiodide*, m. p. 187—188°]; iodocodide, but not β-chlorocodide (*H* d-*tartrate*, $[\alpha]_D^{20}$ +8·3° in H_2O), also reacts with MgMeI to form (I). The "dihydrodeoxycodeine" obtained by Freund (A., 1920, i, 757) by electrolytic reduction of α- or β-chlorocodide absorbs 4H on catalytic reduction to β-tetrahydrodeoxycodeine, and is therefore named *deoxycodeine* B (II) (+½H_2O), m. p. 119—120° (*hydrochloride*; *hydriodide*, m. p. 245°). The "dihydrodeoxycodeine" prepared by interaction of chlorodihydrocodide with NaOMe in MeOH at 140° (G.P. 414,598) is similarly proved to be *deoxycodeine* C (III) (+H_2O), m. p. 105—106° [*hydriodide* (+H_2O), m. p. 160—165° (sinters at 135—140°); *hydrochloride* (+H_2O), m. p. 114°; *methiodide*, m. p. 236—240°]; it is insol. in aq. alkalis, does not form a Me ether or an Ac derivative, and is generally without phenolic properties. The absence of geometrical isomerism at C_{14}



(I.) and (II.) (III.)

requires the existence of two "phenolic" deoxycodeines according as the double linkings are at C

and C_7 or C_6 and C_8 and four " non-phenolic " forms of which (III) represents one.

II. " α-Tetrahydrodeoxycodeine " (A., 1920, i, 757) obtained by reduction of α-chlorocodide or deoxycodeines *A* or *B* with Na and 95% EtOH or electrolytically, is actually a *dihydrodeoxycodeine* (A), b. p. 160—170°/1 mm., m. p. 134—136° ($+\frac{1}{2}H_2O$), $[\alpha]_D^{22}$ −27·1°, −26·7° in EtOH (*methiodide*, m. p. 250—251°). It is reduced by H_2 and PtO_2 in MeOH to " β "-tetrahydrodeoxycodeine. The following additional *dihydrodeoxycodeines* are described: *B* ($+\frac{1}{2}H_2O$), m. p. 128—131°, $[\alpha]_D^{20}$ −106·9° [*hydrochloride*, m. p. 154—156° (decomp.); *hydriodide*, m. p. 255—256° (sinters 244—246°); *methiodide*, m. p. about 175°], produced by electrolytic reduction of deoxycodeine *C*; *C* ($+\frac{1}{2}H_2O$), m. p. 109—111°, $[\alpha]_D^{24}$ −61·6° in 96% EtOH [*hydrochloride*, m. p. 241—242° (sinters 157—163°); *hydriodide*, m. p. 242—243°; *methiodide*, m. p. 245—246°], accompanies *A* in the product of electrolytic reduction of chlorodihydrocodide (*loc. cit.*), and has previously been confused with deoxycodeine *B*: *D*, m. p. 106—107°, $[\alpha]_D^{20}$ −82·5° [*H tartrate*, m. p. 123—125°; *hydriodide*, m. p. 250—251° (decomp.); *methiodide*, m. p. 256°] is obtained by reduction of β-chlorocodide with H_2 and Pd–$BaSO_4$ (A., 1921, i, 124), and is the only non-phenolic dihydrodeoxycodeine yet known; *E* m. p. 139—140°, is prepared by electrolytic reduction of bromocodeinone (A., 1924, i, 1229). All of these dihydro-derivatives pass on complete reduction into β-tetrahydrodeoxycodeine, which is therefore the only known tetrahydro-derivative; consequently it is extremely unlikely that isomerism can occur at C_{14}, and five isomeric dihydrodeoxycodeines only, all of which are now known, can exist. Measurement of [α] is more trustworthy as a means of comparison in this series than the method of mixed m. p.

H. A. PIGGOTT.

Derivatives of *p*-arsanilic acid. II. *p*-Arsonomalonanilic acid and related compounds. G. T. MORGAN and E. WALTON (J.C.S., 1931, 1743—1748; cf. this vol., 636).—Compounds of the type (I) have been prepared. In many cases the Na salts have trypanocidal action in mice. The p_H quoted below refer to aq. solutions. (I) *p*-$H_2O_3As·C_6H_4·NH·CO·CH_2·CO·NRR'$ [$·CO_2Et$ (II)] *Et* p-*arsonomalonanilate* (II), cryst. (*Na* salt, $+H_2O$, p_H 6), could not be obtained from $CH_2(CO_2Et)_2$ and *p*-arsanilic acid, but was prepared from carbethoxyacetyl chloride (improved prep.), *p*-arsanilic acid, and NaOH. This yielded the following cryst. derivatives of type (I) when condensed with the appropriate amine under the conditions stated: *methylamide* (in the cold) (*Na* salt, $+H_2O$, p_H 6—6·5); *amide* (0·880 aq. NH_3 at 75°) (*Na* salt, $+3H_2O$, p_H 6—6·5); *dimethylamide* (at 75°) (*Na* salt, $+H_2O$, p_H 6·5); *ethylamide* (at 75°) (*Na* salt, p_H 7·5); *piperidide* (at 0°) (*Na* salt, $+H_2O$, p_H 7·3). The *acid* obtained by hydrolysing (II) decomposed at 188—193°, and with SO_2 and a trace of I in conc. HCl gave p-*dichloroarsinomalonanilic acid*, $AsCl_2·C_6H_4·NH·CO·CH_2·CO_2H$, m. p. 128—133°, hydrolysed by dil. NaOH to p-*arsinomalonanilic acid*. This or the preceding chloride was converted by $SOCl_2$ at 20° into the trichloride, which with NH_2Ph at 0°, and subsequent hydrolysis by dil. NaOH gave p-*arsinomalonanilide*, oxidised by H_2O_2 to *malonanilide*-p-*arsinic acid* (I; R=H : R'=Ph) (*Na* salt, $+2·5H_2O$, p_H 8·5). Malonyl chloride (improved prep.), and *p*-arsanilic acid yielded *malonanilide*-pp'-*diarsinic acid* ($(p\text{-}H_2O_3As·C_6H_4·NH·CO)_2CH_2$), darkening on drying (*Na* salt).

Malonanilino-n-*propylamide*-p-*arsinic acid*, cryst. (*Na* salt, p_H 6·5) was prepared from (II) and cold aq. NH_2Pr^a. Succinanilino-*p*-arsinic acid and cold alcoholic NH_2Pr^a gave *succinanilino*-n-*propylamide*-p-*arsinic acid*, cryst. (*Na* salt, Na_2 salt, p_H 10).

R. S. CAHN.

Mercury derivatives of *cyclo*hexyl- and benzylphenols. J. W. HAUGHT, C. E. GARLAND, and H. A. H. PRAY (J. Amer. Chem. Soc., 1931, 53, 2697—2700).—The following derivatives of *o*- and *p*-benzyl- and *o*- and *p*-*cyclo*hexyl-phenols are prepared by the usual methods: *diacetoxymercuri*-o-*benzylphenol*, decomp. 115—125°, *diacetoxymercuri*-, decomp. 110—115°, *dichloromercuri*-, decomp. 128—134°, and *anhydromercurihydroxymercuri*-, decomp. 245—250°, -p-*benzylphenols*; *diacetoxy*-, decomp. 135—140°, *dichloro*-, decomp. 155—160°, and *dihydroxy*-, decomp. 230—235°, -*mercuri*-o-cyclo*hexylphenols*; *diacetoxy*-, decomp. 105—110°, *dichloro*-, decomp. 225—230°, and *dihydroxy*-, decomp. 255—260°, -*mercuri*-p-cyclo*hexylphenols*.

H. BURTON.

Effect of heat on the chemical composition of proteins. I. Elementary composition and diamino-acids. K. YAMAFUJI (Bul. Sci. Fak. Terkultura Kjusu, 1930, 4, 101—107).—When muscle proteins are heated at 140° in sealed tubes at varying p_H the reaction tends to approach neutrality. The NH_3 and H_2S evolved increase with a higher p_H. Cystine, arginine, lysine, and NH_2-N generally decrease slightly, although there is a slight increase of arginine at p_H 3·4.

P. G. MARSHALL.

Sources of error in organic elementary analysis. VIII. Ignition of the combustion tube and origin of the water occurring thereby. J. LINDNER (Ber., 1931, 64, [*B*], 1560—1567; cf. A., 1930, 940).—Pure CuO (granular or wire-form), finely-divided Ag, and $PbCrO_4$ readily yield their H_2O when ignited in air. Less ready evolution of H_2O is observed from the asbestos filling. Hard glass tubes in the initial stages of heating yield H_2O in noticeable amount, which gradually diminishes to a small quantity depending on the temp. of ignition. Quartz behaves similarly at temps. usual in combustion analysis, but yields markedly smaller amounts than those obtained with hard glass. Asbestos, air-dried or transitorily ignited, gives much larger amounts of H_2O, but complete removal could not be effected. The H_2O slowly attracted by thoroughly ignited asbestos can be reduced to its former degree only by protracted ignition.

H. WREN.

Detection of carbon disulphide. S. L. MALOWAN (Z. anal. Chem., 1931, 84, 406—407).—A note on previous work (this vol., 638).

H. F. GILLBE.

Conductivity method for the analysis of binary mixtures of the volatile fatty acids. E. I. FULMER, E. E. MOORE, and R. L. FOSTER (J. Physical Chem., 1931, 35, 1227—1231; cf. J. Bact., 1930, 19,

5).—For binary mixtures of formic, acetic, propionic, and n-butyric acids the antilog. of $\kappa \times 10^3$ is a linear function of % composition; this can be used as a basis for analysis. L. S. THEOBALD.

Colour reaction of ephedrine. J. SIVADJIAN (J. Pharm. Chim., 1931, [viii], **14**, 61—63; cf. A., 1930, 1460).—A reply to Hartung and others (this vol., 724). The peculiar reddish-violet colour is specific for compounds of the ephedrine type. Ephedrine and ψ-ephedrine may be distinguished from each other. R. K. CALLOW.

Determination of citrates, salicylates, and benzoates by the mercurimetric method. A. IONESCU-MATIU and (MME.) POPESCO (J. Pharm. Chim., 1931, [viii], **14**, 54—61).—The citrate (Na or Mg) is treated with $HgSO_4$ solution, oxidised by $KMnO_4$, and the ppt. of complex Hg salt is dissolved in HNO_3–H_2SO_4 and Hg determined by adding Na nitroprusside and titrating with NaCl (cf. A., 1927, 687; 1928, 1230). Salicylates and benzoates give ppts. of the Hg salts directly and Hg is determined in the same way. Aspirin may be determined after hydrolysis. R. K. CALLOW.

Determination of sulphosalicylic acid. E. PRSCHEVALSKI and V. PESCHKOVA (Trans. Inst. Pure Chem. Reag., 1931, **10**, 8).—The free H_2SO_4 is determined by $BaCl_2$ in the usual manner, and the total SO_4'' after oxidising with $KMnO_4$. E. S. HEDGES.

Colorimetric determination of tryptophan. T. RUEMELE (Z. anal. Chem., 1931, **84**, 81—89).—A crit. study of the method of Tillmans and Alt (A., 1926, 189). Accurate results are obtained by adherence to standardised conditions. Not more than 2 drops of a 2% CH_2O solution should be used and 45 min. should elapse after this has been added before comparison of the colours is made. A. R. POWELL.

Potassium ferrocyanide as a microchemical reagent for the identification of strychnine. V. D. GNESIN (Farm. Zhur., 1930, 293—295).—Characteristic crystals are described. CHEMICAL ABSTRACTS.

Anhydrous distillation method for the determination of certain metals in organic compounds. I. Mercury. E. P. FENIMORE and E. C. WAGNER.—See this vol., 1025.

Biochemistry.

Determination of respiratory capacity by micro-determination of iron in the blood. J. M. CLAVERA (Anal. Fís. Quím., 1931, **29**, 392—398).—The method of Fontes and Thivolle for the determination of Fe in blood may be used for determining the respiratory capacity, which is equal to 40 times the Fe content (in mg. per c.c.). The error is less than 2%. H. F. GILLBE.

Deformability and wetting properties of leucocytes and erythrocytes. S. MUDD and E. B. H. MUDD (J. Gen. Physiol., 1931, **14**, 733—751).—A microscopical study of the behaviour of blood-cells at an oil–water interface. The surface of the leucocyte is hydrophilic, that of the erythrocyte hydrophobic. A. COHEN.

Staining of reticulocytes by brilliant-cresyl-blue. Influence of solutions of substances. C. W. HEATH and G. A. DALAND (Arch. Int. Med., 1931, **48**, 133—145).—The staining of reticulocytes (rabbit and man) by brilliant-cresyl-blue is inhibited by liver extracts, NH_2-acids, and a variety of org. and inorg. substances to an extent which varies with their concentrations. The inhibitory influence is not related to the efficacy of the liver extracts in anæmia, and is decreased by long contact between blood-cells and inhibitors. The effects are probably due to changed permeability of the cells under the influence of the inhibitors. A. COHEN.

Determination of hæmoglobin in blood. O. ORIAS (Compt. rend. Soc. Biol., 1930, **105**, 305—306; Chem. Zentr., 1931, i, 2240).—A comparison of methods. A. A. ELDRIDGE.

Simplification of the Osgood–Haskins hæmoglobin method. E. E. OSGOOD and H. D. HASKINS (J. Lab. Clin. Med., 1931, **16**, 482—486).—A solution of acid hæmatin is used as a standard. CHEMICAL ABSTRACTS.

Crystalline forms of hæmin, and conditions of their preparation. K. LINDENFELD (Rocz. Chem., 1931, **11**, 532—542).—Hæmin is obtained in hexagonal plates on adding a $CHCl_3$–pyridine solution to 80% AcOH containing NH_4Cl or NaCl at 60°; similar polymorphs of the ordinary Teichmann form are obtained from bromo-, iodo-, and thiocyano-hæmin in a similar way. The polymorphs are unstable, and are rapidly converted into Teichmann crystals at 100°. R. TRUSZKOWSKI.

Physical properties of normal blood-sera of man and some mammals, and of serum-proteins isolated by acetone. C. ACHARD, A. BOUTARIC, and M. DOLADILHE (Compt. rend., 1931, **193**, 271—276).—Colloidal suspensions of the proteins in an equal vol. of H_2O have almost the same optical density and viscosity as whole serum; addition of salts and the extracts increases the optical density and decreases the no. of particles. The no. of particles per g. of dried protein is sensibly the same in the sera from man, horse, and ox. C. C. N. VASS.

Fractionation of serum-proteins and absorption spectra of the fractions. J. GRÓH and E. FALTIN (Z. physiol. Chem., 1931, **199**, 13—24).—The mean extinction coeffs. for the serum-globulin and -albumin from the horse and ox agree, but the differences observed between samples from a particular species are often considerable. Fractional precipitation with $(NH_4)_2SO_4$ yields fractions showing a steady decrease in coeff., the tryptophan and to some extent the tyrosine contents showing a parallel diminution. None of the fractions is homogeneous. J. H. BIRKINSHAW.

Protein coagulation and its reversal. Serum-albumin. M. L. ANSON and A. E. MIRSKY (J. Gen. Physiol., 1931, **14**, 725—732).—The prep. of sol. cryst. serum-albumin from a denatured product obtained by the action of acid $COMe_2$ on the native protein is described. It appears that the more sol. is the denatured protein, the more easily is denaturation reversed. A. COHEN.

Temperature stability and denaturation of serum-albumin. K. O. PEDERSEN (Nature, 1931, **128**, 150—151; cf. A., 1930, 1197).—Heat treatment of serum-albumin within the p_H-stability region forms aggregation products which vary in size and no. according to p_H, temp., time of heating, and the nature of the salts in solution. Removal of these products leaves an unchanged portion of serum-albumin. Heat treatment of amandin forms some smaller particles with a large portion unchanged. Outside the p_H-stability region ($p_H<3\cdot8$) serum-albumin is split up into smaller particles by heating, and mobilities expected for denatured serum-albumin are obtained. Serum-albumin solutions at p_H 3·5 are changed by ultra-violet light. L. S. THEOBALD.

Osmotic pressure of colloids. XVI. Daily fluctuation and arterio-venous difference of the osmotic pressure of the colloids of blood-serum. E. KYLIN (Arch. exp. Path. Pharm., 1931, **161**, 91—103).—The average osmotic pressure exerted by the colloids of arterial blood during a fasting period is 343 mm. H_2O and that of venous blood 337 mm. After food the arterial colloidal osmotic pressure rises to 355—359 mm., whilst the venous osmotic pressure rises after food taken with little H_2O and falls when much H_2O is taken. P. G. MARSHALL.

Use of interferometer for serum-protein and protein fraction determinations. W. J. DIECKMANN (J. Lab. Clin. Med., 1931, **16**, 513—519).—Methods are described. CHEMICAL ABSTRACTS.

Determination of blood-proteins by a direct micro-Kjeldahl method. R. S. HUBBARD (J. Lab. Clin. Med., 1931, **16**, 500—503).—The digested material is nesslerised directly; precipitation of the reagent is prevented by the use of Na K tartrate. CHEMICAL ABSTRACTS.

Occurrence of proteolytic enzymes in serum. Criticism of Yokota's work. H. J. FUCHS and M. VON FALKENHAUSEN (Biochem. Z., 1931, **237**, 87—89).—The results of Yokota (this vol., 641) are shown to be erroneous, due to an imperfect removal of proteolytic enzymes from the fibrin. F. O. HOWITT.

Chemical nature of the depressor substance of blood. K. ZIPF (Arch. exp. Path. Pharm., 1931, **160**, 579—598; cf. A., 1930, 811).—Defibrinated blood is freed from protein by precipitation with trichloroacetic acid, and the depressor principle is isolated from the filtrate by successive precipitation of its Hg, Pb, and Ba salts. It is identical with adenylic acid. A. COHEN.

Spectrophotometric determination of allantoin in the blood of mammals and in the seed of plants. R. FOSSE, A. BRUNEL, and P. E. THOMAS (Compt. rend., 1931, **193**, 7—11; cf. this vol., 976).—The concentration of allantoin in the sera of the ox, horse, sheep, and pig varies from 10·7 to 26·9 mg. per litre. In 40 out of 50 plants the allantoin content of the seed varied from 0·02 to 0·41 g. per kg., but reached 1·78 g. per kg. in *Phaseolus mungo* and 3·3 g. per kg. in *Dolichos sinensis*. C. C. N. VASS.

Acetylcholine in ox-blood. II. C. BISCHOFF, W. GRAB, and J. KAPFHAMMER (Z. physiol. Chem., 1931, **199**, 135—168; cf. A., 1930, 1464).—In 29 out of 32 animals examined the blood was shown by biological test to contain acetylcholine. The essential conditions for successful testing are (*a*) the filtrate from the blood–EtOH mixture after evaporation in vac. must not be alkaline, (*b*) after deproteinisation the solution must not be kept long and must be maintained at a low temp. Of the three protein precipitants trichloroacetic acid, sulphosalicylic acid, and $H_4P_2O_7$, the last is preferred, since it gives a more suitable p_H. J. H. BIRKINSHAW.

Blood-ammonia. L. STANOYEVITCH (Bull. Soc. Chim. biol., 1931, **13**, 579—587).—Blood drawn directly into the reagents contains 0·026 mg. NH_3-N per 100 c.c. NH_3-N increases during muscular work but falls to its initial val. after 2 hr. rest. On autolysis *in vitro* the rate of formation of NH_3-N varies with temp.; the precursor is thought to consist of 2 substances, one of which decomposes at room temp. in 24 hr., whilst the other requires a higher temp. and has a variable time factor. C. C. N. VASS.

Effect of muscle extracts on blood-sugar in the rabbit. F. AMANTEA (Arch. Farm. sperim., 1931, **52**, 189—196).—Injection of extract of ox-muscle has in general a slight hypothermic action on guinea-pigs. The injection of muscle extracts into rabbits has a variable effect on the temp.; homologous extracts lower the blood-sugar, whilst extracts from other animals have little effect. R. K. CALLOW.

Determination of cholesterol in blood-plasma and -serum. J. C. FORBES (J. Lab. Clin. Med., 1931, **16**, 520—521).—The cholesterol is extracted without heat in presence of "doucil," a water softener. CHEMICAL ABSTRACTS.

Influence of nerve excitation on the cholesterol and fat content of blood flowing from the extremities. J. SCHEFFER and G. BARDOS (Biochem. Z., 1931, **236**, 493—499).—Excitation of the ischiadic nerve in the dog increases the cholesterol content of the blood in the femoral or saphenous vein and, to a smaller extent, in that of the femoral artery. Simultaneous excitation of the cruralis nerve inhibits this increase. The total fat does not rise parallel with the cholesterol level so that the quotient total fat/cholesterol decreases during stimulation, which brings about liberation of cholesterol from subcutaneous and bone-marrow tissue. F. O. HOWITT.

Dichlorofluorescein as an adsorption indicator for the determination of blood-chloride. A. E. OSTERBERG (Proc. Staff Meetings Mayo Clinic, 1930, **5**, 300).—Plasma or serum (2 c.c.), $COMe_2$ (7 c.c.), and H_2O (to 10 c.c.) are centrifuged; 5 c.c. of the solution is treated with the indicator (Kolthoff, Lauer, and Sunde), and titrated with $N/3456$-$AgNO_3$. CHEMICAL ABSTRACTS.

Blood-phosphorus in man. M. JAVILLIER and M. FABRYKANT (Bull. Soc. Chim. biol., 1931, **13**, 687—696).—The mean vals. in mg. per litre for venous blood collected at rest while fasting were, total P 358·4, inorg. P 36·6, lipin-P 115·7, nucleoprotein-P 26·5. In disease total P was 183—1055, lipin-P 53—268, and inorg. P 23—60. C. C. N. VASS.

Titrimetric determination of inorganic phosphorus in blood-serum. L. CANNAVO (Biochem. Z., 1931, **237**, 136—138).—From 1 c.c. (not deproteinised) Ca is removed by $(NH_4)_2C_2O_4$ and phosphate precipitated as $MgNH_4PO_4$ in presence of Na citrate. The ppt. is converted into NH_4 phosphomolybdate, which is dissolved in 3 c.c. of 0·02*N*-NaOH and titrated with 0·02*N*-HCl. Vals. for some pathological sera are given. F. O. HOWITT.

Possible transition of inorganic to organised matter. M. COPISAROW (Kolloid-Z., 1931, **56**, 67—71).—A discussion of published work on inorg. structures resembling organised matter in form. E. S. HEDGES.

Paracrystalline organisms. F. RINNE (Kolloid-Z., 1931, **56**, 71—77).—Sepia spermatozoa are gel-like, paracryst., living organisms, which constitute a transition between artificial liquid crystals and organised matter. E. S. HEDGES.

Cholesterol content of shrimp waste. R. F. ABERNETHY and F. C. VILBRANDT (J. Amer. Chem. Soc., 1931, **53**, 2796—2797).—Shrimp oil (this vol., 272) contains 19·08% of cholesterol. H. BURTON.

Cholesterol and protoplasm structure. IX. Summary of I—VIII. G. PFEIFFER (Biochem. Z., 1931, **236**, 457—463).—In a survey of the amounts of cholesterol and its derivatives in various tissues (cf. A., 1929, 90; 1930, 945, 1204; this vol., 507, 644, 975) the functions of these compounds are discussed with reference to interfacial and protective colloid action, O_2 adsorption, H_2-acceptor action, synthetic processes, and their bearing on protoplasmic structure and immuno-behaviour. F. O. HOWITT.

Modification of the Kumagawa–Suto method for the determination of the lipin content of organs. E. LEBORDE and ENVER (Bull. Soc. Chim. biol., 1931, **13**, 712—713).—The operation is carried out in one stage, avoiding the evaporation to dryness of the EtOH-extract prior to hydrolysis with EtOH–KOH. C. C. N. VASS.

Colour reactions of the nucleic acids. P. THOMAS (Z. physiol. Chem., 1931, **199**, 10—12).—A tryptophan reagent (0·1% in 50% aq. HCl) is recommended for the detection of thymus-nucleic acids since it gives characteristic colour reactions with these and with the monosaccharides. J. H. BIRKINSHAW.

Camel flesh. G. A. MAKARYTSCHEV (Z. Fleisch-Milchhyg., 1931, **41**, 181—182, 207—212; Chem. Zentr., 1931, i, 2406).—The flesh contained H_2O 75·51—79·90, protein 18·68—21·37, fat 0·80—2·52, ash 0·51—0·86%, and gave a positive reaction for glycogen. A. A. ELDRIDGE.

Comparative copper determinations in hen embryos. A. LOESCHKE (Z. physiol. Chem., 1931, **199**, 125—128).—The Cu content of the liver of the embryo is only about $\frac{1}{4}$ to $\frac{1}{5}$ that of the whole egg but the percentage is 12—20 times as great. J. H. BIRKINSHAW.

Sulphur content of some South African wools. F. N. BONSMA (J. Text. Inst., 1931, **22**, T305—313).—There is a considerable variation in the S content of wools from different sheep fed on the same diet, but although the S content is largely an inheritable characteristic, it may be altered by, *e.g.*, limitation of the cystine supply in the natural diet. As long as the demand for cystine for the production of wool by the animal is satisfied by its food, the wool maintains the normal S content, but when the supply is inadequate a reduction in S content follows. B. P. RIDGE.

Biochemistry of sulphur. X. Cystine content of meat and fish. M. X. SULLIVAN and W. C. HESS (U.S. Pub. Health Rep. Suppl., 1931, no. 94, 13 pp.).—Cystine was determined in meat and fish (haddock, halibut, and salmon) using fresh or $COMe_2$–Et_2O dehydrated defatted material and also hydrolysed samples. The colorimetric method of Sullivan (A., 1930, 488) gives results comparable with those by the iodometric method of Okuda (A., 1929, 730; 1191), but lower than those by the colorimetric method of Folin (*ibid.*, 1093). Higher vals. (0·26% for wet material) are found for fish than for meat (0·19%) which, however, has a slightly higher glutathione content. F. O. HOWITT.

Separation of iodine from thyroid gland pulp by ultra-violet irradiation and from iodised protein by irradiation with *X*-rays. F. LIEBEN and H. KRAUS (Biochem. Z., 1931, **236**, 182—186).—I is liberated from suspensions of human thyroid gland pulp under the action of ultra-violet light (0·5—2·7% of the total I being set free) and from iodised caseinogen and thyroxine under the action of *X*-rays (less than 1% of the total I set free). P. W. CLUTTERBUCK.

Detection and determination of glucosamine. F. ZUCKERKANDL and L. MESSINER-KLEBERMASS (Biochem. Z., 1931, **236**, 19—28).—A method for the determination of 1—5 mg. of glucosamine depends on the red colour produced when glucosamine monoacetate is treated with alkali and Ehrlich's reagent, the limits of error being not greater than 6%. Ovomucoid contains only half of its carbohydrate as glucosamine, the remainder consisting probably of mannose (up to 10%). P. W. CLUTTERBUCK.

***Haliotis*-indigo, the blue pigment of the shells of *Haliotis californiensis*.** N. SCHULZ and M. BECKER (Biochem. Z., 1931, **236**, 99—106).—The separation and purification of the pigment are described and preliminary tests place it in the indigo group. P. W. CLUTTERBUCK.

Histological and chemical examination of the gills of *Anodonta cygnœa*, Lin. M. DUBUISSON and J. VAN HEUVERSWYN (Arch. Biol., 1931, **41**, 37—74).—Certain concretions found in the gills of *A. cygnœa* contain Fe, Mn, and $CaCO_3$. Their formation and function in relation to the yellowish-brown pigment of the tissue are discussed. A. G. POLLARD.

Elimination of choline from lecithin and the choline content of cerebrospinal fluid. I. H. PAGE and E. SCHMIDT (Z. physiol. Chem., 1931, **199**, 1—9).—Lecithin is not hydrolysed by boiling in EtOH or when kept for a longer period at 37°. It is only slowly attacked in aq. emulsion at p_H 5·6—8·2. Fresh serum or brain extract has no action on it. The choline content of cerebrospinal fluids was 0·1—1·0 mg. per litre except in a case of Lues univ. ac., when 1·3 mg. was attained. J. H. BIRKINSHAW.

Determination of pancreatic enzymes in duodenal contents. E. HOLLANDER (J. Lab. Clin. Med., 1931, **16**, 460—465).—The steapsin and trypsin are determined by measuring the time (normally 5 min.) necessary for the neutralisation of 1 c.c. of $0·1N$-NaOH by the fatty or NH_2-acids formed by the action of 1 c.c. of duodenal contents on olive oil or gelatin, respectively. The amylopsin activity is determined by determining the amount (normally 1·9 c.c. or less) of substrate required to reduce 5 c.c. of Benedict's quant. sugar reagent after the action of 1 c.c. of duodenal contents on sol. starch. A decrease in the activity of the enzymes is usually associated with disease of the gall bladder. CHEMICAL ABSTRACTS.

Proteolytic enzymes in intestinal and pancreatic juices. E. LE BRETON, I. MOCOROA, and E. STULZ (Compt. rend., 1931, **193**, 79—81).—Only abnormal pancreatic secretions contain erepsin or kinase or both, whereas erepsin and enterokinase are always present in the intestinal juice. C. C. N. VASS.

Characterisation of semen in legal investigations. R. MARCILLE (Ann. Chim. anal., 1931, [ii], **13**, 193—203).—Semen may be detected microchemically by Florence's reagent (1·8 g. I; 2·4 g. KI; 45 c.c. H_2O), which gives characteristic brown, prismatic crystals with choline hydrochloride at a limiting dilution of 1 : 70,000 at room temp. or 1 : 400,000 at 12°. The stain is extracted with water, protein precipitated by EtOH, the filtrate evaporated, and the limiting dilution of the aq. extract which gives a positive reaction is determined. Dried semen gives a positive reaction in a dilution of 1 : 1000 or 1 : 4000, and is thus readily distinguished from other materials containing choline in comparatively small amount. Putrefaction interferes with the test. Bogarius' reagent is not sufficiently sensitive. The microscopical detection of spermatozoa is described. R. K. CALLOW.

Absorption spectrum of bilirubin in different solvents. P. MULLER and L. ENGEL (Z. physiol. Chem., 1931, **199**, 117—124).—The absorption of bilirubin in (so-called) alcoholic solution differs from that exhibited in $CHCl_3$ solution (cf. this vol., 644). J. H. BIRKINSHAW.

Detection and determination of indican in urine. FISCHER and HUPPMANN (Pharm. Ztg. 1931, **76**, 810—812).—The urine is treated with 10% of basic Pb acetate solution and 11 c.c. of the filtrate are boiled with 10 c.c. of a saturated solution of acenaphthenequinone in AcOH and 2 c.c. of fuming HCl. The red 1-acenaphthene-2'-indoleindigo formed is extracted with hexahydrotoluene and determined colorimetrically. The prep. of the dye from indoxyl and acenaphthenequinone is described. R. K. CALLOW.

Photometric determination of acetone in urine. C. URBACH (Biochem. Z., 1931, **236**, 164—173).—The method is described and its advantages over other methods are discussed. P. W. CLUTTERBUCK.

Micro-determination of the organic acids of urine by ether extraction. M. LAFARGUE (Bull. Soc. Chim. biol., 1931, **13**, 703—709).—2 c.c. of protein-free urine saturated with $(NH_4)_2SO_4$ and acidified with conc. H_2SO_4 are continuously extracted with EtOH-free Et_2O for 1½ hr., the extract is diluted with H_2O and titrated with $0·02N$-NaOH, using cresol-red as indicator. C. C. N. VASS.

Phenol test for urinary albumin. W. B. CLAPP and B. COHEN (New England J. Med., 1930, **203**, 1237—1238).—A ring test, employing saturated aq. PhOH containing glycerol (*d* 1·045), detects albumin in a concentration of 0·004%. CHEMICAL ABSTRACTS.

Excretion of uric acid. J. NEEDHAM (Nature, 1931, **128**, 152—153).—Facts concerning the development of the chick embryo are quoted in support of the view that a circulation of base as well as of H_2O takes place in the excretion of uric acid (cf. this vol., 976). L. S. THEOBALD.

p_H Values in routine urine analysis. O. B. PRATT and H. O. SWARTOUT (J. Lab. Clin. Med., 1931, **16**, 471—475).—Misleading vals. are discussed. CHEMICAL ABSTRACTS.

Distribution of amino-acids in blood in anæmia; criticism of the new Folin method of determination of amino-acids in the blood. A. SIMON (Arch. exp. Path. Pharm., 1931, **160**, 599—609).—An increase in the ratio of NH_2-N in blood-corpuscles to that in the plasma is found in dogs suffering from anæmia and after splenectomy. The ratio of the concentration of diffusible NH_2-N in corpuscles to that in the plasma is greater in canine than in human anæmia. Folin's method for the determination of NH_2-acid (A., 1930, 630, 1305) is criticised, since it gives low results due to absorption of NH_2-acids by the contracted cells. B. LEVIN.

Catalase action and glutathione content of red blood-corpuscles in anæmia. E. BACH and E. BACH (Biochem. Z., 1931, **236**, 174—181).—The catalase content and the reducing power in the cold (caused chiefly by the glutathione content) in various types of anæmia are investigated. In true pernicious anæmia a parallel increase takes place in both catalase and glutathione contents of the cells. In secondary anæmia the catalase and glutathione contents are not increased. In acute loss of blood, the relative glutathione content of human red cells is increased, and the catalase content is also increased in the cells of lower animals. P. W. CLUTTERBUCK.

Effect of adrenaline-free suprarenal extract on the specific dynamic action of foodstuffs. A. E. KOEHLER (Science, 1931, **74**, 78).—In cases of asthenia, continued administration of the extract results in a diminution of its beneficent effect and a

diminution or disappearance of the sp. dynamic action of foodstuffs. L. S. THEOBALD.

Cancer research and the scientific method. E. McDONALD (Science, 1931, **74**, 55—60).—An address. L. S. THEOBALD.

Hormones in cancer. F. BISCHOFF, L. C. MAXWELL, and H. J. ULLMANN (Science, 1931, **74**, 16).—With one possible exception, none of the well-established hormones or glandular products affects the rate of growth (or final mortality) of transplantable rat sarcomata or carcinomata. L. S. THEOBALD.

Respiration of Jensen sarcoma and mouse carcinoma. B. KISCH (Biochem. Z., 1931, **237**, 226—243).—The respiration-increasing action of certain substances [salts with bivalent and tervalent elements, " omega " (A., 1930, 949, 1036), glycine, and alanine] is greater with normal than with tumour tissue from the same rat. The respiration-inhibiting action of high concentrations of Al salts, borates, and NH_2-acids occurs both with normal and tumour tissue. Hence it appears that tumour tissue has reached the max. rate of respiration for the experimental conditions. F. O. HOWITT.

Mitogenetic spectrum analysis. I. N. KANNEGIESSER. **II. Carcinoma and cornea epithelium.** L. GURWITSCH (Biochem. Z., 1931, **236**, 415—424, 425—431).—I. Blood glycolysis and three different types of oxidation were examined by the method of spectrum analysis of mitogenetic radiation. Typical spectra are obtained, that of glycolysis possessing a range of 190—200 and 212—220 mμ and that of oxidation 223—234 mμ.

II. The duplex nature of mitogenetic radiation of carcinoma is due to glycolytic and proteolytic action. That of the epithelium of the cornea of rabbit is normally glycolytic, but is proteolytic during inanition. F. O. HOWITT.

Carcinogenic potency of mineral oils. C. C. TWORT and J. M. TWORT (J. Ind. Hygiene, 1931, **13**, 204—226).—A revised method of expressing carcinogenic potency is described. Refined Scottish shale lubricating oil was found to be more potent than any refined petroleum-well oil. The potency of crude shale oil did not decrease until the retorting temperature fell below 400°. The potency of refined petroleum lubricating oil may vary as much as 30 times in different samples. Potency is decreased by addition of lanolin or sperm oil; saponifiable oils showed no activity. In general the more saturated mineral oils are less potent. The fluorescence of oils may be related to their potency. Chrysene has definite carcinogenic activity. R. K. CALLOW.

Production of dental caries in rats fed on an adequate diet. C. A. HOPPERT, P. A. WEBBER, and T. L. CANNIFF (Science, 1931, **74**, 77—78).—Dental caries in rats is not due primarily to a deficiency of vitamin or mineral salts, but is probably caused by bacterial decomp. of foodstuffs lodged in the teeth. L. S. THEOBALD.

Partition of potassium in healthy or pathological muscle. A. LEULIER, B. POMME, and R. DELAYE (Compt. rend., 1931, **193**, 202—204).—There is a diminution of K in the musculature affected by certain amyotropic conditions arising from cerebral or spinal lesions. C. C. N. VASS.

Acid-soluble phosphorus of blood in normal individuals and diabetics. R. MEIER and E. THOENES (Arch. exp. Path. Pharm., 1931, **161**, 119—140).—The mean total acid-sol. P of blood in normal man is 55 mg. per 100 c.c., made up by inorg. P 8·5, easily hydrolysable esters 12·0, and esters hydrolysed with difficulty 34·5 mg. 0·1*N*-HCl will hydrolyse 13% in 3 hr. The lowering of total acid-sol. P in diabetes, which is most noticeable in the state of coma (to 35·8 mg. per 100 c.c.), occurs largely at the expense of the esters which are hydrolysed only with difficulty, the changes which these esters undergo being independent of the H_2O content of the serum. Insulin treatment brings about a lowering of inorg. P, increases the fraction of esters hydrolysed with difficulty, and produces a temporary decrease in the easily hydrolysable fraction. Phosphoric esters occur entirely in the corpuscles. P. G. MARSHALL.

Initial hypoglycæmia after extirpation of the pancreas. H. HORSTERS (Arch. exp. Path. Pharm., 1931, **160**, 692—698).—A discussion of the cause of the hypoglycæmia observed in dogs within a few hr. after pancreatectomy (cf. this vol., 758). A. COHEN.

Formation in articular exudates of fibrin apart from blood-fibrinogen ; role of white cells. M. PIETTRE and B. CELAN (Compt. rend., 1931, **193**, 83—85).—The exudate formed in polyarthritis in the calf contains fibrin in three forms: free, mixed with the formed elements, and dispersed in the liquid phase. The formation of the reticulum proceeds as when white cells are treated with dil. HCl or distilled H_2O. C. C. N. VASS.

Occurrence of heavy metals in human gallstones. R. SCHONHEIMER and W. HERKEL (Klin. Woch., 1931, **10**, 345—346; Chem. Zentr., 1931, i, 2218—2219).—Cu, Zn, Mn, and Fe were found in considerable quantities. A. A. ELDRIDGE.

Hæmophilia. C. LA F. BIRCH (Science, 1931, **74**, 16—17).—Introduction of the female sex hormone (ovarian extract) into two young males rendered them symptom-free for several months. The blood platelets are resistant to hypo- and hyper-tonic salt solutions. L. S. THEOBALD.

Effect of diet on hookworm infestation in dogs. A. O. FOSTER and W. W. CORT (Science, 1931, **73**, 681—683).—Dogs fed on a diet deficient in vitamins and inorg. salts develop hookworm infestations, but recover when fed on an adequate diet. L. S. THEOBALD.

Urinary p_H and alveolar carbon dioxide in hyperchlorhydria. C. S. HICKS (Austral. J. Exp. Biol., 1931, **8**, 133—138).—Ingestion of food in one case was immediately followed by secretion of an acid urine which gradually became more alkaline. Alveolar CO_2 changes ran parallel to the urinary p_H. P. G. MARSHALL.

Intelligence and body chemistry. G. J. RICH (Science, 1931, **74**, 21—22).—No significant correlations between blood-Ca and -P and intelligence in children could be found (cf. this vol., 977). L. S. THEOBALD.

Colloid chemistry of insanity. I. W. D. BANCROFT and G. H. RICHTER (J. Physical Chem., 1931, **35**, 1606—1623).—The effects of different reagents on the nervous system are discussed, and it is suggested that mental disorders are of two types, the one resulting from increased and the other from decreased dispersion of the colloids of the nervous system.
L. S. THEOBALD.

Bilirubin liver-function test. I. I. R. JANKELSON and S. L. GARGILL (New England J. Med., 1931, **204**, 547—549).—Blood-bilirubin is determined at 5 min. and 3 hr. intervals following intravenous injection of bilirubin. CHEMICAL ABSTRACTS.

Cinchophen oxidation test of the function of the hepatic cells. S. S. LICHTMAN (Arch. Int. Med., 1931, **48**, 98—125).—A colorimetric determination of "oxycinchophen" in urine is based on the yellow colour produced by HCl, which is sensitive in dilutions of 0·0002%. Following oral administration of 0·45 g. of "cinchophen," the 24 hr. excretion of "oxycinchophen" is used as a test of liver function. In normal subjects this excretion is 30—100 mg., but higher vals. (about 200 mg.) are given for cases of various liver disorders. A. COHEN.

Ration for the production of rickets in chicks. E. B. HART, O. L. KLINE, and J. A. KEENAN (Science, 1931, **73**, 710—711).—A ration containing 19—20% of protein, 0·9—1% Ca, and 0·5—0·6% P is detailed.
L. S. THEOBALD.

Histochemical investigation of the initial lesions of experimental pulmonary silicosis. A. POLICARD (Compt. rend., 1931, **193**, 197—199).—In white rats breathing rock dust containing 82% SiO_2 the particles are filtered by the alveoli. The particles of SiO_2 are attacked by the cellular juices and the resulting fibrosis with its degenerated cytoplasm rich in SiO_2 constitutes an excellent medium for the tubercle bacillus. C. C. N. VASS.

Serum-calcium and -inorganic phosphorus during parathyroid tetany. A. VON BEZNÁK (Biochem. Z., 1931, **236**, 362—371).—Strychnine convulsions in normal and parathyroidectomised dogs result in an increase in blood-Ca and -inorg. P. In venous blood of the contracted muscle, the inorg. P is greater than in resting muscle whilst the Ca content is unchanged. The tetany of parathyroidectomy produces a decrease of muscle-creatinephosphoric acid with a concomitant increase of inorg. P.
F. O. HOWITT.

Cell metabolism. J. JANY and C. SELLEI (Biochem. Z., 1931, **236**, 348—361).—An exact criterion of cell metabolism is provided by the energy quotients and $W^{O_2}_{CO_2}/W_{O_2}$, where $W^{O_2}_{CO}$ is the heat from aerobic glycolysis of the tissue for 1 hr., $W^{N_2}_{CO}$ that from anaerobic glycolysis, W_{O_2} the basic heat of respiration, and W the total heat evolution under aerobic conditions, so that $W = W_{O_2} + W^{O_2}_{O_2}$. Changes in these quotients for various tissues indicate that the kidney cortex has little glycolytic function and possesses typically aerobic metabolism, whilst the medulla produces sufficient heat by glycolysis to support anaerobic metabolism. Grey cerebral cortical tissue is more highly glycolytic, yet is not suited for anaerobic existence. Tissue from rat carcinoma exhibits amongst all tissues considered the greatest adaptation for glycolysis and anaerobiosis.
F. O. HOWITT.

Basal-metabolic rates of vegetarians. G. WAKEHAM and L. A. HANSEN (Science, 1931, **74**, 70—71).—Basal-metabolic rates in young women who have been vegetarians for 5 years or more are less than in non-vegetarians. L. S. THEOBALD.

Metabolic experiments on rabbits with hormone preparations. H. HORSTERS (Z. ges. exp. Med., 1930, **73**, 167—179; Chem. Zentr., 1931, i, 2354).—Determinations of blood-albumin, -P, -Ca, -NaCl, and -cholesterol, urinary P_2O_5 and NaCl, and fæcal P_2O_5 are recorded. A. A. ELDRIDGE.

Relation of life to electricity. IV. Electromotive action of homologous fatty acids; exhaustion as an electrochemical sequence of a chemical splitting of higher molecular compounds. R. BEUTNER and J. LOZNER (Protoplasma, 1931, **12**, 380—393; cf. this vol., 866).—Solutions of homologous fatty acids in fats and in amyl acetate gradually decrease in stainability, e.m.f., and p_H with decreasing mol. wt. These changes are shown to accompany the exhaustion of living tissue with the gradual breakdown of high-mol. compounds.
A. G. POLLARD.

Bile acid : fat ratio of intestinal contents and its relation to fat absorption. O. FÜRTH and H. MINIBECK (Biochem. Z., 1931, **237**, 139—158).—The cholic acid : total fats ratio was determined in the intestinal contents of infants, cream-fed cats, and fat-fed rats, vals. of $\frac{1}{8}$— $\frac{1}{6}$—$\frac{1}{20}$, and $\frac{1}{1\cdot5}$—$\frac{1}{8}$, respectively, being obtained. Thus rats are best adapted for fat absorption. The results indicate that the dissolving action of bile acids on fat does not follow *in vitro* experiments, but is increased by the presence of small amounts of phosphatides and that, especially with increased fat ingestion, the bile acids convey fat into the blood- and lymph-streams and then return to the intestinal lumen for further use. F. O. HOWITT.

Fat and glycogen metabolism of resting and exercised rats. T. OSUKA (Z. physiol. Chem., 1931, **199**, 81—92).—The increased total fat of resting rats receiving an addition of yeast to their diet is found in parts other than the liver; the increased glycogen is present in the liver. With adequate diet, the total body-fat is the same for exercised rats whether they receive yeast or not, but is smaller than for resting rats. Exercise does not affect the liver-fat. The glycogen of the yeast-fed exercised rats is higher than in absence of yeast. Exercise promotes glycogen storage in the liver at the expense of the body-fat.
J. H. BIRKINSHAW.

Glycolysis and amylolysis in muscle after fatigue. E. BECCARI (Biochem. Z., 1931, **236**, 113—121).—Fatigue of muscle causes a decrease in glycolytic but does not affect amylolytic power. The effect is independent of the p_H changes.
P. W. CLUTTERBUCK.

Biochemistry of fatigue. I. Influence of "training" on the lactic acid content of muscle after work. A. PALLADIN, L. PALLADIN, and E. PERSOVA (Biochem. Z., 1931, **236**, 268—275).—Mus-

cular activity by frequent electrical stimulation affects rabbit muscle so that, unlike "untrained" muscle, no increase of lactic acid content occurs on further stimulation. Hence lactic acid formation is not a trustworthy criterion of work performance. Stimulation of "untrained" muscle results in a decrease of creatinephosphoric acid and a more than correspondingly greater formation of H_3PO_4, indicating a simultaneous degradation of hexosephosphate. In "trained" muscle stimulation produces formation of creatinephosphoric acid, indicating a synthesis; comparison with the data of Ferdmann and Feinschmidt (A., 1929, 1193), however, points to a fission of the acid on excitation of "trained" muscle. H_3PO_4 is increased to a smaller extent than in "untrained" muscle. F. O. Howitt.

Muscular contraction without formation of lactic acid ("alactacidic"). V. Henriques and E. Lundsgaard (Biochem. Z., 1931, **236**, 219—225).—The latent period, contraction time, course of contraction, maximal tension developed, and the action current for the contraction of muscle, the lactic acid formation of which has been completely inhibited by iodoacetic acid, are the same as for normal muscle and the role of lactic acid formation in muscular contraction should be regarded as of a secondary nature. P. W. Clutterbuck.

Energetics of muscular contraction when formation of lactic acid is prevented. O. Meyerhof, E. Lundsgaard, and H. Blaschko (Biochem. Z., 1931, **236**, 326—347; cf. A., 1930, 1312).—In muscle poisoned with iodoacetic acid the amount of heat liberated for a definite amount of creatinephosphoric acid hydrolysis is not const. For weak stimulation the calorific equiv. is 160 g.-cal. per g. of liberated H_3PO_4. With anaerobic resting muscle higher vals. are obtained, extensive hydrolysis giving a final val. of about 450 g.-cal. Hence when lactic acid formation is prevented a heat-supplying reaction independent of phosphagen hydrolysis occurs. Part of the excess heat is due to hydrolysis of adenylpyrophosphoric acid and part to the evolution from resting anaerobic muscle. 80% of the heat due to contraction alone is accounted for by phosphagen hydrolysis. F. O. Howitt.

Poisoning of frog muscle-extract by iodoacetate. K. Lohmann (Biochem. Z., 1931, **236**, 444—456).—The hexosediphosphoric acid of Harden and an aldosemonophosphoric acid of the Embden type were isolated from the musculature of the intact iodoacetate-poisoned frog. Formation of phosphoric ester in frog muscle-pulp or -extract is less on addition of iodoacetate than on that of fluoride. Inhibition of lactic acid formation from glycogen and hexosediphosphate is a well-marked time reaction. In completely poisoned muscle-extracts H_3PO_4 liberation from hexosediphosphate is almost completely whilst esterification of glycogen is only partly inhibited. Et urethane inhibits the poisoning action of iodoacetate. With high concentrations of iodoacetate lactic acid formation from hexosediphosphate is inhibited before that from glycogen, whilst with that from methylglyoxal inhibition is much less marked. F. O. Howitt.

Formation of lactic acid and hydrolysis of creatinephosphoric acid in anaerobic activity of muscle. O. Meyerhof and W. Schulz (Biochem. Z., 1931, **236**, 54—86).—The time course of lactic acid formation with short (2 sec.) tetanus in N_2 and O_2 at high and low temp., and of the isometric coeffs. of decomp. of phosphagen and of lactic acid formation for short tetani and for series of single twitches at different temps. in normal and curarised muscle is investigated and the results are shown to remove some of the essential discrepancies between the findings of the chemical and myothermic methods. With max. contraction and with indirect stimulation in short tetanus, a considerable part of the lactic acid arises after relaxation and independently of the temp. (4° and 18°). The lactic acid formation within and immediately following tetanus is the same in an O_2-saturated as in an anaerobic muscle. The lactic acid time coeffs. with and without recovery confirm the older results of Embden rather than those of the author and remove the contradiction between the appearance of positive anaerobic heat and the simultaneous endothermic resynthesis of creatinephosphoric acid, the energy for the latter being accounted for by the energy of exothermic formation of lactic acid. The K_{mL} val. for a single twitch is independent of the stimulation interval, but for a short series of twitches is dependent on the total tension developed (no. of stimuli), being for 30—60 stimuli 255×10^6, for 120 stimuli 150×10^6, and for complete fatigue 115×10^6. With a high degree of curarisation (trimethyloctylammonium iodide) the K_{mL} value for 30—60 twitches is 180×10^6. The K_Z val. for the decomp. of phosphagen in curarised muscle is considerably increased. The increase of the K_{mL} val. of curarised muscle is equiv. in energy val. to the lowering of the K_{mL} val. in the same muscle. Within the tetanus, O_2 is without influence on the decomp. of phosphagen. P. W. Clutterbuck.

Breakdown and resynthesis of phosphagen in frozen and thawed muscles. E. Kreps (Proc. Roy. Soc., 1931, **B**, **108**, 545—552).—As with glycogen (A., 1929, 1102), the max. rate of breakdown of phosphagen in frozen frogs' muscles occurs at —2·6°. On thawing, phosphagen is recovered completely if the muscles are frozen for 24 hr. at a temp. not lower than —1·5°. There is no recovery below —2·5°, and partial recovery at intermediate temp. owing to variations in muscle fibres. Recovery is dependent on O_2. A. Cohen.

Oxygen uptake of frozen and thawed muscles. E. C. Smith (Proc. Roy. Soc., 1931, **B**, **108**, 553—559).—The O_2 uptake of frozen frogs' muscles decreases to zero at —4°. The initial O_2 uptake is recovered on thawing muscles frozen 24 hr. at a temp. not lower than —2·4°. When frozen below —3°, muscles can recover only 10% of the O_2 uptake of muscles in resting condition. Loss of contractility and ability to synthesise glycogen and phosphagen is not due to destruction of the respiratory function, since oxidation of lactic acid is still possible in irreversibly frozen muscle. A. Cohen.

Creatine–creatinine metabolism. I. Urinary creatinine and diet. K. Eimer (Z. ges. exp. Med.,

1930, **74**, 738—749; Chem. Zentr., 1931, i, 2357).—A large increase in the intake of meat causes increased urinary creatinine and N, but not creatine.

A. A. ELDRIDGE.

Liver and nitrogen metabolism. F. GOEBEL (Med. Doswiad. Spolecz., 1929, **10**, 16 pp.; Chem. Zentr., 1931, i, 2357).—The N distribution in the normal dog's urine is: urea 85·2—89·6, NH_3 3·4—4·6, oxyproteic acids 1·3—1·8, Et_2O-sol. 2·7—4·0; with Eck's fistula the NH_3-N : urea-N ratio and the total N were disturbed, and the oxyproteic acid was increased.

A. A. ELDRIDGE.

Structure of mentholglycuronic acid obtained by feeding menthol. A. DA CRUZ (Compt. rend. Soc. Biol., 1930, **105**, 815—816; Chem. Zentr., 1931, i, 2222).—Fission of biosynthetic mentholglycuronic acid with β-glucosidase gives *d*-glycuronic acid.

A. A. ELDRIDGE.

Utilisation of pentosans in the animal organism. O. FURTH and P. ENGEL (Biochem. Z., 1931, **237**, 159—188).—The total carbohydrate content of the liver of rats fed with various diets was determined. Fats and proteins are not good glycogen formers. Cellulose freed from sol. carbohydrate and pectin, galactose, hydropectan, and crude arabinose (hydrolysed cherry-gum) exhibit weak but definite glycogen formation. Cherry- and tragacanth-gums are without action. Orally introduced xylan in 5 phloridzinised rabbits gave an increase in sugar excretion and *D*/*N* ratio in only 2 cases. In adrenalinised and partly starved rabbits oral administration of xylan when the urinary sugar is nil results in the appearance of reducing sugar in the urine. Hence pentosans are utilised and transformed into reducing sugars by the organism.

F. O. HOWITT.

Intermediary carbohydrate metabolism. IX. Intravenous galactose assimilation under the influence of hormones, hunger, and feeding. X. The first phase of dextrose assimilation. M. WIERZUCHOWSKI (Biochem. Z., 1931, **237**, 92—102, 103—128).—IX. The assimilation of galactose administered intravenously to normal dogs at the rate of 2 g. per kg. per hr. for 10 hr. is not affected by the type of feeding, by hunger, or by adrenaline or thyroxine administration. An average of 25·36% is metabolised and 74·64% excreted in the urine. Insulin, however, increases the assimilation, the galactosuria being reduced throughout the experimental period.

X. The first phase of assimilation of dextrose administered intravenously to dogs at the rate of 2 g. per kg. per hr. is attended by a blood-sugar curve which exhibits (*a*) a rise, (*b*) a flat portion, and (*c*) a fall. This first phase, which is sp. for dextrose, is eliminated by increasing the daily administration of carbohydrate. It appears only once during the period of dextrose administration despite any variation in rate and is not influenced by performance of work, which also has no action on the degree of dextrose assimilation. Insulin administration affects the phase mainly during the period of (*a*), simultaneous adrenaline administration resulting in a normal phase. 1 γ of the latter hormone nullifies the assimilation of an average of 27·7 mg. of dextrose.

F. O. HOWITT.

Influence of exclusive and mixed diet, and of addition of salts on the urinary excretion and the composition of blood. W. VON MORACZEWSKI and S. GRZYCKI (Arch. exp. Path. Pharm., 1931, **160**, 703—719).—The proportions of the substances excreted in the urine of dogs fed on a mixed diet, or on one composed exclusively of fat, carbohydrate, or protein, vary. Diuresis is increased by overfeeding of fat or carbohydrate. The latter also increases the excretion of creatinine, which is also increased by the addition to all the diets of salts such as KCl and NH_4Cl. A parallel effect is also observed with the excretion of P. The alkali reserve of the blood is lowered on a diet of fat, whilst addition of salts has a similar effect. Fat in the diet increases the amount of blood-Ca. Overfeeding, generally, leads to an increase in the amounts of NH_3 and uric acid excreted.

B. LEVIN.

Mineral metabolism in infancy. III. Substitution of cow's milk for human milk in infant feeding. S. V. TELFER (Glasgow Med. J., 1930, **33**, 265—284).—With cow's milk the intake of Ca, Mg, and P is much greater than with human milk; the mineral retention (except of Fe) is increased, but the proportionate mineral retention falls. The fat is less effectively utilised. The urinary H_3PO_4 is greater with cow's milk.

CHEMICAL ABSTRACTS.

Calcium requirements of dairy heifers. J. B. LINDSEY, J. G. ARCHIBALD, and P. R. NELSON (J. Agric. Res., 1931, **42**, 883—896).—Heifers on a high-Ca ration showed higher Ca-storage but lower % retention than those on a low-Ca ration. A high Ca content in the ration was necessary to ensure adequate P-storage. The Mg balance averaged a small positive value for high-Ca rations and a small negative value for low-Ca rations. The intake of all elements per unit wt. and the retention per unit wt. showed a similar, proportional decline with increasing age. The 2 : 1 ratio of Ca : P retained, irrespective of the ratio of the intake, was very uniform for both types of ration and for animals of all ages. The storage of mineral substances was definitely lower with animals on low-Ca ration, but no ill effects were observed.

A. G. POLLARD.

Sulphur and growth. L. BINET and J. MAGRON (Compt. rend., 1931, **193**, 115—117).—0·1% aq. $Na_2S_2O_4$ promotes the growth of *Lepidum sativum* and the metamorphosis of the tadpole.

C. C. N. VASS.

Toxicity limit of ozone. F. TOUL (Coll. Czech. Chem. Comm., 1931, **3**, 333—335).—Concentrations of 0·05—0·07% of O_3 in air have no effect on the larvæ of *Tenebrio molitor*; above 0·12%, O_3 is definitely toxic.

H. BURTON.

Effects of dilution on the lethal properties of a poison. T. N. SETH (J. Pharm. Exp. Ther., 1931, **42**, 333—341).—In measurements of the time taken for the heart of the tadpole to cease beating when the animal is placed in solutions containing a poison such as $HgCl_2$ in varying concentrations, it is observed that an increase in the dilution of the poison causes, up to a point, a decline in its lethal properties. Further dilution enhances its lethal effect, but still further dilution again decreases the effect. It is

suggested that the lethal effect of a poison which dissociates in solution depends on both the undissociated mols. and the ions formed. B. LEVIN.

Modifications of the alcohol and water contents of the blood following administration of alcohol and water. A. GALAMINI and G. LAMANNA (Atti R. Accad. Lincei, 1931, [vi], **13**, 143—148).—While fasting, different individuals show different H_2O contents of the blood, the max. usually occurring at about 11 a.m. Administration of small quantities (200—300 c.c.) of H_2O causes lowering of the H_2O content of the blood, sometimes preceded by a slight increase. Lowering of the H_2O content is produced also by ingestion of EtOH or of large amounts of dextrose in the form of grapes, although the amount of H_2O introduced in the latter case may be relatively high. When Marsala is taken at intervals, the EtOH content of the blood shows, not a regular increase, but successive increments, sometimes interrupted by decreases. The H_2O content of the blood varies inversely to the EtOH content. T. H. POPE.

Etiology and therapeutic modifiability of the specific toxic action of methyl alcohol. E. KEESER (Arch. exp. Path. Pharm., 1931, **160**, 687—691).—CH_2O is found in the abdominal fluid and vitreous body of rabbits poisoned with MeOH, and is formed by the action of fresh vitreous body (calf) on MeOH. In the latter case, the addition of $(NH_4)_2CO_3$ leads to the formation of hexamethylenetetramine. The organs of rabbits receiving MeOH and $(NH_4)_2CO_3$ show less injury than those of rabbits receiving MeOH alone. The results support the view that the toxic effects of MeOH are due to CH_2O formation.
A. COHEN.

Blood-lipins and fixation of ethyl chloride by whole blood. L. SCOTTI-FOGLIENI (Compt. rend. Soc. Biol., 1931, **105**, 959—960; Chem. Zentr., 1931, i, 2219—2220).—Blood-lipins do not influence the amount of EtCl retained; the amount is more probably determined by the red corpuscles.
A. A. ELDRIDGE.

Insulin and the blood-sugar level under ether anæsthesia. H. ESCHWEILER (Arch. exp. Path. Pharm., 1931, **161**, 21—33).—Injection of insulin ½ hr. before the beginning of anæsthesia is of advantage in counteracting the hyperglycæmic effect of Et_2O, since the administration of the anæsthetic coincides with the hypoglycæmic stage of insulin action.
P. G. MARSHALL.

Influence of magnesium chloride on the narcotic and toxic effects of sodium barbital. H. G. BARBOUR and W. F. TAYLOR (J. Pharm. Exp. Ther., 1931, **42**, 321—331).—When 2 parts of $MgCl_2$ and 1 part of Na-barbital are injected simultaneously into rabbits, the min. lethal dose is much higher than that calc. by a simple summation of the two separate effects, the $MgCl_2$ exercising a " protective antagonism." Similarly, $MgCl_2$ injected simultaneously with Na-barbital may hasten the onset of narcosis, and lessen its duration, with no corresponding increase in toxicity. B. LEVIN.

Toxicology of benzene. A. M. TSCHERNIKOV, I. D. GADASKIN, and F. V. KOVSCHAR (Arch. exp. Path. Pharm., 1931, **161**, 214—228).—A detailed account of the symptoms of acute C_6H_6 poisoning (dilatation of the pupils, fall in blood-pressure, paralysis of the respiratory centre, etc.) is given and these are compared with the results of PhOH poisoning. PhOH in the blood is determined colorimetrically by coupling with diazotised *p*-nitroaniline.
P. G. MARSHALL.

Resorption of salicylic acid following intratracheal or subcutaneous injection. W. BLUME and P. BREUNIG (Arch. exp. Path. Pharm., 1931, **161**, 181—195).—Salicylic acid (Na salt) is rapidly absorbed from the trachea, making its appearance in the blood in 1 min. and the urine in 10 min. The max. concentration occurs in 3 min. in the blood and in 1 hr. in the urine. Absorption occurs less rapidly after subcutaneous injection. P. G. MARSHALL.

Influence of quinone on cells. G. LEJHANEC, I. A. PARFENTJEV, and B. SOKOLOFF (J. Pharm. Exp. Ther., 1931, **42**, 343—353).—Benzoquinone added to a 36% aq. suspension of yeast (p_H 9·3) increases the O_2 consumption in a dilution of 1 in 500,000. This effect is more marked in salt solution (p_H 5·6) than in H_2O. At the same time, the life of the cells is shortened, and their multiplication inhibited.
B. LEVIN.

Mechanism of antiglycosuric action of santonin. A. LEULIER and A. ROCHE (Compt. rend., 1931, **193**, 81—82).—In the rabbit, 2 hr. after injection santonin exerts an action antagonistic to that of phloridzin; the action lasts for 5—6 hr. and is probably due to an elevation of the dextrose threshold val. of the kidney. C. C. N. VASS.

Active principle of guarana. G. BERTRAND and B. CARNEIRO (Compt. rend., 1931, **193**, 276—278).—The active principle is caffeine. β-Guarinine, described by Nierenstein (1910) is impure caffeine.
C. C. N. VASS.

Biological determination of morphine. L. MAIER (Arch. exp. Path. Pharm., 1931, **161**, 163—172).—Straub's morphine reaction (Biochem. Z., 1912, 39, 216) forms a basis for its biological determination. By injection of crude neutral organ extracts (in forensic cases) into mice as little as 0·02 mg. can be detected.
P. G. MARSHALL.

Neutralisation of [toxicity of] strychnine sulphate. A. C. MARIE (Compt. rend. Soc. Biol., 1930, **105**, 744—745, 846—847; Chem. Zentr., 1931, i, 2226).—Strychnine is detoxicated for mice by $NaMnO_4$. Guinea-pigs are not trustworthy test-animals. Strychnine is also detoxicated for mice by admixture with guinea-pig's blood and dried horse adrenals. The protective action is attributed to the colouring matter of the blood. A. A. ELDRIDGE.

Effect of vomicine on blood-sugar. E. RUICKOLDT (Arch. exp. Path. Pharm., 1931, **161**, 59—63).—Intravenous administration of vomicine to rabbits causes a rise in blood-sugar (to $>$200 mg. per 100 c.c.) which is independent of convulsions caused by this drug and is unaffected by adrenalectomy when large doses are given. Administration of ergotamine prevents this rise in blood-sugar, which is also reduced by the action of adrenaline. P. G. MARSHALL.

Curare-diabetes in the frog. E. GEIGER (Arch. exp. Path. Pharm., 1931, **161**, 88—90).—Contrary to

the conclusions of Langendorff (Pflüger's Archiv, 1887, 139) curare never produces glycosuria following extirpation of the liver. Small doses are more lethal in frogs with extirpated livers than in normal animals (0·3 mg. per 100 g.), whilst the paralysing dose is almost the same (0·05 mg. per 100 g.).

P. G. MARHSALL.

Pharmacology of hops. H. STEIDLE (Arch. exp. Path. Pharm., 1931, **161**, 154—162).—Both hop dust and hop oil produce symptoms of paralysis in frogs, the toxicity varying according to the locality from which the material is obtained, the season, and the duration of storage. P. G. MARSHALL.

Toxicity of aluminium compared with that of iron, nickel, and other metals. G. BERTRAND and S. SERBESCU (Compt. rend., 1931, **193**, 128—131).—The toxicities of Cu, Ni, Cd, Co, Zn, Mn, Fe^{II}, Fe^{III}, and Al have been contrasted by intraperitoneal injections of the cryst. sulphates or chlorides into guinea-pigs, the time of survival being measured. The toxicity of Al is comparable with that of Fe and less than that of Cu and Ni. C. C. N. VASS.

[Blood-]coagulating action of inorganic and organic calcium salts. R. DOURIS and M. PLESSIS (Compt. rend. Soc. Biol., 1930, **105**, 757—759; Chem. Zentr., 1931, i, 2220).—For equal amounts of Ca, the rapidity of coagulation diminished in the order: chloride, hypophosphite and benzoate, lactate and acid malate. A. A. ELDRIDGE.

Partition of gallium in the organism. C. LEVADITI, J. BARDET, A. TCHAKIRIAN, and A. VAISMAN (Compt. rend., 1931, **193**, 117—119).—Ga has been determined spectrographically and colorimetrically in the ash of the tissues and blood of the rabbit after intramuscular injection of Ga tartrate. Ga gives with resorcinol and NH_3 a bluish-violet colour the intensity of which depends on the quantity of resorcinol; for the same amount of reagent the rate of development of the colour is proportional to the amount of Ga present. Ga remains in the organism at least 69 days after injection; it circulates in the blood, accumulates first in the kidney and liver, but is rarely present in the brain. C. C. N. VASS.

Toxicity of several allotropic modifications of germanic oxide. J. H. MULLER (J. Pharm. Exp. Ther., 1931, **42**, 277—297).—The min. lethal dose of the colloidal form when injected intraperitoneally into guinea-pigs is 400 mg. per kg. body-wt., and that of the cryst. form is 300 mg. per kg. A marked tolerance is developed by its administration in sub-lethal amounts. B. LEVIN.

Amalgam [toxicity] question. P. BORINSKI (Zahnarztl. Mitt., 1929, 4 pp.; Chem. Zentr., 1931, i, 2225).—Absorption of Hg occurs from dental amalgams, chiefly in the first 3 months, but also during 15 months or longer. Little difference between Cu and Ag amalgams was observed.

A. A. ELDRIDGE.

Occurrence of small quantities of mercury in urine and fæces. P. BORINSKI (Klin. Woch., 1931, **10**, 149—153; Chem. Zentr., 1931, i, 2225).—Hg (up to 10^{-5} g. per day) was excreted by 56% of (75) persons who had not been in contact with Hg, or those carrying old dental amalgam fillings. Markedly higher results were obtained with persons carrying new fillings or those otherwise brought into contact with Hg. Nearly all foodstuffs contain traces of Hg; it is estimated that the daily intake from this source is 5×10^{-6} g. A. A. ELDRIDGE.

Salt effects on eggs and nauplii of *Artemia salina*, L. E. BOONE and L. G. M. BAAS-BECKING (J. Gen. Physiol., 1931, **14**, 753—763).—The hatching of eggs of the brine shrimp is not affected by the reaction of its environment between p_H 2·0 and 13·0. The highly toxic effect of K salts is slightly antagonised by Na salts, in which nauplii are formed, and to a smaller extent by Mg and Ca. A. COHEN.

Salt effects on swarmers of *Dunaliella viridis*, Teod. L. G. M. BAAS-BECKING (J. Gen. Physiol., 1931, **14**, 765—779).—The organism may be grown in M—$4M$-NaCl solutions at 6—9 without decrease in the size of the cells. It is sensitive to the toxic effects of Ca and Mg, which are, however, antagonistic. The Mg : Ca ratio which permits development of the organism rises from 4—5 in M-NaCl to 20 in $4M$-solution. A. COHEN.

Colloid chemistry of the nervous systems. I. Sodium thiocyanate therapy. I. W. D. BANCROFT and J. E. RUTZLER, jun. (J. Physical Chem., 1931, **35**, 1185—1211).—Further examples of the antagonistic effect of NaCNS on the physiological action of certain drugs support the reversible coagulation theory of narcosis (this vol., 513). NaCNS alleviates the effects of strychnine and other drugs on rabbits (this vol., 649), but "nembutal" and EtOH are not antagonised to any marked degree. Na poisoning may be produced by too much NaCNS in the presence of a strong narcotic. Na tartrate augments the action of morphine hydrochloride, whilst NaCNS antagonises it, indicating the existence of a lyotropic series of ions connected with the peptisation of colloids coagulated by morphine. A theory based on the peptisation of coagulated protein colloids of the brain for relief of drug addiction is proposed.

L. S. THEOBALD.

X-Radiation and regeneration in *Amblystoma*. E. G. BUTLER (Science, 1931, **74**, 100—101).—X-Radiation prevents normal regeneration of the fore-limb of the embryo of *Amblystoma* at any stage of development, but has no apparent effect on normal growth and differentiation. L. S. THEOBALD.

"Omega"-catalysis of oxidative glycine fission. B. KISCH (Biochem. Z., 1931, **236**, 380—386).—In the oxidative deamination of glycine by "omega"-catalysis (cf. A., 1930, 949, 1036) added phosphate functions as a buffer and is replaceable by $NaHCO_3$. "Omega"-catalysis is ineffective for alanine, dihydroxyphenylalanine, glutamic acid, taurine, and also for glycine Et ester and glycylglycine, indicating that these latter compounds are neither hydrolysed nor directly deaminated under the experimental conditions. Thus the "omega"-catalyst exhibits a marked specificity of action similar to that of enzymes.

F. O. HOWITT.

Inhibiting effect of oxidase on the reduction of sulphur by potato and gladiolus juice. J. D. GUTHRIE (Contr. Boyce Thompson Inst., 1931, **3**,

125—130).—Treatment of potato tubers or gladiolus corms with $CH_2Cl{\cdot}CH_2{\cdot}OH$ reduces the ability of the expressed juices to reduce S to H_2S. This effect is increased by boiling the juice or carrying out the reaction in an atm. of N_2. Addition of unboiled juice decreases the H_2S production from boiled juice. Fresh juice probably contains oxidase which oxidises either H_2S as formed or the reducing agents responsible for its formation. A. G. POLLARD.

Influence of reaction of medium on the regeneration of peroxidase inactivated by heat. S. PRONIN (Biochem. Z., 1931, **236**, 107—112).—Regeneration of heat-inactivated peroxidase of horseradish occurs most completely in neutral solution. P. W. CLUTTERBUCK.

Molecular statistics of an enzyme action. J. B. S. HALDANE (Proc. Roy. Soc., 1931, **B**, **108**, 559—567).—Mathematical treatment of available data leads to the following results. About 2×10^5 mols. of H_2O_2 are destroyed per mol. of catalase; the mean life of the active enzyme–substrate mol. is about 10^{-7} sec., and the velocity coeff. for its formation exceeds 7×10^6. A. COHEN.

Dismutation of methylglyoxalylacetic acid into *d*-α-hydroxyglutaric acid by an enzyme of animal cells. S. FUJISE (Biochem. Z., 1931, **236**, 237—240).—Methylglyoxalylacetic acid is converted by animal glyoxalase into *d*-α-hydroxyglutaric acid, the yield being 78·3—86·7%. P. W. CLUTTERBUCK.

Crystalline amylase. M. L. CALDWELL, L. E. BOOHER, and H. C. SHERMAN (Science, 1931, **74**, 37).—Isotropic, elongated crystals of amylase, n 1·54 (approx.), showing slight double refraction, have been obtained from carefully-buffered aq. EtOH solutions of pancreatic amylase. Formation and yield are both dependent on p_H, and the smallness and instability of the crystals necessitate a special technique. L. S. THEOBALD.

Synthetic action of amylase on dextrins of various origin. S. NISHIMURA (Biochem. Z., 1931, **237**, 133—135).—Achroodextrin prepared by the action of α-amylase (pancreatic extract) on starch is much more readily polymerised by the synthetic action of purified amylase (cf. this vol., 653) than are those prepared by the action of β-amylase (malt) or acid hydrolysis on starch, the synthetic action being followed by I coloration. F. O. HOWITT.

Effect of thiocyanates on amylase activity. I. Potato amylase. F. E. DENNY. **II. Salivary amylase.** L. P. MILLER (Contr. Boyce Thompson Inst., 1931, **3**, 277—285, 287—296).—I. The saccharogenic activity of expressed potato juice was decreased by Na and K thiocyanates. The amylolytic activity was much less affected. Similar effects were obtained with dialysed juice. No stimulative action was observed. The stimulation of sprouting and the decreased starch content of potatoes following immersion in thiocyanate solutions are not the results of direct action on the amylase.

II. With all concentrations of KCNS, the activity of salivary amylase was increased at high p_H and decreased at low p_H, with varied intermediate effects. With increasing concentration of KCNS the optimum p_H for starch hydrolysis by the dialysed amylase in the presence of phosphate buffers moved to the alkaline side. With NaCl in the normal concentration found in saliva and at p_H 6·6, addition of KCNS up to $0{\cdot}06M$ produced no effect. In the absence of NaCl amylase activity was increased. A. G. POLLARD.

Effect of potassium cyanide on the amylase activity of potato juice. F. E. DENNY (Contr. Boyce Thompson Inst., 1931, **3**, 297—307).—Small additions of KCN to potato juice increased the amylase activity in slightly acid solution (p_H 6—7), the effect decreasing as the neutral point was approached. Dialysis of the juice almost prevented the action of KCN. The fraction of potato juice necessary to the activating effect of KCN diffuses through collodion more slowly than reducing sugars. A. G. POLLARD.

Cholam diastase. I. Electrodialysis and electro-osmosis. D. NARAYANAMURTI and R. V. NORRIS (Proc. XV Indian Sci. Cong., 1928, 166).—The activity of cholam malt diastase can be increased, and the ash and protein contents decreased, by electrodialysis. In electro-osmotic experiments the ratio of liquefying power to saccharifying power was different in different fractions. CHEMICAL ABSTRACTS.

Enzymic processes in germinating barley. I. Development of diastatic activity. J. WEICHHERZ and R. ASMUS (Biochem. Z., 1931, **237**, 20—72).—Germinating barley grains were examined histologically by normal and polarised light. The development of diastatic activity during germination indicates a progressive liberation of diastase due to proteolytic action of papain. The diastatic activity of grain extracts when papain is added, however, is seldom attained under natural conditions. The activity–time curve is determined by the type and age of the barley. The greater is the diastatic activity the greater is the stimulating action on it by the following substances: Et_2O, EtOH, MeOH, Et and Ph urethanes, MeCHO, saponin, Hg-chlorophenol and -nitrophenol, $HgCl_2$, and H_3PO_4. The following are inhibitory: $CHCl_3$, EtCl, chloral hydrate, Pr, Bu, and amyl alcohols, HCN, NH_2Ph, CS_2, eosin, methylene-blue, and tannin. Stimulation is due to increase in cell permeability, which runs parallel with both development of diastatic activity and readiness of germination. F. O. HOWITT.

Cyclising enzymes. O. FERNANDEZ and B. PIZARROSO (Anal. Fís. Quím., 1931, **29**, 369—373).—Unsuccessful attempts have been made to detect plant enzymes which might transform hexoses and methylpentoses into inositol or phloroglucinol. H. F. GILLBE.

Chondrosulphatase. C. NEUBERG and E. HOFMANN (Naturwiss., 1931, **19**, 484—485).—The enzyme decomposes chondroitinsulphuric acid and the ester sulphates of the mustard-oil glucosides. A. J. MEE.

Specificity of phosphatase. J. TAPADINHAS (Compt. rend. Soc. Biol., 1930, **105**, 811—813; Chem. Zentr., 1931, i, 2345).—Phosphatase from *Euphorbia pulcherrima*, Wild, readily (78%) splits monobornylorthophosphoric acid, whilst diphenylpyrophosphoric acid is split only to the extent of 29%. A. A. ELDRIDGE.

Crystalline pepsin. III. Preparation of active crystalline pepsin from inactive denatured pepsin. J. H. Northrop (J. Gen. Physiol., 1931, **14**, 713—724; cf. A., 1930, 1317).—The activity of pepsin solutions, inactivated at p_H 10·5, is partly recovered by titration to p_H 5·4 and keeping for 24—48 hr. at 22°. The inactivation and its reversal are not due to an inhibitory substance. The reactivated pepsin is isolated from solution by fractional precipitation with $MgSO_4$ after partial precipitation of inactive protein by H_2SO_4. It has the same physical characteristics and activity as the original material, providing further evidence that the proteolytic activity is a property of the mol. itself. A. Cohen.

Action of pepsin on solutions of monoamino-acids alone or in mixtures. A. Blanchetière (Compt. rend., 1931, **193**, 256—257).—In the hydrolysis of glycine and alanine by pepsin, the initial rapid rate of disappearance of NH_2-N, as determined by Sørensen's method, soon decreases. Since the solution always gives a positive Abderhalden and Kamm reaction part at least of the NH_2-N which disappears is diketopiperazine-N, and accordingly the diketopiperazines produced in the enzymic hydrolysis of proteins are at least in part degradation products. Glycerol has an adverse action in peptide synthesis. The carbamate method of determining NH_2-N gives higher results than Sørensen's method. R. Brightman.

Examination of pepsin according to the [Dutch] pharmacopœia. C. G. van Arkel (Pharm. Weekblad, 1931, **68**, 657—660).—The amounts of residue of coagulated egg albumin left after the action of various pepsin solutions have been determined. S. I. Levy.

Tryptic digestion of iodoproteins. G. Barkan and G. Kingisepp (Arch. exp. Path. Pharm., 1931, **160**, 610—627).—The ultrafiltrate from the tryptic digestion of an iodoprotein contains, besides a preponderating amount of organically bound I, a small amount of iodide. Two I fractions are present in the ultrafiltrate, one precipitable by $Ag^{\cdot}$ in acid solution, and the other not. These two fractions appear to be mutually convertible and in equilibrium. The bearing of these results on earlier work is discussed. B. Levin.

Edestin as substrate for nephelometric determination of proteolytic enzymes. K. G. Stern (Biochem. Z., 1931, **236**, 464—473).—The use of edestin and nephelometric measurement following precipitation by sulphosalicylic acid is recommended for the investigation of proteolytic enzymes. F. O. Howitt.

Specific action of metallic salts on the urease of the amœbocytes of *Limulus*. L. Loeb and I. Lorberblatt (Biochem. Z., 1931, **236**, 298—311).—The sp. relation between metal constituents of inorg. salts and the activity of urease prepared from the amœbocytes of the blood-serum of *Limulus* (king crab) is not due to any influence on the cell protoplasm. The activity of urease extracted by $CaCl_2$ solution is decreased by presence of 0·5*M*-NaCl, and the earlier is the addition of NaCl the greater is the inhibition. This phenomenon occurs with other metallic salts. Hence definite metallo-urease compounds are formed and are stabilised with age so that replacement of the metal by another becomes more difficult with passage of time. Combination probably occurs, not with the urease, but with a co-enzyme or protein. F. O. Howitt.

Antiurease. J. B. Sumner and J. S. Kirk (Science, 1931, **74**, 102).—Rabbits have been immunised to cryst. urease by graded injections of this substance. Serum from these animals strongly inhibits the power of the urease to hydrolyse urea. L. S. Theobald.

Influence of structure on the kinetics of desmolases. System: uric acid, surviving liver. S. J. Przylecki and E. Mystkowski (Biochem. Z., 1931, **236**, 122—130).—The greater part of the uric acid of tissue is present in the sorbed condition, the amounts being regulated by an equilibrium between the free and sorbed acid. Decomp. of uric acid takes place entirely within the cell. Addition of PrOH (by a reversible reaction) causes almost complete elution of sorbed uric acid and so accelerates the action of uricase, and it also increases the permeability of the cell to uric acid. P. W. Clutterbuck.

Kinetics of the action of uricase. M. Z. Grynberg (Biochem. Z., 1931, **236**, 138—163).—The decomp. of uric acid with shaken suspensions of uricase is much more rapid in O_2 than in air. Addition of boiled uricase solutions slightly inhibits, but of filtered boiled uricase solution and of saturated solutions of allantoin has no effect on the reaction velocity. The reaction involves the utilisation of 1 atom of O and 1 mol. of H_2O and the formation of 1 mol. of CO_2. The absorption of O_2 and the oxidation of uric acid do not depend on, but the R.Q. decreases with, the age of the enzyme extract. The decomp. of uric acid is proportional, within limits, to the amount of uricase, and increases with the concentration of uric acid. Addition of small amounts of PrOH and BuOH accelerates and of large amounts inhibits the reaction. The inhibition is proportional to the amount of alcohol and independent of the amount of uric acid and is reversible with BuOH, but irreversible with PrOH. P. W. Clutterbuck.

p_H sensitivity of respiring and fermenting yeast. The shift of fermentation to respiration. K. Trautwein and J. Wassermann (Biochem. Z., 1931, **236**, 35—53).—The dependence of fermentation and respiration on the p_H is determined for 2 top and bottom yeasts. The respiration of top is usually greater than of bottom yeast. The respiration- and fermentation-p_H curves at first run parallel; the respiration and fermentation optima practically fall together, but in the later portions, the respiration curve flattens out and proceeds asymptotically to the *x* axis. At p_H 8 fermentation practically ceases, but from this point respiration proceeds with almost const. velocity up to p_H 10·8 and then suddenly decreases and ceases at p_H 11·8. P. W. Clutterbuck.

Oxidation-reduction potential of complex iron compounds in yeast. T. B. Coolidge (Nature, 1931, **128**, 223).—$(NH_4)_2SO_4$ precipitates protein, cytochrome "c," and a complex Fe compound from

an alkaline yeast-extract. The Fe compound, separated by ultra-filtration, has an oxidation potential which lies close to that at which the spectrum of cytochrome "c" appears. The Fe is not present as $Fe^{\cdot\cdot}$ or $Fe^{\cdot\cdot\cdot}$. L. S. THEOBALD.

Phytochemical reduction of oxaloacetic acid to malic acid. S. FUJISE (Biochem. Z., 1931, **236**, 231—236).—Oxaloacetic ester added to a yeast fermentation of sucrose is reduced to *l*-malic acid. P. W. CLUTTERBUCK.

Dismutation of thienylglyoxal. S. FUJISE (Biochem. Z., 1931, **236**, 241—246).—In contact with fresh unwashed yeast, thienylglyoxal [p-*nitrophenylhydrazone*, m. p. 234°; *semicarbazone*, m. p. 222° (decomp.)] is dismuted to l-α-*thienylglycollic acid*, m. p. 84·5—85°, α^{20} −98·07°. P. W. CLUTTERBUCK.

Acetoacetic acid and yeast. E. FRIEDMANN (Naturwiss., 1931, **19**, 400).—Fermenting yeast transforms acetoacetic acid into *d*-β-hydroxybutyric acid in presence or absence of dextrose, both reactions being influenced by bromo- or iodo-acetic acid. A second acid is also formed. F. O. HOWITT.

Action of monoiodoacetic acid on respiration and fermentation. P. B. JENSEN (Biochem. Z., 1931, **236**, 211—218).—The fermentation of dextrose and dihydroxyacetone by *S. Ludwigii* is inhibited by a concentration of 1/5000 of the acid, but to a much smaller extent than the dextrose fermentation by pressed yeast. Formation of dextrose could not be detected when the dihydroxyacetone fermentation is inhibited by iodoacetic acid. Fermentation of pyruvic acid by pressed yeast is also inhibited by the acid, but much more feebly than the dextrose fermentation. The methylene-blue reduction by the yeast and by the Schardinger enzyme is only slightly affected by the acid. P. W. CLUTTERBUCK.

Effect of iodine on the carbon dioxide production of fermentation yeasts. K. SCHARRER and G. CLAUS (Arch. Mikrobiol., 1930, **1**, 343—364).—The activity of yeasts was slightly decreased by treatment with 0·006—0·01% I as KI, stimulated with 0·01—2·5% I, and reduced by higher concentrations. NaI gave similar results. No stimulation occurred with KIO_3 and with 0·001% I in this form fermentation was reduced. Slightly increased activity was produced by 0·0001—0·0005% of KIO_4 with a subsequent decrease at higher concentration. Elementary I had a smaller inhibitory effect than KIO_3 or KIO_4. A. G. POLLARD.

Influence of magnesium and calcium chlorides on some fermentations. E. KEESER (Arch. exp. Path. Pharm., 1931, **160**, 663—686).—The effect of the addition of $CaCl_2$ and $MgCl_2$ on, *e.g.*, the fermentation of yeast and the hydrolysis of gelatin by trypsin depends on the concentration in which they are added as well as on the p_H. The bearing of the results on the theory of enzymes is discussed. B. LEVIN.

Action of sea-water on alcoholic fermentation. L. SANZO and F. PIRRONE (Atti R. Accad. Lincei, 1931, [vi], **13**, 140—143).—When added to dextrose solutions in proportions below 20%, sea-H_2O accelerates alcoholic fermentation appreciably (20—24% for 13% of the H_2O), proportions above 20% causing marked retardation. The accelerative influence is greatest with freshly collected sea-H_2O and decreases somewhat to a const. val. after about 48 hr. if the H_2O is kept before being added to the sugar solution. T. H. POPE.

Action of marine algæ on the alcoholic fermentation of sugar solutions. F. PIRRONE (Atti R. Accad. Lincei, 1931, [vi], **13**, 137—140).—In the fresh state, or still more when dry, addition of *Ulva lactuca* (L.), Lejol, to dextrose solution greatly increases its rate of alcoholic fermentation, as measured by the amount of CO_2 liberated, the max. effect being obtained if the alga is dried in presence of ultra-violet rays. The action is due to org. substances, sol. in H_2O, EtOH, or Et_2O at room temp. T. H. POPE.

Action of bile salts on some fermenting organisms. F. BOAS and G. NEUMULLER (Arch. Mikrobiol., 1930, **1**, 35—59).—Addition of bile salt to nutrient media reduced the tolerance of *S. cerevisiæ* to NaCl (0·6—0·8*M*), but accelerated the growth of the organism where the NaCl concentration was small (0·3*M*). Similar effects occurred with relatively high concentrations of NaCl (1—1·6*M*) in nutrients containing a biocatalyst. With *S. anamensis* the crit. NaCl concentration at which stimulation ceased was lower. The effect of bile salts on *Torula* was less intense. A. G. POLLARD.

Growth-promoting substance of yeast. N. NIELSEN (Biochem. Z., 1931, **237**, 244—246).—Aq. extracts of yeast contain a substance which promotes the growth of *Avena* coleoptiles. It is sol. in EtOH or Et_2O, insol. in light petroleum, thermolabile, and probably identical with "rhizopin" extractable from fungi. F. O. HOWITT.

Growth regulators from bacteria. P. B. JENSEN (Biochem. Z., 1931, **236**, 205—210).—Three of four micro-organisms isolated from saliva were able, on growing on a meat-peptone–agar medium, to form substances which accelerate the growth of the coleoptile of *Avena*. The power of forming these growth-promoting substances is widespread amongst bacteria. P. W. CLUTTERBUCK.

Amœboid motion as the product of protein swelling. S. W. WHITEHOUSE (Science, 1931 **73**, 325—326).—HCl, lactic acid, AcOH, H_2SO_4, urea *p*-phenylenediamine, and NaOH solutions of sufficient concentration cause the formation of pseudopodia and movement of the amœba towards the reagent. The effectiveness of the reagent concerned is in the same order as its action on protein. Inorg. salts inhibit movement of the amœba, stimulated by acid, in the order tervalent cations>bivalent>univalent. L. S. THEOBALD.

Molecular organisation in amœbic protoplasm. A. A. SCHAEFFER (Science, 1931, **74**, 47—51).—Data which support the view that the protoplasm of amœbæ consists primarily of sp. mols. organised into patterns are presented. L. S. THEOBALD.

Phototropic sensitivity of *Phycomyces* as related to wave-length. E. S. CASTLE (J. Gen. Physiol., 1931, **14**, 701—711).—The max. growth

response of the sporangiophores of *Phycomyces* is observed on exposure to light of wave-length 400—430 mμ. This is discussed in relation to the absorption spectrum of the photo-sensitive substance.
A. COHEN.

The yield law and *Aspergillus niger*. R. MEYER (Arch. Mikrobiol., 1930, 1, 277—303).—The mathematical treatment of experimental data of nutrient-growth curves is criticised. The slope (tangential) of the N-growth curve for *A. niger* is independent of the P present, and *vice versa*. The N-curve in the presence of high P concentration shows a point of inflexion near the origin, and the abscissal val. of the max. increases and, later, decreases as the proportion of P is raised. A. G. POLLARD.

Autolysis of *Aspergillus niger*. G. BEHR (Arch. Mikrobiol., 1930, 1, 418—444).—In acid media with $(NH_4)_2SO_4$ as a source of N, autolysis of *A. niger* occurs at p_H 1 and is characterised by relatively small losses of wt. of mycelium, the elimination of protein, peptone, polypeptide, NH_2-acids, and NH_3, an increased chitin content, and the production of yellow pigment. Neutral autolysis occurs at p_H 6·5 approx. There is a rapid destruction of mycelium with the production of NH_3, but no other N compounds, complete destruction of chitin, and the formation of humic substances and a violet pigment. There is no evidence that org. acids are the products of a deamination process. A. G. POLLARD.

Distribution of magnesium in fungus mycelium. A. RIPPEL and G. BEHR (Arch. Mikrobiol., 1930, 1, 271—276).—No Mg could be extracted from the mycelium of *Aspergillus niger* by means of org. solvents (EtOH, Et_2O, CS_2, $CHCl_3$, $COMe_2$). During growth and autolysis changes in the Mg and ash contents of the mycelium were not proportional. During autolysis in acid media the Mg decreased much less rapidly than the ash content.
A. G. POLLARD.

Action of carbon dioxide on heterotrophes. A. RIPPEL and F. HEILMANN (Arch. Mikrobiol., 1930, 1, 119—136).—The accelerated growth of *Aspergillus* resulting from increasing concentration of CO_2 may be represented by a typical nutrient-growth curve. The effect of CO_2 was more marked in acid media.
A. G. POLLARD.

Influence of acetate and phosphate on the activity of the amylase of *Aspergillus oryzæ*. M. L. CALDWELL and M. G. TYLER (J. Amer. Chem. Soc., 1931, 53, 2316—2320).—The amylase has an activity dependent on p_H, and the nature and concentration of the buffer. An increase of NaOAc concentration from 0·01 to 0·1N leads to a slight decrease not observed with Na_2HPO_4 as buffer provided the p_H is suitably adjusted. The max. activity is shown at p_H 5·3—5·5 in 0·01N-NaOAc, which is recommended for measurements with this enzyme.
H. A. PIGGOTT.

Colouring matter of *Penicilliopsis*, Solms-Laubach. A. BLOCHWITZ (Ber. deut. bot. Ges., 1931, 49, 319—323).—The solution of the colouring matter in Et_2O and EtOH is intense yellow. Alkalis produce a blood-red colour and the colouring matter by this treatment loses its solubility in Et_2O and becomes sol. in H_2O. The solubility in $CHCl_3$ is similarly affected and the substance is therefore acidic. An EtOH solution gradually becomes blood-red on keeping, due to the formation of an ester. P. G. MARSHALL.

Biochemistry of micro-organisms. I. Introductory. H. RAISTRICK and W. RINTOUL. **II. Quantitative methods and technique of investigation of the products of metabolism of micro-organisms.** J. H. BIRKINSHAW and H. RAISTRICK. **III. Quantitative examination by the carbon balance-sheet method of the types of products formed from dextrose by species of *Aspergillus*.** J. H. BIRKINSHAW, J. H. V. CHARLES, H. RAISTRICK, and J. A. R. STOYLE. **IV. Quantitative examination by the carbon balance-sheet method of the types of products formed from dextrose by species of *Penicillium* (including *Citromyces*).** J. H. BIRKINSHAW, J. H. V. CHARLES, A. C. HETHERINGTON, H. RAISTRICK, and C. THOM. **V. Quantitative examination by the carbon balance-sheet method of the types of products formed from dextrose by species of *Fusarium*.** J. H. BIRKINSHAW, J. H. V. CHARLES, H. RAISTRICK, and J. A. R. STOYLE. **VI. Quantitative examination by the carbon balance-sheet method of the types of products formed from dextrose by miscellaneous species of fungi.** J. H. BIRKINSHAW, J. H. V. CHARLES, A. C. HETHERINGTON, and H. RAISTRICK. **VII. Kojic acid (5-hydroxy-2-hydroxymethyl-γ-pyrone).** J. H. BIRKINSHAW, J. H. V. CHARLES, C. H. LILLY, and H. RAISTRICK. **VIII. Determination of kojic acid.** J. H. BIRKINSHAW and H. RAISTRICK. **IX. Production of mannitol from dextrose by species of *Aspergillus*.** J. H. BIRKINSHAW, J. H. V. CHARLES, A. C. HETHERINGTON, and H. RAISTRICK. **X. Determination of mannitol in fermentation solutions.** H. RAISTRICK and W. YOUNG. **XI. Citromycetin, a new yellow colouring matter produced from dextrose by species of *Citromyces*.** A. C. HETHERINGTON and H. RAISTRICK. **XII. New methoxydihydroxytoluquinone produced from dextrose by species of *Penicillium* of the *P. spinulosum* series.** J. H. BIRKINSHAW and H. RAISTRICK. **XIII. New type of mucilaginous material, luteic acid, produced from dextrose by *Penicillium luteum*, Zukal.** H. RAISTRICK and M. L. RINTOUL. **XIV. Production and chemical constitution of a new yellow colouring matter, citrinin, produced from dextrose by *Penicillium citrinum*, Thom.** A. C. HETHERINGTON and H. RAISTRICK. **XV. Molecular structure of citrinin.** F. P. COYNE, H. RAISTRICK, and R. ROBINSON. **XVI. Production from dextrose by *Penicillium spiculisporum*, Lehman, of a new polybasic fatty acid, $C_{17}H_{28}O_6$ (the lactone of γ-hydroxy-ββ-dicarboxypentadecoic acid).** P. W. CLUTTERBUCK, H. RAISTRICK, and M. L. RINTOUL. **XVII. Products of dextrose metabolism formed by various species of fungi (*Helminthosporium*, *Clasterosporium*, etc.).** J. H. BIRKINSHAW and H. RAISTRICK. **XVIII. Biochemical characteristics of species of *Penicillium* responsible for the rot of citrus fruits.** J. H. BIRKINSHAW, J. H. V. CHARLES, and H. RAISTRICK

(Phil. Trans., 1931, B, 220, 1—10, 11—26, 27—54, 55—92, 93—98, 99—126, 127—138, 139—152, 153—172, 173—208, 209—244, 245—254, 255—268, 269—296, 297—300, 301—330, 331—354, 355—367).—I. The types of products formed by a large number of moulds were examined quantitatively by the C balance-sheet method in order to select those organisms giving considerable yields of products other than mycelium and CO_2. The selected moulds were then grown on a larger scale for detailed investigation. A Czapek–Dox synthetic medium was used, with dextrose as sole source of C. Pure and authenticated cultures only were employed. The results show that (1) the C balance sheets may be used as a biochemical method of classification in some families of moulds; (2) the first stage of the breakdown of dextrose may be a Cannizzaro reaction with production of mannitol and gluconic acid; (3) the mould products are very sp.; (4) moulds show remarkable powers of synthesis. Many of the products resemble the lichen acids.

II. The mould is cultivated and aerated daily in a closed system retaining all products of metabolism. The volatile products and CO_2 are absorbed in H_2SO_4 and KOH, respectively. The O_2 absorbed (and hence the R.Q.) is determined by analysis of the vitiated air. After the incubation the mycelium is separated from the solution and dried. The compounds in solution are divided into the classes (1) residual dextrose, (2) CO_2 in solution, (3) volatile acids, (4) non-volatile acids, (5) volatile neutral compounds, (6) non-volatile neutral compounds (including synthetic compounds). C is determined in each class by wet combustion (in 1 and 2 by calculation), a balance sheet is constructed, and C unaccounted for obtained by difference.

III—V. The C balance sheets for a large number of species of each of the genera *Aspergillus*, *Penicillium*, and *Fusarium* are arranged in groups, the species in each group having similar characteristics. In the case of the *Aspergilli*, the groups follow closely the accepted morphological classification of Thom and Church. With the *Penicillia* a less close agreement is found. Thom's diagnoses of the species employed are given in an appendix. With the *Fusaria* only a rough biochemical classification was attainable. Their main characteristic is the production of large amounts of EtOH. With each genus a selection was made of organisms suitable for intensive investigation: many of these were found in the *Penicillia*.

VI. C balance sheets were prepared for a number of miscellaneous species and selections made for further examination. The family *Dematiaceæ* includes the largest proportion of interesting species.

VII. The best yield of kojic acid was obtained with *A. parasiticus*, Speare, although it is formed by most species of the *A. flavus-oryzæ* group, and is claimed as a diagnostic test for this group. It is also given by *Penicillium daleæ*, Zaleski. Kojic acid is obtained from starch, sucrose, lactose, dextrose, lævulose, galactose, xylose, arabinose, mannitol, and glycerol.

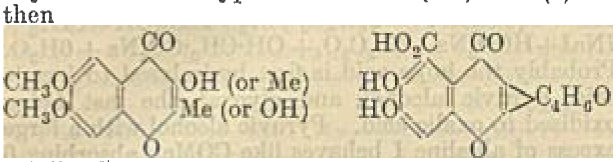
VIII. Kojic acid may be determined by oxidation with alkaline I as in the Willstatter–Schudel method for aldose, if 90 min. are allowed for reaction and at least 4 times the theoretical amount of I is used. 1 Mol. of kojic acid requires 10 I. Allowance is made for dextrose present as determined polarimetrically. The products of reaction agree quantitatively with the equation: $C_6H_6O_4+5I_2+11NaOH=CHI_3+7NaI+HCO_2Na+Na_2C_2O_4+OH{\cdot}CH_2{\cdot}CO_2Na+6H_2O$. Probably the kojic acid is first hydrolysed to formic acid, pyruvic alcohol, and glyoxal, the last being oxidised to oxalic acid. Pyruvic alcohol with a large excess of alkaline I behaves like $COMe_2$, absorbing 6 I, but yields $OH{\cdot}CH_2{\cdot}CO_2H$ and CHI_3.

IX. Three groups of *Aspergilli*, white species, *A. elegans*, and *A. nidulans*, gave considerable yields of mannitol (shown as "C unaccounted for" in the balance sheets). Good yields are not obtained unless aeration is restricted. Two white species, *Ac* 55 and *Ac* 56, both give about 40% "unaccounted for"; with *Ac* 55 this is mostly mannitol, but *Ac* 56 also produces glycerol in fair amount. A mycelium of *Ac* 55 may be used to ferment a fresh quantity of dextrose solution supplied in place of the exhausted medium, yields of mannitol approaching 50% of the dextrose fermented being thus obtained. Other metabolic products are small amounts of succinic and malic acids from *Ac* 55 and malic acid and glycogen from *Ac* 56.

X. A method for determination of mannitol consists in the removal of residual dextrose by yeast fermentation, purification with $Pb(OAc)_2$, removal of glycerol by Et_2O–EtOH extraction, and measurement of rotation in presence of 6% borax. Tables are given connecting rotation with amount of mannitol present. The Ac val. gives a confirmation. A rapid method, carried out in presence of dextrose, is based on the observation that 0·9% dextrose with 6% borax is optically inactive; below 0·9% it is lævorotatory (min. at 0·5%). The solution is adjusted to 0·9% or 0·5% dextrose and 6% borax and the rotation interpreted by means of tables.

XI. Various strains of *Citromyces* give a yellow dye. The acidified filtered solution on evaporation deposits *citromycetin* (I), $C_{14}H_{10}O_7,2H_2O$, darkens at 263°, m. p. 283—285° (decomp.), anhyd. at 150°, gives an olive-green colour with $FeCl_3$ [Ac_2 derivative, m. p. (from abs. EtOH) 223—224° (decomp.), (from aq. KOAc with HCl) 235—236° (decomp.); *K* salt, $C_{14}H_9O_7K,H_2O$; *Ba* salt, $(C_{14}H_9O_7)_2Ba,3H_2O$; *hydrobromide*; *Me* ester of O-Me_2 derivative, m. p. 178°; O-Me_2 derivative, m. p. 217—218° (decomp.)]. Boiling (I) with dil. acid gives CO_2 and a monobasic acid, *citromycin* (II), $C_{13}H_{10}O_5$, darkens 255—260°, m. p. 285—290° [Ac_2 derivative, m. p. 221—222°; *K* salt, $C_{13}H_{10}O_5$, $C_{13}H_9O_5K$; *hydrobromide*; *hydriodide* (also obtained from HI and (I) and all Zeisel determinations); O-Me_2 derivative, m. p. 225—227° (with Me_2SO_4), also $+H_2O$, m. p. 183—185° (with MeI and KOH)]. 1 Mol. of (I) absorbs 8 I in alkaline solution. Hydrolysis of (I) with 33% aq. KOH under N_2 liberates $COMe_2$, CO_2, AcOH, and a small amount of 3 : 5 : 6-trihydroxyphthalic acid. Hydrolysis of the Me ester of *O*-dimethylcitromycetin with KOH in EtOH gives a *hydroxydimethoxybenzopyrone* (III), m. p. 177—180°, a *hydroxydimethoxyphthalic acid* (IV), m. p. 181—182° (decomp.) (*dimethoxyethoxyphthalic anhydride*, m. p. 195—196°), and a *product*, m. p. 242—243°. Boiling HI converts (IV) into 2-hydroxyquinol-5-carboxylic acid, m. p. 214—215° (decomp.), which on sublimation yields hydroxyquinol. (IV) is probably 3-hydr-

oxy-5 : 6-dimethoxyphthalic acid. (III) and (I) are then

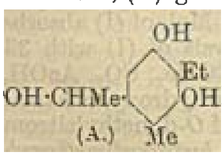


XII. Certain strains of *P. spinulosum* produce large amounts of citric acid and a dihydroxymethoxytoluquinone (I), m. p. 202—203·5°, purplish-black crystals (Ac_2 derivative, m. p. 139·5°), which is reduced by Zn and HCl to the corresponding quinol (Ac_4 derivative, m. p. 192·5—194°). NH_2OH has no action on (I).

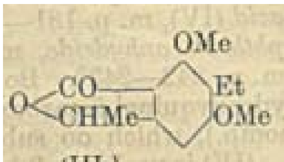
XIII. *P. luteum*, Zukal, produces a colloidal material, *luteic acid* (*Na* salt, $[\alpha]_{5461}$ −47°), which on hydrolysis with N-H_2SO_4 gives dextrose and malonic acid. Hydrolysis with 0·25N-$Ba(OH)_2$ gives malonic acid and a polysaccharide, *luteose*, −46·4°, yielding dextrose on acid hydrolysis. The polysaccharide unit of luteic acid is a condensation product of 2 mols. of dextrose with 1 of malonic acid with loss of 2 mols. of H_2O, in which one CO_2H group is free, whilst the other is combined and the CHO groups are linked in such a way as to destroy their aldehydic properties.

XIV. *P. citrinum* yields a yellow colouring matter, obtained cryst. on acidification of the metabolism solution (optimum temp. for production 28—32°). *Citrinin* (I), $C_{13}H_{14}O_5$, m. p. 166—170° (decomp.), $[\alpha]_{5461}$ −42·8° [*Ac* derivative, an oil; Et_2 derivative, b. p. 170—210°/1 mm.; *Br* compound, m. p. 121°; *phenylhydrazide*, m. p. 207° (decomp.)], is a monobasic acid, which on reduction gives dihydrocitrinin, not isolated [Ac_2 derivative darkens at 200°, m. p. 322—323° (decomp.)]. Hydrolysis of (I) with 2N-H_2SO_4 gives 1 mol. of CO_2, 1 mol. of HCO_2H, and two isomerides, $C_{11}H_{16}O_3$, *product A*, m. p. 128—130°, $[\alpha]_{5461}$ −43·7° [Ac_3 (with Ac_2O and NaOAc), m. p. 90—91°, Ac_2 derivative (with Ac_2O and pyridine), Me_2, b. p. 136—138°/1 mm., *Me*, m. p. 144—147°, and $AcMe_2$, b. p. 136—138°/1 mm., derivatives], and, in small amount, its *racemate B*, m. p. 169—170°. Oxidation of the Me_2 compound of A with alkaline $KMnO_4$ gave a dimethylated *product* (III), $C_{13}H_{16}O_4$, m. p. 122—124°, probably a lactone. Fusion of A with KOH gives a phenolic *substance*, $C_9H_{12}O_2$ (IV), m. p. 97—99° (Me_2, b. p. 89—91°/1 mm., and *Me*, m. p. 63—65° derivatives). Oxidation of the Me_2 derivative of (IV) yields a *product* (V) $C_8H_7(OMe)_2\cdot CO_2H$, m. p. 97—99°, and a *product* (VI) $C_7H_5(OMe)_2\cdot CO_2H$, m. p. 142—146°.

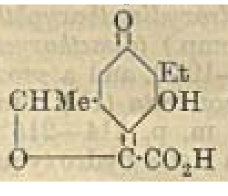
XV. From colour reactions the Me_2 compound of (IV) is a methylethylresorcinol Me_2 ether. The Me_2 ether of orsellinic acid with Br gives 2 : 6 - (or 2 : 4) - *dibromo-orcinol Me_2 ether*, m. p. 168—169°, (V) gives no precipitate; (VI) gives a cryst. derivative. (IV) has then the constitution 6-methyl-2-ethylresorcinol. Product A, the lactone (III), and citrinin (I) are as shown.



(A.)



(III.)



(I.)

XVI. *P. spiculisporum*, Lehman, produces succinic acid and *γ-hydroxy-βδ-dicarboxypentadecolactone* (I), m. p. 145—146°, $[\alpha]_{5461}$ −14·76° (*Na* salt, $[\alpha]_{5461}$ +14·98°). Hydrolysis with dil. NaOH opens the lactone ring, giving the *hydroxytricarboxy-acid* (II), m. p. 134—135° [*Ac* derivative, unstable], reconverted into (I) on heating. (I) or (II) at 180° eliminates 1 or $2H_2O$, respectively, and gives *dehydrated I* (III), m. p. 41°, hydrolysed by alkali to an isomeride of (I), a *tricarboxylic acid* (IV), m. p. 87°, which reverts to (III) at 100°. With diazomethane (I) yields an Me_2 ester (V); with diazoethane (II) gives an Et_3 ester (VI). (V) with aq. NH_3 gives a *Me ester diamide*, m. p. 178·5°, and *Me_2 ester amide*, m. p. 78·5°. Fusion of (I) with KOH gives lauric, oxalic, and succinic acids and CO_2. Oxidation of (I) with acid $KMnO_4$ or of (II) with $KMnO_4$ in $COMe_2$ yields *γ-ketopentadecoic acid* (VII), m. p. 92·6°, which by Clemmensen reduction gives pentadecoic acid. Oxidation of NH_4 pentadecoate with H_2O_2 gave (VII). (VII) was synthesised as follows: *n*-octyl iodide was condensed with Et malonate to *Et* n-*octylmalonate*, b. p. 169°/17 mm.; n-*octylmalonic acid*, m. p. 108°, decomp. 140°, was heated to remove CO_2, thus forming *n*-decoic acid, m. p. 31°. Et *n*-decoate, b. p. 131°/17 mm., was reduced with Na to *decyl alcohol*, b. p. 127°/16 mm., and the latter with HI gave *decyl iodide*, b. p. 132°/15 mm. Condensation of the iodide with Et acetoacetate in presence of Na yielded *Et α-acetyl*-n-*dodecoate*, b. p. 170°/16 mm.; the latter with γ-carbomethoxypropionyl chloride and Na gave (VII). (VII) was also isolated from the metabolism solution.

XVII. The main metabolic products of *Helminthosporium geniculatum* are EtOH and mannitol; subsidiary products are glycerol and MeCHO. A *Clasterosporium* species gives mannitol and EtOH with smaller amounts of glycerol, MeCHO, succinic and probably malic acid. *Aspergillus Wentii* produces gluconic acid (present as free acid and lactone) and small amounts of mannitol and glycerol, but no EtOH. *Fumago vagans* gives gluconic acid, smaller amounts of glycerol and succinic acid, but no mannitol. It also produces a *polysaccharide*, $[\alpha]^{18}_{\text{g yellow}}$ +217°, composed entirely of dextrose units. A strain of *Penicillium chrysogenum* forms gluconic acid and mannitol.

XVIII. *Penicillium digitatum*, Saccardo, gives EtOAc in fair amount together with EtOH and a *polysaccharide*, $[\alpha]^{20}_{61}$ +299°, $[\alpha]^{20}_{\text{Hg yellow}}$ +270°, composed entirely of dextrose units. *Penicillium italicum*, Wehmer, yields a product giving an emerald-green colour with $FeCl_3$ and a purple colour with bleaching-powder solution. These colour tests are of value for diagnosis of the species. J. H. BIRKINSHAW.

Tannin-decomposing micro-organisms. A. RIPPEL and J. KESELING (Arch. Mikrobiol., 1930, 1, 60—77).—Of a no. of moulds examined, only *Penicillium*, *Citromyces*, and *Aspergillus* were able to utilise tannin as a sole source of C. Tannase production by fungi occurred only in the presence of tannin, but was not associated with the ability to utilise tannin. A. G. POLLARD.

Effect of iron, zinc, and copper on the growth and pigmentation of moulds. O. METZ (Arch. Mikrobiol., 1930, 1, 197—250).—The general

effect of Fe, Zn, and Cu on pigmentation, growth, and spore production was similar for numerous fungi examined, but characteristic minor differences among individual species occurred. Details of these effects and of variations produced in the p_H, NH_3 and sugar contents of the media are recorded. A. G. POLLARD.

Hypothesis of mitogenetic radiation acting on the multiplication of bacteria. (MLLE.) CHOUCROUN (Compt. rend., 1931, **192**, 1674—1677).—The work of Sewertzova (Ann. Inst. Pasteur, 1931, **46**, 337) on the activation of *B. mesentericus* by the yeast *Nadsonia* has been confirmed; if the sheet of Pb is enclosed between two quartz plates which form the base of the culture flask the dissymmetry of multiplication of the bacteria no longer obtains. Mitogenetic action is thus due to a material effect which is propagated only along certain substances.
C. C. N. VASS.

Biological gas reactions. I. Carbon monoxide. F. FISCHER, R. LIESKE, and K. WINZER (Biochem. Z., 1931, **236**, 247—267).—The bacterial reduction of CO to CH_4 in presence of H_2 necessitates a 10 : 1 ratio of $H_2 : CO$ for total reduction. With higher CO content the reaction takes place in two stages, viz., $CO+H_2O=CO_2+H_2$ and $CO_2+4H_2=CH_4+2H_2O$, which, after an initial incubation period, proceed simultaneously with a possible concomitant reduction of CO directly to CH_4. Part of the CH_4 is not liberated, but is utilised in synthetic processes of the cell, small amounts of org. acids, aldehydes, and higher hydrocarbons being detectable. Bacteria appear to be able to assimilate CO_2 directly, but not CO. Comparison is made between the biological reduction of CO and that by inorg. catalysis.
F. O. HOWITT.

Formation of hydrogen sulphide in the rabbit's intestine in relation to diet. M. DEGANELLO (Arch. Farm. sperim., 1931, **52**, 181—184).—Sulphides may be detected in the fæces of rabbits fed on cabbage, bran, and hay, and free H_2S appears after 15 days. With a diet of bran and hay no H_2S is formed. With a diet of cabbage alone the formation of H_2S is observed in the large intestine, but the amount decreases in the rectum. R. K. CALLOW.

Proteolytic enzymes of gelatin-liquefying bacteria. A. I. VIRTANEN and J. TARNANEN (Naturwiss., 1931, **19**, 397).—*B. fluorescens liquefaciens* secretes a proteinase which hydrolyses caseinogen and gelatin with little increase of NH_2-N. Filtration of the centrifugate of a 15—20-hr. culture results in a liquid containing all this enzyme. The bacteria cells contain peptone- and dipeptide-splitting enzymes which do not readily pass out from the normal cell and also an enzyme reversibly eliminating NH_3 from aspartic acid, giving rise to fumaric acid.
F. O. HOWITT.

Molybdenum as a catalyst in the biological fixation of nitrogen. H. BORTELS (Arch. Mikrobiol., 1930, **1**, 333—342).—The growth of *Azotobacter chroococcum* in an N-free nutrient was stimulated by the addition of 0·0005% of Na_2MoO_4.
A. G. POLLARD.

Immunising action of diphtheria antitoxins purified with aluminium hydroxide. S. SCHMIDT and A. HANSEN (Compt. rend. Soc. Biol., 1930, **105**, 334—336; Chem. Zentr., 1931, i, 2220).—The prep. may be purified with $Al(OH)_3$ without loss of antitoxic power. A. A. ELDRIDGE.

Refractometric determination of proteins. I. Numerical value of the refractive index constant a for antitoxic globulins. T. D. GERLOUGH and W. WHITE (J. Physical Chem., 1931, **35**, 1328—1335).—For the diphtheria, tetanus, scarlet-fever, and erysipelas antitoxic globulins the increment in n corresponding with a change in protein concentration of 1 g. per 100 c.c. (constant a) has the value 0·00184 for concentrations between 3 and 17 g. per 100 c.c. NaOH lowers n. Euglobulin, pseudoglobulin, albumin, and pneumococcus antibody have the same value for a.
L. S. THEOBALD.

Determination of the size of sub-visible virus by centrifuging. Small-pox vaccine and fowl-plague viruses. H. BECHHOLD and M. SCHLESINGER (Biochem. Z., 1931, **236**, 387—414).—The determination of the size of sub-visible viruses by methods of dispersivity and centrifuging is discussed. Centrifuging at 10,000 r.p.m. permits a determination of size up to a diameter of 0·05 μ and by fractional centrifuging a discrimination of various particle sizes is possible. Filtration through membranes calibrated by filtration of known organisms indicates a diameter of 0·2 μ for small-pox vaccine virus, whilst centrifuging gives 0·21—0·23 μ and for fowl-plague virus 0·12—0·13 μ. That these vals. refer to the actual agent is indicated by the changes in concentration on fractional centrifuging. F. O. HOWITT.

Colorimetric and potentiometric methods for p_H determination of solid bacteriological media, using a dilution method based on the buffer equation. M. W. LISSE, O. G. JENSEN, and R. P. TITTSLER (J. Bact., 1931, **21**, 383—394).—Agar media may be diluted sevenfold (and remain liquid) without change of p_H. The effect of the drift of quinhydrone electrodes is eliminated by the extrapolation of vals. obtained after successive intervals of time. Quinhydrone vals. average 0·16 p_H lower than those of the H_2 electrode. Colorimetric methods using bromothymol-blue gave accurate vals.
A. G. POLLARD.

Physical properties and bactericidal power of solutions of certain phenyl-substituted acids. T. C. DANIELS and R. E. LYONS (J. Physical Chem., 1931, **35**, 2049—2060).—The bactericidal activity of a number of Ph-substituted acids shows a marked parallelism with the solubility, the distribution coeff. between oil and H_2O, and the adsorption by activated C. The power of reducing the surface tension of H_2O is of only secondary importance. Data are given for m. p., solubility, $[H^{\cdot}]$ of 0·01—0·002N solutions, viscosity, and surface tension of solutions of the acids; ε-phenylhexoic acid has m. p. 16°. H. F. GILLBE.

Adrenal cortical hormone. G. A. HARROP, J. J. PFIFFNER, A. WEINSTEIN, and W. W. SWINGLE (Science, 1931, **73**, 684).—Normal and bilaterally adrenalectomised dogs show no characteristic changes in blood constituents or in respiratory metabolism when treated with adequate doses of cortical extract. Blood non-protein-N and urea rise, however, and

respiratory metabolism falls when a healthy bilaterally adrenalectomised animal is deprived of adequate supplies of the extract. The serum-K concentration steadily rises, secretion of urine diminishes, and urinary N and urea are suppressed. Excretion of creatine and creatinine diminishes later. Changes in blood-creatinine do not occur until the animal is very ill. L. S. THEOBALD.

Effects of cortico-adrenal extract on the gonads. E. L. COREY and S. W. BRITTON (Science, 1931, **74**, 101—102).—The extract, prepared by Swingle and Pfiffner's method, produces precocious sexual maturity in the albino rat, especially in the female. L. S. THEOBALD.

Determination of adrenaline in the adrenals. T. KONSCHEGG (Klin. Woch., 1931, **10**, 408—409; Chem. Zentr., 1931, i, 2219).—Zanfrogenini's method gives low results, which depend on the time elapsing between filtration and determination. The max. is reached in 3—4 days; values then obtained accord with those afforded by other methods. A. A. ELDRIDGE.

Electrodialysis of adrenaline. W. DEVRIENT, S. THYSSEN, and B. SOKOLOFF (J. Pharm. Exp. Ther., 1931, **42**, 299—319).—Among the reduction products at the cathode, obtained by the electrolysis of adrenaline in acid or alkaline solution, using varying c.d., were detected cyclic alcohols and ketones, cresol, quinol, and $NHMe_2$, whilst in the oxidation products at the anode were found diketoquinone, quinhydrone, PhCHO, methylaminoacetopyrocatechol, and an unidentified red product. The last is presumed to be an unstable oxidation product, formed from 2 mols. of adrenaline, which acts as an autocatalyst in the anodic oxidations, its catalytic action being more marked under the influence of light. The highest degree of oxidation was obtained between p_H 6·9 and 7·2. B. LEVIN.

Connexion between blood-cholesterol and adrenaline-sensitivity. M. VON BABARCZY (Arch. exp. Path. Pharm., 1931, **160**, 699—702).—There is no definite relation between blood-pressure response to adrenaline and blood-cholesterol. Since the latter is influenced by several factors, a relationship between it and the vegetative nervous system is not precluded. A. COHEN.

Action of insulin on adrenaline secretion. H. POLL (Naturwiss., 1931, **19**, 397—398).—The intervals required for the disappearance of the $K_2Cr_2O_7$ reaction for adrenaline in physiological saline solutions containing adrenaline-secreting ganglionic cells of the leech in presence of various amounts (10—60 units) of insulin were determined. The results, which give a logarithmic curve, are discussed mathematically. F. O. HOWITT.

Significance of the suprarenal cortex in the prevention of insulin shock. D. H. BØGGILD (Biochem. Z., 1931, **236**, 372—379).—Characteristic blood-sugar curves of normal and adrenalectomised dogs after intravenous insulin injection following starvation and carbohydrate-feeding are given. With massive insulin dosage adrenaline production by the organism does not affect the precipitous fall of blood-sugar, but contributes towards the rapid recovery to the normal level. F. O. HOWITT.

Mechanism of insulin action. I. Ammonia formation during muscular activity. H. SCHWARZ and M. TAUBENHAUS (Biochem. Z., 1931, **236**, 474—492).—Muscular work in man induces an increase in blood-NH_3 which, however, does not appear or is substantially less when insulin is previously administered. The diminished NH_3-production is a reversible process; administration of sugar inhibits this action of insulin, which is probably due to an inhibition of adenylic acid degradation. The relation between the blood-sugar-lowering action of insulin and the change of NH_3 metabolism following work together with the possible analogous changes in creatinephosphoric acid are discussed. F. O. HOWITT.

Mechanism of insulin action. H. SCHWARZ and M. TAUBENHAUS (Klin. Woch., 1931, **10**, 313—314; Chem. Zentr., 1931, i, 2355).—In slightly fatiguing work a marked increase in blood-NH_3 occurs unless insulin is injected. The increase is connected with the decomp. of adenylic acid to inosic acid; the fission is arrested by insulin. A. A. ELDRIDGE.

Insulin. Effects on normal rabbits protected from hypoglycæmia by ingestion of dextrose. R. F. LOEB, E. G. NICHOLS, and B. H. PAIGE (Arch. Int. Med., 1931, **48**, 70—81).—Although there are marked individual differences in the blood-sugar of rabbits receiving the same treatment, it appears that small doses of insulin (7 units per kg. body-wt.) are more effective on hyperglycæmia produced by administration of dextrose than large ones (75 units). Glycogen deposition in the liver is suppressed by insulin in the presence of hyperglycæmia. No histological effects are observed on the adrenals, neither is there a toxic effect on normal rabbits receiving 300—500 units of insulin. A. COHEN.

Extraction of insulin from blood. S. MAUGERI (Aten. Parm., 1929, **1**, 113—117; Chem. Zentr., 1931, i, 2240).—Defibrinated blood (10 c.c.) is rubbed to a homogeneous mass with finely-powdered picric acid (0·08 g.) and $COMe_2$ (8 c.c.), centrifuged, and the residue is washed with 8 c.c. of 70% $COMe_2$ followed by 8 c.c. of H_2O. $COMe_2$ is removed from the liquid in a desiccator, the ppt. formed being centrifuged, washed with Et_2O followed by alcoholic HCl (2 c.c.), and again centrifuged. The acid liquid is then treated with 10 vols. of $COMe_2$, the ppt. (containing insulin) being centrifuged, washed with Et_2O, and dried over H_2SO_4. A. A. ELDRIDGE.

Insulin reaction of the leucocytes of the blood. W. STOCKINGER and K. KOBER (Klin. Woch., 1931, **10**, 389—392; Chem. Zentr., 1931, i, 2219). A. A. ELDRIDGE.

Mol. wt. of insulin. B. SJOGREN and T. SVEDBERG (J. Amer. Chem. Soc., 1931, **53**, 2657—2661).—A more detailed account of work previously reviewed (this vol., 658). H. BURTON.

Thyroxine in muscle. B. KOMMERELL (Arch. exp. Path. Pharm., 1931, **161**, 141—153).—A myxœdematous condition develops in thyroidectomised dogs fed on a meat-free diet, and a rise in the basal metabolism occurs when meat from a normal animal is

given. No rise occurs when meat from a thyroidectomised animal is administered. Thyroxine occurs, in small amount, in the muscles of normal, but not of thyroidectomised animals. P. G. MARSHALL.

Thyroxine and nutrition. B. KOMMERELL (Arch. exp. Path. Pharm., 1931, **161**, 173—180).—The stimulating effect of thyroxine on the basal metabolism of thyroidectomised dogs lasts several days longer with a meat diet than with pure carbohydrate feeding, although the maximal effect obtainable is independent of the type of diet. The R.Q. is similarly affected. P. G. MARSHALL.

Concomitance of male and female sexual hormones. S. LOEWE, H. E. VOSS, and E. ROTHSCHILD (Biochem. Z., 1931, **237**, 214—225).—All sexual hormone preps., including those from one kind of organ, contain both male and female sexual hormones. The ratio of the activity of the female sexual hormone (F.S.H.) to that of the male sexual hormone (M.S.H.), as shown by animal tests, is designated by Q, the val. of which varies from 0·15 for M.S.H. preps. to 620 for F.S.H. preps., demonstrating the non-identity of the two hormones. Highly-purified crystalline F.S.H. has the val. for Q of 620, indicating a contamination with traces of M.S.H. The F.S.H. from yeast and bile also contains M.S.H. F. O. HOWITT.

Action of sexual hormones (ovarian and anterior pituitary) on the gas exchange. A. VON ARVAY (Biochem. Z., 1931, **237**, 199—213).—The typical action on the œstrous cycle of normal and spayed rats due to administration of ovarian preps. is accompanied by an increase in basal metabolism. Anterior pituitary extracts have a similar action in normal female but not in spayed or male rats, indicating a liberation of the ovarian hormone under the influence of the extract, which, however, also exhibits the power to inhibit œstrus and to reduce the O_2 consumption in female rats. This latter effect is not correlated to the inhibition of œstrus, but is a specific metabolic action of the anterior pituitary extract, being apparent also in male and ovariectomised female rats. F. O. HOWITT.

Carotene and vitamin-*A*. (MLLE.) D. VAN STOLK, J. GUILBERT, and H. PENAU (Compt. rend., 1931, **193**, 209—210).—Attempts to fractionate the pigment from carrots are described. Xanthophyll is shown to be absent. A. A. LEVI.

Pure carotene and vitamin-*A*. D. VAN STOLK, J. GUILBERT, H. PENAU, and H. SIMONNET (Bull. Soc. Chim. biol., 1931, **13**, 616—633).—A more detailed account of work already noted (this vol., 880).

Relation of the growth-factor to carotene. H. VON EULER, V. DEMOLE, A. WEINHAGEN, and P. KARRER (Helv. Chim. Acta, 1931, **14**, 831—833).—The extract, prepared in the usual way, of yellow (autumn) chestnut leaves gave no carotene spectrum, and also showed no marked vitamin-*A* effect, thus indicating the dependence of the latter on the presence of carotene. The statements that a H_2O-sol. active extract can be prepared from the wheat germ, and that no active substance, but a toxic one, exists in the fat-sol. materials (B., 1925, 520) are not confirmed. H. A. PIGGOTT.

Carotene from lettuce and its relation to vitamin-*A*. H. S. OLCOVICH and H. A. MATTILL (Proc. Soc. Exp. Biol. Med., 1930, **28**, 240—241).—Lettuce (150 kg.) lipins afforded 200 mg. of carotene. When kept at room temp., or in 24 hr. at 105°, the hexagonal crystals became isometric, bleached, and inactive. Carotene is best preserved in Et laurate containing 0·1% of quinol. Vitamin-*A*-deficient rats were cured of xerophthalmia by daily doses of 0·005 mg. of carotene. CHEMICAL ABSTRACTS.

Vitamin of growth. II. Action of α- and β-carotene on rats. R. KUHN and H. BROCKMANN (Ber., 1931, **64**, [*B*], 1859—1864).—The growth-promoting power of α-carotene is of the same order of magnitude as that of β-carotene. Treatment of carotene with diazomethane has little effect on its growth-promoting power. Within the limits of experimental error, the activity of β-carotene does not depend on its origin from carrot through the di-iodide, from spinach, or from nettle exclusively by fractional crystallisation. β-Carotene from paprika behaves somewhat differently. Pronounced changes in the effect of mixtures of α- and β-carotene are not caused by heating at 110° or by fractional adsorption on fibrous $Al(OH)_3$. It is improbable that a hydrocarbon with properties intermediate between those of α- and β-carotene is present in carrot. *iso*Carotene appears to be inactive. As far as unchanged hydrocarbon persists in the rat, there is no mutual transformation of α- and β-carotene. Preps. of carotene with approx. the same growth-promoting power do not lead to the production of equal quantities of vitamin-*A* in the liver, as judged by the behaviour towards $SbCl_3$. H. WREN.

Influence on growth of the isomeric carotenes and their first hydrogenation products. H. VON EULER, P. KARRER, H. HELLSTRÖM, and M. RYDBOM (Helv. Chim. Acta, 1931, **14**, 839—842).—Both α- and β-carotenes exert a marked influence on the growth of animals, the ratio of their activities being about 8 : 10, but they become more nearly equal as the treatment is continued. Conversion of carotene into its tri-iodide, and decomp. of this with $Na_2S_2O_3$. does not affect its physiological activity. The dihydrocarotenes have the same activities as the corresponding carotenes when given in three times the quantity. H. A. PIGGOTT.

Behaviour of the vitamin-*A* content of butter on heating. A. SCHEUNERT and E. WAGNER (Biochem. Z., 1931, **236**, 29—34).—The domestic operations of baking, roasting (meat), and browning do not materially decrease the vitamin-*A* content of butter as shown in feeding experiments with young growing rats. Considerable but not complete injury is caused by heating in an open pan at 160—200° for a long time. P. W. CLUTTERBUCK.

Manner of action of the vitamin-*B* complex. I. E. ABDERHALDEN. **II.** E. ABDERHALDEN and V. VLASSOPOULOS (Pflüger's Archiv, 1931, **226**, 723—737, 808—815; Chem. Zentr., 1931, i, 2256—2257).—I. Convulsive symptoms in pigeons receiving polished rice can be effectively treated by administration of dried liver, kidney, muscle, or brain of normal pigeons or of those which died or were killed during convul-

sions. The liver is the most efficacious. In many cases thyroxine is effective. So-called vitamin action is probably a complex process.

II. The dehydrase activity of the liver, muscle, and cerebral tissue of pigeons suffering from the effects of an exclusive diet of polished rice is less than that of normally fed or fasting pigeons. If yeast or the above tissues (I) were administered during convulsions the dehydrase activity increased. Lack of vitamin-*B* or -B_1 leads primarily to disturbance of oxido-reduction processes, and the observed symptoms result from defective conversion of metabolic products. A. A. ELDRIDGE.

Action of rice phosphatase. S. BELFANTI (Giorn. Chim. Ind. Appl., 1931, **13**, 270—274).—The deficiency of enzymes like phosphatase, phytase, and those acting on fats and carbohydrates is claimed to be the cause of avitaminosis-*B*. Vitamin-*B* is probably identical with these enzymes. O. F. LUBATTI.

Isolation of the antineuritic vitamin. A. SEIDELL and V. BIRCKNER (J. Amer. Chem. Soc., 1931, **53**, 2288—2295).—The method of adsorption on fuller's earth, re-extraction with alkali, benzoylation of the residue after adjustment of the p_H to 3·0 and removal of inorg. salts, and precipitation of the active substance with $COMe_2$ has yielded extracts of the antineuritic vitamin more potent than Jansen and Donath's crystals. H. A. PIGGOTT.

Irradiated ergosterol. A. WINDAUS (Proc. Roy. Soc., 1931, **B**, **108**, 568—575).—An account of work, in part previously abstracted (this vol., 881). Irradiated ergosterol is treated with maleic anhydride at room temp. for 3 days. The fraction which does not react yields a cryst. highly-antirachitic substance, $C_{27}H_{42}O$, m. p. 122—123°, $[\alpha]^{18}_D$ +138°, $[\alpha]^{18}_i$ +169° in $COMe_2$, with main absorption band at 265—270 mμ. The relationship of this product to "calciferol" (this vol., 881) is discussed. It is thought that the mol. formula, the alcoholic OH group, and double linkings of ergosterol are not changed by conversion into vitamin-*D*, but that a steric rearrangement occurs. A. COHEN.

Influence of wave-length in ergosterol irradiation. F. LAQUER (Deut. med. Woch., 1931, **57**, 243—244; Chem. Zentr., 1931, i, 2356).—Ergosterol protected from radiation of wave-length less than 280 mμ is in large doses at least as toxic as totally irradiated ergosterol. A. A. ELDRIDGE.

Activation of ergosterol with radium emanation. R. B. MOORE and T. DEVRIES (J. Amer. Chem. Soc., 1931, **53**, 2676—2681).—Activation of ergosterol by Nt gives a product which is about 0·01 as potent as that obtained by ultra-violet irradiation. The rate of activation, but not the potency, is increased by stirring. H. BURTON.

Effects of ultra-violet rays on the vitamin-*D* content of plants as compared with the direct irradiation of the animal. M. LOJKIN (Contr. Boyce Thompson Inst., 1931, **3**, 245—265).—Plants grown under greenhouse conditions do not produce vitamin-*D*. Ultra-violet rays from the solar spectrum produce very slight antirachitic properties in lettuce, lucerne, spinach, and soya bean. Rays from Hg-vapour lamps have much greater effect. Cabbage was unaffected by either source of radiation. Cut plants had greater antirachitic properties than whole plants after exposure to Hg lamps. Irradiated plants retained their activity for at least 24 hr. The effects of various light filters are recorded and control experiments with rats described. The min. exposure to ultra-violet rays required to produce vitamin-*D* in plants is much greater than that requisite for the complete protection of the animal by direct irradiation. A. G. POLLARD.

Vitamin content of the sour milk preparations yoghurt, kephir, and saya. K. A. FORSTER (Biochem. Z., 1931, **236**, 276—297).—Compared (biologically) with the fresh milk from which they were derived, yoghurt is richer in *A* and *D*, but contains less *B* and *C*, kephir is weaker in *A*, *C*, and *D* and of equal content in *B*, whereas saya is much richer in *A* and *C* and about equal in *B* and *D*. An increased vitamin content is due to bacterial synthesis. F. O. HOWITT.

Structure of protoplasm. W. SEIFRIZ (Science, 1931, **73**, 648—649).—Details of the structure of the hyaline protoplasm of onion cells as revealed by the Spierer lens are described. L. S. THEOBALD.

Physico-chemical studies on proteins. V. Comparative study of the peptisation of the protein complex in various seeds and grains. E. V. STAKER and R. A. GORTNER (J. Physical Chem., 1931, **35**, 1565—1603).—The peptisation produced by 0·5*M* aq. salt solutions has been studied. A lyotropic series of anions is recognisable for most of the protein complexes. With barley, oats, and wheat the order is $KF<K_2SO_4<KCl<KBr<KI$; with the pea it is $SO_4<Cl<F<Br<I$; with radish and rape meals the order is the same as for barley, and with mustard meal it is $F<I<SO_4<Br<Cl$. Legumes show some variation; for the halogens the order is $F<Cl<Br<I$. In the case of maize, millet, and teosinte meals the lyotropic effect is much less pronounced, and for sorghum seeds none could be demonstrated. The effects for Brazil nut, hemp, flax, and sunflower meals are discussed. The peptisation of the various groups of related seeds is distinct and characteristic for each group. Protein "solubility" is in reality protein peptisation and the existence of true plant "albumins" as definite chemical entities is questioned. L. S. THEOBALD.

Action of bromine on plant-tissues. F. M. WOOD (Ann. Bot., 1931, **45**, 421—423).—Plant-tissues which give a pink colour with Cl_2 give a dark red colour with Br. Washing with hot H_2O destroys traces of oxonium salts and renders the sections more transparent. The cortical tissues of *Cycas revoluta*, *Larix europœa*, and *Bambusa* sp. give a blue colour with Na_2HPO_4 after washing with cold H_2O. The use of Cl_2 is preferable to that of Br. P. G. MARSHALL.

Stimulated development of the winter buds of *Hydrocharis norsus ranae*, L. M. MATSUBARA (Planta [Z. wiss. Biol.], 1931, **13**, 695—715).—The dormant period of the winter buds is arrested by fumigation with HCN (gas from 1·0—1·5 g. KCN in 3 litres at 0—5°). Subsequent development occurs

only if the buds are exposed to light. Treatment with AcOH or with H_2 produces a similar but smaller effect. A. G. POLLARD.

Microchemical and morphological study of the developing endosperm of maize. L. LAMPE (Bot. Gaz., 1931, **91**, 337—376).—Changes in the starch, total- and reducing-sugar contents in the developing cells are recorded. A. G. POLLARD.

Influence of increasing amounts of iodide, iodate, and periodate on germination and early development of culture plants. K. SCHARRER and W. SCHROPP (Biochem. Z., 1931, **236**, 187—204).—The influence of increasing amounts of KI, KIO_3, and KIO_4 on germination and development of wheat, rye, barley, and oats in lower moor and sandy clay soil is investigated. Higher doses of I injure germination and further development, iodide having the most and periodate the least injurious effect. The sensitivity of the plants decreases in the following order: oats, wheat, rye, barley. The yield of crop is decreased by high I doses, most strongly with iodide and least with periodate. The injury to germination, embryonic development, and yield on addition of iodide is less in the sandy clay than in the lower moor soil, due to its reaction and colloidal content, the I being largely precipitated by the Ca content. P. W. CLUTTERBUCK.

Translocation of materials in the vascular bundles of the higher plants. W. SCHUMACHER (J. wiss. Bot., 1930, **73**, 770—821; Bied. Zentr., 1931, **60 A**, 200—201).—The translocation of N takes place through the sieve tubes of the phloem. Attempts to induce artificial movement through the parenchyma were unsuccessful. A. G. POLLARD.

Fat metabolism of leaves. I. Detached and starved mature leaves of Brussels sprout (*Brassica oleracea*). A. C. CHIBNALL and P. N. SAHAI (Ann. Bot., 1931, **45**, 489—502).—An Et_2O extract of the leaves was similar in composition to that of cabbage leaves. No change in the phosphatides or glycerides occurs in detached leaves, even when these are kept in the dark until the chlorophyll has almost disappeared. Sugars in the lamina increase during such isolation. In leaves kept in the dark a continuous breakdown of protein occurs (22·3—13·2 g. per kg.) despite the abundance of carbohydrate present. P. G. MARSHALL.

Gas contained in *Valonia utricularis* (Roth), Ag. S. COLLA (Atti R. Accad. Lincei, 1931, [vi], **13**, 149—153).—When kept submerged, the gas present in this alga contains CO_2 (2·5—7·1% according to the age of the organism) only in the morning. The content of O_2 increases as the day advances and may reach 70% in very bright weather (cf. A., 1930, 1072). T. H. POPE.

Katharometer in measurement of respiration. W. STILES and W. LEACH (Ann. Bot., 1931, **45**, 461—488).—An apparatus is described for use with a closed glass respiration chamber, by means of which both CO_2 and O_2 changes can be measured. The sensitivity of the moving-magnet galvanometer can be varied, but in actual use a deflexion of 1 mm. corresponds with a change in CO_2 content of 0·007%. P. G. MARSHALL.

Phæohæmin *b*. O. WARBURG and W. CHRISTIAN (Biochem. Z., 1931, **235**, 240—242).—The prep. of hæmin from phæophorbide *b* is described; the spectrum is closely related to that of *Spirographis* hæmin (this vol., 109). P. W. CLUTTERBUCK.

Pigment of the elderberry (*Sambucus nigra*, Linn.). T. J. NOLAN and H. M. T. CASEY (Proc. Roy. Irish Acad., 1931, **40**, **B**, 56—66; cf. A., 1927, 252).—The chlorides of chrysanthemin and "*sambucicyanin*," a bimol. compound of chrysanthemin and a pentose glucoside of cyanidin, were isolated. The pentose is not rhamnose. A. A. LEVI.

Formation of anthocyanin pigments in the flower of *Iris germanica*. A. GUILLERMOND (Compt. rend., 1931, **193**, 112—114).—Oxyflavonols are the precursors of anthocyanins; occasionally both substances are absorbed in the cells by colloids of unknown constitution. C. C. N. VASS.

Micro-chemical characteristics and cytological mode of formation of anthocyanin pigments. A. GUILLIERMOND (Compt. rend., 1931, **192**, 1581—1583).—In certain flowers anthocyanin is present in the vacuoles in true solution or admixed, or as a complex adsorption colloid with the tannins. Anthocyanin arises as a transformation of hydroxyflavonols. C. C. N. VASS.

Chemical effect of a Mendelian factor for flower colour. R. S. MONCRIEFF (Nature, 1931, **127**, 974—975).—In *Pelargonium* the effect of the factor which converts salmon-coloured flowers into rose is to substitute cyanin almost completely for pelargonin. L. S. THEOBALD.

Chlorophyll defect. H. VON EULER and D. RUNEHJELM (Arkiv Kemi, Min., Geol., 1931, **10**, **A**, no. 10, 8 pp.).—Ungerminated barley contains more catalase than barley after several days' germination. That the catalase content of chlorophyll-defective mutants of barley is less than that of normal grains is confirmed (cf. A., 1930, 498). The chlorophyll-defective tissue of certain species of *Pelargonium*, in contrast to barley, contains more total Mg than that normal in chlorophyll. F. O. HOWITT.

Chlorophyll defect. H. VON EULER and O. MORITZ (Arkiv Kemi, Min., Geol., 1931, **10, A**, No. 11, 15 pp.).—A yellow mutant of barley showed no difference in catalase activity between the green and chlorophyll-poor parts of the germinated seed. In chlorophyll-defective cabbage the decrease in catalase activity with age is related to the chlorophyll content, the former decreases both in yellow and white leaves parallel with decrease in ability to turn green, this being true also for the etiolated cotyledons of *Cucurbita*. That no parallelism exists between catalase activity and chlorophyll content is shown by chlorophyll-free tissue being rich in catalase. The tryptophan content of chlorophyll-free cotyledons is higher than normal. F. O. HOWITT.

Chlorophyll mutants of barley. H. NILSSON (Arkiv Kemi, Min., Geol., 1931, **10, A**, No. 12, 34 pp.).—The amylase activities of homo- and hetero-zygotic and white chlorophyll-defective homozygotic barley show no difference. The O_2-consumption of green parts of the embryo is greater than that of the white,

no difference existing between mono- and heterozygotes. Presence of KNO_3 (0·2—0·3%) in the culture media has no influence on the O_2-consumption. Green leaves have a slightly higher ash than white.

F. O. HOWITT.

Carotenoid of *Citrus aurantium*. P. G. F. VERMAST (Naturwiss., 1931, **19**, 442—443).—The properties of xanthophyll from fruits are examined. That from *C. aurantium* is the same as that obtained by Tswett, and has vitamin-*A* properties.

A. J. MEE.

Sapogenin of guaiacum bark. II. Identity of guagenin with the sugar-beet sapogenin. E. WEDEKIND and W. SCHICKE (Z. physiol. Chem., 1931, **198**, 181—184; cf. this vol., 491).—Beet resin-acid, when hydrolysed by dil. H_2SO_4, yields a sapogenin identical with guagenin. The guagenin regenerated from the Ac derivative gives combustion figures which correspond closely with the formula $C_{30}H_{48}O_3$.

J. H. BIRKINSHAW.

Distribution of saponins. L. ROSENTHALER (Pharm. Zentr., 1931, **72**, 417—418).—A discussion of the relationships between terpenes and saponins. The fact that plants which are rich in the one substance are poor in the other is explained by the different initial polymerisation of the C_5 isoprene residue; on the one hand terpenes are formed and on the other sapogenins which by further condensation with sugars give saponins.

E. H. SHARPLES.

Natural polylævans. II. Polylævans of the leaves of *Yucca filamentosa*. III. Formation of polylævans in *Helianthus tuberosus*. H. H. SCHLUBACH and W. FLORSHEIM (Z. physiol. Chem., 1931, **198**, 153—164; cf. A., 1929, 914).—II. The MeOH extract of dried yucca leaves, after removal of hexoses and sucrose by fermentation, gave a dilævan agreeing in rotation with sinistrin *A* and yielding 3 : 4 : 6-trimethyl-*h*-fructose after methylation and hydrolysis. The yucca product is hydrolysed by yeast enzyme.

III. The leaves of *Helianthus tuberosus* harvested in July and September contain no polylævans, although these are present in the axes (cf. A., 1925, i, 618).

J. H. BIRKINSHAW.

Presence of maclurin in sapwood of the cutch-producing acacias. M. NIERENSTEIN (J. Indian Chem. Soc., 1931, **8**, 143—145).—Extraction of the sapwood of *Acacia catechu, A. catechuoides*, and *A. Sundra* affords maclurin (0·4 g. per kg.) but no quercetin. The biosynthetic relationships of *l*-leucomaclurin glycol with acacatechin, *iso*acacatechin, and maclurin are discussed.

J. W. BAKER.

Principal sugar of Kaa-he-e (*Stevia Rebaudiana*, Bertoni). II. Products of enzymic hydrolysis of stevioside: dextrose and steviol. M. BRIDEL and R. LAVIEILLE (Compt. rend., 1931, **193**, 72—74).—Stevioside, $C_{38}H_{60}O_{18}$, is hydrolysed by the digestive juices of the edible snail to dextrose and a phenol, *steviol*, $C_{20}H_{30}O_3$, m. p. 217°; $[\alpha]_D$ −94·66°.

C. C. N. VASS.

Rebaudin of Dieterich and impure stevioside. M. BRIDEL and R. LAVIEILLE (Bull. Soc. Chim. biol., 1931, **13**, 656—657).—The rebaudin of Dieterich is impure stevioside.

C. C. N. VASS.

Biochemistry of *Salix*. III. A new β-glucoside, salipurposide, from the bark of *Salix purpurea*, L. C. CHARAUX and J. RABATE (Bull. Soc. Chim. biol., 1931, **13**, 590—597).—Extracts of the bark of male and female trees have been prepared and their rotations and reducing powers before and after enzymic hydrolysis determined. *Salicopurposide*, $C_{21}H_{22}O_{10}$, was extracted in 1·87% yield from the bark by 90% EtOH and crystallised from H_2O, $[\alpha]_D^{19}$ −116·87°. It is non-reducing, but yields on hydrolysis 42·5% of dextrose and 61·6% of a phenol, *salipurpol*, $C_{15}H_{12}O_5$, m. p. 256·5°.

C. C. N. VASS.

Salireposide, new glucoside from the bark of *Salix repens*, L. N. WATTIEZ (Bull. Soc. Chim. biol., 1931, **13**, 658—667).—The bark is extracted with 70% EtOH in presence of $CaCO_3$. After distillation of the EtOH and removal of chlorophyll, salireposide crystallises on keeping; subsequent treatment with basic Pb acetate ppts. salicoside. Anhyd. *salireposide*, m. p. 206°, $[\alpha]_D$ +36·78°, is non-reducing; on hydrolysis with dil. H_2SO_4 it yields dextrose, BzOH, and an unknown phenol.

C. C. N. VASS.

Gaultherioside, a new glucoside obtained from *Gaultheria*. J. RABATE and S. RABATÉ (Bull. Soc. Chim. biol., 1931, **13**, 604—615).—In addition to monotropitin and sucrose, the EtOH extract of fresh *G. procumbens*, L., contains a mixture of sugars from which after hydrolysis *gaultherioside*, m. p. 185°, $[\alpha]_D$ −58·07° (anhyd.), containing 1·44% H_2O has been isolated. It is non-reducing and on hydrolysis with dil. H_2SO_4 yields dextrose, xylose, and EtOH. It is not hydrolysed by rhamnodiastase.

C. C. N. VASS.

Pollen and pollen extracts. VII. Glucoside from certain grass pollens. M. B. MOORE and E. E. MOORE (J. Amer. Chem. Soc., 1931, **53**, 2744—2746).—An aq. extract of the pollens of *Dactylis glomerata*, L., and *Phleum pratense*, L., gradually deposits crystals of *dactylin*, $C_{23}H_{28}O_{15}$, m. p. 183—185° (corr.), hydrolysed by 5% H_2SO_4 to 1 mol. of a substance, m. p. 298—300° (corr.; decomp.), and 2 mols. of (probably) a hexose. Dactylin is not hydrolysed by emulsin.

H. BURTON.

Pectic substances of the carrot and their decomposition by *Bacillus carotovorus*. H. W. BUSTON and H. F. KIRKPATRICK (Ann. Bot., 1931, **45**, 519—525).—The protopectin content of the cortex is approx. twice that of the stele. If the powdered tissue is extracted with boiling *N*/75 HCl, only the protopectin is removed, the middle lamella pectin being unattacked, whilst $(NH_4)_2C_2O_4$ extracts all pectins. The pectins of the cortex and stele have similar constitutions, as evidenced by the furfuraldehyde, uronic anhydride, and OMe-group contents, and both are equally efficient as nutrients for *B. carotovorus*.

P. G. MARSHALL.

Plant gums. F. WEINMANN (Biochem. Z., 1931, **236**, 87—98).—The separation of *d*-glycuronic acid from gum-arabic and cherry gum and its purification are described.

P. W. CLUTTERBUCK.

Harmine: preparation from the root *Peganum harmala*, L. A. D. ROZENFELD (Farm. Zhur., 1930, 183—186).—A 3% yield was obtained.

CHEMICAL ABSTRACTS.

Plant chemistry. XVIII. Crystalline protein in the secretions of the *Anacardiaceæ*. H. MOLISCH (Ber. deut. bot. Ges., 1931, **49**, 324—327).—A cryst. protein is present in *Manganifera*, *Odina*, *Schinus*, and *Rhus*. P. G. MARSHALL.

Tyramine and hydroxytyramine, precursors of the black pigments of *Sarothamnus scoparius*, Wimm. H. SCHMALFUSS and A. HEIDER (Biochem. Z., 1931, **236**, 226—230).—Hydroxytyramine (*tricarbomethoxy*-compound, m. p. 92—93°; *tribenzoate*, m. p. 141°) and tyramine (*dicarbomethoxy*-compound, m. p. 99—100°) are the precursors of black pigments in broom pods. P. W. CLUTTERBUCK.

Chemical composition of tobacco. I. Organic bases and acids of fresh leaves. K. YAMAFUJI (Bull. Agric. Chem. Soc. Japan, 1931, **7**, 121—132).—An aq. extract is treated with $Pb(OAc)_2$ and the ppt. discarded. After removal of Pb the filtrate is made alkaline and distilled in steam; nicotine passes over (3 g. per kg.). Phosphotungstic acid ppts. adenine, histidine (with some arginine), and betaine from the residual liquid after acidification with H_2SO_4. If the powdered leaf is extracted with very dil. HCl and $Pb(OAc)_2$ added, the acids are precipitated. The salts are decomposed by H_2S and the acids esterified and fractionally distilled. Malic (1·3%), citric (0·6%), and oxalic acids (0·09%) are present. P. G. MARSHALL.

[Degradation of nicotine in tobacco.] A. FAITELOWITZ (Biochem. Z., 1931, **237**, 90—91).—The contention of Fodor and Reifenberg (this vol., 402) concerning the results of the author (A., 1930, 1484) is refuted. F. O. HOWITT.

Effect of evaporation and radiation on nicotine solutions. J. HIGGINS, P. L. EWING, and H. A. MCGUIGAN (J. Pharm. Exp. Ther., 1931, **42**, 213—216).—Nicotine assayed by means of its action on the dog's blood-pressure is not destroyed when heated in a closed vessel at 100°, but is destroyed when irradiated by means of a Hg vapour lamp. The effect of irradiation by a C arc lamp is only small. W. O. KERMACK.

Leguminous bacteria and plants. X. Activity of leguminous bacteria and the utilisation of fixed nitrogen from nodules of legumes by non-leguminous plants. A. I. VIRTANEN and S. VON HAUSEN (Z. Pflanz. Düng., 1931, **21 A**, 57—69).—N compounds formed in root nodules of legumes diffuse into the soil and are utilisable, as such or after ammonification, by other non-leguminous crops. In a mixed crop of peas and oats the latter gained additional N if the ratio of peas : oats was 1 : 1 or 2, but with a smaller ratio the growth of both plants declined. This effect varies with the p_H of the medium. Similar results are obtained with other combinations of crops. A. G. POLLARD.

Constituent of *Euphorbia formosana*, Hay. I. J. SHINODA and C. PING-KUN (J. Pharm. Soc. Japan, 1931, **51**, 50—51).—Acidification of a MeOH extract of the roots of *E. formosana*, Hay, and extraction with Et_2O gives an acidic substance, m. p. 337—338°, containing 2 OMe and 2 OH groups (Ac_2 *derivative*, m. p. 298—300°), and yielding ellagic acid (tetra-acetate, m. p. 342—343°) on demethylation. It is, therefore, an *ellagic acid* Me_2 *ether*, which, because it is not identical with the product previously described (A., 1905, i, 900), and because of its colour reaction with $FeCl_3$, contains the OH groups in different C_6H_6 rings. R. S. CAHN.

Chemical composition of mulberry leaves. Y. KISHI (Bul. Sci. Fak. Terkultura Kjusu, 1931, **4**, 173—190).—The protein in dried leaves and H_2O in fresh leaves decrease from spring to autumn. The p_H of the leaf sap increases slightly from spring onwards. P. G. MARSHALL.

Chemical examination of the roots of *Hygrophyla spinosa*. N. H. GHATAK and S. DUTT (J. Indian Chem. Soc., 1931, **8**, 23—28).—Exhaustion of the dried roots of *H. spinosa* with EtOH or other org. solvents yields a phytosterol (cf. J.C.S., 1920, **117**, 1624), *hygrosterol*, $C_{28}H_{46}O$, m. p. 194°, $[\alpha]_D^{15}$ (in $CHCl_3$) +27·8° (*Ac* derivative, m. p. 208°; *hydrobromide*, m. p. 59°; *dibromohydrobromide*, m. p. 138—139°; *digitonide*, decomp. 220—230°), together with maltose and an oil. G. DISCOMBE.

Nutmeg oil. E. BUREŠ and H. MLADKOVA (Časopis Českoslov. Lék., 1930, **10**, 317—323; Chem. Zentr., 1931, i, 1987).—The oil of *Nigella sativa* seeds (33·4%) had d^{15} 0·8960, acid val. 29·42, sap. val. 201·98, ester val., 172·56, I val. 107·40, Reichert-Meissl val. 3·379, Polenske val. 0·535, Hehner val. 89·25, Ac val. 23·89. Myristic and telfairic acids were isolated. A. A. ELDRIDGE.

Paeony seed oil. E. BUREŠ and B. ŠUSTEROVA (Časopis Českoslov. Lek., 1930, **10**, 293—299, 323—325; Chem. Zentr., 1931, i, 1987).—Characteristic data are recorded. A. A. ELDRIDGE.

Expressed Brazil-nut oil. H. A. SCHUETTE and W. W. F. ENZ (J. Amer. Chem. Soc., 1931, **53**, 2756—2758).—The expressed oil (B., 1930, 1162) contains myristin (0·48%), palmitin (13·74%), stearin (5·45%), olein (42·79%), and linolein (26·54%). The olein and myristin contents are lower than those of the residual oil (*loc. cit.*), but the stearin content is higher. H. BURTON.

Occurrence of calcareous and siliceous substances in plant cells. F. NETOLITZKY (Bull. Fac. Stiinte Cernauti, 1928, **2**, 320—325; Chem. Zentr., 1931, i, 2070).—A discussion. A. A. ELDRIDGE.

Preparation of skeletal substances from incrusted cellwalls with the aid of chlorine dioxide. III. The whole-number relation of $3C_6H_{10}O_5$ of cellulose to $1C_5H_8O_4$ of sparingly soluble xylan to $1CO{\cdot}CH_2$ of acetyl in the skeletal substance of red beechwood (*Fagus sylvatica*). E. SCHMIDT, Y. C. TANG, and W. JANDEBEUR (Cellulosechem., 1931, **12**, 201—212; cf. this vol., 606).—Delignification of wood by ClO_2 is carried out in a single stage in presence of aq. pyridine, and the above whole-number ratio in the resulting skeletal substance is confirmed. The total OAc content of the wood is contained in the sparingly sol. xylan portion, which is regarded as a polymeric acetylxylose anhydride. A. A. LEVI.

Chemical composition of red beechwood. R. RUNKEL and G. LANGE (Cellulosechem., 1931, **12**, 185—200).—A method for delignification involving the min. destruction of the natural fibrous structure of the

wood is described, and the whole-number ratio between sparingly sol. xylan and cellulose in the skeletal substance (this vol., 606) is confirmed. The distribution of the OMe and OAc groups, and of the substances yielding furfuraldehyde among the constituents of the wood is discussed, and the "genuine lignin" content estimated. A. A. LEVI.

Determination of the base content of wood. K. BEAUCOURT (Biochem. Z., 1931, 235, 79—85).—The electrolytic determination of Ca, Mg, and Fe separately and in mixtures in terms of g. OH (B., 1928, 346) is trustworthy and has a max. error of 2%. The method is applied to the determination of base content of salt-rich samples of wood, the results being reproducible with an error of less than 5%. P. W. CLUTTERBUCK.

Chemical aspect of the drying of timber. II. The drying of a softwood. W. G. CAMPBELL and J. BOOTH (Biochem. J., 1931, 25, 756—762).—Air-drying reduces the pentosans and H_2O-sol. material in the wood of silver fir. Lignin is enhanced at the expense of the furfuraldehyde-yielding complexes, and cellulose at that of the H_2O-sol. material of the green wood. Kiln-drying precludes the addition to cellulose and part of the additions to lignin. Oven-drying of green wood induces hydrolysis of the wood substance which is responsible for a slight error in moisture determination. S. S. ZILVA.

Sugar beet and molasses (nitrogen and raffinose). E. SAILLARD (Compt. rend., 1931, 192, 1748—1750).—The amounts of sugar, protein-N, NH_3-N, and NH_2-N in sugar beet and the rainfall for the periods 1904—1913, 1920—1929, 1930 are recorded; also the dry wt., polarisation after precipitation with basic Pb acetate, dextrose after inversion, and N-content of molasses for the years 1925—1931. In wet seasons the largest amount of sugar and the lowest amount of N are elaborated. In molasses the difference between the direct polarimetric reading and the amount of sugar following inversion increases as the amount of N decreases; this difference was traced in 1931 to the accumulation of raffinose in the roots in the last stages of cultivation. C. C. N. VASS.

Potassium in sugar beet. H. COLIN and P. BILLON (Compt. rend., 1931, 192, 1746—1748).—Selective cultivation of sugar beet has reduced the mineral content. Formerly the ash contained 50% K_2O and the combined MgO and CaO reached 20%; at the present time sugar beet contains approx. 3% of ash with 20% K_2O, but the greater part of the K is present as K salts of organic acids. C. C. N. VASS.

Potassium deficiency of fruit trees. T. WALLACE (J. Pomology, 1931, 9, 111—121).—Fruit trees on K-deficient soils are distinguished by the appearance of leaf scorch and chlorosis and by the decreased K content of leaves, shoots, main stem, and pulp (but not stones) of the fruit. There is a corresponding increase in the dry matter content of the fresh material. The response to applications of dung and K-manures is reflected in the composition of the treated trees. A. G. POLLARD.

Plant tissue fluids. I. Effects of age and environment on the tissue fluids of French beans (*Phaseolus vulgaris*). C. N. ACHARYA and B. N. SASTRI (J. Indian Inst. Sci., 1931, 14, A, 1—9).—Specimens of fluids from various tissues were taken at various stages of growth and examined for sp. gr., n, osmotic pressure, reaction, total solids, mineral ash, total N, sugar content, and diastatic activity. The changes observed are correlated with the translocation incident on flowering and with the changes in metabolism following differences in rate of growth, photosynthesis, or respiration. F. O. HOWITT.

Hydrogen-ion concentration of potato tubers. J. M. ROBERTSON and A. M. SMITH (Biochem. J., 1931, 25, 763—769).—In the early stages of development the underground stem and the heel end of the tuber are most acid and the average acidity of the tuber increases with maturity. In the dormant state the acidity does not vary much in different parts of the tuber, but when sprouting begins the active eyes are most acid. The acidity of the tuber is independent of environment and is not influenced by large variations in soil acidity. The differences in acidity due to variety and storage are not significant. Comparatively large changes in acidity are associated with certain diseases. S. S. ZILVA.

Blackening of potatoes after cooking. C. K. TINKLER (Biochem. J., 1931, 25, 773—776).—Potatoes contain a substance in greatly varying amounts which on treatment with HNO_2 and an alkali gives a red colour. The amount of the red substance varies exactly with the amount of blackening which takes place on cooking. Fe may have a pronounced influence on the degree of blackening. S. S. ZILVA.

Changes in chlorosis-infected leaves of *Abutilon*. H. VON EULER, W. HERTZSCH, S. MYRBÄCK, D. RUNEHJELM, and A. FORSSBERG (Arkiv Kemi, Min., Geol., 1931, 10, B, no. 13, 6 pp.).—The catalase content of chlorosis-infected leaves of *A. striatum* is directly proportional to the degree of green colour. The NH_2 : total-N ratio is higher for the white parts for which spectrophotometric observations indicate a low content of all the chlorophyll pigments, and for which the tryptophan content is below normal. F. O. HOWITT.

Determination of small quantities of mixed reducing sugars and its application to the determination of the products of hydrolysis of starch by taka-diastase. E. M. WIDDOWSON (Biochem. J., 1931, 25, 863—879).—The method combines the principle of Hanes' modification of Hagedorn and Jensen's method and the iodometric method. It can be applied to the determination of small quantities of mixtures of dextrose, lævulose, and of dextrose and maltose and to the dextrose and maltose obtained by the hydrolysis of starch by taka-diastase. In the latter case the experimental error was within 1%. There is no loss of sugar when dextrose–maltose solutions are cleared with basic Pb acetate and Na phosphate. Clear solutions from EtOH extracts of apples should be decolorised with charcoal before analysis. S. S. ZILVA.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

OCTOBER, 1931.

General, Physical, and Inorganic Chemistry.

Aston's dark space. A. Günther-Schulze and F. Keller (Z. Physik, 1931, **71**, 238—245).—The thickness of Aston's dark space increases inversely as the gas pressure for He, Ne, A, H_2, and N_2.
A. B. D. Cassie.

New phenomenon in the dark space of the glow discharge. A. Günther-Schulze and F. Keller (Z. Physik, 1931, **71**, 246—249).—A cathode containing Mg shows a dark space immediately beyond the cathode; this space is $\frac{1}{8}$ the thickness of Aston's dark space, and is bordered on the anode side by a glow due to the Mg triplets at 5172 Å. A. B. D. Cassie.

Spectrum of doubly-ionised carbon C III. I. S. Bowen (Physical Rev., 1931, [ii], **38**, 128—132).—With new experimental data 54 lines of C III and 14 additional lines of C II are classified. The former lead to an ionisation potential of 47·7 volts.
N. M. Bligh.

Wave-length standards in the spectra of carbon and tin in the Schumann region. R. V. Zumstein and D. S. Marston (Physical Rev., 1931, [ii], **38**, 305—308).—In the region 2000—1500 Å. the strong lines of C I and Sn II were measured by comparison with Fe. The C arc lines 1930 have a lower wave-length than from the vac. spark (cf. A., 1929, 860); the Sn wave-lengths are 1899·875, 1831·75, 1811·206, 1757·91, and 1699·39 Å. (cf. A., 1928, 2).
N. M. Bligh.

Spectra of the corona discharge. H. Oyama (Tech. Rep. Tohoku, 1931, **10**, 1—10).—Spectrograms of the corona discharge along Cu and Pt wires show that the d.-c. discharge can develop continuously to the state of the glow discharge. The spectra obtained are those of the N band systems, no emission due to mol. ions of O being observed. A. R. Powell.

Influence of electric fields on ultra-violet lines in the neon spectrum (Ne I and Ne II). N. Ryde (Z. Physik, 1931, **71**, 124—136).—The Stark effect in the ultra-violet region of the arc and spark spectra of Ne was determined, and is discussed.
A. B. D. Cassie.

Emission of *D* lines by sodium vapour irradiated with yellow light. A. Jabłoński and P. Pringsheim (Z. Physik, 1931, **70**, 593—602).—Emission of *D* lines by Na vapour saturated at 300° is due to absorption of light in a small spectral region near the *D* lines, and is probably a fluorescence by weakly bound Na_2 mols. A. B. D. Cassie.

Absorption line width in sodium vapour. S. A. Korff (Physical Rev., 1931, [ii], **38**, 477—486; cf. A., 1929, 1129).—Spectrograms of the *D* lines of Na in absorption were measured on a densitometer.
N. M. Bligh.

Absorption spectrum of aluminium hydride. L. Farkas (Z. Physik, 1931, **70**, 733—749).—The absorption spectrum of AlH was photographed between 4000 and 4500 Å. with various pressures of H_2 in the absorption tube; the relation of the width of observed lines in the three bands of this region to predissociation in the $^1\Pi$ state is discussed.
A. B. D. Cassie.

Band spectrum of the green flame of phosphorus. E. D. Ludlam (Nature, 1931, **128**, 271).—Preliminary details of the band spectrum of the green flame obtained when H_2 containing some P vapour is burned in air are given. L. S. Theobald.

[Energy] levels in diatomic sulphur vapour. II. J. Genard (Bull. Acad. roy. Belg., 1931, [v], **17**, 583—592; cf. this vol., 540).—Resonance series excited by certain Hg, Ag, and Cu lines are in better agreement with the author's equation $1/\lambda=1/\lambda_0-734n''+2\cdot9n''^2$ than with Rosen's (A., 1927, 608).
N. H. Hartshorne.

Photographic measurement of excitation functions in the argon spectrum. O. Fischer and W. Hanle (Z. wiss. Phot., 1931, **30**, 141—146).—Spectra of A by electron impact (cf. A., 1930, 131, 1490) at 15—100 volts have been photographed in the visual region. Arc line excitation potentials are about 15 volts, spark line about 35 volts.
J. Lewkowitsch.

Vacuum spark spectrum of K and Ca between 100 and 1100 Å. E. Ekefors (Z. Physik, 1931, **71**, 53—88).—A vacuum spectrograph and glass grating at grazing incidence were used to give high dispersion in this region, and wave-lengths of K and of Ca were measured and tabulated. A. B. D. Cassie.

Hyperfine structure in the spectra of copper and gold. R. Ritschl (Naturwiss., 1931, **19**, 690).—The splitting up of resonance lines in the spectrum of Cu is in agreement with Shenstone's val. of 3/2 for the nuclear moment. For Au the val. of the nuclear moment is 3/2, which disagrees with Frisch's zero val. W. R. Angus.

Optical dissociation of rubidium iodide. A. C. S. van Heel and G. H. Visser (Z. Physik, 1931, **70**, 605—613).—The heat of dissociation of RbI into $Rb_{(^2P_1}$ $I_{(^2P_2)}$ and into $Rb_{(^3P_1,\,^3P_2)}+I_{(^2P_2)}$, kg.-cal. per mol. A. B. D. Cassie.

Hyperfine structure in the spectra of some elements. S. Frisch (Z. Physik, 1931, **71**, 89—92).—Sr, Ag, and Mo have zero nuclear moment; the moment for Cu is small. A. B. D. Cassie.

Black-body [radiation] at the m. p. of palladium; comparison of the tube and filament

methods. S. Nikitine (J. Phys. Radium, 1931, [vii], 2, 205—226; cf. A., 1929, 967).—The filament method is described and discussed in detail; results by the two methods are in satisfactory agreement.
N. M. Bligh.

Effect of hyperfine structure on the polarisation of cadmium resonance radiation. A. C. G. Mitchell (Physical Rev., 1931, [ii], 38, 473—476).—Assuming the nuclear moment of two kinds of isotopes, the polarisation of Cd resonance radiation (λ 3261) is calc. and compared with experimental data.
N. M. Bligh.

Infra-red spectrum of Sn I. H. M. Randall and N. Wright (Physical Rev., 1931, [ii], 38, 457—462).—Wave-lengths, approx. relative intensities, and classifications of 45 new lines are tabulated.
N. M. Bligh.

$^3P\bar{P}$ groups in singly-ionised antimony and arsenic. K. R. Rao and A. L. Narayan (Proc. XV Indian Sci. Cong., 1928, 80—81).—The probable multiplets discovered in Sb II and As II are tabulated.
Chemical Abstracts.

Doublets in As III, Sb III, and Bi III. K. R. Rao and A. L. Narayan (Proc. XV Indian Sci. Cong., 1928, 80).—Vals. for As (3 pairs), Sb, and Bi (2 pairs each) are tabulated. Chemical Abstracts.

Forbidden lines in the high-frequency discharge of mercury, cadmium, and zinc. J. Okubo and E. Matuyama (Nature, 1931, 128, 224).—The forbidden lines $1S-2p_1$ of Hg and $1S-2p_1$ and $1S-2p_3$ of Cd, but none of Zn, have been observed. The marked effects of a rise in temp. on the spectrum of Hg are described. L. S. Theobald.

Temperature radiation of thallium vapour. K. Majumdar and P. K. Kichlu (Proc. XV Indian Sci. Cong., 1928, 84).—Emission begins at 1800°. At 1900°, 5350 A. was obtained in emission and 3775 Å. in absorption. Chemical Abstracts.

Hyperfine structure of heavy elements. G. Breit (Physical Rev., 1931, [ii], 38, 463—472).—Mathematical. N. M. Bligh.

Ultimate rays and absorption lines. A. T. Williams (Compt. rend., 1931, 193, 358—360).—On the ground of the author's previous results (cf. A., 1928, 929; 1929, 2, 366; 1930, 125) it is concluded that very few ultimate rays are absorption lines. The ultimate rays are not always among the most readily produced absorption lines (cf. A., 1926, 314).
C. A. Silberrad.

Spectroscopic classification of the elements according to ground states. C. H. D. Clark (Proc. Leeds Phil. Soc., 1931, 2, 225—229).—Previous classifications are criticised and an improved table, as a basis for discussion of the relation between spectroscopic ground states and the valencies of atoms, is given.
N. M. Bligh.

Effect of surface films on exploring electrodes in gas discharges. W. E. K. Middleton and T. Alty (Canad. J. Res., 1931, 4, 498—504).—The presence of org. vapours in a H_2 discharge is shown to influence the current collected by an exploring electrode placed in the discharge. W. Good.

Method of obtaining spectral purity with a monochromator in the ultra-violet. C. Leiss (Z. Physik, 1931, 71, 156—160).—The different chromatic foci of two ordinary lenses may be used to give purity of spectrum in the ultra-violet. A. B. D. Cassie.

Vacuum fluorite spectrograph. G. Cario and H. D. Schmidt-Ott (Z. Physik, 1931, 69, 719—723).—Descriptive. W. Good.

[Vacuum fluorite spectrograph.] C. Leiss (Z. Physik, 1931, 71, 161).—The fluorite vacuum spectrograph for the Schumann region described by Cario and Schmidt-Ott (preceding abstract) is essentially that described by Leiss (*ibid.*, 1927, 44, 135—138).
A. B. D. Cassie.

Reflecting power and grating efficiency in the extreme ultra-violet. H. M. O'Bryan (Physical Rev., 1931, [ii], 38, 32—40).—Various angles of incidence were investigated for the region 200—1000 Å. Vals. for glass and Au mirrors at 388 and 770 Å. were measured for all angles of incidence. The influence of reflecting power, groove form, and surface smoothness on grating efficiency is discussed.
N. M. Bligh.

Interference in thin metallic films. H. W. Edwards (Physical Rev., 1931, [ii], 38, 166—173).—The colour of thin metallic films sputtered on glass or on other metals is explained by interference, and is investigated mathematically. N. M. Bligh.

Non-existence of photon spin. A. Kastler (J. Phys. Radium, 1931, [vii], 2, 159—164).—The negative result (no photon spin) obtained by Frisch with the resonance line of Hg has been confirmed with Na *D* radiation. Theoretical consequences are discussed.
W. Good.

Collision broadening of spectral lines and energy exchange on collision. A. Jabłonski (Z. Physik, 1931, 70, 723—732).—Theoretical.
A. B. D. Cassie.

Structure of the spectra of stripped atoms. K. Bechert (Z. Physik, 1931, 69, 735—741).—Theoretical. W. Good.

Λ-type doubling and electron configurations in diatomic molecules. R. S. Mulliken and A. Christy (Physical Rev., 1931, [ii], 38, 87—119).—Theoretical. N. M. Bligh.

Solar component of cosmic radiation. V. F. Hess and W. S. Pforte (Z. Physik, 1931, 71, 171—178).—Cosmic radiation traversing 10 cm. of Pb shows a distinct max. near mid-day. A. B. D. Cassie.

Photovisual star sizes. E. Hertzsprung (Z. wiss. Phot., 1931, 30, 171—173).—The relations between temp., photovisual strength of black-body radiation, and the corresponding star sizes are calc. for the photographic region about 550 mμ.
J. Lewkowitsch.

Atomic synthesis and stellar energy. I. R. D'E. Atkinson (Astrophys. J., 1931, 73, 250—295).—A synthesis theory of stellar energy and of the origin of the elements is developed in which the heavier elements are built up stepwise in stellar interiors from lighter ones. L. S. Theobald.

Precision X-ray spectrometer and the wavelength of Mo-$K\alpha_1$. A. H. Compton (Rev. Sci. Instr., 1931, [ii], 2, 365—376).—An ionisation spectrometer with two or more crystals in series is described;

it gives $\lambda=707{\cdot}830\pm0{\cdot}002$ X for Mo-$K\alpha_1$, and $1-\mu=(2{\cdot}10\pm0{\cdot}15)\times10^{-6}$ for calcite. N. M. BLIGH.

Occurrence of a continuous spectrum during bombardment by cathode rays. I. Preliminary. II. "Aeona effect." III. Thorium in high vacuum. W. M. COHN (Z. Physik, 1931, **70**, 662—666, 667—678, 679—694).—I. The spectrometer and microphotometer required to study a continuous spectrum in an X-ray tube are described.

II. A continuous spectrum extending from 6500 to 2150 Å. appears with the "auto-electronic" discharge between a pointed cathode and cylindrical anode situated in vac.; it is not a temp. emission, and appears superposed on spectra due to foreign gases.

III. A cylindrical Th anode gave a continuous spectrum extending from 6800 to 2200 Å., and Th when heated to 850° by cathode-ray bombardment emitted this spectrum, which was absent when the Th was heated to this temp. by ordinary means. A. B. D. CASSIE.

Scattering of X-rays by neon and argon. G. HERZOG (Z. Physik, 1931, **70**, 583—589).—Theoretical. Scattering due to Ne is calc., and the curves for Ne and A are compared with experimental results. A. B. D. CASSIE.

Scattering of X-rays by helium. G. HERZOG (Z. Physik, 1931, **70**, 590—592).—Theoretical. Scattering due to He is calc. and agrees with experiment. A. B. D. CASSIE.

X-Ray absorption coefficients of mercury vapour in the region of its L-absorption discontinuities. F. M. UBER (Physical Rev., 1931, [ii], **38**, 217—224).—Coeffs. were determined by an improved method and apparatus. N. M. BLIGH.

Scattering of X-rays by gases and crystals. G. E. M. JAUNCEY (Physical Rev., 1931, [ii], **38**, 1—5; cf. this vol., 896).—Deductions from formulæ previously obtained and the relation of the const. to the at. structure factor are discussed. N. M. BLIGH.

Temperature and diffuse scattering of X-rays from crystals. Y. H. WOO (Physical Rev., 1931, [ii], **38**, 6—14).—Debye's expression for diffuse scattering is amended to take account of modified radiation; the result is discussed in relation to the temp. factor. N. M. BLIGH.

Atomic scattering power of copper and oxygen in cuprous oxide. G. A. MORTON (Physical Rev., 1931, [ii], **38**, 41—44).—At. F-curves for the Cu and O in Cu_2O were obtained for $K\alpha$ radiation of Cu from measurement of the principal powder reflexions, and were identical with those for metallic Cu and for O in NiO. N. M. BLIGH.

Absorption of scattered X-rays and Compton's theory of scattering. S. R. KHASTGIR (Proc. XV Indian Sci. Cong., 1928, 88—89). CHEMICAL ABSTRACTS.

Relative absorption of primary and scattered X-rays by silver and tin. S. R. KHASTGIR (Proc. XV Indian Sci. Cong., 1928, 88).—The theory of wave-length change on scattering is untenable. The greater absorbability of the primary radiation is due to the J-transformation in Ag. CHEMICAL ABSTRACTS.

Partial absorption of X-ray quanta. A. J. ALICHANOV and L. A. ARZIMOVITSCH (Z. Physik, 1931, **69**, 853—856).—A beam of X-rays (Cu-$K\alpha$) was passed through a layer of paraffin (also $C_{10}H_8$, graphite, and H_2O) and examined spectroscopically. The phenomenon of partial absorption found by Ray (this vol., 277) was not observed. W. GOOD.

Partial absorption of X-rays. M. BOTZKES (Z. Physik, 1931, **71**, 151—155).—Calculation shows that the probability of partial absorption of Cu-$K\alpha_1$ radiation by C is 10^3 times less than that of ordinary photo-electric absorption; experiments gave no positive proof of partial absorption (cf. this vol., 277). A. B. D. CASSIE.

Part-absorption in X-rays. B. B. RAY and B. B. DATTA (Nature, 1931, **128**, 224—225; cf. A., 1930, 1334).—The conflicting results of different authors are discussed; they are due, apparently, to the thickness of the absorption screens used. L. S. THEOBALD.

Resolving power attainable in X-ray spectroscopy by photographic methods. S. K. ALLISON (Physical Rev., 1931, [ii], **38**, 203—211; cf. this vol., 137).—Mathematical. Equations for resolving power are deduced. N. M. BLIGH.

Total reflexion of X-rays. H. KIESSIG (Ann. Physik, 1931, [v], **10**, 715—768).—The total reflexion of X-rays by glass and Ni mirrors was obtained. W. R. ANGUS.

Relativistic theory of the photo-electric effect. I. K-absorption of X-rays. H. HALL. **II. Photo-electric absorption of ultra-γ-radiation.** H. HALL and J. R. OPPENHEIMER (Physical Rev., 1931, [ii], **38**, 57—70, 71—79).—Mathematical. N. M. BLIGH.

Fall of potential in the initial stages of electrical discharges. J. C. STREET and J. W. BEAMS (Physical Rev., 1931, [ii], **38**, 416—426).—The rate of potential fall through air, N_2, H_2, and CO_2 increased with rise of pressure. N. M. BLIGH.

Cathode fall of an arc. R. C. MASON (Physical Rev., 1931, [ii], **38**, 427—440).—On both classical and quantum theory, for the same val. of cathode fall, the electrons from a thermionic arc have energies several volts greater than those from a high-field arc. N. M. BLIGH.

Probability law governing ionisation by electron impact in mercury vapour. C. R. HAUPT (Physical Rev., 1931, [ii], **38**, 282—295).—The law found by Lawrence (cf. A., 1927, 85) is verified by an improved apparatus; further ionisation potentials at 12·3, 12·45, 12·85, and 13·2 volts were found and interpreted. N. M. BLIGH.

Ionisation of helium, neon, and argon. R. L. WOMER (Physical Rev., 1931, [ii], **38**, 454—456).—In the region of the normal ionisation potentials of these gases there is only one ionisation potential for each. N. M. BLIGH.

Ionisation in gas-filled photo-electric cells. (i) The inert gases in cæsium on silver photo-electric cells. (ii) Time lag in gas-filled photo-electric cells. W. F. TEDHAM (Phil. Mag., 1931, [vii], **12**, 224—232).—The relative efficiencies of the

rare gases as fillings for photo-electric cells have been studied. Current–voltage curves have been determined for each gas at varying pressures and vals. of the anode potential. F. J. WILKINS.

Photo-electric sensitivity curves for clean metals at various temperatures. R. H. FOWLER (Physical Rev., 1931, [ii], 38, 45—56).—A theory of the effect of temp. on sensitivity is developed. Experimental data are explained by the effect of temp. on the no. of electrons available for extraction on Sommerfeld's theory of metals. An improved method of finding thresholds from curves is described. N. M. BLIGH.

Origin of the appearance of the selective photo-electric effect. R. SUHRMANN (Z. wiss. Phot., 1931, 30, 161—171).—Experiments are detailed showing that selective electron emission from an irradiated alkali metal surface appears only when, between the K etc. layer and the conducting support, there is a fine layer of a substance, penetrable by electrons, which can combine with the K. The action of a glow discharge in H_2 is the formation of a layer of hydride, the heat of reaction then vaporising some K, which condenses on the hydride. The selective effect with polarised light on a mirror surface is also considered. J. LEWKOWITSCH.

Photo-electric effect. J. FRENKEL (Physical Rev., 1931, [ii], 38, 309—320).—The theory for a H-like atom is developed by wave mechanics, and extended to take account of the mobility of the nucleus. N. M. BLIGH.

Photo-electric properties of thin unbacked gold films. R. P. WINCH (Physical Rev., 1931, [ii], 38, 321—324).—The films, on exposure to ultraviolet light, showed a rapid increase in emission and shift in long-wave limit. Solid Au and Ag under similar treatment showed a corresponding but slower effect. Results are explained by surface outgassing by ejected electrons. N. M. BLIGH.

Photo-electric properties of mercury films. D. ROLLER, W. H. JORDAN, and C. S. WOODWARD (Physical Rev., 1931, [ii], 38, 396—400).—For Hg films deposited on oxidised Fe the variation, with film thickness, of photo-electric current excited by Hg arc lines was investigated. The conclusion that threshold wave-lengths for solid and liquid Hg are the same is confirmed. N. M. BLIGH.

Photo-electric properties of zinc single crystals. J. H. DILLON (Physical Rev., 1931, [ii], 38, 408—415; cf. A., 1927, 505).—Photo-electric properties were measured and tabulated after outgassing polycryst. and cleft emitting surfaces by irradiation with ultra-violet light, and thermally evaporating some of the Zn. In the stable condition produced a difference in long-wave limits of the two types of surface of approx. 260 Å. was observed. N. M. BLIGH.

Effect of adsorbed K^+ ions on the photo-electric threshold of iron. A. K. BREWER (Physical Rev., 1931, [ii], 38, 401—407; cf. A., 1930, 972).—The fraction of surface covered with K was investigated by the change of emissivity; the emissivity is proportional to the positive ion current. N. M. BLIGH.

Burning-out process of glowing (tungsten) wires in vacuum. L. PRÁSNIK (Z. Physik, 1931, 69, 832—834).—A reason is given for the increase in the amount of material vaporised throughout the burning process with a rise of temp. W. GOOD.

[Internal degree of freedom of an electron.] E. SCHRÖDINGER (Z. Physik, 1931, 70, 808—810).—An alternative mathematical derivation of the time mean of operators used by Fock (this vol., 666). A. B. D. CASSIE.

[Internal degree of freedom of an electron.] V. FOCK (Z. Physik, 1931, 70, 811).—Remarks on the note by Schrödinger (preceding abstract). A. B. D. CASSIE.

Affinity. IV. T. DE DONDER (Bull. Acad. roy. Belg., 1931, [v], 17, 653—663; cf. this vol., 685).—Mathematical. Electronic gas, treated as if containing an infinite no. of constituents, is shown to have a potential energy independent of temp. C. W. GIBBY.

Theory of the rotating electron. Extension of Schrödinger's analogy between optical and mechanical phenomena. A. E. LEVASCHOV (Bull. Univ. Asie Centr., 1929, 18, 37—44).

Crystal interference of spinning electrons. H. HELLMANN (Z. Physik, 1931, 70, 695—698; cf. this vol., 889).—Theoretical. A. B. D. CASSIE.

Present position of Dirac's electron theory. G. RUMER (Physikal. Z., 1931, 32, 601—622).

Motion of a Dirac electron in a magnetic field. L. D. HUFF (Physical Rev., 1931, [ii], 38, 501—512).—Mathematical.

Scattering of slow electrons by atoms. W. P. ALLIS and P. M. MORSE (Z. Physik, 1931, 70, 567—582).—Theoretical. The Ramsauer effect is treated as the optical problem of scattering by colloidal particles of diameter comparable with the wave-length of light; results agree with experiment. A. B. D. CASSIE.

New electron inertia effect and the determinations of m/e for the free electrons in copper. S. J. BARNETT (Phil. Mag., 1931, [vii], 12, 349—360).—Maxwell showed that if a current in a circular or cylindrical coil of wire free to move about its axis is altered, the free electricity will be accelerated and the coil itself will be accelerated in the opposite direction, the changes of angular momenta being equal in magnitude and opposite in sign. This effect has now been demonstrated experimentally, and it has provided a method for determining the val. of m/e for free electrons in Cu: $2m/e$ is $1{\cdot}10 \pm 0{\cdot}03 \times 10^{-7}$ e.m.u. compared with the standard value of $1{\cdot}13 \times 10^{-7}$. F. J. WILKINS.

Experimental electron distributions in atoms of monatomic gases. E. O. WOLLAN (Physical Rev., 1931, [ii], 38, 15—22).—Radial electron distribution in the atoms of He, Ne, and A is calc. from data (cf. this vol., 781) for the intensity of X-rays scattered by gases; results are in good agreement with those of wave mechanics, and show more detail than those from crystal reflexion data. Evidence of zero point energy is given by the difference between electron distribution in A and Cl_2 at 0° abs. N. M. BLIGH.

Transmission of electron bundles through screens. E. SEITZ and G. HARIG (Physikal. Z., 1931, **32**, 635—639).—The structure of patterns obtained on a photographic plate when a bundle of electrons has passed through a series of screens is discussed.

A. J. MEE.

Extraction of electrons from metals by metastable atoms. II. H. S. W. MASSEY (Proc. Camb. Phil. Soc., 1931, **27**, 460—468; cf. A., 1930, 1231).—Previous theoretical investigations are extended to the metastable He atom and the angular distribution of the ejected electrons. N. M. BLIGH.

Excitation energy by electron impact in helium. R. WHIDDINGTON and J. E. ROBERTS (Proc. Leeds Phil. Soc., 1931, **2**, 201—205).—Excitation energies in He using electrons of about 120 volts energy have been measured with increased precision, and give values slightly exceeding, by an amount more than the probable error, those calc. from spectroscopic data. N. M. BLIGH.

Collision of electrons with simple atomic systems and electron exchange. H. S. W. MASSEY and C. B. O. MOHR (Proc. Roy. Soc., 1931, **A**, **132**, 605—630).—Oppenheimer's methods (A., 1928, 1170) are applied to the scattering of electrons in He and H_2. The effect of electron exchange on the scattering by heavy atoms should be considerable up to quite high voltages (*e.g.*, 500 volts in Ne).

L. L. BIRCUMSHAW.

Electron emission from Langmuir probes and from the cathode of the glow discharge through gases. M. L. E. OLIPHANT (Proc. Roy. Soc., 1931, **A**, **132**, 631—645).—Measurements have been made to determine the positive ion and electron currents at the surface of a simplified form of cathode, a negatively-charged Langmuir probe in the positive column of an arc discharge through various gases. The theory of the cold probe as developed by Langmuir and Mott-Smith (Gen. Elect. Rev., 1924, **26**, 449) assumes that the electron emission is zero, but evidence of electron emission is given both by observation of the current–voltage characteristic of such a probe and by measurement of the heating effect of the positive ions. The results are discussed from the viewpoint of the glow discharge.

L. L. BIRCUMSHAW.

Stereophotographic models of electron motion in Stark effect. R. W. WOOD (Physical Rev., 1931, [ii], **38**, 346—350).—The electron motion, precessing orbit, and other characteristics of the Stark effect are illustrated by stereoscopic photographs of a rotating wire frame. N. M. BLIGH.

Pictorial representations of the Dirac electron cloud for hydrogen-like atoms. H. E. WHITE (Physical Rev., 1931, [ii], **38**, 513—520; cf. this vol., 889).—Mathematical. The angular and radial probability density factors are treated separately, and combined by means of a mechanical device which when photographed represents closely the electron cloud. N. M. BLIGH.

Velocity losses of slow electrons in nitrogen. H. LOHNER (Ann. Physik, 1931, [v], **9**, 1004—1016).—For the determination of the velocity losses a more sensitive Lenard method was used. The following crit. potentials of N_2 were established with an accuracy of $\pm 0{\cdot}1$ volt: 2·45, 3·1, 3·6, 4·15 volts.

W. GOOD.

Angular distribution of scattering of slow electrons by gas molecules. C. RAMSAUER and R. KOLLATH (Naturwiss., 1931, **19**, 688—689).—Electron velocities of 1—20 volts and scattering angles of 15—167° were used. The scattering by A mols. and the scattering of 1·8 volt electrons by mols. of Ne, H_2, CO, and CO_2 are discussed. W. R. ANGUS.

Breadth of Doppler bands in non-homogeneous canal rays. H. STRAUB (Ann. Physik, 1931, [v], **10**, 670—672).—The breadth of the displaced line is practically independent of pressure; the intensity of the original line depends on pressure.

W. R. ANGUS.

Calculation of the mobility of unimolecular ions. H. R. HASSÉ and W. R. COOK (Phil. Mag., 1931, [vii], **12**, 554—566; cf. A., 1926, 219).—Theoretical. N. H. HARTSHORNE.

Recombination of ions in the normal arc. E. H. BRAMHALL (Proc. Camb. Phil. Soc., 1931, **27**, 421—429).—Experimental results for the Cu arc are in agreement with theory. The coeff. of recombination, α, is $5{\cdot}7\times10^{-9}$ and varies approx. as $t^{2\cdot5}$, where t is the ionised gas temp. N. M. BLIGH.

Diffraction of proton wave. Y. SUGIURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, **16**, 29—40).—A strong proton stream was diffracted by thin Pt and W films sputtered on glass plates, and measured by a sensitive electrometer. Proton beams of different wave-lengths showed diffraction patterns expected by Bragg's condition for *X*-rays.

N. M. BLIGH.

Discharge and ionisation by the passage of protons through gases. F. GOLDMANN (Ann. Physik, 1931, [v], **10**, 460—484).—Measurements have been made using protons of 500—400 volts in H_2, of 1500—4000 volts in A, and of 1000—4000 volts in He, produced by a new electron bombardment device designated an "ion nozzle." In H_2 and A protons are discharged, but do not influence ionisation; in He neither discharge nor ionisation was detected. At the higher pressure phenomena appear which are due to excitation and ionisation collisions with fast neutral atoms. W. R. ANGUS.

Determination of the equilibrium between the atoms and the molecules of an alkali metal vapour by a molecular-beam method. L. C. LEWIS (Z. Physik, 1931, **69**, 786—809).—The atoms in mol. beams of Na, K, and Li are magnetically deviated. The intensity of the beam was measured by the Langmuir–Taylor method and the equilibrium consts. of the reactions, $2Na \rightleftharpoons Na_2$, etc., were determined. Measurements at different furnace temps. gave the heats of dissociation. W. GOOD.

Mobility of Na^+ ions in N_2 and H_2 as a function of time. L. B. LOEB (Physical Rev., 1931, [ii], **38**, 549—571).—Mobilities measured in highly-purified N_2 and H_2 for time interval ranges of 10^{-5} to 10^{-1} sec. indicate three classes of ions in each gas. The nature, life in sec., and mobility in cm. per sec. per volt cm.

in H_2 are: atom ion Na^+, 10^{-4}, 17·5; $\rightarrow$ mol. additive product, 10^{-3}, 13·5; $\rightarrow$ normal ion, —, 8·4, respectively. Corresponding data in N_2 for ions which are similarly interpreted are: 5×10^{-3}, 3·75; $\rightarrow$ 10^{-2}, 3·0; $\rightarrow$ —, 1·6. N. M. BLIGH.

Conductivity electrons and ferromagnetism. III. J. DORFMAN, R. JAANUS, K. GRIGOROW, and M. CZERNICHOWSKI (Z. Physik, 1931, **70**, 796—807).—Correction of an error in earlier work (cf. A., 1929, 127, 751) shows that the Thomson effect gives no information regarding the role of conductivity electrons in ferromagnetism. Measurements of Thomson coeffs. for Fe in a temp. range including the Curie point are given. A. B. D. CASSIE.

At. wt. of chlorine. Solubility of silver chloride. O. HONIGSCHMID (J. Amer. Chem. Soc., 1931, **53**, 3012—3013).—The at. wt. of Cl is $35·456_3$ (cf. A., 1927, 806; 1930, 1337) after correcting for solubility of AgCl. J. G. A. GRIFFITHS.

New isotopes of strontium and barium. F. W. ASTON (Nature, 1931, **128**, 221).—The application of high resolution to accelerated anode rays reveals Sr^{87}, and Ba^{137}, Ba^{136}, and Ba^{135}. L. S. THEOBALD.

Isotopes. S. RAY (Proc. XV Indian Sci. Cong., 1928, 69, 161).—It is postulated that the val. of e is 0·005 of that determined by Millikan.

CHEMICAL ABSTRACTS.

Possibility of isotopes in radon. N. AHMAD (Proc. XV Indian Sci. Cong., 1928, 140).—Since fresh and old samples have equal rates of decay, the differences observed by others cannot be due to the presence of isotopes. CHEMICAL ABSTRACTS.

Mass spectra of glasses, salts, and metals. H. MURAWKIN (Ann. Physik, 1931, [v], **9**, 977—980).—Supplementary (cf. this vol., 546). W. GOOD.

Natural system of atomic nuclei. H. C. UREY (J. Amer. Chem. Soc., 1931, **53**, 2872—2880; cf. A., 1930, 518).—Theoretical. From a study of the proton–electron curve for at. nuclei, the existence of undiscovered isotopes between A^{36} and Cu^{63} is predicted. The isotopic isobars Io^{230} and U-Y are predicted. It is suggested that Barton's "clusters" of nuclei are related to regions of nuclear instability. This is discussed in relation to the abundance of the elements. J. G. A. GRIFFITHS.

Periodic arrangement of atomic nuclei. Prediction of isotopes. H. L. JOHNSTON (J. Amer. Chem. Soc., 1931, **53**, 2866—2871; cf. A., 1928, 344).—Theoretical. The atoms are arranged in order of isotopic mass no., classified into 4 types distinguished by the no. (0—3) of "free" protons in the nuclei, and further classified by the no. of "free" electrons in the nuclei. From the regularities observed, many undiscovered isotopes are predicted and certain isobaric triplets are indicated. Harkins' abundance rules are modified. J. G. A. GRIFFITHS.

Thermodynamical aspects of the origin of elements. L. FARKAS and P. HARTECK (Naturwiss., 1931, **19**, 705—706).—The relative abundance of individual elements appears to correspond roughly with the equilibrium distribution at high temp. The equilibrium concentration of a nucleus containing N protons and n electrons is expressed by an equation. W. R. ANGUS.

Radioactive constants as of 1930. Report of the International Radium-Standards Commission. M. CURIE, A. DEBIERNE, A. S. EVE, H. GEIGER, O. HAHN, S. C. LIND, ST. MEYER, E. RUTHERFORD, and E. SCHWEIDLER (J. Amer. Chem. Soc., 1931, **53**, 2437—2450).—The report deals with basic vals., units, and consts. The term "proton number" is proposed in place of "isotopic weight." Owing to the discovery of the isotopes O^{18} and O^{17} it is proposed, for the purposes of at. structure and radioactivity, to choose O^{16}=16·0000, from which H=1·0078 and He=4·00216. Avogadro no. is $6·0644\times10^{23}$ (e=$4·770\times10^{-10}$) or $6·0265\times10^{23}$ (e=$4·80\times10^{-10}$); no. of α-particles emitted per sec. from 1 g. of Ra is $3·7\times10^{10}$, and in the relation $k=k_0\times(\text{Range})^{2/3}$, k_0=$6·3\times10^4$. Radioactive consts., the range and ion production of α-particles, and absorption coeffs. for β- and γ-rays are tabulated.

J. G. A. GRIFFITHS.

Distribution of radioactive substances in the free atmosphere. J. PRIEBSCH (Physikal. Z., 1931, **32**, 622—629).—The vertical distribution of radioactive substances in the free atm. is calc. There is a small decrease with increasing height above the surface of the earth in the quantities of niton, Th emanation, and Th-B. A. J. MEE.

Activity of radioactive substances by means of the torsion balance. J. ZAHRADNÍČEK (Physikal. Z., 1931, **32**, 630—634).—A method for determining the activity of radioactive sources by means of a torsion balance is described. The construction and sensitivity of the balance are described.

A. J. MEE.

Scintillation curves given by the α-rays of polonium. G. DESTRIAU (J. Phys. Radium, 1931, [vii], **2**, 148—158).—Factors influencing the form of scintillation curve are examined experimentally.

W. GOOD.

Anomalous scattering of α-rays. M. MUSKAT (Physical Rev., 1931, [ii], **38**, 23—31).—Mathematical. A modification of the wave-mechanical expression for the scattering function is applied to the anomalous scattering by Mg (cf. A., 1925, ii, 1109).

N. M. BLIGH.

β-Transformation. B. M. SEN (Phil. Mag., 1931, [vii], **12**, 439—441).—Theoretical. It is shown that radioactive properties are a consequence of increasing at. no. N. H. HARTSHORNE.

Absorption method of investigating the high-velocity limits of continuous β-ray spectra. N. FEATHER (Proc. Camb. Phil. Soc., 1931, **27**, 430—444).—The theoretical basis for the use of absorption measurements to determine the max. energies in the continuous spectra of β-ray bodies is analysed.

N. M. BLIGH.

Artificial disintegration without capture of the projectile. E. C. POLLARD (Proc. Leeds Phil. Soc., 1931, **2**, 206—216).—Theoretical. General energy and momentum conditions are considered; the max. range proton occurs when both α-particle and nuclear remnant move away together. N. M. BLIGH.

Natural vibration of ionised gases. J. PLACINTEANU (Compt. rend., 1931, **193**, 286—288).—The same period (cf. this vol., 666) is reduced in three different ways on the assumption that Thomson's hypothesis (cf. A., 1929, 231) is equiv. to that of a double layer supporting ion-electron systems, vibrating as a whole. The mechanical model of Jonescu leads to unsatisfactory results. C. A. SILBERRAD.

Calculation of zero order eigenfunctions. N. M. GRAY and L. A. WILLS (Physical Rev., 1931, [ii], **38**, 248—254).

Wave functions of many-electron atoms. J. E. LENNARD-JONES (Proc. Camb. Phil. Soc., 1931, **27**, 469—480).—The Hartree equations deduced by Fock for the many-electron atom are obtained by an improved method. N. M. BLIGH.

Use of the Ritz method in polarisation problems in wave mechanics. Polarisation forces between two hydrogen atoms. J. PODOLANSKI (Ann. Physik, 1931, [v], **10**, 695—714).—Mathematical. W. R. ANGUS.

Quantum theory and electron pair linking. W. HEITLER (Physical Rev., 1931, [ii], **38**, 243—247).—Mathematical. N. M. BLIGH.

Interaction between atoms with *s*-electrons. N. ROSEN (Physical Rev., 1931, [ii], **38**, 255—276; cf. Heitler, A., 1927, 923).—Calculations are generalised and extended to atoms other than H_2. Results for a normal Na_2 mol. and the repulsion of two normal He atoms are in fair agreement with experiment. N. M. BLIGH.

Low-velocity inelastic collisions. C. ZENER (Physical Rev., 1931, [ii], **38**, 277—281).—Mathematical. N. M. BLIGH.

Triatomic hydrogen ion H_3^+. H. S. W. MASSEY (Proc. Camb. Phil. Soc., 1931, **27**, 451—459).—Mathematical. Quantum mechanics shows that nuclear symmetry considerations decide the stability of the mol. N. M. BLIGH.

Collision of two particles taking into account retardation of forces. C. MØLLER (Z. Physik, 1931, **70**, 786—795).—Mathematical. A. B. D. CASSIE.

Copper salts as light filters. I—III. W. V. BHAGWAT and N. R. DHAR (J. Physical Chem., 1931, **35**, 2383—2390, 2391—2400, 2401—2411).—I. Absorption by solutions of $CuCl_2$, $CuSO_4$, and $Cu(NO_3)_2$ in the visible and ultra-violet regions has been determined. $CuCl_2$ is a better light filter than $CuSO_4$ or $Cu(NO_3)_2$ and is as good as Wratten filters 62 and 74 for the region 4900—5770 Å. Mol. and ionic absorptions are discussed.

II. Absorption in the visible and ultra-violet regions has been measured for picric acid, methyl-violet, $CoCl_2$, and didymium nitrate alone and in conjunction with Cu salts. Ammoniacal $CuCl_2$ is a good filter for the region 4000—4590 Å. and $CuCl_2+CoCl_2$ is convenient for the transmission of 2961 Å. and 3248—3274 Å.

III. Data are recorded for combinations of Cu salts with K_2CrO_4, $K_2Cr_2O_7$, H_2CrO_4, methylene-blue, and crystal-violet. Convenient solutions of light filters are tabulated. L. S. THEOBALD.

Selective thermal radiation of coloured and pure fused quartz. R. W. WOOD (Physical Rev., 1931, [ii], **38**, 487—490).—The absence of visible radiation of pure quartz below the m. p. is attributed to the displacement, with rise of temp., of the ultra-violet absorption band towards the visible. Quartz–Nd rods containing Nd_2O_3 when heated emitted (and absorbed) 7 bands, the wave-lengths of the centres being 8730, 8270, 7504, 6717, 5944, 5340, and 4570 Å. N. M. BLIGH.

Effect of temperature on the ultra-violet band spectrum of ozone and the structure of this spectrum. O. R. WULF and E. H. MELVIN (Physical Rev., 1931, [ii], **38**, 330—337; cf. A., 1930, 1226).—The bands in the region 3400—2300 Å., studied over the range −78° to 250°, show a small increase in contrast with fall of temp., found photometrically to be a decrease in absorption between the bands. Results are explained, a partial vibrational analysis is deduced, and effects on the O_3 in the upper atm. are discussed. N. M. BLIGH.

Absorption spectra of the Ce^{+++} ion in solution. D. M. BOSE and S. DATTA (Nature, 1931, **128**, 271).—Data for a solution of $CeCl_3$ are recorded and discussed. L. S. THEOBALD.

Absorption spectra and optical dissociation of hydrides of the oxygen group. C. F. GOODEVE and N. O. STEIN (Trans. Faraday Soc., 1931, **27**, 393—402).—The extinction coeffs. of H_2O, H_2S, H_2Se, and H_2Te have been measured over a wide range of thicknesses and pressures and utilised to construct the absorption curves. With H_2O, H_2S, and H_2Se the position of the threshold corresponds with the thermochemical heat of dissociation into normal H_2 mols. and ^1D non-metal atoms, and assuming that the same is true of H_2Te the heat of dissociation of this gas is calc. to be −17·5 kg.-cal. The photochemical decomp. of H_2Te into H_2 and Te has been observed. Both H_2O and H_2Te have a second threshold, which probably corresponds with dissociation into H_2 and ^1S non-metal atoms. R. CUTHILL.

Continuous absorption spectra of gaseous alkali halides in the ultra-violet. H. D. SCHMIDT-OTT (Z. Physik, 1931, **69**, 724—734).—These are investigated with the aid of a new method which is also suitable for the investigation of difficultly volatile substances. W. GOOD.

Ultra-violet transmission of liquids. E. H. HARVEY (J. Amer. Pharm. Assoc., 1930, **19**, 1173—1179; 1931, **20**, 643—648).—Previous knowledge is summarised and the $(CO_2H)_2$–$UO_2(OAc)_2$ method is adapted to the measurement of the absorption of ultra-violet light by essential, fatty, and crude oils and other liquids. E. H. SHARPLES.

Absorption spectra of cobaltous compounds. III. Pyridine and quinoline complexes and solutions. W. R. BRODE (J. Amer. Chem. Soc., 1931, **53**, 2457—2467; cf. A., 1928, 1089).—The blue solutions of Co halides in quinoline are stable at room temp., and the absorption spectra are almost identical with those of the blue solutions of the Co halides in pyridine at higher temp.; this indicates

the absence of solvent effect and the probability that neither pyridine nor quinoline is directly linked to the Co. The substitution of heavier halogens shifts the absorption bands further towards the red in acid than in pyridine or quinoline solutions, and for a given halide, the band in acid solution is of lower frequency than in pyridine or quinoline, suggesting a Co-complex involving fewer halogen ions in the org. solvents. The complex $Co(C_5H_5N)_2Cl_2$ [and $Co(C_{10}H_7N)_2Cl_2$] in EtOH, $CHCl_3$, and ligroin affords an absorption spectrum with bands of different intensities, but at the same frequencies as $CoCl_2$ in pyridine or quinoline. Different absorption spectra, like those of Co halides in EtOH, are afforded by Co pyridinium (or quinolinium) halides ($CoX_2,2C_5H_5N,2HX$; cf. A., 1929, 1028) in EtOH. The addition of quinoline or HCl and LiCl to $CoCl_2$ in EtOH produces absorption spectra characteristic of $CoCl_2$ in quinoline or HCl, respectively. The halogen acid, the pyridine–quinoline, and an intermediate absorption system are considered to exist in a blue Co solution.

J. G. A. GRIFFITHS.

Absorption of light by aqueous copper glycine solutions. R. LUTHER and W. EICHLER (Z. wiss. Phot., 1931, **30**, 174—176; cf. B., 1931, 91).—The absorption coeffs. of 0·02*M* aq. Cu glycine solution have been measured from 700 to 313 mμ.

J. LEWKOWITSCH.

Ultra-violet light absorption of ethyl alcohol purified by different methods. P. A. LEIGHTON, R. W. CRARY, and L. T. SCHIPP (J. Amer. Chem. Soc., 1931, **53**, 3017—3019).—Small absorption in the region 2500—3000 Å. indicates absence of impurities. Drying of EtOH over CaO should be performed in N_2, since O_2 causes slow oxidation. Still lower absorption is afforded by EtOH dried with Al–Hg. Other methods are less satisfactory.

J. G. A. GRIFFITHS.

[Ultra-violet] absorption spectra, structure, and dissociation energies of gaseous halogen cyanides. R. M. BADGER and S. C. WOO (J. Amer. Chem. Soc., 1931, **53**, 2572—2577).—Regions of continuous absorption only are found, with the following long wave-length limits: ClCN, $\lambda > 2270$ Å.; BrCN, >2450; ICN, >2900 and >2100. The heats of dissociation into normal products, computed from the chemical heats of formation, are approx. those expected for the rupture of the C–halogen linking. The higher spectroscopic dissociation energies indicate optical dissociation into a normal halogen atom and an excited CN radical. J. G. A. GRIFFITHS.

Ultra-violet absorption spectra of cyanogen and the cyanogen halides. R. B. MOONEY and H. G. REID (Nature, 1931, **128**, 271—272).—CNCl at 760 mm., and CNBr at 76 mm., show continuous absorption from 2240 to 1840 Å. and 2540 to 1840 Å., respectively. CNI at room temp. has a continuous absorption with a long wave-length limit at approx. 2150 Å. At 100—125° another region of continuous absorption appears. The absorption spectrum of $(CN)_2$ is discontinuous with 40 bands, some showing rotation structure, between 2380 and 1860 Å. The heat of dissociation of $(CN)_2$ into 2(CN) is probably >81 kg.-cal. The discrepancy between this and the thermochemical val. (66 kg.-cal.) may be accounted for by vibration of CN mol. L. S. THEOBALD.

Spectrographic study of compounds of tartaric acid with copper. J. GIUNTINI (Compt. rend., 1931, **193**, 340—342; cf. A., 1930, 1516).—The absorption at various wave-lengths from λ 2340 to 7000 by a series of mixtures of tartaric acid and CuO indicates that part of the Cu in $C_4H_4O_6Cu_2,nH_2O$ forms a complex. C. A. SILBERRAD.

Ultra-violet absorption and isomerism of maleic and fumaric acids. A. WASSERMANN and A. SMAKULA (Z. physikal. Chem., 1931, **155**, 366—377).—The absorption of the above acids, their *l*-menthyl and dimethyl esters, and maleic anhydride has been measured in various solvents over the range about 300—190 mμ. The absorption data do not conflict with Anschutz' cyclic formula for maleic acid (cf. A., 1928, 737). R. CUTHILL.

Ultra-violet absorption spectra of acetylene and formaldehyde. G. HERZBERG (Trans. Faraday Soc., 1931, **27**, 378—384).—Both spectra exhibit two regions of discontinuous absorption, corresponding with two stable excited electronic levels of the mols. Henri and Schou's analysis of the longer wave-length system of CH_2O (A., 1928, 935) is corrected.

R. CUTHILL.

Ultra-violet absorption of geometrically isomeric stilbenes and cinnamic acids. A. SMAKULA and A. WASSERMANN (Z. physikal. Chem., 1931, **155**, 353—365).—The absorption in various solvents of the *cis*- and *trans*-isomerides has been measured over the region about 320—190 mμ. The frequency corresponding with the max. of the band due to the ethylene linking is lower for the stilbenes than for the cinnamic acids, and lower for a *trans*- than for the corresponding *cis*-compound, whilst the band is deeper for a *trans*- than for the *cis*-compound.

R. CUTHILL.

Co-ordination. II. Absorption spectra of metallic derivatives of benzoylcamphor. T. M. LOWRY, H. BURGESS, I. J. FAULKNER, and R. C. TRAILL (Proc. Roy. Soc., 1931, **A**, **132**, 387—397)—The mol. extinction coeffs. of benzoylcamphor (enolic and ketonic forms) and the Li, Na, Be, $Cu^{\cdot\cdot}$, Al, $Cr^{\cdot\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, and $Co^{\cdot\cdot\cdot}$ *derivatives* in alcoholic solution, the $Cu^{\cdot\cdot}$ *derivative* in $CHCl_3$, and the Be and $Th^{\cdot\cdot\cdot\cdot}$ *derivatives* in hexane have been determined. The spectra of the first two metallic compounds each include two max. at wave-lengths corresponding with those of the single max. of the two forms of the parent compound, but the max. are displaced in the Be derivative and in the case of the other metals only one max. lies within the range of experiment. The selective absorption of these compounds is considered due to polar activation of the unsaturated system. This is evidently not destroyed by co-ordination, although it may be modified by the presence of a metallic atom. The alkali metal derivatives behave as metallic salts and not as co-ordination compounds.

L. L. BIRCUMSHAW.

Visible and ultra-violet absorption spectra of carotene and xanthophyll and the changes accompanying oxidation. H. J. MCNICHOLAS (Bur. Stand. J. Res., 1931, **7**, 171—193).—The

frequencies of the absorption bands for pure carotene and xanthophyll in $EtOH-Et_2O$ solution appear to form a regular sequence extending throughout the visible and ultra-violet spectral range and converging towards the lower frequencies in accordance with a simple parabolic law. Imposing a periodic variation in intensity on this progression of bands gives the appearance of 3 adjacent spectral regions of selective absorption, which are partly resolved into overlapping component bands. During oxidation both spectra pass through the same characteristic series of changes, indicating two definite stages in the oxidation. Carotene is not oxidised to xanthophyll in this process. The data support the view that different xanthophylls may represent distinct stages in the oxidation of a single pigment. E. S. HEDGES.

Some results of infra-red spectrography. R. MECKE (Z. wiss. Phot., 1931, **30**, 77—84).—A review, with reference to atm. absorption bands in the solar spectrum. J. LEWKOWITSCH.

New absorption bands of ammonia, methyl bromide and iodide, and carbon dioxide in the infra-red spectrum. W. W. SLEATOR (Physical Rev., 1931, [ii], **38**, 147—151).—An NH_3 band with centre at 15·9 μ is observed in detail; MeBr and MeI bands are reported at 16·4 and 18·8 μ, respectively; greater complexity is found for the 15 μ CO_2 band. N. M. BLIGH.

Infra-red absorption bands of hydrogen cyanide in gas and liquid. F. S. BRACKETT and U. LIDDEL (Smithsonian Miscell. Coll., 1931, **85**, 1—8; cf. Badger, this vol., 667).—An improved automatic recording apparatus was used. Data of 15 bands for the liquid, and 3 bands for the gas are tabulated. The computed heat of dissociation is 5·5 volts. Accepted fundamentals are confirmed. N. M. BLIGH.

Reflexion power of metals in thin layers for the infra-red. R. B. BARNES and M. CZERNY (Physical Rev., 1931, [ii], **38**, 338—345; cf. Murmann, A., 1929, 753).—The reflexion power for the infra-red and visible spectra was investigated for Ag mirrors and for glass mirrors protected by a film of Sb, with reference to dependence on the thickness of the reflecting layer. A new equation governing the relation is deduced. N. M. BLIGH.

Intensity of Raman scattering in gases. S. BHAGAVANTAM (Nature, 1931, **128**, 272).—Estimated intensities of the Raman lines of simple gases favour Manneback's theory (A., 1930, 840). L. S. THEOBALD.

Raman effect of carbon dioxide. E. FERMI (Z. Physik, 1931, **71**, 250—259).—The double Raman lines at 1285 and 1388 $cm.^{-1}$ may be due to resonance between a fundamental inactive frequency near 1300 $cm.^{-1}$ and the first harmonic of the 673 $cm.^{-1}$ vibration. A. B. D. CASSIE.

Constitution of nitric acid. A. DADIEU and K. W. F. KOHLRAUSCH (Naturwiss., 1931, **19**, 690—691).—Raman displacements for 64% and 100% HNO_3 are compared with those obtained for alkyl and aryl nitrates and nitrites. It is concluded that in an aq. solution of HNO_3 (64%) a considerable fraction of the acid is present in the form of the ψ-acid, $HO{\cdot}NO_2$, whilst 100% acid appears to consist entirely of $HO{\cdot}NO_2$ mols. The displacement 1038 $cm.^{-1}$ is found in the 64% HNO_3 solution only and characterises the NO_3' ion. W. R. ANGUS.

Raman effect in a sodium nitrate crystal. J. CABANNES and E. CANALS (Compt. rend., 1931, **193**, 289—290).—Revised figures for the Raman lines of $NaNO_3$ are 103·1, 190·1, 730·4, 1074·2, 1391·4, and 1678·5 $cm.^{-1}$ The polarisation of the inactive frequency, 1074·2, differs from that of the other two of the fundamental frequencies of the NO_3' ion, 730·4 and 1391·4, precisely as in calcite (cf. this vol., 998). A large untwinned crystal of $NaNO_3$ was obtained by slowly cooling the fused salt. C. A. SILBERRAD.

Fine structure of Raman lines in liquids. A. LANGSETH (Nature, 1931, **128**, 225).—The isotope effect in CCl_4, $SnCl_4$, etc. has been observed. Raman lines in the spectra of liquids have a characteristic structure resembling unresolved vibration-rotation bands. Conc. aq. NH_3 gives a strong band due to the NH_3 mol.; this band shows a distinct rotation structure, which is described. PhMe gives a number of Raman lines of which two, commonly ascribed to the C–H vibration, show rotation structure. L. S. THEOBALD.

Raman spectra of certain organic liquids. C. S. MORRIS (Physical Rev., 1931, [ii], **38**, 141—146). —Measurements are tabulated for 19 compounds from different series. Comparison with infra-red absorption data is made. It is suggested that anti-Stokes lines may have slightly greater frequency shifts than the corresponding Stokes lines. N. M. BLIGH.

Chemical theory of fluorescence. S. S. BHATNAGAR and K. G. MATHUR (Proc. XV Indian Sci. Cong., 1928, 141—142).—Illumination of aq. solutions of eosin, fluorescein, or acriflavine produces small changes in n, the changes diminishing at higher concentrations as the intensity of the fluorescence light decreases. Gelatin and NaOH retard the photo-decomp. of the fluorescent substances. CHEMICAL ABSTRACTS.

Solarisation of fluorite, and the law of lumino-transformation. S. IIMORI and E. IWASE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, **16**, 41—67).—The photo-luminescence of green fluorite was investigated photographically. The luminosity reaches a max. and shows, under excitation by ultra-violet rays, a gradual decrease termed solarisation. The mechanism must be partly irreversible, such transformation being termed lumino-transformation. The end-product can be restored by the action of γ- or X-rays. N. M. BLIGH.

Relation between photoconductivity and photovoltaic effect. R. AUDUBERT and J. ROULLEAU (Compt. rend., 1931, **193**, 291—292).—The variation of resistance on illumination of electrodes of CuO, Cu_2O, $CuO+Cu_2O$, CuI, and Ag_2S in association with a reversible electrode, $Hg|Hg_2Cl_2$ or Ag|AgI, both in aq. KCl or aq. KI, measured by Mance's method is 10—12 times that by Kohlrausch's. The values of $\Delta R/R$ with 10 lumens for Cu_2O are respectively 0·30—0·35 and 0·05—0·07; for Ag_2S and CuO very small, and for CuI nil. C. A. SILBERRAD.

Variations of sensitiveness of cuprous oxide photo-cells with the spectrum. P. Auger and C. Lapicque (Compt. rend., 1931, **193**, 319—321).—The cell is a Cu plate (positive) supporting a layer of Cu_2O covered by a transparent film of Au or Ag (negative) and illuminated by a monochromatised C arc (cf. this vol., 9). Measuring sensitiveness as the ratio of the illuminating power (in microwatts) to the current, after allowing for the absorption due to the film of metal, const. results were obtained. Sensitivity rises from λ 4000 to a max. at λ 4850, and almost vanishes at λ 6250. C. A. Silberrad.

Effect of electric fields on the emission of photo-electrons from oxide cathodes. W. S. Huxford (Physical Rev., 1931, [ii], **38**, 379—395).—Using $BaCO_3$–$SrCO_3$ mixtures sprayed on Ni and baked out, long-wave limits were obtained from the current–incident radiation wave-length graph. The theory that emission of electrons takes place from outer layers of the oxide coating is confirmed. N. M. Bligh.

Theory of rectification. C. Wagner (Physikal. Z., 1931, **32**, 641—645).—Electronic conduction in $Cu^{\cdot}$ compounds and its increase by the presence of excess of electronegative elements is supposed to be due to the presence of Cu ions, which act as places of electron deficiency in the normal Cu lattice. A theory for the action of Cu–Cu_2O rectifiers based on this assumption is given. A. J. Mee.

Electromotive force between two metals in relative motion. J. B. Seth, B. Gulati, and S. Singh (Phil. Mag., 1931, [vii], **12**, 409—429).—The max. vals. of the e.m.f. developed when pieces of Al, Mg, Zn, Sn, Co, Cd, Pb, Mn, Bi, Ni, Pt, Sb, As, Au, Te, Cu, and Ag are held in contact with the polished rim of a rapidly revolving steel disc are, in the order stated, from -730 mv. (e.m.f. directed from metal to steel) to $+123$ mv., the smallest being -3 mv. (Sb). The vals. for Cu and Ag are much higher than Lafay's (Compt. rend., 1928, **186**, 133), and his laws regarding the influence of contact pressure and speed of the disc hold only to a limited extent. It is concluded that the effect is due to voltaic contact potential. N. H. Hartshorne.

Dependence of conductivity on the field intensity in rock-salt crystals. B. Hochberg (Z. Physik, 1931, **70**, 635—640).—Deviations from Ohm's law observed with natural rock-salt (cf. A., 1930, 1504) disappear when the crystal has been tempered near its m. p. A. B. D. Cassie.

Protons and the electrical conductivity of metals. II. Resistance measurements. A. Coehn and H. Jürgens (Z. Physik, 1931, **71**, 179—204; cf. A., 1930, 836).—Protons moving under the influence of an electrical field in a Pd wire transported $0{\cdot}4\times10^{-5}$ amp. of a current of 1·25 amp.: this phenomenon was detected in Pd–Ag alloys up to 20% Ag. Resistance increases with proton content up to normal saturation, after which it diminishes. A. B. D. Cassie.

Conductivity of gases in uniform electric fields. S. P. McCollum and E. L. Jones (Phil. Mag., 1931, [vii], **12**, 384—392).—A crit. discussion of the hypotheses which have been put forward to describe the method by which energy is transferred in collisions between electrons and atoms, particularly in relation to the theory of conductivity in the positive column of discharges. F. J. Wilkins.

Electrical conductivity and the structure of thin metallic layers. I. Present knowledge; general relationship between electrical conductivity and structure. W. Reinders and L. Hamburger (Ann. Physik, 1931, [v], **10**, 649—669).—The distribution of atoms in thin layers of a metal condensed from its vapour in a completely unregulated manner, the relation between the electrical conductivity and the structure by considering the possible structural changes, and the abnormal temp. coeff. of the resistance in thin metallic layers and its relation to the abnormal separation of atoms are discussed. W. R. Angus.

Validity of Ohm's law for Cu_2O. E. Engelhard and B. Gudden (Z. Physik, 1931, **70**, 701—705).—The conductivity of Cu_2O shows no deviations from Ohm's law (cf. A., 1930 1504); theoretically, none is expected. A. B. D. Cassie.

Variation with frequency of the dielectric constant and damping of solid insulators. R. Weber (Z. Physik, 1931, **70**, 706—710).—The dielectric const. and damping of insulators (vulcanite, glass, and rubber) commonly used in condensers vary appreciably with frequency. A. B. D. Cassie.

Orientation of dipole molecules in a viscous medium. J. W. Williams and J. L. Oncley (J. Rheology, 1931, **2**, 271—283).—The region in which the dielectric const. of a polar liquid decreases with increasing frequency determines a time of relaxation for the mols., which has been evaluated, using Stokes' law for the rotation of a particle in a viscous medium. There are several objections to using the ordinary viscosity coeff. to measure the resistance offered to a rotating mol. The type of system to which the theory may properly be applied is indicated. E. S. Hedges.

Dielectric constants and their variation with very intense fields. A. Günther-Schulze and H. Betz (Z. Physik, 1931, **71**, 106—123).—Oxide layers were obtained of sufficient stability for measurement of their dielectric consts. in fields up to 12×10^6 volts per cm. Al_2O_3, Sb_2O_4, Bi_2O_3, and ZrO_2 showed no variation, but the dielectric const. of Ta_2O_5 showed a 10% variation, and that of WO_3 a 260% variation. A. B. D. Cassie.

Electric moment and molecular structure. V. Polymethylene bromides. C. P. Smyth and S. E. Kamerling (J. Amer. Chem. Soc., 1931, **53**, 2988—2998).—Dielectric const. and density data for solutions, chiefly in heptane, at temps. between $-40°$ and $90°$ are tabulated. Vals. of the polarisation for $Br[CH_2]_2Br$ are much higher in C_6H_6 than in heptane (cf. A., 1930, 980). Using mol. refractions, the following electric moments are evaluated (heptane solutions): $Br[CH_2]_2Br$, 0·79, 0·98, $1{\cdot}05\times10^{-18}$ e.s.u., $Br[CH_2]_3Br$, 2·07, 2·15, 2·19 at $-30°$, $10°$, and $50°$, respectively, $Br[CH_2]_5Br$, 2·39, 2·48, $Br[CH_2]_{10}Br$, 2·69, 2·75 at $0°$ and $60°$, respectively. These results are compared with calc. vals. For the first two com-

pounds, the observed vals. are low owing to proximity of the two bromide dipoles. Long C chains are rod-like and do not bend appreciably even in the externally applied electric fields. J. G. A. GRIFFITHS.

Dipole moment of semi-polar linkings. J. DE VRIES and W. H. RODEBUSH (J. Amer. Chem. Soc., 1931, **53**, 2888—2893).—Dielectric const. and density data of C_6H_6 solutions at 25° are given and the following electric moments are evaluated: Ph_2S $1{\cdot}565\times10^{-18}$ e.s.u., Ph_2SO 4·17, and Ph_2SO_2 5·05. The results indicate a high val. for the dipole moment of the semi-polar linking (cf. this vol., 23).

J. G. A. GRIFFITHS.

Dielectric coefficients of gases. I. Rare gases and hydrogen. H. E. WATSON, G. G. RAO, and K. L. RAMASWAMY (Proc. Roy. Soc., 1931, **A**, **132**, 569—585; cf. A., 1928, 107).—The following mean vals. of $(\epsilon-1)_{25^\circ}\times10^6$ at 1 atm. and 25°, −79°, and −191°, respectively, were obtained: He, 66·7, —, 65·4; Ne, 122·9, —, 123·3; A, 504·4, 506·0, 510·3; Kr, 768, 769, —; Xe, 1238, 1242, —; H_2, 251·8, —, 251·5. None of these gases except A has an electric moment detectable by the experimental method used, $0{\cdot}05\times10^{-18}$ being an upper limit for Kr and Xe. The value for A appears to be $0{\cdot}03\times10^{-18}$, and for the remaining gases $<0{\cdot}015\times10^{-18}$.

L. L. BIRCUMSHAW.

Dielectric constants of aqueous solutions. R. WEBER (Z. Physik, 1931, **70**, 711—722).—Dielectric consts. were determined at different concentrations for aq. solutions of KCl, $BaCl_2$, $La(NO_3)_3$, oxalic, malonic, and succinic acids, carbamide, and thiocarbamide. The temp. variation of the dielectric consts. of H_2O, carbamide solutions, and of $La(NO_3)_3$ in H_2O, were also determined. An apparatus for distilling H_2O in vac. and for making up solutions without contact with air is described.

A. B. D. CASSIE.

Dipole moment of the polymorphic forms of methyl tartrate and the existence of racemic compounds in solution. A. WEISSBERGER and R. SANGEWALD (Z. physikal. Chem., 1931, **B**, **13**, 383—386; cf. this vol., 894).—The indefinite m. p. of "low-melting" Me *d*-tartrate is due to the existence of two polymorphs, m. p. 48° and 50°. In C_6H_6 solution the dipole moments of this prep. and the "high-melting" form (cf. J.C.S., 1904, **85**, 765) are identical, viz., $2{\cdot}9\times10^{-18}$ e.s.u. Dipole measurements of C_6H_6 solutions of this compound and a *d–l* mixture, and of Me *d*-mandelate and a *d–l* mixture, show no evidence of the formation of racemic compounds.

N. H. HARTSHORNE.

Studies in dielectric polarisation. I. Benzene solutions of furan, ethyl mercaptan, and ethyl sulphide. E. C. E. HUNTER and J. R. PARTINGTON (J.C.S., 1931, 2062—2070).—The dielectric consts. of solutions of various concentrations were measured at 20° by an apparatus on the heterodyne principle (cf. A., 1924, ii, 292). The following results for $\mu\times10^{18}$ are given: EtSH 1·39, Et_2S 1·57, furan 0·63. Comparison of corresponding compounds shows that replacement of O by S raises the moment in the sulphide, and lowers it in the mercaptan; one of H by Et raises it in the S series, but lowers or leaves it unchanged in the O series. The polarity of Et_2S and thiophen is attributed to the mols. being V-shaped (cf. A., 1925, ii, 479); the moment of Et_2S calc. on the vector moment theory is 1·68.

C. A. SILBERRAD.

Temperature variation of the electric moment of ethylene chloride. C. T. ZAHN (Physical Rev., 1931, [ii], **38**, 521—527).—Mol. polarisations measured over a temp. range of 32—270° and over a pressure range at each temp. show a departure from the Debye theory, and explanations are discussed in detail. The assumption of variation with temp. of the electric moment and calculation of the latter show hindrance to free rotation (cf. Meyer, A., 1930, 980, 1331).

N. M. BLIGH.

Refractometric value of fluorine in organic compounds. G. SCHIEMANN (Naturwiss., 1931, **19**, 706).—The val. of the at. refraction of F from the measurement of the *d* and *n* of some 30 aromatic compounds containing F agrees well with that of Swarts for aliphatic F compounds. F has a refraction val. less than H. F compounds show similar variations to analogous compounds of the other halogens. W. R. ANGUS.

Influence of the solvent on optical rotation. W. KUHN, K. FREUDENBERG, and R. SEIDLER (Z. physikal. Chem., 1931, **B**, **13**, 379—382).—$[M]_{Hg}^{18}$ (λ=5780 Å.) for OMe·CHPh·CO·NMe_2 is −25°, whilst for a 2% solution in hexane it is +250°. This is explained by the theory that optical rotation is the sum of positive and negative quantities, which depend on the absorption bands, and are altered to different extents by solvents. N. H. HARTSHORNE.

Complex indicatrix of stibnite. A. CISSARZ (Z. Krist., 1931, **78**, 445—461).—The reflecting powers of the three principal planes of stibnite for green, orange, and red light have been measured, and the principal sections of its complex indicatrix determined.

C. A. SILBERRAD.

Electro-optical Kerr effect in gases. E. C. STEVENSON and J. W. BEAMS (Physical Rev., 1931, [ii], **38**, 133—140).—The effect in CO_2 was investigated as a function of density and temp. at high pressures and field strengths; results were in agreement with theory. N. M. BLIGH.

Theory of metals. I. Proper values and functions for the linear atomic network. H. BETHE (Z. Physik, 1931, **71**, 205—226).—Theoretical.

A. B. D. CASSIE.

Exchange energy. P. STARODUBROWSKY (Z. Physik, 1931, **70**, 812—816).—Calculation, to a first approximation, of the exchange energy of a diat. mol. shows that this has a sharp max. for homogeneous mols. and rapidly becomes negligible as heterogeneity of the mol. increases.

A. B. D. CASSIE.

Structure of the groups XO_3. J. C. SLATER (Physical Rev., 1931, [ii], **38**, 325—329; cf. this vol., 548).—Structural explanations of such radicals as NO_3 and ClO_3 as valency or as ionic compounds are not mutually exclusive, a combination of the two being possible. Directional properties of the valency lead to the observed coplanar structure for the NO_3 and the pyramidal structure for the ClO_3 type.

Energy relations show that the valency model is more stable and more probable than the purely ionic structure. N. M. Bligh.

Reaction of hydrogen peroxide with some metallic ions. IV. True nature of "per-acids" and the alleged "acid nucleus theory." S. Hakomori (Tech. Rep. Tohoku, 1931, **10**, 11—24; cf. this vol., 569).—A theoretical paper in which oxy-acids and per-acids are considered to consist of "acid nuclei" combined with H_2O and H_2O_2, respectively, by means of "induction valency." A. R. Powell.

Triple collisions. M. Volmer (Z. physikal. Chem., 1931, **B**, **13**, 299—300).—The life period of an activated mol. of N_2O is discussed in relation to the mechanism of the synthesis of this gas. N. H. Hartshorne.

Complex isomerism. E. Hertel and K. Schneider (Z. physikal. Chem., 1931, **B**, **13**, 387—399; cf. A., 1928, 998; this vol., 210).—By analogy with the picrates of aromatic amines (cf. A., 1924, i, 1179) the yellow form of 2 : 6-dinitrophenol–4-bromo-α-naphthylamine is the result of co-ordination between the OH of the phenol and the NH_2 of the amine, whilst in the red form co-ordination between an NO_2 of the former and the nucleus of the latter is responsible. *X*-Ray measurements support this view. Both forms are monoclinic and have the space-group C_{2h}^5, the red having J_a 14, J_b 8, J_c 14·5 Å., β 102° 6′, and the yellow J_a 9·5, J_c 13·5, J. 13·8 Å., β 105° 19′. *X*-Ray data for 4-bromo-α- and -β-naphthylamine are given. N. H. Hartshorne.

Anisotropy in magnetic materials. O. Dahl and J. Pfaffenberger (Z. Physik, 1931, **71**, 93—105).—The magnetic anisotropy of crystals may be applied to determination of fibre structure. The method was applied to Fe, Ni, and Fe–Ni alloys. A. B. D. Cassie.

Method of measuring magnetic susceptibilities. P. Kapitza and W. L. Webster (Proc. Roy. Soc., 1931, **A**, **132**, 442—459).—A detailed account is given of a method of measuring magnetic susceptibilities which does not involve the measurement of the force exerted on the body. The balance system is entirely separate from the body, which can therefore be subjected to almost any physical force without interfering with the measurements. The method may be used to study the influence of such factors as pressure, elastic strain, and temp. on the magnetisation of feebly magnetic substances. L. L. Bircumshaw.

Magnetic moment of the diatomic sulphur molecule. E. J. Shaw and T. E. Phipps (Physical Rev., 1931, [ii], **38**, 174—178).—An investigation was made by the Stern–Gerlach mol. ray method. Results prove that the mol. has a magnetic moment due to electron spin; the indicated configuration is $^3\Sigma$. N. M. Bligh.

Change of magnetic moment of nitric oxide with temperature. R. Stossel (Ann. Physik, 1931, [v], **10**, 393—436).—The magnetic susceptibility of NO has been determined at five different temps. within the range 135·5—289·2° abs., using a small balance and a compensation field. The apparatus was calibrated for O_2. At const. temp. a direct proportionality exists between pressure and susceptibility. The magnetic moment and the Bohr magneton no. of NO vary with temp. in the manner predicted by van Vleck (cf. A., 1928, 572). W. R. Angus.

Magnetic moment of the palladium atom. A. N. Guthrie and M. J. Copley (Physical Rev., 1931, [ii], **38**, 360—364).—The Gerlach–Stern method was used. No splitting of the beam of Pd atoms was observed, indicating that the atom in its normal state has zero magnetic moment, in agreement with spectroscopic results. N. M. Bligh.

Structural demagnetising field of ferromagnetic substances and its experimental determination. R. Forrer and J. Martak (J. Phys. Radium, 1931, [vii], **2**, 198—204).—The assumption of a structural demagnetising field H_s is necessary to explain the inclination, varying with heat treatment, of the hysteresis curves of ferromagnetic substances, and its experimental determination is described. A knowledge of H_s is necessary for the determination of true residual magnetism. N. M. Bligh.

Magnetic behaviour of ammonium manganese sulphate hexahydrate at low temperatures. K. S. Krishnan (Z. Physik, 1931, **71**, 137—140).—$MnSO_4,(NH_4)_2SO_4,6H_2O$ resembles other paramagnetic crystals, and does not show anisotropy of the magnetic moment of Mn^{++} as suggested by Jackson and de Haas (A., 1928, 1081). A. B. D. Cassie.

Polymerisation vs. association and condensation. E. C. Bingham and L. W. Spooner (Ind. Eng. Chem., 1931, **23**, 785—786).—The degree of association of an org. substance (ascertained by abs. temp.–fluidity measurements) depends on its constitution; thus certain polar groups, *e.g.*, OH, COO, NH_2, CO, Cl, and SH, and their relative freedom from surrounding alkyl groups accentuate association. Polymerisation and condensation are less effective than association in lowering fluidity. S. S. Woolf.

Surface tension of liquid metals. IV. Mercury. L. L. Bircumshaw (Phil. Mag., 1931, [vii], **12**, 596—602; cf. A., 1928, 1084).—The surface tension of Hg determined by the method of max. bubble pressure varies linearly from 480 dynes per cm. at 20° to 492 dynes per cm. at − 30°, and thereafter to − 37° appears to pass through a max. at −33°. When the bubble is held for a time at a pressure just below that necessary to detach it, a decrease in the surface tension is observed. The reason for this is discussed. N. H. Hartshorne.

Surface energy of liquids. H. Margenau (Physical Rev., 1931, [ii], **38**, 365—371).—Intermol. forces, thermodynamic relations, and a statistical theory of surface energy are discussed. Results calc. for liquid He, Ne, A, N_2, Cl_2, O_2, and Hg are in satisfactory agreement with experimental data. N. M. Bligh.

Ionisation chamber method of measuring the relative intensities of *X*-ray spectrum lines. S. K. Allison and V. J. Andrew (Physical Rev., 1931, [ii], **38**, 441—453).—An improved ionisation chamber is described. The relative ionisation currents produced by the $L\alpha_1$, β_1, γ_1 lines of W in MeI, MeBr, A,

SO_2, and air, and by the U *L* series in Kr were measured. N. M. BLIGH.

Comparison standards for the powder spectrum method: nickel and cadmium oxides. C. J. KSANDA (Amer. J. Sci., 1931, [v], 22, 131—138).—CdO has *a* 4·689±0·003 Å., n_{Li} 2·49; NiO *a* 4·171 ±0·003 Å., n_{Li} 2·37, and bunsenite the same, its face-centred cubic cell containing 4 mols. Both are recommended as standards for the powder method, and a table of consts. and intensities of diffraction lines for both and for NaCl is given. C. A. SILBERRAD.

Graphic or mechanical method of evaluating Debye–Scherrer diagrams for cubic, tetragonal, hexagonal, and rhombic symmetries. F. EBERT (Z. Krist., 1931, 78, 489—495; cf. A., 1922, ii, 624).—A process is described, and exemplified by application to WC, PdF_2, and $HgCl_2$. C. A. SILBERRAD.

Graphic method of determining indices from powder photographs. E. SCHNEIDER (Z. Krist., 1931, 78, 503—510).—The method applies to hexagonal, rhombohedral, and tetragonal crystals (cf. A., 1922, ii, 624). C. A. SILBERRAD.

Supercooling and nuclei formation in homogeneous liquid metals. A. LANGE (Z. Metallk., 1931, 23, 165—171).—The mechanism of nuclei formation from molten metals is considered mathematically and the process is shown to follow the law of radioactive disintegration. A. R. POWELL.

Architecture of the solid state. W. L. BRAGG (Nature, 1931, 128, 210—212, 248—250).—Kelvin lecture. L. S. THEOBALD.

Preferred orientation in silver foil produced by cold-rolling. C. B. HOLLABAUGH and W. P. DAVEY (J. Rheology, 1931, 2, 284—290).—The cold-rolling of Ag produces two preferential orientations of crystals, which are not affected by the % reduction per pass or the abs. reduction per pass through the rolls. The single preferential position described in the literature falls within the range of orientation now found, but is not in the mean position. E. S. HEDGES.

Growth of metal crystals in metal vapour. M. STRAUMANIS (Z. physikal. Chem., 1931, B, 13, 316—337).—The condensation of Zn and of Cd vapour in evacuated glass vessels takes place most rapidly and with the formation of the largest crystals at those places where the temp. is just below the m. p. of the metal. Here truncated hexagonal pyramids with "stepped" sides are formed, prism faces being rarely encountered. In the "etch" pits produced on evaporation of the metals this structure is inverted. The results are discussed in the light of Kossel's and Stranski's theories of crystal growth. N. H. HARTSHORNE.

Theory of crystal growth. H. BRANDES and M. VOLMER (Z. physikal. Chem., 1931, 155, 466—470).—From the theory previously described (A., 1927, 504) it is deduced that the formation of two-dimensional nuclei on the (001) face of an NaCl crystal will occur by preference on the edges and corners. The relationship of the theory to that of Stranski (A., 1928, 1178) is examined. R. CUTHILL.

Equilibrium forms of homopolar crystals. I. N. STRANSKI and R. KAISCHEV (Z. Krist., 1931, 78, 373—385; cf. A., 1928, 1178; this vol., 288).—A detailed theoretical discussion of the conditions of growth and dissolution of various types of homopolar crystals, showing that such crystals can never appear in simple forms. C. A. SILBERRAD.

Crystal structure of N_2O_4. S. B. HENDRICKS (Z. Physik, 1931, 70, 699—700).—Polemical against Vegard (this vol., 548). *X*-Ray photographs are not inconsistent with an N_2O_4 mol., and from other data this is preferred to a linear NO_2 mol. for the solid structure. A. B. D. CASSIE.

Crystal structures of trioxides of chromium, molybdenum, and tungsten. H. BRAKKEN (Z. Krist., 1931, 78, 484—488).—The following data are given (in this order): *a*, *b*, *c* (in Å.), β (where not 90°), mols. in unit cell, space-group, distances (in Å.) metal–O and O–O: CrO_3, rhombic (or approx.), 8·46, 4·77, 5·70, 4, 2·07, 2·77, and 2·82; MoO_3 (cf. this vol., 289) 3·954, 13·285, 3·694, 4, V_h^{16}, 2·0—2·5, 2·7—3·5; WO_3 triclinic, 7·28±0·05, 7·48, 3·82, αγ very near 90°, β near to 90°, 4, C_i, 1·66—1·91, 2·46—3·02. C. A. SILBERRAD.

Gradual transition in sodium nitrate. I. Physico-chemical criteria of transition. F. C. KRACEK (J. Amer. Chem. Soc., 1931, 53, 2609—2624).—Full details are given of results previously published (this vol., 549). J. G. A. GRIFFITHS.

Space-group of potassium dithionate. W. H. BARNES and G. V. HELWIG (Canad. J. Res., 1931, 4, 565—569).—The space-group is either D_3^1 or D_3^2; in unit cell a_0=9·77 and c_0=6·28 Å. R. CUTHILL.

Explanation of the results of Spangenberg and Neuhaus on the growth of spherical polished sodium chloride crystals. I. N. STRANSKI (Naturwiss., 1931, 19, 689—690).—An explanation of the occurrence of (100) faces, with a small number of (210), (110), and (111) faces in polished NaCl crystals is given by calculating and comparing the nos. of uniform and repetition faces to be expected. W. R. ANGUS.

Habit-variation in crystals of potassium permanganate. H. E. BUCKLEY (Z. Krist., 1931, 78, 412—421; cf. this vol., 414).—The effects of rate of growth and the presence of the ions Cr_2O_7'', S_2O_6'', ClO_3', SO_4'', CrO_4'', and SeO_4'' on the habit of crystals of $KMnO_4$ are described and explanations discussed. C. A. SILBERRAD.

Crystal structure of arsenic tri-iodide, AsI_3. (MISS) D. HEYWORTH (Physical Rev., 1931, [ii], 38, 351—359).—Investigations were made by Laue, powder, and oscillation photographs. The structure is a layer lattice, space-group C_{3i}. The rhombohedron has two mols. per unit cell, *r* 8·25 Å., α 51° 20′. The I ions are in hexagonal close packing; each As ion is surrounded by 6 I ions. N. M. BLIGH.

Space lattice of cobaltous ammonium sulphate hexahydrate. F. HALLA and E. MEHL (Z. anorg. Chem., 1931, 199, 379—383).—The space-group is C_{2h}^5, and the dimensions of the unit cell, which contains 2 mols., are *a* 9·23, *b* 12·49, and *c* 6·23 Å. R. CUTHILL.

Crystalline form of new cobaltammines. L. W. Strock and T. P. McCutcheon (J. Amer. Chem. Soc., 1931, **53**, 2852—2866; cf. A., 1929, 780).—The prep. of *oxalato-* and *carbonato-tetramminocobaltic dichromate, chromate, chlorate*, and *perchlorate* is described. Solubilities of the oxalato-compounds are recorded, but the carbonato-compounds decompose rapidly in H_2O. Crystallographic data for the oxalato-compounds and the carbonato-chromate are recorded. The carbonato-dichromate does not crystallise. It is suggested that the $[Co(NH_4)_4,C_2O_4]$ ion has a definite skeleton structure in crystals and the substitution of various anions merely alters the shape and dimensions of this structure. Since the structural type is found to be const., the axial ratios afford a measure of the deforming influence of the series of substituted anions on the structure of the oxalato-group and indicate the following order of increasing effect: Cr_2O_7'', ClO_4', ClO_3', CrO_4''. J. G. A. Griffiths.

Crystal structure of epidote. I. D. J. Bujor (Z. Krist., 1931, **78**, 386—411; cf. this vol., 415).—The unit cell has a 8·84, b 5·60, c 10·10 Å., β 115° 23′, and contains 2 mols. of $Al_2(Al,Fe)OHCa_2(SiO_4)_3$. Epidote is pyro-electric but not piezo-electric. C. A. Silberrad.

Crystal structure of vesuvianite. B. E. Warren and D. I. Modell (Z. Krist., 1931, **78**, 422—432; cf. A., 1930, 734).—The unit cell has a 15·63, c 11·83 Å., and contains 2 mols. of $Ca_{10}Al_4(Mg,Fe)_2Si_9O_{31}(OH)_4$; space-group D_{4h}^4. C. A. Silberrad.

Crystal structure of bastnasite. I. Oftedal (Z. Krist., 1931, **78**, 462—469; cf. A., 1930, 1099).—Revised data are a 7·094±0·007, b 9·718±0·008 Å. with 6 mols. of $RFCO_3$ (R=Ce, La, etc.) in the unit cell; space-group D_{3h}^4. A complete structure is worked out. The crystals are piezo-electric. C. A. Silberrad.

Crystal structure of manganite. A. Ferrari and A. Scherillo (Z. Krist., 1931, **78**, 496—502).—The unit cell has a 4·41, b 5·19, d 2·83 Å., and contains 2 mols. of MnO(OH). The Mn forms a body-centred lattice (cf. A., 1930, 983). C. A. Silberrad.

X-Ray investigations of liquid crystals. III. Anisole-1:5-diaminonaphthalene. K. Herrmann and A. H. Krummacher (Z. Physik, 1931, **70**, 758—764).—Aligning the mols. of anisole-1:5-diaminonaphthalene with a magnetic field gives an X-ray diagram with lines due to inter- and to intra-mol. interference (cf. this vol., 289). A. B. D. Cassie.

Anisotropic liquids ("liquid crystals") in electric fields. W. Kast (Z. Physik, 1931, **71**, 39—52).—Debye X-ray diagrams were obtained for *p*-azoxyanisole at 124° subjected to const. electric fields of 220—7200 volts per cm., and to alternating fields of 650 volts per cm. and of frequencies of 25,000—600,000 hertz. The const. field photographs indicate a dipole directed along the nematic particle and of magnitude greater than 10^{-14} e.s.u., giving 10^6 mols. per particle; the alternating fields indicate a time of relaxation of $1·7\times10^{-6}$ sec. A. B. D. Cassie.

Crystal structure of resorcinol. A. N. Sarkar (Proc. XV Indian Sci. Cong., 1928, 92).—The space-group is C^{10} and the mols. are asymmetric. Chemical Abstracts.

Lattice structure of some simple sugars. K. Andress and L. Reinhardt (Z. Krist., 1931, **78**, 477—483).—The following data are given (in this order): a, b, c (in Å.), β (where not 90°), mols. in unit cell, space-group: *l*-arabinose 6·48, 19·30, 4·81, 4, V^4 (D_2p222); *l*-xylose 9·21, 12·48, 5·56, 4, V^4 (D_2p222); *l*-rhamnose monohydrate 7·84, 7·84, 6·61, 95°, 2, C_2^2 (C_2p2). The dimensions of the unit cell imply that the mol. of arabinose is long and narrow, that of xylose short and broad (in agreement with the open-chain and 5-carbon ring structure respectively), as is the case with mannose and sorbose compared with dextrose and lævulose (cf. A. 1930, 983; this vol., 152). C. A. Silberrad.

Electrolytic investigations with single crystals of zinc. K. H. Kreuchen (Z. physikal. Chem., 1931, **155**, 161—198).—In contact with a $ZnSO_4$ solution the (0001) principal cleavage plane of a single crystal of Zn is positive in respect of a Zn polycrystal in contact with the same solution. The difference in potential rises considerably immediately after immersion in the electrolyte, then passes through a max., and slowly falls, approaching zero in few days. The single-crystal electrode behaves similarly when combined with a Cu or Cd electrode. Kossel's theory of crystal growth (A., 1930, 1506) indicates that there can be no strictly reversible equilibrium between a completed lattice plane and its ions in solution, for the plane corresponds with an energy threshold. The growth of a single crystal by electrolysis in a solution of $ZnSO_4$ containing H_3BO_3 has been observed. Current measurements have been made with capillary cells having Zn single crystals as electrodes. R. Cuthill.

Influence of hydrostatic pressure on the critical temperature of magnetisation for iron and other materials. L. H. Adams and J. W. Green (Phil. Mag., 1931, [vii], **12**, 361—380).—Pressure has no effect on the Curie point of Fe, Ni, magnetite, meteoric Fe, and Ni-steel with 35% Ni up to pressures of 4000 atm. The vol. change during the magnetic transformation must be very small. F. J. Wilkins.

Transverse effect of magnetostriction. G. Dietsch and W. Fricke (Physikal. Z., 1931, **32**, 640).—Two methods for the investigation of the transverse effect of magnetostriction are given. A. J. Mee.

Change of resistance of nickel in a magnetic field. H. H. Potter (Proc. Roy. Soc., 1931, **A**, **132**, 560—569).—The change of resistance of a Ni wire has been studied in transverse and longitudinal fields up to 7000 gauss for temps. from −183° to 460°. In the neighbourhood of the Curie point the change is independent of the direction of the field and varies with field and temp. in a manner analogous to the variation of the magneto-caloric effect. The resistance change is proportional to the energy of magnetisation. This holds both in the ferromagnetic state and in the quasi-paramagnetic state above the Curie point (cf. A., 1930, 1505). L. L. Bircumshaw.

Magnetisation and the magneto-caloric effect. F. Bitter (Physical Rev., 1931, [ii], **38**, 528—548).—The mechanism of magnetisation is surveyed, and available experimental data on the magneto-caloric effect for Ni, Fe, and Co are discussed in relation to the Weiss and Akulov theories. N. M. Bligh.

Mechanical properties of rock-salt. V. D. Kusnetzov and V. A. Semencov (Z. Krist., 1931, **78**, 433—444; cf. A., 1929, 989; 1930, 845).—Some 40 samples of rock-salt gave elastic limits varying from 198 to 3180 g. per sq. mm., tensile limits 2160 to 4210 g. per sq. mm., and elastic moduli 2950 to 6390 kg. per sq. mm. C. A. Silberrad.

Thermocouples with elements of longitudinally and transversely magnetised wires of nickel and iron. W. H. Ross (Physical Rev., 1931, [ii], **38**, 179—181).—Thermal e.m.f. developed for the single ferromagnetic substances were investigated. N. M. Bligh.

Thermoelectric power of nickel in the neighbourhood of the Curie point. K. E. Grew (Proc. Leeds Phil. Soc., 1931, **2**, 217—220; cf. Dorfman, A., 1929, 751).—The thermoelectric power of Ni with reference to Pt was measured; the change in the sp. heat of electricity in Ni at the Curie point was $4{\cdot}9\times10^{-24}$ g.-cal. per electron per degree. N. M. Bligh.

Determination of certain physical constants of krypton and xenon. F. J. Allen and R. B. Moore (J. Amer. Chem. Soc., 1931, **53**, 2522—2527; cf. A., 1930, 986, 1508).—Details of the results previously recorded are given. The b. p. are Kr $-152{\cdot}9\pm0{\cdot}3°$ and Xe $-107{\cdot}1\pm0{\cdot}3°$. J. G. A. Griffiths.

Thermal expansion and atomic heat of solid mercury. L. G. Carpenter and F. H. Oakley (Phil. Mag., 1931, [vii], **12**, 511—522).—The mean curve of the authors' experimental vals. for the cubical expansion coeff. $\times10^5$ of solid Hg is linear and runs from 12·8 at 180° abs. to 17·0 at the m. p., $\pm3\%$. C_v calc. from these figures and previous determinations of C_p (A., 1930, 1243) remains constant at 6·08—6·09 from 200° to 220° abs., and then rises to 6·13 at 234° abs. N. H. Hartshorne.

Influence of cold-working [of metals] on the specific heat. J. A. M. van Liempt (Naturwiss., 1931, **19**, 705).—The difference between the sp. heats of cold-worked and recryst. metal has been expressed by a formula; results are in agreement with experimental values of Gaudino (this vol., 155) for Cu, Ni, and Pb wires. W. R. Angus.

Density of sulphur dioxide. D. LeB. Cooper and O. Maass (Canad. J. Res., 1931, **4**, 495—497).—The density of SO_2 has been measured. Equations of five isothermals are given. The normal density found is 2·9262. W. Good.

Vapour density of selenium tetrabromide and the existence of selenium dibromide. D. M. Yost and J. B. Hatcher (J. Amer. Chem. Soc., 1931, **53**, 2549—2553).—V. d. data for mixtures of the composition $Se : Br_4$ indicate complete decomp. into Br_2 and *selenium dibromide* in the range 250—500°. The latter, alone, is produced by vaporising mixtures of the composition $Se : Br_2$, but on condensation, a mixture of Se_2Br_2 and $SeBr_4$ is produced. Attempts to volatilise Se_2Br_2 afford $SeBr_2$ (*g*) and Se (*l*). Polymorphism of $SeBr_4$ is indicated. J. G. A. Griffiths.

Constants of van der Waals' equation. S. Ray (Kolloid-Z., 1931, **56**, 159—166).—Although the actual values of the consts. a and b vary greatly for different gases and vapours, the ratio a/b is practically const. for all substances. E. S. Hedges.

Quantum theory of the equation of state. J. C. Slater (Physical Rev., 1931, [ii], **38**, 237—242).—The quantum analogue of the expression relating probability of a system and potential energy is deduced, and free energy computed therefrom. From a qual. application for an imperfect gas He and H_2 are expected to show quantum effects in their equations of state. N. M. Bligh.

***P–V–T* relations of ammonium chloride and bromide, and the effect of pressure on the volume anomalies.** P. W. Bridgman (Physical Rev., 1931, [ii], **38**, 182—191).—Measurements were made of the vol. as a function of pressure at 3 temps. and a pressure range of 12,000 kg. per sq. cm. Discontinuities, differing for the two substances, were found in the slope of the vol. isotherms, and correspond with those in the thermal expansion. Results are discussed thermodynamically. N. M. Bligh.

Vapour pressure of hydrogen selenide and hydrogen telluride. N. O. Stein (J.C.S., 1931, 2134—2138).—The v. p. of H_2Se between 173° and 228·8° abs. and of H_2Te between 195° and 273° abs. are given by: H_2Se (liquid) $\log_{10} p = -1030/T+6{\cdot}27$, (solid) $-1380/T+7{\cdot}96$; H_2Te (liquid) $-1005/T+5{\cdot}53$, (solid) $-1220/T+6{\cdot}39$. The mol. heats (kg.-cal.) of vaporisation and of fusion, and Trouton's const. are respectively: H_2Se 4·71, 1·57, 20·4; H_2Te 4·58, 0·97, 16·7. No association is therefore indicated. C. A. Silberrad.

Interchange of molecules between a liquid and its vapour. T. Alty and F. H. Nicoll (Canad. J. Res., 1931, **4**, 547—558).—Measurements of the rate of evaporation under low pressures show that with H_2O many of the vapour mols. impinging on the liquid surface are reflected, whereas with CCl_4 and C_6H_6 there is little or no reflexion. R. Cuthill

Viscosity, thermal conductivity, and diffusion in gas mixtures. XVIII. Measurement of the viscosity of chlorine and hydrogen iodide. M. Trautz and H. Winterkorn (Ann. Physik, 1931, [v], **10**, 511—528).—Apparatus for measuring the viscosity of and HI is described. The viscosity of SO_2 and air were first measured to test the apparatus and results were obtained in good agreement with previous vals. Vals. for Cl_2 and HI are obtained for temps. from 20° to 250° and their temp. functions calc. η for Cl_2 is lower than previously recorded vals. Vals. of $M\Theta$ for the H halides are practically identical with those of the inert gas occupying the next position in the periodic system to the halide. W. R. Angus.

Viscosity, heat conductivity, and diffusion in gas mixtures. XV. Viscosity of H_2, N_2O, CO_2, and C_3H_8 and their binary mixtures. M. Trautz

and F. Kurz. XVI. **Viscosity of H_2, CH_4, C_2H_6, C_3H_8, and their binary mixtures.** M. Trautz and K. G. Sorg. XVIII. **Viscosity of NH_3 and of its mixtures with H_2, N_2, O_2, and C_2H_4.** M. Trautz and R. Heberling (Ann. Physik, 1931, [v], 9, 981—1003; 10, 81—96, 155—177).—XV. The coeff. of viscosity has been determined at 26·9°, 126·9°, 226·9°, and 276·9°.

XVI. The viscosities were measured by the transpiration method at 20°, 100°, 200°, and 250°.

XVIII. The viscosity of NH_3 has been measured between 20°, and 700°. Empirical relations are discussed in each case. W. Good.

Dynamic azeotropism. VI. (Mlle.) G. Schouls (Bull. Acad. roy. Belg., [v], 1931, 17, 630—644; cf. this vol., 676).—A continuation of the previous mathematical considerations.

N. H. Hartshorne.

Magnetism of binary mixtures. Aqueous solutions of acids. J. Farquharson (Phil. Mag., 1931, [vii], 12, 283—290).—Susceptibility-concentration measurements made with aq. solutions of HCl indicate the formation of hydrates at concentrations from 3 to 10 H_2O; measurements were not made in solutions with less than $3H_2O$. The hexahydrate is indicated by a max. on the curve, whilst the other hydrates give minima, suggesting differences in the way in which the water mols. are linked to the Cl^-. The gram-ionic susceptibility of free Cl^- is calc. to be $-30{\cdot}66\times10^{-6}$. The H_2SO_4–H_2O curve has a flat max. at a concentration of H_2SO_4,H_2O and another which is sharp at 15·1% H_2SO_4; there is also a slight break at the concentration $H_2SO_4,3H_2O$. The gram-ionic susceptibility of $SO_4^{=}$ is given as $-39{\cdot}0\times10^{-6}$.

F. J. Wilkins.

Diffusion in metals. G. von Hevesy and W. Seith (Z. Elektrochem., 1931, 37, 528—531).—The diffusion coeff. of Au in Pb at 150° is 4×10^{-3} sq. cm. per day; that of Pb in Au is only 3×10^{-11} sq. cm. per day at 141°. Inter-metallic diffusion is generally one-sided, but loses this character as the metals become more similar, as in the series Au–Pb, Ag–Pb, Bi–Pb, Tl–Pb, Sn–Pb, Pb–Pb. The solubility of sparingly sol. metals in other metals can be calc. from the diffusion const. The solubility of Ag in Pb at 285° is 0·13 at. %. E. S. Hedges.

Diffusion of metals in the solid state. S. Tanaka and C. Matano (Mem. Coll. Sci. Kyoto, 1931, A, 14, 59—66).—The diffusion of various metals has been investigated by measuring the change in the electrical resistance of metal foils made by alternately electroplating the one metal on the other. W. Good.

X-Ray investigation of the tin–antimony alloys. E. G. Bowen and W. Morris-Jones (Phil. Mag., 1931, [vii], 12, 441—462).—The following phases have been found at room temp.: 0—9 at.-% Sb, solid solution, simple tetragonal, a_0 increases from 5·818 to 5·836 Å., c 0·546; 9—40 at.-% Sb, mixture of simple tetragonal and NaCl structure; 40—54 at.-% Sb, solid solution, NaCl structure, a_0 decreases from 6·126 to 6·110 Å., but there is a break at 50 at.-% Sb and $a_0=6{\cdot}120$ Å., which shows that the solvent in this field is SbSn; 54—90 at.-% Sb, mixture of NaCl and face-centred rhombohedral structures; 90—100 at.-% Sb, solid solution, face-centred rhombohedral, a_0 6·220, α increases from 86° 30′ to 87° 24′. No evidence for the existence of Sn_3Sb_2 found by previous workers was obtained. The changes in the lattice on either side of SnSb can be qualitatively explained by using ionic, but not at., radii, but those near pure Sn and Sb can be satisfactorily explained by using at. radii.

N. H. Hartshorne.

Investigation of gold–copper alloys by the diffraction of fast electrons. O. Eisenhut and E. Kaupp (Z. Elektrochem., 1931, 37, 466—473).—An apparatus for the investigation of the structure of solids by means of electron diffraction is described. The method has certain advantages over the X-ray diffraction procedure, and by its means a tetragonal structure can be recognised in 50% Au–Cu alloys after short heat treatment. 50/50 Au–Cu and 50/50 Au–Al alloys after heating at 400° develop a zinc-blende type of lattice. The velocity of formation of individual mixed crystals of Au and Cu is doubled for a rise of 10°.

E. S. Hedges.

System calcium–bismuth. E. Kurzyniec (Bull. Acad. Polonaise, 1931, A, 31—58).—Thermal analysis shows the existence of two compounds, Ca_3Bi_2 (m. p. 928°) and $CaBi_3$. There are two eutectics, at 270° and 786°. Microscopic analysis agrees with the above.

A. J. Mee.

Interatomic forces in binary alloys. G. Scatchard (J. Amer. Chem. Soc., 1931, 53, 3186—3188; cf. this vol., 900).—Polemical. The available data are insufficient to decide between the theories of Langmuir and van Laar. J. G. A. Griffiths.

Metallographic investigation of ternary alloys of the iron–carbon–tungsten system. III. Equilibrium diagram of the system. S. Takeda (Tech. Rep. Tohoku, 1931, 10, 42—92).—The liquidus and solidus of the system Fe–W–C have been determined for alloys containing <4% C and <80% W and the complete ternary diagram as well as numerous pseudo-binary diagrams are reproduced. In the binary system Fe_3C–W a metastable double carbide, η, with 1·8% C and 70% W is formed by the peritectic reaction: liq.$+$W $\rightleftharpoons \eta$, and this phase forms a eutectic with θ. The η-phase occurs in the ternary system Fe–Fe_3C–W in a number of metastable equilibria. Thus in the metastable system there exist nine monovariant reactions and four non-variant reactions; the latter are liquid$+\zeta$ $\varepsilon+\eta$, liquid$+\varepsilon \rightleftharpoons \delta+\eta$ (at 1380° and 28% W, 1% C), liquid$+\delta \rightleftharpoons \gamma+\eta$ (1335°, 27% W, 1·4% C), liquid $\rightleftharpoons \gamma+\theta+\eta$ (1085°, 17% W, 3·7% C). On slow cooling or annealing θ decomposes into Fe and graphite and η into Fe and WC and the equilibrium diagram of this stable system has been tentatively constructed.

A. R. Powell.

Magnetic alloys and their properties. H. H. Potter (Phil. Mag., 1931, [vii], 12, 255—264).—The ternary alloys Ag–Mn–Al are ferromagnetic, having a max. saturation intensity of about 70 units per c.c. at a composition corresponding with Ag_5MnAl. They possess an enormous coercive force which, in the most magnetic specimens, may be more than 20 times that of the hardest permanent magnet steels. The Curie point is at about 360°. The Mn–Sn system contains

two magnetic compounds. The first, $SnMn_4$, has a saturation intensity of about 100 units and a Curie point at 150° (approx.); the second, presumably $SnMn_2$, is unique in having a high saturation intensity (about 470 units) and a low Curie point (about 0°).
F. J. WILKINS.

Metallurgical problems of aluminium and aluminium alloys. G. SACHS (Z. Elektrochem., 1931, **37**, 436—447).—A review of published work on the prep. and properties of single crystals of Al, equilibria, structure, and properties of Al alloys, and corrosion and surface treatment of Al and its alloys.
E. S. HEDGES.

Improvement of alloys, especially light metals and beryllium alloys. G. MASING (Z. Elektrochem., 1931, **37**, 414—429).—A discussion of published work on the effects of plastic deformation in the cold and heat treatment on the hardness, electrical conductivity, elasticity, vol., lattice consts., and magnetic susceptibility of alloys. E. S. HEDGES.

Diffusion of liquids. B. GERLACH (Ann. Physik, 1931, [v], **10**, 437—459).—The following binary mixtures have been investigated: H_2O–MeOH; H_2O–EtOH; H_2O–PrOH; CCl_4–$PhNO_2$; CCl_4–C_6H_6; $PhNO_2$–MeOH. Experimental details and the theory of diffusion are discussed. The diffusion coeffs. of one constituent into the other, the inner viscosity, and the mol. radius have been determined for each substance. Only with CCl_4 is there good agreement between the experimental val. of the mol. radius and the val. calc. from the kinetic theory of gases.
W. R. ANGUS.

Intertraction or barophoresis. N. K. ADAM (Kolloid-Z., 1931, **56**, 138—141).—Intertraction is due to vertical streams brought about by differences of *d* when two liquids having different diffusion coeffs. are placed in contact. E. S. HEDGES.

Solubility of sulphur dioxide in sulphuric acid and the existence of the monohydrate. J. A. N. FRIEND (J.C.S., 1931, 2225—2226).—Available data over the range 55—84% H_2SO_4 give a linear relation: $S=10{\cdot}0-0{\cdot}0852x$, where S is the solubility of SO_2 in g. per 100 g. of solvent and x is % H_2SO_4 in solvent. Assuming these solutions to be mixtures of H_2O and H_2SO_4,H_2O, the relation becomes: $S=10{\cdot}0\times\%$ free $H_2O+2{\cdot}8\times\%$ H_2SO_4,H_2O, where 10·0 and 2·8 are the extrapolated solubilities in H_2O and pure monohydrate, respectively. C. W. DAVIES.

Determination of solubility of sparingly soluble liquids in water. H. SOBOTKA and J. KAHN (J. Amer. Chem. Soc., 1931, **53**, 2935—2938).—With a minute quantity of Sudan IV as indicator, the solubilities in H_2O at 20° of the Et esters of the straight-chain monocarboxylic acids between propionic and hexoic acid and of the dicarboxylic acids between malonic and sebacic acid have been determined. Refractive indices of the esters are recorded.
J. G. A. GRIFFITHS.

Tears of strong wine. M. LOEWENTHAL (Phil. Mag., 1931, [vii], **12**, 462—472).—The classical explanation of the marginal film and "tears" which form when a strongly alcoholic liquid is placed in an open vessel is inadequate. The presence of H_2O in the liquid is immaterial, but that of H_2O in the air is an important condition. Thus abs. EtOH shows the phenomenon, but aq. EtOH exposed to dry air does not. MeOH, $COMe_2$, glacial AcOH, and probably any volatile liquid sol. in H_2O show the effect, which may also be produced by mixing a volatile but insol. liquid, *e.g.*, $CHCl_3$, with a sol. one, *e.g.*, PhOH. With some mixtures, however, H_2O is not essential; *e.g.*, C_6H_6+light petroleum acts vigorously in dry air. Volatile liquids may also be rendered active in dry air by dissolving various solids in them. The experimental facts are held to show that the marginal film is driven upwards by the "interface pressure" postulated by Leslie (*ibid.*, 1802, **14**, 193) and not drawn upwards by surface tension.
N. H. HARTSHORNE.

Liquid–liquid separation of sodium soaps by sodium sulphate. E. L. LEDERER (Kolloid-Z., 1931, **56**, 204—206).—The soap content of the separated layer may be expressed by the empirical formula $(x-s)/(a-s)-[(c-c_0)/(g-c_0)]^m$, where c is the total concentration of electrolyte used, c_0 the crit. value, g the limiting concentration of alkali, s the concentration of soap, x the concentration of soap in the separated layer, a the highest value possible for x, and m is a const. E. S. HEDGES.

Solubilities of the thiocyanates of the metals. K. MASAKI (Bull. Chem. Soc. Japan, 1931, **6**, 163—165).—The solubilities of the thiocyanates of Pb, Cd, Zn, and Co in H_2O have been measured at 18°.
F. J. WILKINS.

Solubility of silver oxide in water at various temperatures. R. P. P. MATHUR and N. R. DHAR (Z. anorg. Chem., 1931, **199**, 387—391).—The solubility has been determined at 20—80°. The rhythmic precipitation of Ag_2O when $AgNO_3$ diffuses into a gelatin gel containing NaOH has been observed, the ppt. disappearing, however, on exposure to light.
R. CUTHILL.

Solubility of potassium per-rhenate in water and some physico-chemical constants of its solutions. N. A. PUSHIN and D. KOVAC (Z. anorg. Chem., 1931, **199**, 369—373).—Data for the system $KReO_4$–H_2O between the cryohydric point at $-0{\cdot}060°$ and 100° have been obtained, and the viscosity, d, and n of aq. solutions of $KReO_4$ at 20° and 30° determined. R. CUTHILL.

Solubility, conductivity, and b.-p. elevation of inorganic and organic compounds in liquid hydrogen fluoride. K. FREDENHAGEN (Z. Elektrochem., 1931, **37**, 684—694).—A review of published work, emphasising the analogy between HF and H_2O.
E. S. HEDGES.

Molecular magnitude and phase distribution. II. J. N. BRONSTED and E. WARMING (Z. physikal. Chem., 1931, **155**, 343—352).—When colloidally dispersed As_2S_3 or Cr_2O_3 is brought in contact with two conjugate solutions of H_2O, BuOH, and EtOH it remains entirely in one phase until the temp., T, approaches the crit. temp., T_c, when the log. of the distribution ratio becomes proportional to $\sqrt{(T_c-T)}$. A theoretical basis for this relation is given.
R. CUTHILL.

Adsorption phenomena with mercury. H. CASSEL (Z. Elektrochem., 1931, **37**, 642—645).—By

measuring the max. drop pressure the adsorption of the vapours of several easily condensible org. liquids has been determined at a surface of Hg. Two different types of isotherms were obtained. At low pressures, Henry's law is obeyed by non-polar C_6H_6, hexane, and *cyclo*hexane and by polar Et_2O, *iso*amyl alcohol, and BuOH. Dipole mols. of small polarisability (H_2O, MeOH, $MeNO_2$) produce little or no lowering of surface tension, especially at low pressures. The results offer no support for the dipole theory of adsorption. For small amounts of adsorbed material the heat of adsorption of EtOH is less and that of C_6H_6 is greater than the heat of vaporisation. With increasing thickness of the adsorbed layer the heat of adsorption of EtOH rises, whilst that of C_6H_6 falls, eventually reaching values which are only slightly greater than the heats of vaporisation.

E. S. Hedges.

Adsorption of polar and apolar substances on mercury. H. Cassel and F. Salditt (Z. physikal. Chem., 1931, **155**, 321—342).—The adsorption of various vapours on Hg has been determined by measuring their effect on the surface tension, γ, at 50°. If γ is plotted against the v. p., the axis of γ is tangential to the resulting isotherm when the adsorbate is Bu^aOH, *iso*amyl alcohol, *n*-hexane, *cyclo*hexane, or C_6H_6, and at low v. p. Henry's law is valid for the distribution between the surface and the extended phase. When dipolar substances, such as H_2O, $MeNO_2$, MeOH, EtOH, Pr^aOH, and allyl alcohol, are adsorbed, however, the isotherm meets the γ axis practically at right angles, which shows that the adsorbed substance is associated. In general, a modified van der Waals equation is applicable to the adsorbed substance. The results show that dipole moment is of only minor importance in determining degree of adsorption. It seems, however, that the intensity of adsorption increases with increase in the mol. refractivity of the adsorbate, although the presence of double linkings causes complications.

R. Cuthill.

Binding of gases (hydrogen, nitrogen) by highly-dispersed metals (iron, nickel) precipitated from the vapour phase. W. Frankenburger, K. Mayrhofer, and E. Schwamberger (Z. Elektrochem., 1931, **37**, 473—482).—When the vapours of Fe or Ni are condensed on a cold surface the fresh condensate takes up large quantities of H_2 or N_2, but relatively small quantities of gases are taken up when the condensate is left for some time. Probably the structure of the initially highly dispersed metal changes with time, the number of "active centres" diminishing as the grain size increases. The amount of gas taken up is increased when the metal vapour is mixed with an inert vapour (such as NaCl) before condensing. The condensate then consists of a highly-dispersed solid sol of metal in NaCl and the gas taken up may amount to 6 mols. of H_2 per atom of Fe, increasing with the proportion of NaCl used. Mo shows a similar effect. N_2 is not appreciably taken up by Fe except in the presence of NaCl; A, and mixtures of He and Ne, are not taken up under any of these conditions. These effects appear to be due to sp. adsorption in which van der Waals forces are probably involved.

E. S. Hedges.

System iron–hydrogen. A. Sieverts and H. Hagen (Z. physikal. Chem., 1931, **155**, 314—317).—The absorptive power of Fe powder for H_2 at 800° and 1000° is the same as that of Fe sheet or wire. The Fe powder used by Iwasé (A., 1927, 15) seems to have contained oxide.

R. Cuthill.

Gaseous adsorption. I. Influence of hydrogen sulphide on the rate of adsorption of hydrogen by platinum. E. B. Maxted (J.C.S., 1931, 2203—2207).—H_2S is very strongly adsorbed by Pt; on degassing at 100° an equal vol. of H_2 is evolved, the S remaining on the Pt. Both before, and to a smaller extent after, this treatment the adsorption of H_2 by Pt is markedly retarded, although there is no decrease in the amount ultimately adsorbed. The results afford no obvious confirmation of Taylor's dual mechanism (this vol., 421), but suggest that adsorption as a whole is catalysed by the most unsaturated portions of the surface.

C. W. Davies.

Absorption of nitrogen by iron. A. Sieverts (Z. physikal. Chem., 1931, **155**, 299—313).—The solubility of N_2 in Fe under 1 atm. pressure has been measured between 700° and 1130°, and approx. vals. have been obtained for the solubility in $\alpha(\beta)$-Fe. At a given temp. the amount of N_2 absorbed by γ-Fe is proportional to the square root of the N_2 pressure. The amount of N_2 retained by Fe saturated with N_2 on cooling depends on the surface area and the conditions of cooling; the rate of diffusion of dissolved N_2 is very small below 600°.

R. Cuthill.

Adsorption of nitrogen by condensed atomic platinum. S. H. Bastow (J.C.S., 1931, 1950—1959).—A film of Pt on a very cold glass surface adsorbs N_2 strongly, and the adsorbed N_2 forms NH_3 with H_2 or H_2O. In these reactions the sintering of the Pt film is a source of energy, and it is shown that the N_2 adsorbed by a film which has been partly sintered by warming is less reactive.

C. W. Davies.

Adsorption of hydrogen cyanide and of carbon dioxide at low pressures by activated charcoals. A. J. Allmand and R. Chaplin (Proc. Roy. Soc., 1931, A, **132**, 460—479; cf. A., 1929, 133).—The adsorption isothermals of HCN and CO_2 have been determined for specimens of evacuated activated charcoals at 25° over pressure ranges of 10^{-3} to 0·2 mm. and 10^{-2} to 0·15 mm., respectively. The results with HCN show certain resemblances to those obtained with H_2O vapour. The results with CO_2 indicate the existence of two distinct types of adsorption process, both being active with steam- or air-activated charcoals, but one only with chemically activated charcoals. It is suggested that in the latter, the regions of highest potential are occupied by mineral matter adsorbed during activation; this view is confirmed by further experiments.

L. L. Bircumshaw.

Sorption of gas by mineral. III. Silicic acid minerals. J. Sameshima (Bull. Chem. Soc. Japan, 1931, **6**, 165—173).—The rate of sorption of NH_3 by dehydrated chalcedony, opal, kieselguhr, natural silica gels, and silicious sinter have been measured. The amount x sorbed in time t is given by $x{-}K \log t + k$, where K and k are consts.

F. J. Wilkins.

Adsorption and surface energy at phase boundaries. III. Theories of reversal of adsorption series. B. ILIIN (Z. physikal. Chem., 1931, **155**, 403—416).—A theory of the adsorption of a dissolved substance is elaborated. According as the electric moment of the mols. composing the surface of the solid is greater or less than that of the solvent mols., the solid is lyophilic or lyophobic. If the moment of the solute is less than that of the solvent, *i.e.*, if the latter is a polar liquid, adsorption will or will not occur, depending on whether the solid is lyophobic or lyophilic, respectively, whereas if the solvent is non-polar the adsorption effects are reversed. When, however, this theory is applied to porous adsorbents, such as C, it is necessary to take into account the presence of micro-pores so small as to be impermeable to large mols. The adsorptive characteristics of a sample of C will then be determined, not only by the lyophilic or lyophobic character of its surface, but also by the extent to which the adsorbent surface is made up of micro-pores. Since adsorption in such air-filled pores is essentially adsorption at a gas-liquid interface, the inversion of Traube's adsorption series becomes explicable. R. CUTHILL.

Validity of Traube's rule for active sugar carbon. E. LANDT and W. KNOP (Z. Elektrochem., 1931, **37**, 645—651).—The relative adsorption of propionic and valeric acid from EtOH solutions by active charcoal is in accordance with Traube's rule, but not when adsorption takes place from aq. solutions. E. S. HEDGES.

Hydrolytic adsorption of activated charcoal. J. N. MUKHERJEE and S. P. ROYCHOUDHURY (Nature, 1931, **128**, 412).—A discussion. L. S. THEOBALD.

Adsorption of weak electrolytes from neutral salt solutions. A. SKAAPSKI (Bull. Acad. Polonaise, 1931, **A**, 20—30).—The possibility of determining activity coeffs. by the determination of the adsorption of a weak electrolyte in neutral salt solutions is considered and found not to provide a general method. A. J. MEE.

Adsorption of acids by silica. M. P. LAKHANI (Proc. XV Indian Sci. Cong., 1928, 134).—SiO_2 produced by interaction of SiF_4 with H_2O and dialysed for 7 days did not adsorb HCl or H_2SO_4. CHEMICAL ABSTRACTS.

Adsorption by silica gel from binary mixtures of liquids. B. S. RAO and H. M. CHANNABASAPPA (Proc. XV Indian Sci. Cong., 1928, 133).—Static and dynamic experiments indicated no selective adsorption with mixtures of CCl_4 and CS_2. CHEMICAL ABSTRACTS.

Adsorption and capillary condensation. P. KUBELKA (Z. Elektrochem., 1931, **37**, 637—640).—A theoretical investigation of the condensation of vapours in capillaries leads to the view that capillary condensation plays a greater part in processes of adsorption than has been supposed. E. S. HEDGES.

Inner adsorption in crystalline salts. III. D. BALAREV (Kolloidchem. Beih., 1931, **33**, 279—316; cf. A., 1930, 684).—The mosaic structure of crystals is held to account for the phenomena of inner adsorption, impurities being almost universally distributed in the channels between the "lattice blocks" and sometimes adding to the stability of the crystal as a whole. $BaSO_4$ crystals are always impure and when exhaustively washed disintegrate into the units of the mosaic structure, which are readily peptised. Inner adsorption is characteristic, not only of impurities in crystals, but also of certain types of supposed mixed crystals, electrolytes in gels, and H_2O in pure crystals of "anhyd." salts, hydrophilic colloids and zeolites. The chemical composition of the material thus adsorbed is never in agreement with the simple stoicheiometric relation. E. S. HEDGES.

Distinguishing features between adsorption by a substance in a hydrated and a dehydrated condition. M. P. V. IYER (Proc. XV Indian Sci. Cong., 1928, 132—133).—Certain dehydrated org. acids show scarcely any change in p_H val. or electric charge when kept in contact with neutral salt solutions; changes are observed with hydrated acids. Irreversible coagulation and charge reversal are explained. CHEMICAL ABSTRACTS.

Calculation of the true adsorption. K. S. G. DOSS (J.C.S., 1931, 2027—2028).—A graphical method is given for solving Williams' equation, as modified by Jones and Outridge (A., 1930, 1109), for the true adsorption of one component from a solution. C. W. DAVIES.

Calculation of the heats of adsorption of atomic silver and atomic halogen on silver chloride, bromide, and iodide on the basis of photo-, thermo-, and electro-chemical data. H. H. SCHMIDT (Z. wiss. Phot., 1931, **30**, 147—156).—The discrepancy between the thermochemical and apparent photochemical heat of dissociation of Ag halide is accounted for by the secondary reactions: (*a*) adsorption of Ag and halide atoms on AgBr, (*b*) condensation of these atoms to mols. The heats of these reactions are calc. The primary dissociation is independent of light intensity, but this is not the case for reaction (*b*). Sufficient energy is not available for the condensation of I atoms. The formation of the latent image, reciprocity failure, and other phenomena are discussed in relation to these considerations. J. LEWKOWITSCH.

Method of studying surface films. E. GORTER and W. A. SEEDER (Nature, 1931, **128**, 413).—Waves produced at the surface of a unimol. film of ergosterol or protein by an electrically-driven tuning fork show a diminution of amplitude. L. S. THEOBALD.

Electro-kinetics and significance of surface conductivity. J. W. McBAIN and R. DU BOIS (Z. Elektrochem., 1931, **37**, 651—655).—Theoretical. E. S. HEDGES.

Oxide hydrates and active oxides. XLV. Properties of the interface between two solid phases. G. F. HUTTIG (Z. Elektrochem., 1931, **37**, 631—636).—Experimental results indicate that, in reactions of the type AB (solid)$\longrightarrow$A (solid)+B (gaseous), the independence of v. p. on the amount of solid phase, the velocity with which the saturation pressure is established, and the rate at which the solid phase enters into or catalyses any other reactions must be explained by the peculiar state of mols. at the interface of the solid phases. E. S. HEDGES.

Electro-endosmosis in closed cylindrical tubes of large diameter. B. W. CURRIE (Phil. Mag., 1931, [vii], **12**, 429—438).—The electro-endosmotic velocity of a liquid has a parabolic distribution across closed cylindrical tubes of large as well as of small diameter (cf. Physical Rev., 1924, **23**, 396; A., 1930, 858), and is independent of the diameter of the tube. For H_2O having sp. conductivity $1{\cdot}0$—$1{\cdot}6\times10^{-6}$ mho, the velocity along the axis of a SiO_2 tube is $0{\cdot}69\times10^{-4}$ cm./sec./volt/cm. The cataphoretic velocity of a particle depends on its shape, the correct vals. of the numerical factor appearing in the Debye–Hückel equation being $1/4\pi$ and $1/6\pi$ for a cylinder and sphere respectively. N. H. HARTSHORNE.

Influence of conductivity of electrolytes on the charge of diaphragms. N. SCHONFELDT (Z. Elektrochem., 1931, **37**, 734—736).—The relation between the electrokinetic potential of a porcelain membrane and the concentration (between 0·1 and 1·0%) of the electrolyte is far from linear for solutions of KCl and $BaCl_2$, but approaches a linear form for $AlCl_3$, $Th(NO_3)_4$, and NaOH, which give ions of greater electrokinetic activity. Probably both concentration of electrolyte and adsorbability of ions are involved. E. S. HEDGES.

Influence of reaction electrolytes on periodic structures of lead chromate. H. ERBRING (Kolloid-Z., 1931, **56**, 194—200).—The addition of the reaction electrolyte KOAc in concentrations above a limiting val. affects the conditions of precipitation of $PbCrO_4$ by reaction of $Pb(OAc)_2$ with $K_2Cr_2O_7$. The turbidity max. is displaced in the direction of more $K_2Cr_2O_7$ by adding increasing quantities of KOAc. The reaction appears to be reversible in the sense of the law of mass action. E. S. HEDGES.

General theory of solutions. R. C. CANTELO (J. Physical Chem., 1931, **35**, 2357—2363).—A brief review. L. S. THEOBALD.

Theory of hydrotropic solutions. A. VON KUTHY (Biochem. Z., 1931, **237**, 380—395).—Hydrotropic solutions of org. fluids (amyl alcohol, NH_2Ph, PhCHO, quinoline, $PhNO_2$, and paraldehyde) were investigated and a far-reaching analogy is found with the hydrotropic solutions of solids (benzoic and phthalic acids, brucine). Attention is directed to the similarity of emulsification and hydrotropic solution and a general theory is developed. P. W. CLUTTERBUCK.

Molecular complexity. S. N. SEN (Z. anorg. Chem., 1931, **199**, 427—428).—For solutions of various hydrocarbons and NO_2-compounds in org. solvents the val. of $\log \sqrt{c}/F$, where c is the concentration and F the association factor, is, for a given solute, a const., usually about 1·5, independent of the solvent. R. CUTHILL.

Velocity of diffusion of strong electrolytes in dilute solution. G. S. HARTLEY (Phil. Mag., 1931, [vii], **12**, 473—488).—Theoretical. Three equations for the diffusion velocity are deduced on the basis of the activity function by making different assumptions, and are compared with the experimental results for HCl, KCl, NaCl, KOH, KNO_3, H_2SO_4, and K_2SO_4. N. H. HARTSHORNE.

Theory of molecular volumes of dissolved electrolytes. II. O. REDLICH and P. ROSENFELD (Z. Elektrochem., 1931, **37**, 705—710).—Theoretical. Existing data for solutions of electrolytes in MeOH are examined in the light of previous work (A., 1930, 560, 905). E. S. HEDGES.

Apparent volumes of salts in solution. I. Test of Masson's empirical rule. A. F. SCOTT (J. Physical Chem., 1931, **35**, 2315—2329).—Masson's empirical rule $\phi=am^{0.5}+b$, where ϕ is the apparent mol. volume of a salt in H_2O, m is no. of mols. per litre, and a and b are consts. (cf. A., 1930, 31), is found to be supported by Baxter and Wallace's data (A., 1916, ii, 219). The const. a depends on the valency factor and is related to inter-ionic distances. This suggests that a basis for the equation may be found in the interaction of ionic forces. L. S. THEOBALD.

Electrostriction. A. L. T. MOESVELD and H. J. HARDON (Z. physikal. Chem., 1931, **155**, 238—256).—From vol. measurements with aq. solutions of a series of isomeric complex Co salts it has been possible to determine how much of the contraction which occurs on dissolution really represents electrostriction and would not occur if the constituents of the solution were without charge; the effect of the charge is clearly shown. The hydrolysis of the amides of the fatty acids to the corresponding NH_4 salts is accompanied by a change in vol., which is partly due to the charge on the ions formed. When $AgClO_4$ is dissolved in C_6H_6 the contraction is much greater than when H_2O is the solvent, which indicates that mol. forces, as well as interionic forces, may cause considerable changes in vol. Compressibility measurements with aq. solutions of various electrolytes over a concentration range of about 0·5—5% have shown that electrostriction diminishes considerably as the pressure rises; the results are used to calculate the degree of hydration of the electrolytes. R. CUTHILL.

Interferometric determination of refractive indices of dilute solutions. A. E. BRODSKI and J. M. SCHERSCHEVER (Z. physikal. Chem., 1931, **155**, 417—430).—The refractive indices of aq. solutions of KCl and KNO_3 have been measured by a new interferometric method, which for high dilutions is capable of far greater precision than the refractometer. R. CUTHILL.

Influence of temperature on the equivalent refraction of strong electrolytes in solution. I. P. HÖLEMANN and H. KOHNER. **II.** Z. SHIBATA and P. HÖLEMANN. **III.** K. FAJANS, P. HÖLEMANN, and Z. SHIBATA (Z. physikal. Chem., 1931, **B**, **13**, 338—346, 347—353, 354—371; cf. A., 1929, 1233).—The temp. coeff. of the apparent equiv. refraction at infinite dilution of NaCl, KBr, $NaClO_4$, KCl, NaBr, NH_4Cl, KI, and $BaCl_2$ between 25° and 45° is in all cases positive and lies between 2·5 and $6{\cdot}5\times10^{-3}$, which is much greater than that of the equiv. refraction of free inorg. substances, whether solid, liquid, or gaseous. This is mainly due to a decrease in the refractometric "solution effect" (*i.e.*, the effect due to the forces between the ions and the solvent mols.) with rise of temp., the sum of the "solution effects"

of the cation and anion being therefore negative. The results demonstrate that K˙ and Ba˙˙ and either Cl′ or I′ have a "solution effect" as well as Na˙ (cf. A., 1924, ii, 372). As regards the change of equiv. refraction with concentration (NaCl>KCl)<(NaBr~KBr)<(NaI<KI), and on the assumption that the change is due to association of the ions, the results can be correlated with the osmotic coeffs. of the salts. The effect of temp. on this change is not sufficiently marked to permit any certain conclusions about the temp. coeff. of the association.

N. H. HARTSHORNE.

Electrical and individual properties of electrolyte solutions. E. LANGE and H. STREECK (Z. Elektrochem., 1931, 37, 698—704).—Theoretical considerations suggest that at sufficiently high dilution the properties of equiv. salts will be determined solely by the charges of the ions. Measured heats of dilution of 17 unibivalent salts in $M/5000$ solution still show marked individual properties. The results are discussed in relation to the Debye–Hückel theory.

E. S. HEDGES.

Capillary systems. XII. Mathematical treatment of ideal packing of spheres and the hollow-space volumes of actual structures. E. MANEGOLD, R. HOFMANN, and K. SOLF (Kolloid-Z., 1931, 56, 142—159).—Mathematical.

E. S. HEDGES.

Dielectric relations of disperse systems. R. FRICKE (Kolloid-Z., 1931, 56, 166—170).—A summary of previously published work. E. S. HEDGES.

Formation of silver sol prepared by dispersion in the electric arc. P. S. MACMAHON and S. C. VARMA (Proc. XV Indian Sci. Cong., 1928, 136).—The deposit obtained by Fürth's method contains oxide and nitrate. In N_2 practically no deposit was formed. Finely dispersed Ag appears to become oxidised in air or O_2. CHEMICAL ABSTRACTS.

Properties of silver sols prepared by Kohlschütter's method. R. P. P. MATHUR and N. R. DHAR (Z. anorg. Chem., 1931, 199, 392—399).—Ag sols may be prepared by reduction of a suspension of Ag_2O by H_2 at temp. as low as 50°, the presence of alkali not being essential. With increasing concentration of such sols the concentration of free OH′ ions diminishes, but on ageing, OH′ ions are set free. The constitution of a stable sol is probably represented by $[Ag_6,Ag_2O,H_2O]'H^{\cdot}$. R. CUTHILL.

Tungstic acid hydrosol. A. R. NORMAND and M. C. MUTHANNA (Proc. XV Indian Sci. Cong., 1928, 137).—A fairly sensitive sol is obtained by peptising WO_3 with an acid and an alkali. The coagulating power diminishes in the order RbCl, KCl, NaCl, LiCl; the protective influence increases in the order Cl′, Br′, I′. CHEMICAL ABSTRACTS.

Behaviour of calcium, strontium, and barium fluoride suspensions towards electrolytes. G. G. KANDILAROV (Kolloid-Z., 1931, 56, 200—204).—Suspensions of CaF_2, SrF_2, and BaF_2 in H_2O are positively charged. Capillary-active anions (*e.g.*, those of the fatty acids) are strongly adsorbed and lead to precipitation; other anions are less effective. Dil. solutions of salts of alkali or alkaline-earth metals stabilise the suspensions, but more conc. solutions coagulate them. The changes are traced to exchange adsorption. The greater stabilising effect of the Na salts over K salts is attributed to the greater hydration of the Na ion. E. S. HEDGES.

Organic acid iron solutions. II. Colloidal properties. N. J. HARRAR and F. E. E. GERMANN (J. Physical Chem., 1931, 35, 2210—2218; cf. this vol., 891).—Dialysis, Tyndall effects, and diffusion experiments with the org. acid–Fe combinations previously described support the view that the strength of the acid is the chief factor which determines colour and structure. In many respects the properties of colloidal $Fe(OH)_3$ resemble those of the preps. with weak acids which, however, all appear to contain Fe in true solution. Some type of equilibrium between several different complexes appears necessary to explain the results obtained. L. S. THEOBALD.

Alcogel of silica. B. S. RAO and K. G. DOSS (Proc. XV Indian Sci. Cong., 1928, 133).—Replacement of the H_2O envelope by EtOH becomes progressively difficult with decrease in H_2O content.

CHEMICAL ABSTRACTS.

Viscosity and adsorption in colloidal solutions. E. O. KRAEMER and G. R. SEARS (J. Rheology, 1931, 2, 292—305).—The relative viscosities of dil. solutions of a series of related cellulose nitrates in $COMe_2$ and in "cellosolve" have been measured at 25° and 45°. Applying Einstein's equation, the viscous properties are characterised by the "sp. hydrodynamic vol.," ϕ/c (defined as $[\eta_s-\eta_0]/2{\cdot}5\,\eta_0 c$), which is the sp. vol. of a substance which in the same wt.-concentration would give a suspension having the same viscosity as the colloid if the particles of the suspension were small, compact, rigid spheres. The hydrodynamic properties of highly viscous colloidal solutions are ascribed mainly, although not entirely, to the presence of highly porous, felt-like particles. E. S. HEDGES.

Lyophilic colloids. II. M. VOLMER (Z. physikal. Chem., 1931, 155, 281—284; cf. A., 1927, 308).—An equation connecting the apparent mean mol. wt. with the density and the surface tension of a colloidal dispersion is obtained, and the effect of the charge on the stability investigated. R. CUTHILL.

Determination of charge of a micelle. (MLLE.) S. FILITTI (Compt. rend., 1931, 192, 1731—1733).—Using Marinesco's method (cf. A., 1928, 119) the p_H of a solution of KOH, p_H 11·6—11·7, is shown to be diminished by the addition of 0·4% Congo-red, 0·3% eosin, and 0·5% rose-Bengal to 9·6, 9·1, and 8·3, respectively, and of 1% animal charcoal by about 0·2. The relative lowering is greater for small concentrations of KOH. The effect depends on the extent of surface of the added material, and indicates adsorption of a number of ions per micelle or mol. which increases with decreasing concentration, but tends to a limit, *e.g.*, 11 in the case of rose-Bengal.

C. A. SILBERRAD.

Colloidal chemical analysis. I. J. MUKHERJEE, S. ROYCHOUDHURY, and M. BISWAS (J. Indian Chem. Soc., 1931, 8, 373—389).—Experiments with a hydrosol of $Fe(OH)_3$ show that the coagulating concentration of bi- and ter-valent anions decreases on

dilution, whilst that of KCl remains const. so long as the time of coagulation is const. If the time is made proportional to the dilution the electrolyte shows a sensitisation, indicating a change in the condition of the particles. Ultrafiltration produces a change in the composition of the intermicellar liquid. Measurements of cataphoretic velocity in relation to the composition of the intermicellar liquid do not support the supposed existence of a crit. coagulating potential.

E. S. HEDGES.

Influence of electrolytes on coagulation of ceric hydroxide hydrosol heated at different temperatures. A. R. NORMAND and M. C. MUTHANNA (Proc. XV Indian Sci. Cong., 1928, 135).—The order of diminishing coagulating power of the chlorides with sol dialysed at 28° is Li, Na, K, Rb; with sol dialysed at 28° and heated at 70°, Li, Na, Rb, K; with sol dialysed at 28° and heated at 100°, K, Rb, Li, Na. CHEMICAL ABSTRACTS.

Coagulation of colloids from the viewpoint of Smoluchowski's theory. II. Coagulation of arsenious sulphide sol. S. S. JOSHI and S. M. PRABHU (J. Indian Chem. Soc., 1931, **8**, 337—343).—The Smoluchowski const., β, decreases appreciably soon after the start of coagulation. Contrary to the requirements of the theory, the bimol. const., k, diminishes during coagulation. Slow coagulation cannot be considered as autocatalytic in general.

E. S. HEDGES.

Irreversible processes in colloidal systems and theory of sorption hysteresis. B. ILJIN (Z. physikal. Chem., 1931, **155**, 257—266).—A theory of sorption hysteresis in colloidal systems is described, and an equation for the hysteresis isotherm derived. The methods used are also applicable to such processes as irreversible sedimentation and the irreversible effect of temp. on swelling. R. CUTHILL.

Emulsification at interfaces by an electric current. M. P. V. IYER and P. B. GANGULY (Proc. XV Indian Sci. Cong., 1928, 134).—Emulsification at the interface between $PhNO_2$ and H_2O containing a polyiodide depends on the formation of complex hydrated polyiodide ions in both phases.

CHEMICAL ABSTRACTS.

Micellar structure of graphitic acid. H. THIELE (Kolloid-Z., 1931, **56**, 129—138).—The structure of graphitic acid is related to that of the graphite from which it is obtained, the more cryst. graphite giving a more cryst. product having stronger swelling properties; the optical properties are also related. Graphitic acid swells in H_2O and in other liquids of high dielectric const. and forms hydrosols spontaneously, especially in presence of traces of NaOH, NH_3, and lower amines. Sols are readily formed also in EtOH, $COMe_2$, and AcOH. Two kinds of colloidal solutions (suspensions and micellar solutions), differing in viscosity and in optical properties, are distinguished. The sol particles are negatively charged and are flocculated by cations in the series $K<Ca<Al<Ce$. Small amounts of alkaloids and other high-mol. bases coagulate the sols, but the influence of corresponding acid substances is small. The viscosity and optical anisotropy of the sols increase with increasing size of the flakes. Graphitic acid has no protective effect on red Au sols, but is protected by humic acid, tannic acid, and starch. Rapid coagulation of the sols produces amorphous particles, whilst slow coagulation gives rise to membranes. Adsorption takes place by exchange of cations. E. S. HEDGES.

Soluble starch. B. RASSOW and M. LOBENSTEIN (Kolloidchem. Beih., 1931, **33**, 179—253).—Heat is liberated when NaOCl is added to potato-starch, partly due to decomp. of NaOCl to NaCl and O_2 and partly to oxidation of the starch. The addition of $HClO_3$ accelerates the rate of evolution of heat, but produces a decrease in the total amount of heat evolved. The acidity of the starch causes the formation of HOCl and HCl and the evolution of Cl_2, which acts on the starch together with O_2; the existence of the HCl is too transient to have any hydrolysing effect. The acidity of sol. starch increases with time, especially during the first 3 months, becoming const. after 12—18 months; the increase is due to the oxidation of –CHO groups to $-CO_2H$. Sol. starch contains dextrin-like reducing compounds, the reducing power increasing with the amount of NaOCl treatment of the starch. The viscosity of solutions of sol. starch is considerably lower than that of native starch solutions, and is still further depressed by the addition of K_2CO_3, Na_2CO_3, $NaHCO_3$, or $Na_2B_4O_7$. Sol. starch is coloured rather less strongly than native starch by basic dyes; acid dyes have relatively little effect, but colour the sol. starch more strongly. Analysis of the Ba compounds indicates the presence of di- and tetra-amylose in an exhaustively treated starch and of tetra- and hexa-amylose in a starch treated with less NaOCl.

E. S. HEDGES.

Plant colloids. XXIX. Migration velocity of starch substances. M. SAMEC [with D. ANDRIC] (Kolloidchem. Beih., 1931, **33**, 269—278).—The migration velocity of constituents of potato-starch has been measured by Hittorf's transport method with the Engel–Pauli apparatus. The amylopectin migrates most rapidly, in spite of its strong hydration, and the amylose migrates more rapidly than the erythro-amylose. The PO_4 group must account for a great part of the electric charge. E. S. HEDGES.

Measurements of structure-viscosity of cellulose derivatives in organic solvents and the influence of additions on their viscosity. II. Y. NISIZAWA (Kolloid-Z., 1931, **56**, 179—194; cf. this vol., 1008).—The influence of various substances on the structure-viscosity of cellulose nitrate solutions in $EtOH-Et_2O$ and $COMe_2$ has been examined. H_2O causes a rise of viscosity and a widening of the structure-viscosity region. Inorg. salts lower the viscosity slightly at first and then coagulate the sol, producing a rise of viscosity and an increase of structure-viscosity. Light petroleum and C_6H_6 lower the viscosity, but displace the region of structure-viscosity towards higher pressures, showing that a decrease of viscosity is not necessarily concomitant with decrease of the structural region. Camphor, carbamide, and linseed oil lower the viscosity, and sunflower oil raises it. The addition of EtOH to cellulose nitrate in $COMe_2$ raises the viscosity and the structure-viscosity; amyl alcohol lowers the viscosity. E. S. HEDGES.

Condition of sparingly-soluble substances in gelatin. T. R. Bolam (Nature, 1931, **128**, 222—223).—Liesegang rings of AgCl in gelatin have been obtained (cf. A., 1926, 1005). The conclusion (this vol., 687) that gelatin behaves differently towards AgCl and Ag_2CrO_4 is apparently not justified.

L. S. Theobald.

Condition of sparingly-soluble substances in gelatin. S. C. Bradford (Nature, 1931, **128**, 223). —A criticism (cf. this vol., 687). L. S. Theobald.

Condition of sparingly-soluble substances in gelatin. B. N. Desai (Nature, 1931, **128**, 223).—A reply to criticism (cf. preceding abstracts).

L. S. Theobald.

Evidence in favour of the existence of silver chromate in gelatin in the colloidal condition. Electric conductivity of silver chromate in gelatin. A. C. Chatterji and S. C. Varma (Proc. XV Indian Sci. Cong., 1928, 142—143).—Measurements are stated to support the above view.

Chemical Abstracts.

Growth of lead crystals in silica gels. R. Taft and J. Stareck (J. Chem. Educ., 1930, **7**, 1520—1536).—The effects of variations in the conditions were studied. Chemical Abstracts.

Emulsifying properties of gelatin systems. L. Friedman and D. N. Evans (J. Amer. Chem. Soc., 1931, **53**, 2898—2901; cf. A., 1920, ii, 742).—The variation of concentration of gelatin between 0·25 and 1·5% has, in general, little effect on the stability of emulsions of H_2O with C_6H_6, CCl_4, $CHCl_3$, $PhNO_2$, and cottonseed oil at p_H 3, 4·7, and 6. At p_H 3 and with 0·25% of gelatin, the stability is much less. The emulsifying properties of gelatin change with p_H in a manner closely related with the changes of surface tension and viscosity of its solutions. Gelatin is concentrated at the interface in stable emulsions.

J. G. A. Griffiths.

Membrane potential and adsorption of hydrogen ions by gelatin and albumin. B. N. Ghosh (Z. physikal. Chem., 1931, **155**, 285—288).—Membrane potential may be calc. from the concentration of protein and H ions by means of the principles of adsorption equilibrium. R. Cuthill.

Salting-out of gelatin sols by salt mixtures. E. H. Buchner and G. Postma (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 699—702).—The salting-out effects produced by mixtures of Na_2SO_4 and other Na salts with gelatin sols at 40° and $p_H \simeq 6$ follow the same sequence as with agar sols. Differences in the behaviour of particular salts are discussed.

W. R. Angus.

Influence of surface-active substances on permeability. A. von Kuthy (Biochem. Z., 1931, **237**, 396—405).—Tables show the influence of various surface-active substances (NaOBz, Ph acetate, propionate, and cinnamate) and of MeOH, EtOH, PrOH, carbamide, urethane, and phosphate buffer on the swelling of gelatin and on the diffusion velocity of dyes in gelatin gels. Considerably greater swelling is obtained with the surface-active substances than with H_2O.

P. W. Clutterbuck.

[Union of] gelatin with ammonia and hydrogen chloride. B. C. Belden (J. Physical Chem., 1931, **35**, 2164—2193).—Equilibria between powdered gelatin and NH_3 or HCl have been investigated by the methods previously described (A., 1930, 700). Gelatin and NH_3 show adsorption but no compound formation; the amount of adsorption varies with the sample of gelatin but is independent of the degree of fineness of the powder. The presence of certain impurities lowers adsorption at least temporarily. Adsorption cannot be used as a means of differentiating between various samples. The hydrolysis products of gelatin combine with NH_3 (0·041 g. per g. of hydrolysed product), and this agrees with the assumption that NH_3 unites with the glutamic and aspartic acids, the proline, hydroxyproline, and histidine of the hydrolysed product. After this combination, NH_3 is adsorbed. Gelatin and HCl combine (0·110 g. HCl per g. of gelatin), and then adsorption takes place. Gelatin darkens and finally decomposes in HCl. The hydrolysed products combine with HCl to a greater extent (1 g. to 0·290 g. HCl). The results are opposed to the view that proteins always react stoicheiometrically with acids and bases to form definite compounds.

L. S. Theobald.

Influence of bases on heat-coagulation of proteins. L. Nasch (Biochem. Z., 1931, **237**, 343—346).—In an attempt to obtain a relation between the free NH_2 and CO_2H groups of a protein and the amount of base which inhibits the heat-coagulation of the same protein, it is shown that the amount of NaOH corresponding with these groups is the smallest amount which prevents heat-coagulation of horse-serum proteins and albumin.

P. W. Clutterbuck.

Dielectric constants of albumin solutions. V. Vlassopoulos and F. Blank (Kolloid-Z., 1931, **56**, 176—179).—Measurements of the dielectric consts. of solutions of serum-albumin in the presence of varying quantities of acid and alkali indicate that the NH_2 and CO_2H radicals are symmetrically disposed over the surface of the serum-albumin mol.

E. S. Hedges.

Nature of the biological action of alcohols. M. Mitolo (Mem. R. Accad. Naz. Lincei, 1930, [vi], **4**, 116—165).—Changes in the sp. gr., drop no., and surface tension of solutions of egg-albumin, with or without electrolytes or non-electrolytes, by continued addition of EtOH, are recorded and discussed. The true sp. gr. of all the systems studied is always increased, irrespective of the amount of EtOH added, except that alcohol in precipitating proportion lowers the true sp. gr. of the system, H_2O–egg-albumin–$MgSO_4$. In all cases the drop no. (obtained with the stalagmometer) increases (decreases) and the surface tension diminishes (increases) if the alcohol is added in non-precipitating (precipitating) amount.

T. H. Pope.

Dielectric properties of casein gels. W. Haller (Kolloid-Z., 1931, **56**, 170—176).—A method for measuring the dielectric polarisation of powders is described. The data obtained with moist casein gels indicate that with rising H_2O content the sp. polarisation increases strongly; this cannot be explained by the dipole theory alone. It is probable that the gel is a honeycomb structure isolating spaces containing H_2O of high conductivity. When the H_2O

content reaches 20% the honeycomb structure begins to break down, the dielectric polarisation reaches the val. 1, and simultaneously the electric conductivity rises. The opening of the structure also produces a marked increase in plasticity. E. S. HEDGES.

Extent of dissociation of salts in water. III. W. H. BANKS, E. C. RIGHELLATO, and C. W. DAVIES (Trans. Faraday Soc., 1931, 27, 621—627; cf. A., 1930, 1371).—The degrees of dissociation and dissociation consts. of various uni-univalent and uni-bivalent salts have been calc. from available conductivity data. The corrections for incomplete dissociation remove the anomalies in the activity values of the uni-bivalent salts in dil. solutions.

R. CUTHILL.

Dissociation of alkali salts of carboxylic acids. Heats of dilution and activity coefficients of alkali citrates. A. WASSERMANN (Z. physikal. Chem., 1931, 155, 378—391).—Theoretical. Since the integral heats of dilution of the Na citrates in aq. solution, instead of being positive as would be anticipated from the complete ionisation theory, are negative, it is probable that, in solutions of the normal citrate at least, ionisation is incomplete, and that when further ionisation occurs heat is absorbed. The variation of the activity coeffs. of the citrate ions in a solution of citric acid containing an alkali chloride at a given concentration when the cation of the chloride is varied does not agree with the Debye–Hückel equation, this discrepancy being ascribed to the presence of variable amounts of undissociated citrate. This explanation would require that if the anion instead of the cation of the alkali salt is varied the activity coeffs. will vary normally, and this is so.

R. CUTHILL.

Electrolytic dissociation of transitional-metal salts. I. Copper, zinc, and nickel malonates. D. J. G. IVES and H. L. RILEY (J.C.S., 1931, 1998—2012; cf. A., 1929, 1237).—The conductivities of Cu, Zn, and Ni malonates and of Cu and Zn methyl-, ethyl-, propyl-, *iso*propyl-, dimethyl-, diethyl-, and dipropyl-malonates have been measured in aq. solution at 25° over a wide concentration range. The dissociation consts. are of the order $K=5\times10^{-6}$ for the Cu salts, Ni malonate being stronger and the Zn salts stronger still. A trend in K with increasing concentration, most noticeable in the Cu salts, is probably due to complex anion formation. The dependence of K on the nature of cation and anion is discussed. C. W. DAVIES.

Complex salts. IV. Effect of alkyl substitution on the tendency of the aminoacetate ion to co-ordinate with copper. H. L. RILEY and V. GALLAFENT (J.C.S., 1931, 2029—2034; cf. A., 1930, 1120).—Mixtures of $0.02N$-$CuSO_4$ with various Na aminoacetates have been examined in concentration cells with Cu electrodes. Very stable complexes are present and are assigned formulæ of the type $[Cu(NH_2\cdot CH_2\cdot COO)_3]'$. Substitution in the CH_2 group has little effect on the tendency to co-ordination, but substitution of an NH_2-H atom to form phenylglycine greatly reduces it. C. W. DAVIES.

Effects of hydrocarbon groups on the strength of carboxylic acids. J. O. HALFORD (J. Amer. Chem. Soc., 1931, 53, 2944—2953; cf. this vol., 1127).—The relative strengths of 31 carboxylic acids and 2 phenols in $0.1M$-LiCl in a 60 vol.-% diethylene glycol Bu ether–H_2O mixture have been determined at 23° by means of the Sb electrode, and the results compared with the vals. for H_2O and 50 vol.-% aq. EtOH solutions (cf. A., 1925, ii, 793, 867). Owing to sp. solvent effects, observed relative strengths differing by less than one pK unit (or a factor of 10 in the dissociation const.) are not necessarily indicative of differences of intrinsic acidity. Either lengthening or branching of the hydrocarbon chain of aliphatic acids decreases the strength, but the introduction of aromatic hydrocarbon radicals is without effect.

J. G. A. GRIFFITHS.

Electrometric titration curves of dibasic acids. IV. Corrections for interionic effects and for solvent electrostriction. First and second dissociation constants of some *n*-paraffin-αω-dicarboxylic acids, alkyl- and dialkyl-malonic acids, *s*-di- and -tetra-alkylsuccinic acids, β-alkyl- and ββ-dialkyl-glutaric acids, and cyclic 1 : 1-diacetic acids. Configurations and molecular dimensions of these acids in dilute aqueous solution. R. GANE and C. K. INGOLD (J.C.S., 1931, 2153—2169).—Figures for the acids named are corrected for interionic attraction effects by an empirical extrapolation, and the calculation of r, the distance between the charges of the bivalent anion, is further modified in accordance with calculations outlined elsewhere (cf. following abstract). For the normal acids the applicability of a pliable and extensible mol. model, in which the dominant force is ionic, is tested and discarded in favour of a rigid uniplanar zig-zag model having an intervalency angle of 114° and an increase in length per CH_2 group of 1·29 A. (cf. A., 1929, 126); in the CO_2H group the ionic centre is distant 1·00 Å. from the C atom in the direction of the C·C linking. The deduction from measurements in dil. solutions of this structure implies that it is commonly occasioned by intramol. forces. The data for the substituted acids bear out earlier conclusions (A., 1928, 1083; 1929, 1144), and in their minor variations support the valency deflexion hypothesis. C. W. DAVIES.

Electrical and mechanical conditions in the neighbourhood of a dissolved ion. C. K. INGOLD (J.C.S., 1931, 2179—2190).—The calculation of the mutual potential of two ions in an " ideal " solvent (one which obeys Mosotti's law and is incompressible) is corrected, in the case of H_2O, for the associated nature of the solvent, its optical and electrical anisotropy, the anisotropy of the local inner field, the density variation on account of electrostriction, and the effect of this last factor on the consts. of permanent and temporary polarisation. Vals. are tabulated for the potential, electric intensity, pressure, and density in the neighbourhood of a dissolved ion down to distances of 2.25×10^{-8} cm. C. W. DAVIES.

Degrees of hydration of the alkyl amines in aqueous solution. W. C. SOMERVILLE (J. Physical Chem., 1931, 35, 2412—2433).—F.-p. curves suggest the formation of $NMe_3,10H_2O$ instead of $NMe_3,11H_2O$; the hydrate $NHEt_2,3H_2O$ may exist. The order of

hydration of Me and Et amines appears to be mono< di<tri. A method for deducing degree of hydration from conductivity data, which are tabulated, is suggested. The order of hydration appears to correspond with the order of internal pressure; the greater is the difference between the internal pressure of an amine and H_2O, the greater is the degree of hydration. Densities and viscosities at 0° and 25° for the Me and Et series have been determined. L. S. THEOBALD.

Thermodynamics of nitrogen-oxygen compounds. E. ABEL, H. SCHMID, and W. SIMON (Z. Elektrochem., 1931, **37**, 626—630).—The reaction between Ag and HNO_3 under appropriate conditions reaches an equilibrium for which $_{0_2}p_{NO}/a_{HNO_3}=4\cdot8\times10^7$, where a denotes the activities. The result leads to thermodynamical data for other reactions involving oxides of N. E. S. HEDGES.

Activity coefficients of sulphuric acid in anhydrous acetic acid. A. W. HUTCHISON and G. C. CHANDLEE (J. Amer. Chem. Soc., 1931, **53**, 2881—2888).—The e.m.f., E, of the cell H_2,Pt|0·0025—0·9M-H_2SO_4 in anhyd. AcOH|Hg_2SO_4,Hg has been determined at 25°. The activity coeffs., γ, of H_2SO_4 in anhyd. AcOH have been evaluated by means of Hückel's modification of the Debye–Hückel equation for strong electrolytes and agree with values given by $E=0\cdot181-0\cdot08872\log(\gamma m4^{1/3})$.

J. G. A. GRIFFITHS.

Influence of higher terms of the Debye–Hückel theory in the case of unsymmetric valency type electrolytes. V. K. LAMER, T. H. GRONWALL, and L. J. GREIFF (J. Physical Chem., 1931, **35**, 2245—2288).—The second and third order terms in the complete solution of the Debye equation (A., 1928, 841) are evaluated and their influence is investigated for electrolytes of unsymmetrical valency types. The theoretical curves obtained are compared with e.m.f., f.-p., and solubility data; better agreement results than is the case when only the first approximation of the equation is employed. Further, the vals. required for the closest distance of approach of two ions are more plausible and more consistent. The validity of the Debye–Hückel theory is considered to be established. L. S. THEOBALD.

Relation between relative strengths of acids in two solvents. J. O. HALFORD (J. Amer. Chem. Soc., 1931, **53**, 2939—2943).—Equations relating the strengths of acids in two solvents by means of solubility data are derived and discussed (cf. A., 1927, 828). Results for AcOH, BzOH, salicylic, o-nitrobenzoic, and α-naphthoic acids in H_2O and 50% aq. EtOH are recorded. J. G. A. GRIFFITHS.

Hydrogen effect. L. WOLF (Z. Elektrochem., 1931, **37**, 619—622).—The H effect (A., 1930, 1391) increases with the concentration of neutral salt, is the same for NaCl, KCl, LiCl, and RbCl, and is const. for a given indicator. The magnitude of the true salt error depends more on the nature of the cation than of the anion. E. S. HEDGES.

Third-law calculation of entropy and free energy of ammonia. W. M. D. BRYANT (J. Amer. Chem. Soc., 1931, **53**, 3014—3015).—Recent low-temp. data lead to the mol. entropy 46·7 units at 298·1° abs. Using Giauque's val. for the entropy of H_2 (this vol., 294), the free energy of formation of NH_3 is $\Delta F_{298\cdot1}=-4150$, in better agreement with the experimental val. J. G. A. GRIFFITHS.

***V–T–X* model for binary mixtures as a supplement to Roozeboom's *P–T–X* model.** E. JANECKE (Z. Elektrochem., 1931, **37**, 585—588).—A method for the more complete representation of equilibria is described. E. S. HEDGES.

Affinity. IV. T. DE DONDER (Bull. Acad. roy. Belg., 1931, [v], **17**, 507—515; cf. this vol., 685).—Unary and binary systems containing an infinite no. of constituents are treated mathematically from the viewpoint of the first and second laws of thermodynamics. N. H. HARTSHORNE.

Fusion curves of binary systems forming a chemical compound. A. MLODZIEJOWSKI (Arch. Neerland., 1931, IIIA, **13**, 196—207).—Mathematical.

W. R. ANGUS.

Case of apparently isothermal "mixed m. p." C. W. GIBBY and W. A. WATERS (J.C.S., 1931, 2151—2152; cf. A., 1929, 1299).—For mixtures of 3 : 5-dibromo-4-amino- (m. p. 146·0°) and 3-bromo-5-iodo-4-amino-benzophenone (m. p. 145·9°) the max. f.-p. depression is only 1·4°. C. W. DAVIES.

Properties of metal hydrides. III. Titanium hydride. A. SIEVERTS and A. GOTTA (Z. anorg. Chem., 1931, **199**, 384—386; cf. A., 1930, 534).—The heats of combustion of Ti and $TiH_{1\cdot 73}$ have been found to be 220·1 and 247·8 kg.-cal. per mol., respectively, from which it follows that the heat of formation of $TiH_{1\cdot 73}$ from Ti and H_2 is 31·1 kg.-cal., and that when 1 mol. of H_2 combines with 1·16 g.-atoms of Ti the heat effect is 36·0 kg.-cal. R. CUTHILL.

Thermal dissociation of pyrites. L. D'OR (J. Chim. phys., 1931, **28**, 377—408).—The thermal dissociation of hexadiedric and triglyphic pyrites appears to give rise to a system in monovariant equilibrium comprising a gaseous phase and two solid phases, viz., hemihedral cubic pyrites, and a solution of S in FeS (holohedral hexagonal). The partial pressures of the S mol. (S_2, S_6, S_8) are calculable from $p=T\times10^{-A/T+B}$, where T is the temp., and A and B are consts. which depend on the no. of atoms constituting the S mol. Although it is assumed that no other S mols. are present, there are indications of a fifth mol. (cf. A., 1910, ii, 118) of secondary importance. The data given are therefore only a first approximation although the total pressure is given accurately by Σp. The thermochemical data for the equilibria between FeS_2, FeS, Fe, S (gas and solid), and S_2 are slightly higher (numerically) than those obtained by the indirect calorimetric method. The reaction FeS+S (vapour) FeS_2, which occurs readily in both directions at 500—700°, results from the simultaneous decomp. of FeS_2 into FeS and S or S_2, the former transformation being favoured by a rise in temp. The dissociation pressure data of Allen and Lombard (A., 1917, ii, 194) and of Kamura (B., 1921, 262) are not confirmed. J. GRANT.

M. p. and saturation points of sodium thiosulphate and sodium sulphate by the con-

ductivity method. C. ANAND and H. GOBIND (Proc. XV Indian Sci. Cong., 1928, 173).—Resistance–temp. curves for aq. Na_2SO_4 solutions show at the m. p. (33°) a discontinuity for all concentrations, and a second transition at the saturation point which varies with the concentration of the solution. The curves for $Na_2S_2O_3$ give two transition points; the m. p. varies between 45° and 50° with different concentrations. CHEMICAL ABSTRACTS.

Systems $AgNO_3$–$Ca(NO_3)_2$ and $AgNO_3$–$Ba(NO_3)_2$. A. P. PALKIN (Bull. Univ. Asie Centrale, 1929, **18**, 77—82).—In the system $AgNO_3$–$Ca(NO_3)_2$ there is one eutectic, at 80·7% $AgNO_3$ and 202°; no solid solutions are formed. The system $AgNO_3$–$Ba(NO_3)_2$ contains a eutectic at 96·5% $AgNO_3$ and 207°, *i.e.*, at 1° below the m. p. of $AgNO_3$. A compound $Ba(NO_3)_2,2AgNO_3$ has m. p. (decomp.) in the neighbourhood of 500°. No solid solutions are formed. H. F. GILLBE.

Vapour pressures and latent heats for the system $BaCl_2,8NH_3$–$BaCl_2$–NH_3. L. J. GILLESPIE and E. LURIE (J. Amer. Chem. Soc., 1931, **53**, 2978—2983; cf. A., 1927, 616).—The decomp. pressures of $BaCl_2,8NH_3$ between 0° and 50° are reproduced by $\log p$ (atm.)$=-1998\cdot04/T+7\cdot13333$ with an average deviation of $\pm0\cdot2\%$. Better agreement is obtained with the equation previously developed (this vol., 554). Latent heats of decomp. are calc. The low-temp. data of Huttig and Martin (A., 1923, ii, 72) are said to be in error. J. G. A. GRIFFITHS.

Thermodynamic investigation of the system iron–carbon–oxygen. H. DUNWALD and C. WAGNER (Z. anorg. Chem., 1931, **199**, 321—346).—The equilibrium CO_2 (gas) $+$C (dissolved in γ-Fe)$\rightleftharpoons$ 2CO (gas) has been investigated between 940° and 1070°, the solubility of graphite in γ-Fe at 940° being found by extrapolation to be about 1%. There is no evidence that CO or CO_2 as such is present in the solid phase. From a study of the equilibrium with α-Fe at 800° it appears that when α-Fe and γ-Fe coexist in equilibrium at 800° the concentration of C in the α-phase is about 0·008%, and that the solubility of graphite in α-Fe is about 0·025%. It is calc. that the solubility of O_2 in α-Fe at 800° or γ-Fe at 1000° is less than 0·01% (in equilibrium with wüstite). R. CUTHILL.

Perchlorates. I. C. SMEETS (Natuurwetensch. Tijds., 1931, **13**, 247—253).—The only eutectic in the system $Cu(ClO_4)_2$–H_2O at temps. below 114° occurs at $-50\cdot5°$ and 47% $Cu(ClO_4)_2$; the m. p. of $Cu(ClO_4)_2,6H_2O$ is 82·3°. At temp. above 100° $HClO_4$ is evolved from the solution. The only solid phase in the system $Cu(ClO_4)_2$–$HClO_4$–H_2O, when not more than 70% $HClO_4$ is present, is $Cu(ClO_4)_2,6H_2O$; there is no evidence of the formation of a compound $Cu(ClO_4)_2,2HClO_4,16H_2O$, and the production of a ppt. when the acid is added to a solution of the Cu salt is due solely to suppression of ionisation. H. F. GILLBE.

System $Mg(OH)_2$–KCl–H_2O at 25°. A. P. PALKIN (Bull. Univ. Asie Centrale, 1929, **18**, 73—76).—The solubility of KCl is not influenced by the presence of $Mg(OH)_2$, and that of $Mg(OH)_2$ is independent of the KCl concentration. The probability of the formation of complexes is therefore remote. H. F. GILLBE.

Heterogeneous equilibria between sodium and magnesium sulphates and nitrates and their aqueous solutions. M. A. HAMID and A. PARSHAD (Proc. XV Indian Sci. Cong., 1928, 169).—In addition to the solid phases in the ternary systems at 25°, a new surface in the quaternary system H_2O–Na_2SO_4–$NaNO_3$–$MgSO_4$–$Mg(NO_3)_2$ probably represents the saturation field of the lower hydrate or hydrates of $MgSO_4$. CHEMICAL ABSTRACTS.

System cellulose–sodium hydroxide–water. D. VAN DER WANT (Chem. Weekblad, 1931, **28**, 507—510).—A new method of studying such systems, involving the addition of a substance, *e.g.*, NaCl or NaI, which is not adsorbed by the solid phase, is described. The results obtained show that cellulose combines with both NaOH and H_2O; the quantity of the former which combines increases with increase of the NaOH concentration, whereas the combined H_2O diminishes. There is no evidence of true compound formation, and the effect is ascribed solely to adsorption. H. F. GILLBE.

Determination of the heat of dilution of sulphonitric mixtures. PRÉTAT (Mém. Poudres, 1930—1931, **24**, 119—136).—Heats of dilution have been calc. for mixtures of H_2SO_4 and HNO_3 with variations of 5% in the respective proportions and containing 0, 10, 20, and 30% H_2O, respectively. The figures are expressed by triangular co-ordinates. W. J. WRIGHT.

Affinity. LII. Affinity of sulphur to rhenium. I. R. JUZA and W. BILTZ. **LIII. Affinity of phosphorus to gold and silver.** H. HARALDSEN and W. BILTZ (Z. Elektrochem., 1931, **37**, 498—501, 502—508).—LII. The following results have been obtained: ReS_2 (solid) $=$Re (solid) $+S_2$ (gas) -70 kg.-cal. at 1100—1200°; ReS_2 (solid) $=$Re (solid) $+2$S (solid) -40 kg.-cal., the heat of formation falling between that of PtS and of FeS. A lower sulphide of Re does not exist in equilibrium with S vapour; the solubility of ReS_2 in Re is very small. The compound Re_2S_7 can be prepared indirectly, but not by synthesis.

LIII. Tensimetric analysis has established the existence of Au_2P_3 in equilibrium with P vapour up to pressures of 1 atm., but not of Au_3P_4 or Au_2P. Au_2P_3 is insol. in Au and the system Au–P is completely heterogeneous. In the system Ag–P the compounds AgP_3 and AgP_2 have been recognised. The following vals. for the affinities of these compounds at 774° are given: Au_2P_3 8·71, AgP_3 0·625, AgP_2 1·99 kg.-cal., showing the greater affinity of Au. E. S. HEDGES.

Heats of neutralisation of eugenol and *iso*eugenol. G. G. RAO (Proc. XV. Indian Sci. Cong., 1928, 143).—The vals. (g.-cal. per mol. at 25°) are 6476—6790 and approx. 6550, respectively. CHEMICAL ABSTRACTS.

Transport numbers and constitution of aqueous salt solutions. P. VAN RYSSELBERGHE (Z. Elektrochem., 1931, **37**, 694—698).—A discussion. E. S. HEDGES.

Effect of pressure on the electrical conductivity of solutions of sodium chloride and of other electrolytes. L. H. ADAMS and R. E. HALL (J. Physical Chem., 1931, **35**, 2145—2163).—The electrical conductivities of aq. solutions of NaCl, KCl, and K_2SO_4 at 0°, 25°, and 30° are recorded for pressures up to 4200 bars. At 4000 bars the conductivity of NaCl solutions reaches a max. at approx. 25 wt.-% and then decreases. Pressure slightly decreases the conductivity of dil. solutions, but increases markedly that of conc. solutions. With a rise in pressure the relative resistance R/R_0, where R is the resistance at a given pressure and concentration and R_0 that at 1 atm., decreases to a min. and then increases with dil. solutions, but with conc. solutions (approx. 20%) it increases continuously. In dil. solutions of NaCl, α (defined as Λ/Λ_∞) is increased by pressure, but to an extent smaller than is the case with weak electrolytes; for conc. solutions no definite conclusion concerning the effect of pressure can be reached. The importance of the effect of pressure on the viscosity of the solution in relation to conductivity is discussed.
L. S. THEOBALD.

Effect of ammonia, amines, and pyridine on the mobility of the silver ion. (FRL.) A. BATHE (Z. physikal. Chem., 1931, **155**, 267—280).—Transport measurements with solutions of $AgNO_3$ containing NH_3, NH_2Me, NH_2Et, $NHEt_2$, and pyridine show that the mobility of the complex Ag ion falls as the vol. of the neutral constituent increases. The mobility of the $Ag^{\cdot}$ ion in pure aq. solution indicates that it is associated with 2 mols. of H_2O. R. CUTHILL.

Conductivities of tetraethylammonium and ammonium salts in methyl alcohol. (MISS) A. UNMACK, E. BULLOCK, D. M. MURRAY-RUST, and (SIR) H. HARTLEY (Proc. Roy. Soc., 1931, A, **132**, 427—441; cf. A., 1930, 703).—Measurements have been made of the vals. of Λ_c of NEt_4 and NH_4 salts in MeOH at 25° over the range 0·0001—0·002N. All the salts except NEt_4ClO_4 obey the linear relation $\Lambda_c=\Lambda_0-x\sqrt{c}$. Comparison of the vals. of x with those given by the Debye–Hückel–Onsager equation shows that the deviation from the theoretical slope is greater for the NEt_4 than for the NH_4 salts. The mobilities of the NEt_4^+ and NH_4^+ ions are 62·1 and 58·1, respectively. It is probable that the NEt_4^+ ion is not appreciably solvated. L. L. BIRCUMSHAW.

Polybasicity of several common sugars. A. E. STEARN (J. Physical Chem., 1931, **35**, 2226—2236; cf. A., 1929, 765).—Conductometric data for galactose, dextrose, lævulose, lactose, maltose, and sucrose in NaOH at 23° are recorded. In 2N-NaOH these sugars act as polybasic acids with at least 5 ionising H atoms. Various ionisation consts. are calc. and the limiting equiv. conductances of the univalent sugar ions have been determined. L. S. THEOBALD.

Role of hydrogen linkings in conduction by hydrogen and hydroxyl ions. M. L. HUGGINS (J. Amer. Chem. Soc., 1931, **53**, 3190—3191).—An explanation of the high mobility of solvent ions in H_2O compared with NH_3 is offered. A mechanism of chain conduction is based on the presence of a lone pair of electrons in H_3O^+. An analogous mechanism for liquid NH_3 is excluded, since NH_4^+ has no lone pair. J. G. A. GRIFFITHS.

Absolute potentials and sources of error in their determination. J. BILLITER (Z. Elektrochem., 1931, **37**, 736—739).—A discussion. E. S. HEDGES.

Electromotive behaviour of cupric oxide. B. S. RAO and N. G. CHOKANNA (Proc. XV Indian Sci. Cong., 1928, 145).—If the CuO in the half-cell Pt| CuO, Cu_2O, N-NaOH is first evaporated with alcoholic NaOH and then heated, it tends to give const. potential val. No appreciable ageing effect was observed with Cu_2O when similarly treated.
CHEMICAL ABSTRACTS.

Measurements of temperature at working electrodes. V. B. BRUZS (Z. physikal. Chem., 1931, **155**, 392—402; cf. this vol., 435).—It is shown theoretically that for a reversible electrode the electrolytic Peltier effect is equal to the latent heat of the electrode process unless there is concentration polarisation (cf. A., 1930, 1121). Direct measurement of the Peltier effect at a Cd–Hg electrode in contact with aq. $CdSO_4$ has given a result agreeing satisfactorily with that calc. from e.m.f. data for thermocells. It is possible to calculate the abs. partial sp. heats of ions from Peltier effect data.
R. CUTHILL.

Hysteresis in the Weston standard cell. W. C. VOSBURGH and K. L. ELMORE (J. Amer. Chem. Soc., 1931, **53**, 2819—2831; cf. A., 1929, 1147).—The hysteresis of the cell has been investigated for the sudden temp. fall from 35° to 25°. Gelatin or cork extract increases the hysteresis in acid cells, but carbamide or CH_2O is without effect. It is suggested that the phenomena may be due to adsorption on the Hg_2SO_4 of impurities which retard crystallisation. The increase of hysteresis with decreasing concentration of acid is parallel to or caused by the hydrolysis of Hg_2SO_4, possibly by the deposition on Hg_2SO_4 of the basic sulphate. Cells with no added acid or basic material (neutral cells) show more hysteresis than cells containing basic Cd sulphate, and the e.m.f. of the latter cells are less variable and more reproducible than of the former. Since Hg_2SO_4 is progressively hydrolysed by basic Cd sulphate, the constancy of the e.m.f. of basic cells is due to local equilibrium or a steady rate of change. New acid cells have less hysteresis than basic, but in the former the effect increases and in the latter decreases with age. The effect of O_2 is in the same direction as, but less pronounced than, that produced by adding basic Cd sulphate, hence acid cells should be made in the absence of O_2 or contain enough acid to remain acid after the " clean up " of O_2. J. G. A. GRIFFITHS.

Theory and technique of the thermionic valve potentiometer for the measurement of electromotive force. III. F. MÜLLER (Z. physikal. Chem., 1931, **155**, 451—465).—The theory and construction of a potentiometer suitable for e.m.f. measurements with cells having abnormally high internal resistance or incapable of giving any appreciable current without polarisation are described.
R. CUTHILL.

Potentiometric study of Wurster's red and blue. L. MICHAELIS (J. Amer. Chem. Soc., 1931,

53, 2953—2962; cf. A., 1929, 190).—When p-$Me_2N\cdot C_6H_4\cdot NH_2$ and p-$(Me_2N)_2C_6H_4$ in an acetate buffer at p_H 4·6 and 30° are titrated electrometrically with Br, Wurster's red and blue, respectively, are produced, and steady reproducible potentials are registered by a Pt electrode. Further rapid titration discharges the colour, which, however, is partly restored by keeping, but const. potentials cannot be obtained. The titration curve of the first step is that for a regular reversible oxidation–reduction system, and shows that Wurster's red and blue are not mol. compounds of 1 mol. of a quinonoid type with 1 mol. of a hydroquinonoid type, but radical-like compounds which are intermediate and of the same mol. size as these types. Each of Wurster's compounds therefore has an odd number of electrons.

J. G. A. GRIFFITHS.

Electrolytic valve action. II. Oxide layer on antimony, bismuth, tungsten, zirconium, aluminium, zinc, magnesium. A. GÜNTHER-SCHULZE and H. BETZ (Z. Elektrochem., 1931, **37**, 726—733; cf. this vol., 546).—Zn, Cd, and Mg electrodes show little valve action, but the phenomenon is well shown by Ta, Bi, Sb, Zr, W, and Al, which become coated with films of Ta_2O_5, Bi_2O_3, Sb_2O_4, ZrO_2, WO_3, and Al_2O_3, respectively. The thickness of these oxide films has been measured. The theory that electrolytic valve action is a property of the O_2 gas layer is now replaced by a theory which ascribes the effect to a compact, non-porous layer of oxide. Unidirectional electronic conduction is assumed to occur as in the Cu/Cu_2O dry-plate rectifier.

E. S. HEDGES.

Electrolysis of perchlorates in non-aqueous solutions. A. L. CHANEY and C. A. MANN (J. Physical Chem., 1931, **35**, 2289—2313).—The conductivity of certain metallic perchlorates has been measured for 0·1—0·00001N solutions in furfuraldehyde, "cellosolve," ethylene glycol, and pyridine. Furfuraldehyde is the best ionising medium and the perchlorates of Ba, Ni, Co, Cd, Mn, and Cu have similar conductances. The degree of hydration of the salt has little or no effect. Pyridine resembles furfuraldehyde as an ionising medium, but conductances in ethylene glycol are small. The electrode potentials of Zn, Cd, Co, Ni, Pb, Cu, and Ag in solutions of their perchlorates in furfuraldehyde and "cellosolve" have been determined, and the electrodeposition of some of these metals from perchlorate solutions in furfuraldehyde has been studied. Cu, Pb, Ni, and Co can be successfully deposited from "cellosolve" solutions of their perchlorates. Al has been deposited from a "cellosolve" solution of $Al(ClO_4)_3$ prepared by anodic corrosion. Anhyd. *Pb* and *Cd perchlorates* have been prepared, together with the *dihydrates* of Co, Cu, Mn, Ni, and Zn perchlorates. Furfuraldehyde and "cellosolve" purified by vac. distillation over Ca have κ 3·5—7·3 $\times 10^{-8}$ and 5—10 $\times 10^{-8}$ ohm^{-1}, respectively. Solubility data for the perchlorates in these two solvents are recorded, and a modified vac.-tube potentiometer is described.

L. S. THEOBALD.

Becquerel effect. IV. I. LIFSCHITZ and M. REGGIANI (Z. physikal. Chem., 1931, **155**, 431—450; cf. A., 1930, 433).—The Becquerel effect with valve anodes of Nb and Ta is negative and is produced only by ultra-violet light. Since the magnitude of the effect varies with the electrolyte used, it seems possible that an effect of the second kind is superimposed on the electrode effect. The illumination causes an enormous fall in the internal resistance of the cell, *i.e.*, the valve action is largely destroyed, and the same is true in every case of the Becquerel effect so far examined and also when the effect is of the second kind. It thus appears that in either type of effect both the resistance and the e.m.f. of the cell change, and it is suggested that the resistance of the cell in the dark is due to a film of gas on the electrode, which is destroyed on illumination. With a Pt electrode the electrolyte when illuminated must have the power of destroying the film on the unilluminated electrode. The photo-electric conductivity of the metal oxide on the electrode surface will also play a part in reducing the resistance of the cell. How far the change in the e.m.f. of the cell is a consequence of the changes causing the fall in resistance is uncertain. Carborundum electrodes and valve electrodes of Fe in conc. H_2SO_4, and of Zn and Cd in aq. K_2CO_3 give a well-marked effect, but the effect of the first type seems to be absent with passive metals generally.

R. CUTHILL.

Velocity of unimolecular reaction. A. GANGULI (Phil. Mag., 1931, [vii], **12**, 583—588).—An expression for the velocity coeff. of a unimol. reaction is deduced from the point of view of adsorption and is claimed to give good agreement with the experimental results of Hinshelwood, Ramsperger, and others.

N. H. HARTSHORNE.

Kinetics of gas reactions at constant pressure. A. F. BENTON (J. Amer. Chem. Soc., 1931, **53**, 2984—2988).—Mathematical. Kinetic equations for reactions at const. vol. are not necessarily applicable to reactions at const. pressure, *e.g.*, reactions studied by a flow method. Appropriate equations are developed for uni- and bi-mol. homogeneous reactions, and reactions catalysed at surfaces.

J. G. A. GRIFFITHS.

Kinetics of gas explosions. Thermal decomposition of ozone sensitised by bromine vapour. B. LEWIS and W. FEITKNECHT (J. Amer. Chem. Soc., 1931, **53**, 2910—2934; cf. A., 1930, 425).—The reaction above and below the explosion limit has been investigated between 15° and 70° by means of the change of pressure in mixtures containing 0·5—20 mm. of Br and 15—100 mm. of O_3. The reaction begins only after an induction period ranging from a few secs. to 1 hr.; the velocity increases and an explosion (detonation) occurs if the pressure of O_3 exceeds a critical val., L; otherwise, the velocity attains a max. and then decreases. The induction period varies inversely as P_{O_3}, decreases with rise of temp., is markedly diminished by adding the O_3 before the Br, and, as in the case of the explosion limit, L, and rate of slow decomp., is influenced by the activity of the surface of the vessel. This activity is diminished by $AsBr_3$, H_2O, and other impurities, but is increased by slow decomp. and more particularly by explosions. Such activity persists for several days. With decrease of temp. below 35°,

the pressure of Br has an increasing effect; *L* has a min. and the slow reaction a corresponding max. velocity for 5 mm. of Br. At const. pressure of Br, *L* has a min. at 25° and a max. at 55°. Correspondingly, the 10° temp. coeff. of the slow reaction is <1 between 25° and 55°, and >1 beyond these limits. *L* is increased by packing the vessel; above 25° the reaction occurs mainly in the gas phase, but with fall of temp. the wall reaction becomes predominant. *L* bears a hyperbolic relation to the diameter of cylindrical reaction vessels. *L* is raised in proportion to the pressure of the added inert gases A, CO_2, O_2, N_2, and He (in order of increasing effect). The slow reaction is retarded similarly. A mechanism is proposed which involves an initial adsorption and labile combination of Br and O_3 at the walls. The unstable oxide decomposes more readily with rise of temp., and ejects an active product, possibly O_2^*, which initiates reaction chains propagated in the gas phase. The chains terminate in the gas or on the wall. J. G. A. GRIFFITHS.

Spark ignition of gas mixtures of low inflammability. K. YUMOTO (J. Fuel Soc. Japan, 1931, **10**, 52—53).—The relation between the nature and structure of an electric spark and its power of igniting mixtures of H_2 or CO with air has been examined. R. CUTHILL.

Decomposition of pyrosulphuryl chloride, a homogeneous unimolecular reaction. D. G. HILL (J. Amer. Chem. Soc., 1931, **53**, 3192).—The gas reaction is believed to be $S_2O_5Cl_2 \longrightarrow SO_3+SO_2Cl_2$. At 179°, a fourfold increase of surface by "packing" a pyrex bulb increases the time of half reaction from 7 to 15 min. J. G. A. GRIFFITHS.

Thermal decomposition of straight-chain paraffins. R. E. BURK (J. Physical Chem., 1931, **35**, 2446—2460).—A modified Polanyi–Wigner equation interprets existing data for the early stages of the thermal decomp. of normal paraffins. L. S. THEOBALD.

Investigation of explosions in bombs by means of the Braun tube. J. TAUSZ, H. GORLACHER, and J. LORENTZEN (Z. angew. Chem., 1931, **44**, 693—696).—The processes occurring during the combustion of mixtures of air with H_2, *n*-heptane, CH_4, *n*-hexane, C_2H_4, C_6H_6, *cyclo*hexane, and *cyclo*hexene in a cylindrical bomb have been studied photographically. Details are given of the ionisation period and velocity of propagation in a variety of mixtures; the former increases in the order given above, and it appears therefore that this function is related to the anti-knock properties of a fuel. In several cases the velocity of propagation appears to increase at first with increase of the content of the combustible gas in the mixture, and then to decline. The types of photograph obtained indicate the rate at which the ionisation diminishes after the explosion, and may be employed to differentiate between various types of combustible gas. H. F. GILLBE.

Kinetics of oxidation of cyanogen. H. J. HADOW and C. N. HINSHELWOOD (Proc. Roy. Soc., 1931, A, **132**, 375—387).—C_2N_2 reacts with O_2 giving N_2 and a mixture of CO and CO_2 at 700°, and in Si vessels the reaction takes place chiefly on the surface at a rate proportional to $[C_2N_2]^{\frac{1}{2}}[O_2]^{\frac{1}{2}}$. Oxides of N are not formed, and traces of these oxides do not influence the reaction. The oxidation of the CO produced is inhibited until all the C_2N_2 is oxidised, when an explosion occurs. CO_2 is, however, formed during the entire course of the reaction. Normally, O_2 was added to the reaction vessel after the C_2N_2; reversal of this order causes delay in the establishment of adsorption equilibrium. H_2O vapour facilitates the explosion of the CO, but not the initial oxidation of the C_2N_2. If the initial C_2N_2 pressure exceeds a certain limit depending on the state of the surface and the size of the vessel, explosion occurs. It is suggested that surface oxidation of the C_2N_2 gives activated CO, which either escapes from the surface and can be deactivated by C_2N_2 or reacts with O_2 before deactivation. L. L. BIRCUMSHAW.

Inflammation of mixtures of acetaldehyde and air. M. PRETTRE (Compt. rend., 1931, **193**, 240—242).—By the method applied to pentane (cf. A., 1930, 1255, 1256) similar phenomena are demonstrated as regards MeCHO. With mixtures containing 5—45% MeCHO luminosity begins at 200—210°, the first inflammation occurs at 256—263°, and then only luminosity from 285—290° to about 350°, when inflammation again occurs. Addition of 1% of $PbEt_4$ suppresses the first inflammation, and raises the temp. of the second about 10°. C. A. SILBERRAD.

Propagation of combustion along the surface of an inflammable liquid. I. T. KINBARA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, **16**, 91—108).—The velocity of propagation of combustion along the surface of a liquid contained in a rectangular trough has been measured photographically. The velocity is independent of the width of the trough provided this is greater than 2 cm. The liquids investigated were MeOH, EtOH, and PrOH, $COMe_2$, C_6H_6, and certain pairs formed from two of these or one of them with H_2O. In all cases the curves showing the relation between velocity and temp. are of the same type in which the velocity increases to a max. as the temp. is raised to a crit. val. above which the velocity decreases. The nature of the flame fronts formed at different temps. has been studied, particularly for C_6H_6. F. J. WILKINS.

Technically interesting deduction from the kinetics of nitrous acid. E. ABEL (Z. angew. Chem., 1931, **44**, 667—668).—As the rate of decomp. of HNO_2 is inversely proportional to the square of the NO pressure it follows that the efficiency of HNO_2 as an oxidiser is increased by conditions which tend to retain the NO in the system or by introducing NO independently into the system, preferably under pressure. The same applies to oxidising reactions with HNO_3, as HNO_2 appears in most of these to be the effective oxidising agent. This explains, *e.g.*, the action of HNO_3 on Al; when the acid is kept stationary the attack on the metal is greater than when the acid is stirred so as to accelerate the escape of NO from the system. A. R. POWELL.

Hydrolysis of iodine. H. A. LIEBHAFSKY (Z. physikal. Chem., 1931, **155**, 289—298).—Experi-

mental evidence is outlined showing that the rate of hydrolysis of I is much greater than Abel concluded from his experiments on the catalysis of the decomp. of H_2O_2 by I and I′ (A., 1928, 1194).

R. CUTHILL.

Decomposition of oxalic acid by arsenic acid. G. B. KING and J. H. WALTON (J. Physical Chem., 1931, 35, 2377—2382).—The velocity of reaction between $Na_2C_2O_4$ and conc. solutions of As_2O_5 in H_2O at 140° and 150°, determined by measurements of the CO and CO_2 evolved, shows the reaction to be unimol. with a temp. coeff. approx. 3. H_2O is a marked inhibitor. Determinations of the solubility of $H_2C_2O_4$ in H_3AsO_4 indicate compound formation between the two acids. Decomp. is presumed to occur by formation of an unstable mol. complex, and inhibition is explained on the basis of Taylor's theory of negative catalysis. The decomp. of $H_2C_2O_4$ is similar to that with H_2SO_4 and H_3PO_4.

L. S. THEOBALD.

Chemical kinetics. II. Influence of relative position of electric charge and reacting group on the velocity of the bromopropionate–thiosulphate reaction [at 25°]. V. K. LAMER and M. E. KAMNER (J. Amer. Chem. Soc., 1931, 53, 2832—2852; cf. A., 1930, 168).—Electrostatic considerations indicate that the reaction $CH_2Br{\cdot}CH_2{\cdot}CO_2{}'+S_2O_3{}'' \longrightarrow CH_2(S_2O_3){\cdot}CH_2{\cdot}CO_2{}''+Br'$ should be more rapid than the corresponding reaction with the β-bromopropionic ion, whilst chemical theory predicts the opposite effect. Data are given for the reaction of $S_2O_3{}''$ ions with bromoacetate, α- and β-bromopropionate ions in the presence of $Na^{\cdot}$ at vals. of $\mu^{\frac{1}{2}}$ between 0·04 and 0·53, and with the corresponding 0·0003—0·01*M*-Me esters in H_2O. The rates of the corresponding spontaneous reactions of the Br-compounds with H_2O have been investigated. Me bromoacetate and α-bromopropionate react with $S_2O_3{}''$ 20—45 and 34—100 times as fast, respectively, as the corresponding acid ions, the ratio k_{ester}/k_{ion} decreasing with increasing values of μ. $S_2O_3{}''$ reacts at about equal rates with the β-Br-ion and the ester, since the impacts of $S_2O_3{}''$ on the Br are less influenced by the presence or absence of charge on the carboxyl. Although the α-ester reacts 5—7-fold as fast as the β-ester, the β-ion reacts 3—32-fold as fast as the α-ion. Electrostatic interaction is therefore the dominant factor regulating the velocities of ionic reactions (cf. A., 1930, 426).

The limiting slope predicted by the Bronsted–Debye theory is approached at concentrations less than $\mu^{\frac{1}{2}}=$ 0·06 for the $S_2O_3{}''$–α-bromopropionate′ reaction, but, contrary to this theory, the velocity coeff. for the $S_2O_3{}''$–β-bromopropionate′ reaction increases with decreasing $\mu^{\frac{1}{2}}$, and especially at low vals. of $\mu^{\frac{1}{2}}$. The anomaly cannot be explained on chemical grounds and an explanation based on the assumption of oriented collision is proposed.

J. G. A. GRIFFITHS.

Interaction of epichlorohydrin and *cyclo*hexene oxide with alkali and ammonium halides. H. K. SEN, C. BARAT, and P. P. PAL (Proc. XV Indian Sci. Cong., 1928, 146—147).—Velocity coeffs. were determined under various conditions of dilution and mol. proportion.

CHEMICAL ABSTRACTS.

Mechanism of inversion of sucrose in mixed solvents. A. GANGULI and A. B. MALKANI (J. Physical Chem., 1931, 35, 2364—2370).—Data for the inversion of sucrose by 0·1*N*-HCl in the presence of MeOH, EtOH, $Pr^{\beta}OH$, glycol, glycerol, and $COMe_2$ at 25°, 31°, and 44·5° are recorded and discussed.

L. S. THEOBALD.

Reaction rate in the system solid–solid–gas. R. S. BRADLEY (Phil. Mag., 1931, [vii], 12, 290—296).—It is suggested that decomp. in the system solid–solid–gas takes place only when of the combined gas mols. at the solid–solid interface there are those of which the kinetic energy of vibration exceeds the potential energy. The equations derived from this basis are applied to the figures of Garner and Tanner on the rate of decomp. of $CuSO_4,5H_2O$.

F. J. WILKINS.

Thermal dissociation of ammonia on tungsten. H. R. HAILES (Trans. Faraday Soc., 1931, 27, 601—606).—Measurements of the rate of decomp. at const. NH_3 pressure at 950—1150° abs. and under the pressures 0·7 and 3·7 cm. have shown that the products of reaction have no retarding effect and have given support to Polanyi and Wigner's theory (A., 1929, 404). The crit. increment falls with the pressure, which is ascribed to increase in the heat of adsorption as the degree of saturation of the surface with NH_3 diminishes.

R. CUTHILL.

Dehydration of copper sulphate pentahydrate. J. HUME and J. COLVIN (Proc. Roy. Soc., 1931, A, 132, 548—560; cf. A., 1930, 39, 428).—Vals. for the mean rate of linear propagation of the reaction $CuSO_4,5H_2O \longrightarrow CuSO_4,3H_2O$ through the pentahydrate lattice are derived from measurements in a vac. of the rate of dehydration of $CuSO_4,5H_2O$ at 20°, using uniform small crystals of known size. The effects of increasing the air and H_2O vapour pressure are examined. The results obtained in a vac. and at low pressures of H_2O vapour support the theory that the rate of loss of $4H_2O$ is controlled by the linear rate of advance of the interface between the solid phases. The effective interface is assumed to be that between the penta- and the tri-hydrate, the latter having but momentary existence. Evidence is adduced that a solid hydrate gives rise on decomp. to a layer of material of almost mol. size which possesses two tendencies—to aggregate and to decompose. The surrounding conditions determine which of the two will predominate. Aggregation and slow nucleation account for the persistence in hydrate mixtures of a hydrate which is metastable under the prevailing v.-p. conditions. The results obtained by Garner and Tanner (*loc. cit.*) are discussed.

L. L. BIRCUMSHAW.

Thermal decomposition and detonation of lead azide crystals. W. E. GARNER and A. S. GOMM (J.C.S., 1931, 2123—2134).—The crit. increments of the decomp. of α- (orthorhombic) and (monoclinic) lead azide crystals in a vac. between 210° and 295° are 47,600 and 34,700 g.-cal., respectively, the difference probably accounting for the greater instability of the β-form. The rate of decomp. of the α-form is 10^7 times that calculated from the equation $-dx/dt-\nu\,.\,n\,.\,A\,.\,e^{-E/RT}$ (cf. A., 1928,

1100) and it is therefore suggested that the decomp. is a chain reaction. The infra-red absorption spectra of the two forms between 1 and 10 μ are very similar and the bands are probably those of the N_3 group. From the rate of decomp. immediately preceding detonation and the average time of heating before detonation at different temps., the crit. increment of detonation is calc. to be approx. 200,000 g.-cal. The detonation temp. is lower in a vac. than in air.

N. H. HARTSHORNE.

Condensation on crystals. M. VOLMER and W. SCHULTZE (Z. physikal. Chem., 1931, **156**, 1—22).—Measurements of the rate of growth of crystals of I, $C_{10}H_8$, and P in an atm. of their pure vapours have been made to determine the validity of the theory of two-dimensional nucleus formation, which requires that with decreasing supersaturation the rate of growth falls to zero before equilibrium is attained. The results with I support the theory, at least qualitatively, but with $C_{10}H_8$ conditions are complicated by the orientation of the crystals on the walls of the vessel and by the fact that owing to the migration of the non-oriented crystals the rate of growth is dependent on the frequency of nucleus formation on the 001 faces; similar conditions exist with P.

H. F. GILLBE.

Velocity of dissolution of some zinc–silver alloys in acids. M. CENTNERSZWER and M. STRAUMANIS (Z. physikal. Chem., 1931, **156**, 23—37).—The rate of dissolution of Zn and Zn alloys containing 0·5% Ag in HCl and H_2SO_4 of various concentrations has been determined; the rate is smaller in H_2SO_4 than in HCl. Ag accelerates the dissolution of Zn only if the latter contains impurities. In accordance with the theory of local action, the rise of the velocity coeff. of the dissolution with increase of dilution follows a course parallel with the change of mol. conductivity.

H. F. GILLBE.

Effect of hydrogen-ion concentration on corrosion of tin. J. M. BRYAN (Trans. Faraday Soc., 1931, **27**, 606—620).—Sn is not appreciably attacked by dil. aq. citric acid in absence of O_2. If O_2 is present, the Sn dissolves largely as $Sn^{\cdot\cdot\cdot\cdot}$. The corrosion slowly decreases as the p_H rises from 3·1 to 5·5 as a result of O_2 being rendered unavailable for corrosion through increasing oxidation of Sn^{II} and of the acid. The rate of attack is considerably enhanced by a little Fe^{II} citrate, which apparently acts as O carrier by alternate oxidation and reduction. In absence of O_2, a 0·5% solution of citric acid containing Fe^{III} citrate has a powerful action, the amount of Sn dissolved being an approx. linear function of the concentration of Fe^{III}. The rate of attack is reduced at first by an increase in p_H, but the total amount of Sn dissolved in 20 days is increased, the reason being that as the p_H increases the reduction of the Fe^{III} salt by Sn^{II} is retarded and the available O is thus conserved for corrosive action.

R. CUTHILL.

Colloid theory of corrosion of iron and steel. J. N. FRIEND (Trans. Faraday Soc., 1931, **27**, 595—596; cf. J.C.S., 1921, **119**, 932; 1922, **121**, 41).—Experimental evidence has been obtained showing that the role of the colloidal $Fe(OH)_2$ formed from Fe in contact with aerated H_2O in bringing about corrosion is mechanical, not chemical. If the H_2O is in rapid motion the $Fe(OH)_2$ is carried away; otherwise it adheres to parts of the metallic surface, partly screening them from O_2 and inducing anodic corrosion. Any reaction or process which will retard such screening will also retard anodic attack.

R. CUTHILL.

Laboratory study of atmospheric corrosion of metals. W. H. J. VERNON (Trans. Faraday Soc., 1931, **27**, 582—585; cf. B., 1931, 763).—The products of corrosion of Cu in atms. of 99% relative humidity and containing 0·1—0·75% SO_2 have been examined, the max. basicity observed corresponding with the formula $CuSO_4,3Cu(OH)_2$. Corrosion is maximal in presence of 0·5% of SO_2, falling steadily at lower concentrations.

R. CUTHILL.

Methods and apparatus for determining rates of corrosion of metals. G. GOLLNOW (Chem. Fabr., 1931, 326—328, 335—336, 341—342).—Comparative rates of corrosion are often determined by actual loss of wt. using an intensified corrosive agent to shorten the time required to give measurable results. Such are $NaCl+H_2O_2$ for Al corrosion. Al alloys for airship construction are tested in H_2O at 20° for 3—96 days. A similar type of test is that in which NaCl solutions are caused to impinge on the metal as spray or jets, the physical state of the surface being observed. A number of special tests are described. A general method is afforded by the measurement of the p.d. developed. The vessel with the corrosive reagent is placed under an air-tight glass bell and contains an Hg electrode and the test sample. O_2 is led in and the pressure in the bell, together with the e.m.f. developed, are measured; the O_2 acts as corrosion accelerator. The Todt corrosimeter is based on the theory that the corrosion of Fe in dil. salt solutions is due to O_2 alone, through its action in oxidising $H^{\cdot}$ at the cathode. The depolarisation current which is measured is a function of the O consumption, the electrodes being of Pt and of the sample. The test cell is fitted to take 2 samples so that comparative results under similar conditions can be instantly obtained. The apparatus affords a rapid and trustworthy means of testing protective coatings.

C. IRWIN.

Reaction between oxygen and acetylene in the presence of nitrogen oxides. S. LENHER (J. Amer. Chem. Soc., 1931, **53**, 2962—2967; cf. this vol., 313).—The reaction between C_2H_2 and O_2 in the presence of 1·7—4% of HNO_3 vapour has been investigated by a flow method between 170° and 250°. Explosions occur at higher temp., and at lower temp. with increased rate of flow. 50—60% of the C_2H_2 is oxidised to trimeric glyoxal; some CO and small quantities of CO_2, H_2O, H_2, HCO_2H, and CH_2O are also produced. The reaction is catalysed by NO_2, but is not retarded by excess of O_2 or air. The initial reaction is probably the oxidation of C_2H_2 by NO_2 and the formation of NO. With only 0·01—0·45% of NO_2 in $1C_2H_2:1O_2$ mixtures neither the explosion limit nor the temp. range (260—315°) of the slow oxidation is lowered.

J. G. A. GRIFFITHS.

Catalysis and microchemistry. F. FEIGL (Z. angew. Chem., 1931, **44**, 739—742).—Microanalytical

reactions which depend on catalysis are reviewed. HNO_3 accelerates the reduction of $KMnO_4$ solution by nascent H, and a solution containing Zn, H_2SO_4, and $KMnO_4$ may thus be used to detect NO_3'. Various metals, notably Mo, W, Ti, Zr, and Th, may be detected by their catalytic influence on the reaction between H_2O_2 and S_2O_3'', whereby SO_4'' is formed; the sensitivity limit, in presence of $BaCl_2$, is 0·5—2 microg. Peracids have a similar effect, and in addition accelerate the oxidation of KBr by H_2O_2 in dil. AcOH solution. $Fe^{\cdot\cdot\cdot}$ catalyses the reaction between H_2O_2 and polythionates, SO_4'' being formed, but the sensitivity is comparable only with that of the detection of $Fe^{\cdot\cdot\cdot}$ by CNS'. Combination of the accelerating action of Ag on the oxidation of Cr by H_2O_2 with the diphenylcarbazide reaction yields a method for the detection of 0·15 microg. Cr. Addition of a solution containing Ag to a mixture of $NH_2\cdot NHPh$, AcOH, and Hg_2Cl_2 causes the almost immediate production of a dark coloration; the limit is 0·016—0·005 microg. Ag per c.c., and the sensitivity thus exceeds that of any other reaction for the detection of Ag.

H. F. GILLBE.

Catalytic decomposition of nitroamide. III. Catalysis by bivalent cation bases. J. N. BRONSTED and K. VOLQVARTZ (Z. physikal. Chem., 1931, **155**, 211—224; cf. A., 1925, ii, 982).—Bivalent positive hydroxy-ions, such as $[Co(OH)(NH_3)_5]^{\cdot\cdot}$, strongly catalyse the decomp. of nitroamide in aq. solution, the catalysis const., k, being related to the strength of the ion as a base, K, by the equation $k=GK^{0.84}$. The value of G is much greater than for the bases previously investigated. These results agree with the general theory of acid and basic catalysis (A., 1928, 1336).

R. CUTHILL.

Autocatalysis strongly influenced by concentration and by promoters. A. QUARTAROLI (Gazzetta, 1931, **61**, 466—478).—The velocity of decomp. of H_2O_2 in presence of $CuSO_4$ and NH_3 (A., 1928, 96) rises to a max. as the concentration of Cu decreases. A small change of concentration in a solution already dil. causes an extremely large increase in velocity, ascribed to a change from a weak to a powerful catalyst. Formation of the latter is favoured by the presence of small amounts of Fe or Co. It is suggested that cupric peroxide may be the weak and cuprous peroxide the strong catalyst.

E. E. J. MARLER.

Mechanism of chemical change. II. Catalysis of the mutarotation of beryllium benzoylcamphor. III. Mutarotation of aluminium benzoylcamphor. T. M. LOWRY and R. C. TRAILL (Proc. Roy. Soc., 1931, **A**, **132**, 398—415, 416—427).—II. In CCl_4 and $CHCl_3$ the mutarotation of Be benzoylcamphor is very slow. It is catalysed by pyridine, EtOH, and p-cresol, but not to any extent by a mixture of pyridine and cresol. The velocity coeff. is proportional to the concentration of pyridine, but the "catalysis coeffs." for EtOH and p-cresol decrease with rise of concentration, in accordance with the law of mass action, owing to the formation of a relatively stable complex of solute and catalyst. If the cryst. compound of Be benzoylcamphor with $CHCl_3$ is formulated as a racemate with 4 mols. of $CHCl_3$ of crystallisation, the rotatory power of the unknown β-form of the solute can be calc. from the rotatory powers of freshly prepared solutions of the α-form and of the α- and β-compound with $CHCl_3$. The proportions of the two forms in the equilibrium mixture can then be deduced. The displacement of equilibrium in passing from CCl_4 to $CHCl_3$ and the retardation of mutarotation in presence of pyridine or EtOH are considered to be due to the selective formation of a $CHCl_3$ compound by the α- and β-forms. It is calc. that 46% of the α-form and 64% of the β-form are present as $CHCl_3$ compounds when dissolved in $CHCl_3$. The mechanism of mutarotation is discussed.

III. The mutarotation of Al benzoylcamphor is very rapid in CCl_4 and even more rapid in $CHCl_3$. At a sufficiently low temp., however, a very rapid rise to a max. rotation, followed by a slow fall to a steady val., takes place in both cases. The form of the curves for the mutarotation in CCl_4 and EtOH is given by the equation the const. A being negative. This equation also expresses the form of the mutarotation curves for solutions in CCl_4 catalysed by pyridine but not by EtOH. It is suggested that EtOH may form a complex with the Al compounds.

L. L. BIRCUMSHAW.

Hydrolysis of gelatin. B. N. DESAI and T. R. BOLAM (Proc. XV Indian Sci. Cong., 1928, 144).—The power of gelatin to inhibit the formation of Ag_2CrO_4 from $AgNO_3$ and K_2CrO_4 is at first decreased, then increased, and then decreased by progressive hydrolysis. The p_H is slightly increased, but the val. then shows little variation.

CHEMICAL ABSTRACTS.

Catalysts for the production of hydrogen by means of the water-gas reaction. II. Effect of Cr_2O_3 on activity of Fe_2O_3. R. YOSHIMURA (J. Soc. Chem. Ind. Japan, 1931, **34**, 271—273B).—The activity of Fe_2O_3 in the oxidation of CO rapidly falls at 800°. This deterioration is prevented by addition of 7% of Cr_2O_3, and the deposit of C on the catalyst is lessened. The catalyst promoted with Cr_2O_3 converted 480,000 times its own vol. of CO with a reduction of conversion efficiency from 90% to 86%.

C. IRWIN.

Catalytic decomposition of nitrous oxide. M. S. SHAH (Proc. XV Indian Sci. Cong., 1928, 170).—The thermal decomp. of N_2O is catalysed by ThO_2, C, Al_2O_3, Pt-black, TiO_2, and Pt foil in that order.

CHEMICAL ABSTRACTS.

Action of nitric acid on metals in presence of hydrazine. A. KESĀNS [KESCHAN] (Latvij. Univ. Raksti, 1931, **2**, 145—152).—The autocatalytic effect observed when metals such as Ag, Hg, Cu, As, Bi, or Sb react with HNO_3 is retarded to a much greater extent by N_2H_4 than by $KMnO_4$, $KClO_3$, H_2O_2, or carbamide. The presence of about 0·1% of N_2H_4 in $8N$-HNO_3 is sufficient to suppress the effect for several days, and even in the $3N$-acid at the b. p. the protective action persists for some hours. It is suggested that the N_2H_4 reacts with HNO_2 to form N_3H, and that this immediately reacts with further quantity of HNO_2.

H. F. GILLBE.

Reaction between hydrogen sulphide and sulphur dioxide. B. S. RAO and M. R. A. RAO

(Nature, 1931, **128**, 413).—SO_2 and H_2S in C_6H_6 or CCl_4 react in the presence of Hg even in the absence of H_2O and O_2. A solution of either gas in either of the solvents has no action on Hg. The primary product of the reaction is believed to be thiosulphonic acid which decomposes at the solvent–Hg interface, yielding sulphoxylic acid and HgS.

L. S. THEOBALD.

Mechanism of catalytic hydrogenation with sodium hydride. G. HUGEL and FRIESS (Bull. Soc. chim., 1931, [iv], **49**, 1042—1047).—NaH will catalyse the reduction of polycyclic hydrocarbons such as anthracene, phenanthrene, etc., and those which have a double linking capable of fixing Na. It will not catalyse the reduction of the normal double linking, or the reduction of C_6H_6 or hydrocarbons formed by substitution in C_6H_6. The temp. of optimum activity is 270—320°.

F. J. WILKINS.

Esterification in the gaseous phase with solid catalysts. N. G. GAJENDRAGAD (Proc. XV Indian Sci. Cong., 1928, 148).—SiO_2 or K alum at 230° was employed to catalyse the interaction of MeOH or EtOH with AcOH.

CHEMICAL ABSTRACTS.

Catalytic equilibrium between acetaldehyde and alcohol. W. D. BANCROFT and A. B. GEORGE (J. Physical Chem., 1931, **35**, 2194—2209).—With a finely-divided Ni catalyst the equilibrium value of the reaction EtOH $\rightleftharpoons$ MeCHO+H_2 at 140—145°, approached from both directions with different rates of flow, lies at 3% MeCHO. The catalyst showed a rapid initial poisoning, after which its activity remained approx. const., indicating regions of different activity in the Ni surface. The equilibrium lies at the same point for both used and unused catalyst. H_2O activates the Ni surface for both hydrogenation and dehydrogenation reactions. In the former, the amount of EtOH is increased, probably through a preferential adsorption of H_2O on the catalyst; in the latter, the equilibrium is not displaced, but a used catalyst is activated. Pt–asbestos causes neither hydrogenation of MeCHO nor dehydrogenation of EtOH at 140—145°, and MeCHO is not reduced electrolytically to EtOH with a platinised Pt cathode. In the dehydrogenation, the yield of MeCHO is slightly increased by the presence of O_2. At 180°, an excess of H_2 in the dehydrogenation of EtOH does not markedly affect the % of MeCHO which is decomposed into CO and CH_4.

L. S. THEOBALD.

Hydrogenation of benzene with nickel and platinum. W. D. BANCROFT and A. B. GEORGE (J. Physical Chem., 1931, **35**, 2219—2225).—The rate of flow of H_2 is the important factor in the hydrogenation of C_6H_6 at 180—185° with a Ni or a Pt–asbestos catalyst. With Pt a slow rate is necessary, but for a fixed rate the yield of *cyclo*hexane is greater with Ni. With Ni at 300° the decomp. of C_6H_6 is greater than at 250°; more CH_4 and less C_2H_6, C_3H_8, and unsaturated hydrocarbons are formed. Pt–asbestos at 300° gives less saturated hydrocarbons than Ni, and at 250° the amount of unsaturated compounds is only slightly less than that obtained at 300°. With Pt–asbestos decomp. to saturated hydrocarbons is small even up to 500°. *cyclo*Hexane at 300° with Pt gives results similar to those obtained with C_6H_6 under the same conditions.

L. S. THEOBALD.

Anode sludge formation during the electrodeposition of copper. O. ESSIN (Z. physikal. Chem., 1931, **156**, 41—50).—On the assumption that during reversible electrolysis of Cu salt solutions both the discharge of $Cu^{\cdot\cdot}$ and $Cu^{\cdot}$ at the cathode and the dissolution of Cu at the anode are proportional to the relative ionic concentrations, it is shown that the passage of the current displaces the equilibrium between $Cu^{\cdot\cdot}$ and $Cu^{\cdot}$ at the electrodes. The resulting excess of $Cu^{\cdot}$ at the anode is removed by a reaction $2Cu^{\cdot} \longrightarrow Cu^{\cdot\cdot} + Cu$, and the liberated Cu forms the anode sludge. Such sludge formation can occur in absence of polarisation.

H. F. GILLBE.

Oriented deposits of copper on bismuth. Y. HORI (Nature, 1931, **128**, 412).—The Cu crystals deposited electrolytically from $CuSO_4$ on a cleavage surface of Bi with a low current density show distinct orientations.

L. S. THEOBALD.

Electrodeposition of silver from argentocyanide solutions. II. S. GLASSTONE and E. B. SANIGAR.—See B., 1931, 845.

Electrodeposition of lead dioxide on metals and protection against corrosion. N. ISGARISCHEV and A. KUSNEZOVA.—See B., 1931, 845.

Synthesis of ammonia in the low-voltage arc. A. K. BREWER and R. R. MILLER (J. Amer. Chem. Soc., 1931, **53**, 2968—2978).—The rate of formation of NH_3 in $3H_2 : N_2$ mixtures is independent of pressure, except at the lowest vals., within the limits employed (0·5—0·02 mm.) and is directly proportional to the current flowing through the arc (cf. A., 1929, 891). The lower pressure limit for synthesis depends on the dimensions and type of plate employed. Synthesis does not occur at arc potentials below the ionisation potential of N_2, but the rate increases rapidly between 17 and 23 volts and then increases linearly to 50 volts. The max. rate of synthesis at 0·3 mm. in the 19- and 30-volt arc occurs in a mixture containing 83 vol.-% N_2. The addition of less than 80% of He, Ne, or A to $3H_2 : N_2$ mixtures has only small retarding effects increasing in the order of the mol. wt. (cf. A., 1930, 304). The results indicate that the reaction occurs around N_2^+ and N^+ ions; H_2^+ ions, neutral atoms, and excited mols. are relatively inactive. An evaluation of the rate of ion formation and of the distribution of ions between N_2 and H_2 indicates a yield of about 2 mols. of NH_3 per N_2^+ below 23 volts (24·5, corr. for contact p.d.) and about 1 mol. of NH_3 per N^+ ion.

J. G. A. GRIFFITHS.

Simple photochemical phenomena. A. BERTHOUD (Trans. Faraday Soc., 1931, **27**, 484—492).—A critical examination of the laws of photochemical change. Tolman's theory of the thermal acceleration of photochemical reactions (A., 1923, ii, 813) is unsatisfactory, since it admits of acceleration only with a reaction brought about by light of frequency not much greater than that corresponding with the threshold. The fact that the Grotthus–Draper law is normally rigidly obeyed does not necessarily follow from the theory of deactivation at present accepted.

R. CUTHILL.

Photochemical temperature coefficient. K. W. YOUNG and D. W. G. STYLE (Trans. Faraday Soc., 1931, 27, 493—503).—The factors which may produce a temp. coeff. in a photochemical change are discussed. It seems probable that in many reactions occurring in solution the velocity may be largely dependent on chemical equilibria, *e.g.*, between solvated and unsolvated mols. R. CUTHILL.

Photochemical kinetics in gaseous systems. M. BODENSTEIN (Trans. Faraday Soc., 1931, 27, 409—412).—The methods of investigating the dark reactions which follow the primary photochemical process in a photochemical reaction are reviewed. R. CUTHILL.

Reaction between hydrogen and oxygen under the influence of photochemically-produced hydrogen atoms and the relationship of its mechanism to that of the burning of detonating gas at high temperatures. W. FRANKENBURGER and H. KLINKHARDT (Trans. Faraday Soc., 1931, 27, 431—444).—In the combination of O_2 with H atoms produced from H_2 by optically-excited Hg atoms the yield of H_2O_2 is not affected by variation of the temp. between 50° and 200°, or of the pressure between 1 and 11 atm., but with increase in the O_2 concentration or the rate of flow of the reacting gases rapidly rises to a limiting value. At this point, which corresponds with the elimination of inhibiting influences and side reactions, the yield of H_2O_2 per quantum varies between 1 and 2. Since about 2 mols. of H_2O are formed per mol. of H_2O_2, it is concluded that if the reaction chain in the formation of H_2O is $H+O_2+H_2=H_2O+OH$, $OH+H_2=H_2O+H$, etc. (cf. A., 1929, 11) the latter reaction is, at room temp., negligible compared with the reaction $2OH+M=H_2O_2+M$. It appears that the OH radical is relatively stable. R. CUTHILL.

Acceleration of electrodeposition of hydrogen and oxygen by light of short wave-length. F. P. BOWDEN (Trans. Faraday Soc., 1931, 27, 505—508).—The overvoltage of H_2 at an Hg cathode and of O_2 at a Pt anode is reduced by ultra-violet light. With H_2 the effect of the light decreases with increase in wave-length and disappears at about 4000 Å. R. CUTHILL.

Comparison of efficiency of photochemical reactions and similar reactions produced by gaseous ions. G. R. GEDYE (Trans. Faraday Soc., 1931, 27, 474—478).—The comparison is made by means of published data for the decomp. of NH_3, N_2O, and O_3 and the formation of O_3. R. CUTHILL.

"Chlorknallgas." M. BODENSTEIN (Trans. Faraday Soc., 1931, 27, 413—424).—The Nernst chain theory of the reaction between H_2 and Cl_2 has serious defects, *e.g.*, it fails to account for the catalytic action of traces of H_2O. It is suggested that the Cl atoms only initiate the chains and are not concerned in their propagation, and that the true mechanism is (1) $Cl_2+E=2Cl$, (2) $Cl+H_2O+H_2=HCl+H_2O+H$, (3) $H+Cl_2+H_2=2HCl+H$ (4) $H+O_2+H_2=H_2O+OH$, (5) $H+O_2+Cl_2=HCl+ClO_2$, reactions (4) and (5) being followed by $OH+H+M=H_2O+M$ and $ClO_2+H=HCl+O_2$, respectively. This theory leads to the equation substantiated experimentally by Thon (A., 1927, 323), and also accounts in an approx. quant. manner for the effect of H_2O. The action of inhibitors, such as O_3, is attributed to the competition with the termol. reaction (2) of a bimol. reaction, such as $Cl+O_3=ClO+O_2$. Allmand's observation that the quantum yield decreases with shorter wave-lengths (this vol., 179) is also explained. R. CUTHILL.

Photochemical oxidation of sulphur. R. DUBRISAY and R. PALLU (Compt. rend., 1931, 193, 339—340).—On exposure of flowers of S to ultraviolet light in a quartz vessel containing air at 35—40° without, and with, moisture the first product is probably $H_2S_5O_6$ which then decomposes with formation mainly of SO_2, H_2SO_4 and S (cf. A., 1928, 928; B., 1929, 431; this vol., 806). C. A. SILBERRAD.

Photochemical ozone equilibrium in the atmosphere. R. MECKE (Trans. Faraday Soc., 1931, 27, 375—377).—In the upper atm. there appears to be an equilibrium between O_2 and O_3, the two primary photochemical reactions responsible for this being $O_3+h\nu$ ($<\lambda$ 2655)$=O_2'+O'$ and O_2+O_2'' ($<\lambda$ 2025)$=O_3+O'$. The equilibrium concentration of O_3, however, diminishes so rapidly with increase in the O_2 pressure that at the highest attainable altitudes the amount of O_3 is too small to be detected. R. CUTHILL.

Molecular spectra in relation to photochemical change. R. MECKE (Trans. Faraday Soc., 1931, 27, 359—375).—A survey of the present position. R. CUTHILL.

Comparative study of photographic process in different experimental conditions. J. EGGERT (Trans. Faraday Soc., 1931, 27, 528—533).—The modern theory of the photographic process is reviewed. In respect of the photographic effect on them of visible light, X-rays, or α-particles, emulsions of AgCl, AgN_3, Ag_2C_2, and $Ag_2C_2O_4$ are closely similar. Whereas, however, with AgCl the active spectral absorption corresponds with the spectral sensitivity of the emulsion, with the endothermic Ag compounds this is not so. R. CUTHILL.

Photochemical reaction between iodine and potassium oxalate in aqueous solution. A. J. ALLMAND and K. W. YOUNG (Trans. Faraday Soc., 1931, 27, 515—527; cf. A., 1925, ii, 141).—For the shorter wave-lengths the temp. coeff. rises rapidly with decreasing wave-length. If the solution is stirred, however, the variation largely disappears, and it is probable that in complete absence of diffusion and convection effects the temp. coeff. would be const. at 2·8—3·0 for all wave-lengths below about 580 mμ. The quantum efficiency either increases continuously with increasing wave-length or passes through a max., depending on whether the vals. are determined for a fixed incident intensity of light or a fixed absorbed intensity. It is suggested that in an insolated solution containing I_2 and I′ ions the following processes occur: $I_3'+h\nu=2I+I'$, $I_2+h\nu \longrightarrow 2I$, $I'+I_2 \rightleftharpoons I_3'$, $I'+I$ I_2', $I+H_2O \longrightarrow OH+H^{\cdot}+I'$, $OH+I' \longrightarrow OH'+I$, $2I_2' \longrightarrow I_3'+I'$, $2I \longrightarrow I_2$, $I_2'+I$ —— I_3'. This scheme is extended to various photo-oxidations of I_2 in aq. solution. R. CUTHILL.

Photochemical decomposition of chlorine dioxide in carbon tetrachloride solution. Y. NAGAI and C. F. GOODEVE (Trans. Faraday Soc., 1931, **27**, 508—513; cf. J.C.S., 1923, **123**, 1199).—The quantum efficiency for light of wave-length about 4150 Å. and over a range of concentrations is $1\cdot98\pm0\cdot2$ mols. per quantum. Reaction chains are improbable, and the suggested mechanism is $ClO_2+h\nu \longrightarrow ClO_2^*$, $ClO_2^*(+CCl_4) \longrightarrow Cl+O_2(+CCl_4)$; $Cl+ClO_2 \longrightarrow Cl_2+O_2$, which is in accordance with thermal and spectroscopic data. R. CUTHILL.

Photochemistry of mixtures of chlorine, oxygen, and carbon monoxide. G. K. ROLLEFSON (Trans. Faraday Soc., 1931, **27**, 465—467).—Experimental evidence is described in support of the mechanism for the photochemical formation of $COCl_2$ previously suggested (A., 1930, 433). R. CUTHILL.

Photosensitised formation of hydrogen peroxide in the system hydrogen–oxygen–chlorine. R. G. W. NORRISH (Trans. Faraday Soc., 1931, **27**, 461—464; cf. this vol., 805).—Experimental evidence has been obtained in favour of the view that the retarding action of O_2 on the reaction between H_2 and Cl_2 is due to its reacting with the H atoms propagating the reaction chains, $H+H_2\ \ O_2=H_2O+OH$, $OH+OH+X=H_2O_2+X'$. R. CUTHILL.

Photosensitised decomposition of nitrogen trichloride, and the induction period of the hydrogen–chlorine reaction. J. G. A. GRIFFITHS and R. G. W. NORRISH (Trans. Faraday Soc., 1931, **27**, 451—458).—A general account of recent work on the decomp. of NCl_3 is given (cf. this vol., 179, 578). It appears that in the induction period of the reaction between H_2 and Cl_2 the reaction chains are very much shortened by the action of NCl_3 on the Cl atoms. R. CUTHILL.

Photochemical union of hydrogen and chlorine. J. B. BATEMAN and H. C. CRAGGS (Trans. Faraday Soc., 1931, **27**, 445—450).—Contrary to the findings of Trifonov (A., 1930, 173), H_2 and Cl_2 react in light at Cl_2 pressures below 0·2 mm. and H_2 pressures down to 0·04 mm. R. CUTHILL.

Formation of nitrogen compounds in air and soil under the influence of light. G. G. RAO and N. R. DHAR (Z. anorg. Chem., 1931, **199**, 422—426).—It is probable that the nitrates and nitrites of the atm. are formed principally by photochemical oxidation of NH_3, and that the same process is mainly responsible for nitrification in the soil. R. CUTHILL.

Latent photographic image. New methods of investigation and results. F. WEIGERT [with F. STIEBEL] (Trans. Faraday Soc., 1931, **27**, 533—541; cf. this vol., 442).—The negative dichroism induced in a transparent photographic emulsion by exposure to polarised red light is increased by either previous or subsequent exposure to natural light. It is therefore suggested that the characteristics of the developable photographic latent image are determined by at least two factors, viz., an "activation factor" and a 'form factor." The latter is related to the mode of vibration of the incident light and determines the max. amount of dichroitic developed Ag obtained. The activation factor probably represents some catalytic effect which enables the system to surmount the high level of potential which occurs in the path of reduction of the Ag halide by the developer. It is likely that the catalyst is at. Ag, partly present in the emulsion originally and partly formed during exposure. In support of this theory it is found that if an emulsion which has been exposed to polarised red light is treated with H_2CrO_4 and then exposed to natural red light, positively dichroic Ag is obtained on development. The theory is also capable of accounting for the form of the characteristic curves. R. CUTHILL.

Sensitisations of the first and second types. F. WEIGERT [with (FRL.) F. PRUCKNER] (Trans. Faraday Soc., 1931, **27**, 542—543).—Two types of sensitisation may be distinguished, according as the sensitiser is present in very small amount and the quantum efficiency is much greater than 1, or as a large excess of sensitiser is required and the quantum efficiency is small, often of the order of 0·5. R. CUTHILL.

Relative masses of photo-silver and sensitivity specks in the photographic latent image. S. E. SHEPPARD.—See B., 1931, 906.

Optical sensitisation. W. D. BANCROFT, J. W. ACKERMAN, and C. GALLAGHER (Proc. Nat. Acad. Sci., 1931, **17**, 407—410).—Reduction occurs in pure $FeCl_3$ or $AgNO_3$ solutions on exposure to light in presence of dyes which are reducing agents or become such on irradiation. The reduction is due to light absorbed by both the dye and the $FeCl_3$. Photographic sensitising dyes are considered to act similarly after adsorption on the AgBr. J. LEWKOWITSCH.

Action of light on silver bromide. P. S. MACMAHON and A. C. CHATTERJI (Proc. XV Indian Sci. Cong., 1928, 138—139).—When AgBr in O_2 is exposed to sunlight O_2 is absorbed, probably by Ag produced by photochemical decomp. of the AgBr. CHEMICAL ABSTRACTS.

Wave-length–sensitivity curve of a cæsium oxide photocell; a new light-sensitive instrument for the ultra-violet. T. F. YOUNG and W. C. PIERCE (J. Opt. Soc. Amer., 1931, **21**, 497—501).—A new quartz-enclosed Cs_2O cell is described. The cell has a relatively high response to wave-lengths between 2500 and 3000 Å. A min. occurs at 3200 Å. J. LEWKOWITSCH.

Photochemical formation of carbonyl chloride. VI. Influence of pressure and of the dimensions of the vessel. VII. Formation of carbon dioxide, sensitised by irradiated chlorine. H. J. SCHUMACHER and G. STIEGER (Z. physikal Chem., 1931, B, **13**, 157—168, 169—189).—VI. At room temp. and total pressures up to 100 mm., and in an ordinary vessel, the disappearance of the at. Cl is due to a reaction in the gas phase, $COCl+Cl \longrightarrow CO+Cl_2$, whereas at pressures below 30 mm., at high temp., or in presence of an extensive solid surface the disappearance is attributable to a diffusion effect on the surface. The kinetics of the reaction are discussed.

VII. The formation of CO_2 from CO and O_2 under the influence of photosensitised Cl conforms to the equation $d(CO_2)/dt=k_p[Cl_2]^x[CO]^{1/2}$, where the value

of x is 0·5 at high pressures or in large vessels and rises to 1·0 as the pressure falls or as the surface in contact with the reacting mixture increases; x thus depends on whether the combination of the Cl atoms takes place in the gas or on the walls of the vessel. The probable mechanism of the reaction is described in detail. Calculation of x from the calc. stationary concentration of the Cl atoms yields vals. in close agreement with those obtained experimentally.

H. F. GILLBE.

Kinetics, temperature coefficients, and quantum yields of the photochemical reactions of bromine with propyl, *iso*propyl, and butyl alcohol in radiation of wave-lengths 5660, 6800, and 8500 A. K. N. MALAVIYA and N. R. DHAR (Z. anorg. Chem., 1931, **199**, 418—421; cf. A., 1930, 46).—The quantum yield is far greater than unity and increases with rising temp. and with diminution in the wave-length of the incident light. The temp. coeff. varies from about 1·6 to about 3·0. It seems that the primary process in all the reactions is the activation of Br_2 mols. by the incident light. R. CUTHILL.

Relationship of light intensity to velocity of photochemical reactions of bromine with propyl, *iso*propyl, and butyl alcohol in radiation of wave-lengths 5660, 6800, and 8500 Å. K. N. MALAVIYA, N. R. DHAR, and W. V. BHAGWAT (Z. anorg. Chem., 1931, **199**, 406—417; cf. A., 1930, 46).—The velocity of the above reactions may be directly proportional to the intensity, I, of the incident light or approx. proportional to $I^{\frac{1}{2}}$, depending on the wave-length of the light. In presence of KBr, which has a retarding action, the square-root law is valid in all cases. It is shown theoretically that if a reaction is only slightly accelerated by light the rate of the photochemical change will be proportional to I, whereas if the accelerating effect is considerable the rate will be proportional to a fractional power of I.

R. CUTHILL.

Phototropic and photochemical changes of some camphor derivatives in solution. B. K. SINGH and B. BHADURI (Trans. Faraday Soc., 1931, **27**, 478—483).—The phototropic change of α-naphthylaminocamphor (A., 1925, ii, 195), which occurs in a variety of halogenated solvents, is accompanied by more or less photochemical oxidation to α-naphthyliminocamphor. The oxidation, but not the colour change, results in an increase in rotatory power. Both changes are inhibited by NaOEt or a trace of H_2O. The *d*-, *l*-, and *dl*-compounds undergo identical changes. It is suggested that the solvent plays a part in bringing about the phototropic change.

R. CUTHILL.

Measurement of ultra-violet radiation, especially of the physiologically active ultra-violet (which produces erythema), by means of the photochemical formation of triphenylmethane dyes from the leuco-compounds. (FRL.) E. WEYDE and W. FRANKENBURGER (Trans. Faraday Soc., 1931, **27**, 561—571).—The coloration developed in an EtOH solution of the leuco-cyanide of crystal-violet on exposure to ultra-violet light is, up to a certain degree of conversion, proportional to the intensity of the radiation. Since the quantum efficiency is unity at wave-lengths 2537 and 3130 Å., the abs. energy of monochromatic radiation between these limits can be determined by using a layer of solution of such thickness that absorption is complete and arranging that the coloured substance shall not be formed in sufficient amount to absorb itself. The leuco-sulphite solution is suitable for the measurement of the physiologically active ultra-violet, and the sensitivity spectrum of the solution may be matched to the sensitivity spectrum of the skin in respect of the formation of erythema. R. CUTHILL.

Photosynthesis in tropical sunlight. N. R. DHAR, G. RAO, and A. RAM (Trans. Faraday Soc., 1931, **27**, 554—558).—The formation under the influence of sunlight of CH_2O and occasionally traces of dextrose from CO_2 and H_2O in presence of various metallic salts and org. colouring matters has been observed. In presence of $FeCl_3$, $NiCO_3$, or chlorophyll, CH_2O undergoes in light more or less polymerisation to reducing sugars. Complex nitrogenous substances are not, however, readily formed from CH_2O and NH_3. It is suggested that the part played by chlorophyll in photosynthesis may be represented by the scheme chlorophyll $+ H_2CO_3 =$ chlorophyll peroxide $+ CO$, $CO(\text{nascent}) + H_2O = CH_2O + O$, chlorophyll peroxide $=$ chlorophyll $+ O$, $nCH_2O \longrightarrow$ carbohydrate. R. CUTHILL.

Photosynthesis. E. C. C. BALY (Trans. Faraday Soc., 1931, **27**, 545—551).—The prep. and properties of various types of catalyst for photosynthesis are described. R. CUTHILL.

Photochemical properties of carbonyl group. F. W. KIRKBRIDE and R. G. W. NORRISH (Trans. Faraday Soc., 1931, **27**, 404—408).—Existing data for the photolysis of aldehydes and ketones and new data for the photolysis of CH_2O and methylglyoxal show that decomp. giving CO always occurs when absorption takes place in the CO band between 3500 and 2500 Å., and that in several cases the decomp. is associated with predissociation. It seems probable that the primary reaction is $R'{\cdot}CO{\cdot}R'' = R'{\cdot}R'' + CO$, for the chief product is always $R'{\cdot}R''$. R. CUTHILL.

Mechanism of photo-oxidation of gaseous alkyl halides. J. R. BATES and R. SPENCE (Trans. Faraday Soc., 1931, **27**, 468—474).—When MeI vapour is exposed to the light from a Hg arc a very slow reaction, involving the liberation of I, occurs. If O_2 is added, however, reaction is much more rapid and paraformaldehyde and methylal are formed, $4MeI + 2O_2 = (MeO)_2CH_2 + (CH_2O)_n + H_2O + 2I_2$. A reaction mechanism which leads to the observed velocity equation is suggested. R. CUTHILL.

Application of the photochemical equivalence law to vital processes. O. WARBURG (Trans. Faraday Soc., 1931, **27**, 551—554).—Application of the above law to photosynthesis indicates that 4 elementary reactions are involved in the conversion of a mol. of CO_2 into sugar. The absorption spectrum of the CO compounds of such substances as hæmin may be obtained from measurements of the rate of respiration of cells in presence of CO in light of various wave-lengths and intensities. R. CUTHILL.

Mechanism of formation of nitrogen oxides from the mixture nitrogen–oxygen, under the influence of slow electrons. L. A. M. HENRY (Bull. Soc. chim. Belg., 1931, **40**, 371—384).—Oxides of N are formed from mixtures of N_2 and O_2 by a discharge of electrons when the acceleration is 16·8 volts, the velocity of formation increasing considerably up to 23·1 volts. The vals. correspond with the production of mol. and at. ions of N, respectively. The reactions suggested for the synthesis of NO_2 are: (1) $N_2^+ + O_2 = NO_2 + N^+$; $N_2^+ + O_2 \longrightarrow NO_2^+ + N$; $NO_2^+ + e \longrightarrow NO_2$: (2) $N^+ + O_2 \longrightarrow NO_2^+$; $NO_2^+ + e \longrightarrow NO_2$: (3) $N + O_2 \longrightarrow NO_2$. E. S. HEDGES.

Mechanism of formation of ozone from oxygen by the action of the electronic discharge. L. A. M. HENRY (Bull. Soc. chim. Belg., 1931, **40**, 339—360).—An accelerated discharge of electrons from a heated filament transforms O_2 into O_3 at the accelerating potentials 9·0 and 21·2 volts, corresponding respectively with the excitation of O_2 and its dissociation. The following mechanism is suggested: (1) $O_2'' + O_2 = O_3 + O$; (2) $O^+ + O_2 = O_3^+$; (3) $O + O_2 = O_3$.
E. S. HEDGES.

Theory of the chemical effects produced by rays in gaseous media. W. MUND (Ann. Soc. Sci. Bruxelles, 1931, **51**, B, 128—147).—Conditions for the formation of clusters, the temp. coeff. of reactions promoted by ions, and the influence of the composition of the irradiated gas are discussed theoretically. W. R. ANGUS.

Formation of hydrogen peroxide from hydrogen and oxygen. R. N. PEASE (J. Amer. Chem. Soc., 1931, **53**, 3188—3189; cf. this vol., 320).—Dynamic experiments in a pyrex vessel with $19H_2 : O_2$ mixtures at 530—550° show that even with low total conversion (<0·2% H_2), the highest $H_2O_2 : H_2O$ ratio in the product is 1 : 4. Thus direct formation of H_2O from its elements is not excluded.
J. G. A. GRIFFITHS.

Factors influencing the stability of hypochlorite solutions and a proposed formula for a modified Dakin's solution. H. DAVIS.—See B., 1931, 839.

Deterioration of sodium hypochlorite solution. A. KLING and H. SCHMUTZ.—See B., 1931, 839.

Polysulphides of the alkali metals. IV, V. T. G. PEARSON and P. L. ROBINSON (J.C.S., 1931, 1983—1990; cf. this vol., 807).—IV. RbSH acts similarly to KSH when boiled in EtOH solution with S, and the product is assumed to be Rb_2S_4 or, more probably, Rb_2S_5. Rb_2S_4 is formed when molten Rb reacts with S under PhMe. Hexasulphides of Li, Na, and K when treated with H_2O deposit S and yield pentasulphide solutions, which in the case of Li and less so in the case of Na deposit a little more S when kept. Alkali polysulphides in general when treated with CS_2 lose some S, but a quant. study is prevented by the simultaneous formation of thio- and perthiocarbonates. When treated with HCO_2H they behave differently from $(NH_4)_2S_5$ (A., 1928, 1200) and do not appear to be convenient sources of persulphides. In the cold they give intensely coloured solutions with many org. liquids.

V. The most probable structures for M_2S, MSH, M_2S_2, M_2S_3, M_2S_4, M_2S_5, and M_2S_6 (where M is an alkali metal) are formulated. N. H. HARTSHORNE.

Action of heat on alkali dihydrogen phosphates. L. HACKSPILL and R. LAUFFENBURGER (Compt. rend., 1931, **193**, 397—400).—Determination of the pressure of H_2O vapour in vac. shows that $NaH_2PO_4,2H_2O$ and NaH_2PO_4,H_2O lose all H_2O of crystallisation at 40° and 80° respectively; NaH_2PO_4 passes into $Na_2H_2P_2O_7$ at 190—210°, and into $NaPO_3$ at 380—300°. LiH_2PO_4 behaves similarly. $Na_2H_2P_2O_7,6H_2O$ becomes anhyd. at 60°, and passes into $NaPO_3$ at 280°, or, if the anhyd. salt has been precipitated by EtOH, at 300—305°. KH_2PO_4 passes directly into KPO_3 at 250°; $K_2H_2P_2O_7$ loses half its H_2O rapidly at 250°, possibly due to formation of $K_4H_2P_4O_{13}$, and the remainder slowly at 250—350°. The Rb salts behave similarly. There is no indication of the formation of any other hydrate in any case (cf. A., 1900, ii, 651).
C. A. SILBERRAD.

Action of boric acid on the chlorides and nitrates of the alkali metals. A. P. ROLLET and L. ANDRÈS (Bull. Soc. chim., 1931, [iv], **49**, 1065—1092).—H_3BO_3, in a current of steam, displaces HCl or HNO_3 from the corresponding salts of the alkali metals to form, in most cases, the pentaborate. The solubility of the pentaborates of K, Rb, and Cs in H_2O has been measured from the ice–salt eutectic to the b. p. F. J. WILKINS.

Formation of sodium hydrosulphide from sodium sulphide. M. O. CHARMANDARYAN and K. I. BRODOVICH (J. Appl. Chem., Russia, 1930, **3** 1023—1030).—For aq. $Na_2S + H_2S \longrightarrow 2NaHS$ the reaction coeff. is 0·0126; the max. yield is 89·7%. The adsorption of H_2S by dry Na_2S is accelerated by wetting the Na_2S with NaHS solution.
CHEMICAL ABSTRACTS.

Interaction between hydrated copper oxide and neutral salt solutions. M. P. V. IYER (Proc. XV Indian Sci. Cong., 1928, 170—171).—Pure CuO is positively charged in contact with conductivity H_2O. The p_H developed by shaking with neutral salt solutions depends on the anion more than on the cation. The total quantity of alkali liberated by repeated shaking of a given quantity of the CuO with KCl and $BaCl_2$ was const. CHEMICAL ABSTRACTS.

Per-rhenates of copper, nickel, and cobalt, and the ammines of these compounds. H. V. A. BRISCOE, P. L. ROBINSON, and A. J. RUDGE (J.C.S., 1931, 2211—2213).—The following new *compounds* have been prepared and described: $Cu(ReO_4)_2$, 0, 0·5, 4, and $5H_2O$, and $4NH_3$; $Ni(ReO_4)_2$, 0, 4, and $5H_2O$, and 4 and $6NH_3$; $Co(ReO_4)_2$, 0, 3, and $5H_2O$, and $4NH_3$. N. H. HARTSHORNE.

Solubility in water of the phosphoric acid in calcium phosphate. W. STOLLENWERK (Z. Pflanz. Düng., 1931, **21A**, 321—323; cf. B., 1931, 438).—Decomp. of $CaHPO_4$ by H_2O occurs only in the presence of free H_3PO_4. A Merck preparation contained approx. 6% of free acid. A. G. POLLARD.

New series of ammines of the mercuric iodide class. M. E. VOJATSAKIS (Bull. Soc. chim., 1931, [iv], **49**, 1029—1031).—The prep. of the *compound*

$HgI_4[Zn(NH_3)_6]$ is described. The method has also been applied to the corresponding salts of Cd, Ag, Ni, and Co. F. J. WILKINS.

Active aluminium. G. SAMBAMURTI and N. L. NARASIMHAM (Proc. XV Indian Sci. Cong., 1928, 168).—Al amalgam is readily oxidised by moist air containing traces of CO_2. CHEMICAL ABSTRACTS.

Hexafluorodisilane. W. C. SCHUMB and E. L. GAMBLE (J. Amer. Chem. Soc., 1931, **53**, 3191—3192).—The reaction between Si_2Cl_6 and anhyd. ZnF_2 affords Si_2F_6, m. p. $-18·5°$ at 780 mm., v. p. 760 mm. at $-19°$. The *compound* is instantly hydrolysed by moist air or H_2O. J. G. A. GRIFFITHS.

Germanium. IX. J. S. THOMAS and W. W. SOUTHWOOD (J.C.S., 1931, 2083—2097; cf. this vol., 322).—In its action on org. bases $GeCl_4$ resembles $SiCl_4$ more than the chlorides of the other elements of group IV. With NH_2Ph it forms $GeCl_4,4NH_2Ph$, which is separated by Et_2O into NH_2Ph,HCl and $Ge(NPh,HCl)_2$. With NH_2Et it forms $GeCl_4,4NH_2Et$ and $GeCl_4,6NH_2Et$, the latter being separated by Et_2O into NH_2Et,HCl and $Ge(NEt)_2$. With $NHEt_2$ it gives $GeCl_4,6NHEt_2$, which readily forms a substance in which Ge : Cl : N=1 : 4 : 5. This is separated by Et_2O into $NHEt_2,HCl$, NEt_3,HCl, and $Ge(NEt,HCl)(NEt)$. $GeCl_4$ does not react with tert. bases. With piperidine it gives $C_5H_{11}N,HCl$ and the saturated compound $Ge(NC_5H_{10})_4$. Hence it is concluded that an unstable saturated compound is the first product of the reactions of $GeCl_4$ with org. bases and NH_3. Hydrolysis of the above imides yields primary amines only, showing that they and probably $Ge(NH)_2$ are symmetrical in structure. N. H. HARTSHORNE.

Hyponitrites. I. Sodium hyponitrite. J. R. PARTINGTON and C. C. SHAH (J.C.S., 1931, 2071—2080).—$Na_2N_2O_2$ is satisfactorily prepared by a modification of Divers' method (*ibid.*, 1899, **75**, 97). It forms an octa- and a penta-hydrate. Its slight action with HI in solution is believed to be due to traces of HNO_2 formed by hydrolysis. When heated alone in a vac. it decomposes explosively at 260—265°: $3Na_2N_2O_2=2NaNO_2+2Na_2O+2N_2$, but when mixed with $NaHSO_4$ N_2O, NO, N_2, Na_2SO_4, $NaNO_2$, and, even at red heat, some $NaNO_3$ are formed. It is partly decomposed by H_2O, dil. HCl, and dil. H_2SO_4, giving N_2O, NO, and N_2, but apparently no $NaNO_3$ or $NaNO_2$, and completely decomposed by conc. H_2SO_4, giving the same products and $NaNO_3$ and traces of $NaNO_2$ as well. Acidified $KMnO_4$ oxidises part of it to $NaNO_3$ and the remainder decomposes into N_2O and NaOH, the proportion oxidised depending on the conditions. Equations are suggested for the above reactions. $Na_2N_2O_2$ is apparently not attacked by the common reducing agents. N. H. HARTSHORNE.

Attack of metals and alloys by phosphoric acid. A. PORTEVIN and A. SANFOURCHE.—See B., 1931, 844.

Reaction of violet solutions of chromic salts. C. MONTEMARTINI and A. VERNAZZA (Boll. R. Staz. Sperim. Ind. Pelli, 1931, **9**, 276—192).—Solutions of $Cr_2(SO_4)_3$ and $KCr(SO_4)_2,12H_2O$, when freshly prepared, give at once with ZnO, $Zn(OH)_2$, $5Zn,2CO_2,4H_2O$, or $ZnCO_3$ a pinkish-violet ppt., $Cr_2O_3,4ZnO,SO_3,xH_2O$. SeO_4'' acts similarly to SO_4'', but Cl' and NO_3' do not produce the same reaction. $Cd(OH)_2$ when freshly prepared reacts analogously to $Zn(OH)_2$, but CdO and $CdCO_3$ have no action. Oxides and hydroxides of Pb^{II}, Cu, Mg, Al, Be, Sn^{II}, Sn^{IV}, Mn^{II}, Fe^{II}, Ni, and Co do not show the same behaviour. O. F. LUBATTI.

Energy of activation for bimolecular reactions involving hydrogen and halogens, according to quantum mechanics. H. EYRING (J. Amer. Chem. Soc., 1931, **53**, 2537—2549; cf. this vol., 688).—Theoretical. The application of London's theory to reactions involving 4 atoms shows that the thermal reaction of H_2 with I will involve I_2 mols. only, whilst other halogens will react with H_2 by way of atoms, except in the case of Br, where an ambiguity exists depending on the value (3·5 or 10%) assigned to the ratio of coulombic to total energy of linking. The conversion of para- into ortho-H_2 involves an atom and a mol. rather than two mols. The theory is in accord with the observation that the energy of activation of reactions of the type MeX+Na=Me+XNa decreases with increasing size of the halogen, X (this vol., 174). J. G. A. GRIFFITHS.

Transformation from rose to green manganous sulphide. H. B. WEISER and W. O. MILLIGAN (J. Physical Chem., 1931, **35**, 2330—2344).—The change from rose to green MnS occurs at the b. p. in the presence of a sufficient excess of Na_2S. At room temp. the change readily occurs when $(NH_4)_2S$ in the presence of aq. NH_3 is the precipitant. The crit. concentration of reagents for max. speed of transformation is sharply defined. In the presence of NH_4HS free from NH_3 the change slowly occurs when the rose ppt. is seeded with the green by mixing this form with the reactant before precipitation. Rapid mixing delays the change, and free NH_3 is not essential (cf. A., 1924, ii, 186). The solvent action of Na_2S and $(NH_4)_2S$ on the rose sulphide is an important factor in initiating and accelerating the transformation, but adsorption of NH_3 by the rose ppt. acts protectively and retards it. There is no evidence that the rose ppt. which spontaneously turns to green has the composition $(NH_4)HMn_3S_4$ (cf. *loc. cit.*). *X*-Ray analysis shows that both sulphides are cryst., but are different in mol. structure. Green MnS is probably face-centred cubic with a_0 5·20 Å. and is identical with alabandite. The rose sulphides formed in the presence or absence of free NH_3 are identical in structure, as are the light and dark green sulphides formed with Na_2S and $(NH_4)_2S$, respectively; the difference in colour is due to variation in particle size. L. S. THEOBALD.

Persulphate complexes. R. KLEMENT (Z. anorg. Chem., 1931, **199**, 367—368).—The compound supposed by Duval to be persulphatopentamminocobaltic sulphate (this vol., 53) is really *hydroxypentamminocobaltic persulphate*, $[Co(NH_3)_5OH]S_2O_8$. R. CUTHILL.

Thiosulphatopentacyanocobaltic acid and its salts. Constitution and isomerism of thiosulphuric acid. P. RAY and S. N. MAULIK (Z.

anorg. Chem., 1931, **199**, 353—366).—The above *acid* has been obtained by the action of H_2S on its basic Pb salt, prepared from the K salt (A., 1928, 35). It is present in solution as the normal form, $H_4[(CN)_5\cdot Co\cdot O\cdot S_2O_2]$, but on evaporation red crystals of the *iso*-form, $H_4[(CN)_5\cdot Co\cdot S\cdot SO_3]$, separate, this transformation being irreversible. The following *salts* of the normal acid have been obtained: $X=[(CN)_5\cdot Co\cdot S_2O_3]$: $Na_4X,2H_2O$; PbO,Pb_2X; $(NH_4)_4X,0\cdot5H_2O$; $Li_4X,4H_2O$; Rb_4X; Cs_4X; Tl_4X; $Mg_2X,9\cdot5H_2O$; $Ca_2X,8H_2O$; $Sr_2X,3\cdot5H_2O$; and $Ba_2X,7\cdot5H_2O$. These are all yellow. The *iso*-acid forms brown or red salts. Both acids yield free $H_2S_2O_3$ on hydrolysis, but whereas the acid from the normal isomeride decomposes into S and H_2SO_3 the reaction in the other case is $H_2S_2O_3=H_2S+SO_3$. It is therefore concluded that $H_2S_2O_3$ exists in two isomeric forms which differ in the position of the charge on the anion: $S\cdot SO_2\cdot O''$ and $O\cdot SO_2\cdot S''$, the transformation from the first into the second probably being irreversible. This theory agrees with the general properties of thiosulphates. R. CUTHILL.

[Cyanogen] compounds of rhodium. G. A. BARBIERI (Atti R. Accad. Lincei, 1931, [vi], **13**, 433—439).—The stable complex *thiocyanate* $K_3Rh(CNS)_6$ has been prepared by the action of KCNS on K Rh chloride. By the action of dil. H_2SO_4 on this salt the free *acid* $H_3Rh(CNS)_6$ is liberated and can be extracted with amyl alcohol. With $AgNO_3$ the *salt* $Ag_3Rh(CNS)_6$ is precipitated. The following complex *thiocyanates* and *cyanides* have also been prepared:

$Co(NH_3)_6Rh(CNS)_6$ (orange-red),
$Co(NH_3)_6Rh(CNS)_6,3H_2O$,
$(C_6H_{12}N_4)_2H_2KRh(CNS)_6,4H_2O$ (ruby),
$(C_6H_{12}N_4)_3H_3Rh(CNS)_6$ (red),
$K_3Rh(CN)_6,2C_6H_{12}N_4,3H_2O$,
$Na_3Rh(CN)_6,2C_6H_{12}N_4,5H_2O$,
$Mg_3[Rh(CN)_6]_2,4C_6H_{12}N_4,24H_2O$,
$Ba_3[Rh(CN)_6]_2,4C_6H_{12}N_4,20H_2O$,
$Ba_3[Rh(CN)_6]_2,3C_6H_{12}N_4,18H_2O$,
$CaKRh(CN)_6,2C_6H_{12}N_4,6H_2O$, and
$BaKRh(CN)_6,2C_6H_{12}N_4,4H_2O$.

O. J. WALKER.

Osmium. IV. Action of oxidising agents on osmium sulphide. E. FRITZMANN and E. M. ZUHN (Z. anorg. Chem., 1931, **199**, 374—378; cf. A., 1928, 723).—Neither H_2O_2 nor $(NH_4)_2S_2O_8$ oxidises OsS_4 in either a neutral or an acid medium, but with both reagents present together slight oxidation occurs. In acid solution chlorates and bromates have a powerful oxidising action, whilst perchlorates are rather less reactive. R. CUTHILL.

Nephelometric titrations. III. Effect of extra compounds. C. R. JOHNSON (J. Physical Chem., 1931, **35**, 2237—2244; cf. this vol., 584).—The effect of the presence of 13 inorg. compounds of various types on the equal-opalescence end-point has been investigated. No loss of accuracy in at. wt. determinations need result from this source when suitable precautions are taken. Certain arbitrary features which arise in precise nephelometry are examined. L. S. THEOBALD.

Practical measurement of p_H by the quinhydrone electrode. P. VIGNON (J. Soc. Leather Trades' Chem., 1931, **15**, 367—384).—The purest chemicals obtainable should be used in the Hg_2Cl_2 electrode, which is in the form of a funnel-shaped tube, the lower end of which forms a U-tube free from taps and hermetically sealed. The Pt wire for the Hg_2Cl_2 cell should be washed in H_2CrO_4 solution, then in H_2O, and finally coated with Hg by electrolysis in a 1% $HgNO_3$ and HNO_3. This electrode can be used for one year. In making determinations 0·05—0·10 g. of quinhydrone should be shaken with 10 c.c. of the liquor to be tested. A steady potential and good duplicate readings are quickly obtained with solutions of pyrogallol tan liquors, but not with pyrocatechol tannins. The first readings from several measurements should be averaged for pyrocatechol tans and for sulphited extracts. Before each series of measurements, the apparatus should be tested with a solution of known p_H. An accuracy of 0·03—0·05 is obtained. The free acid in a tannin solution can be determined from the point of inflexion in the titration curve obtained by this electrode.

D. WOODROFFE.

Diphenylaminesulphonic acid as a new oxidation-reduction indicator. L. A. SARVER and I. M. KOLTHOFF (J. Amer. Chem. Soc., 1931, **53**, 2902—2905; cf. this vol., 54).—The oxidation of diphenylaminesulphonic acid by $K_2Cr_2O_7$ involves the following changes: diphenylaminesulphonic acid $\longrightarrow$ diphenylbenzidinesulphonic acid $\longrightarrow$ diphenylbenzidinesulphonic acid-violet; the last forms diphenylbenzidinesulphonic acid-green with unoxidised diphenylbenzidinesulphonic acid. The reaction is not affected by $HgCl_2$, but is markedly catalysed by and is slow in the absence of $Fe^{\cdot\cdot}$. In electrometric titration of the violet compound (absorption spectrum similar to that of diphenylbenzidine-violet) to the green compound with $FeSO_4$ in 0·5—2·0N-H_2SO_4, the colour change reddish-violet to green occurs reversibly at a potential of 0·59—0·6 volt with reference to the saturated calomel electrode. Further addition of $Fe^{\cdot\cdot}$ changes the green substance to pale yellow. Diphenylaminesulphonic acid is preferred to the other indicators (*loc. cit.*), since the colour change is sharper and more brilliant, and tungstate does not interfere.

J. G. A. GRIFFITHS.

Indicator corrections for diphenylamine, diphenylbenzidine, and diphenylaminesulphonic acid. L. A. SARVER and I. M. KOLTHOFF (J. Amer. Chem. Soc., 1931, **53**, 2906—2909; cf. preceding abstract).—Optimal analytical conditions for the use of the indicators in the titration of 0·1—0·001N-$FeSO_4$ with dichromate or vanadate are given and indicator corrections are recorded. Diphenylaminesulphonic acid has the largest correction, but is preferred.

J. G. A. GRIFFITHS.

Determination of hydrogen and methane in the Orsat apparatus. H. PAUSCHARDT.—See B., 1931, 791.

Analysis of chlorine monoxide–chlorine mixtures. J. W. T. SPINKS (J. Amer. Chem. Soc., 1931, **53**, 3015—3016).—The gases are absorbed in KI solution, excess of 0·1N-H_2SO_4 is added, and the I determined. The I liberated by the subsequent addition of slight excess of 0·1N-KIO_3 is a measure of

the excess of H_2SO_4. The method may be applied to ClO_2-Cl_2 mixtures. J. G. A. GRIFFITHS.

Volumetric determination of free hydrofluoric and sulphuric acids. H. GINSBERG (Chem.-Ztg., 1931, **55**, 608).—The solution is titrated with NaOH and methylene-blue to obtain the total acidity; a second portion is evaporated on an oil-bath until the temp. reaches 110°, then heated for a further 45 min. while the temp. is slowly raised to 155—160°, whereby the whole of the HF is expelled without loss of H_2SO_4. The residual acid is diluted and titrated as before, HF being found by difference. A. R. POWELL.

Determination of small quantities of hydrogen sulphide. Determination of sulphur in steel. S. G. CLARKE.—See B., 1931, 845.

Pregl's microchemical determination of nitrogen (micro-Dumas). F. GOVAERT (Ann. Chim. analyt., 1931, [ii], **13**, 229—232).—Possible sources of error are indicated. Air-free CO_2 is best generated by heating magnesite in a horizontal tube 15 cm. long, the rate of flow being controlled by a tap on an attached T-piece, the third arm of which dips below a Hg surface. Air should be removed by evacuation rather than by passage of CO_2, and if the substance is volatile, the appropriate portion of the apparatus should be cooled during this process by enclosing it between two interlocking blocks of Al, the lower ends of which dip in a freezing mixture. The apparatus and technique are described, the error being about 0·06% for N contents of 4—6%. J. GRANT.

Reaction between nitrite and iodide and its application to iodometric titration of these anions. C. A. ABELEDO and I. M. KOLTHOFF (J. Amer. Chem. Soc., 1931, **53**, 2893—2897).—At $p_H > 6$, the reaction between NO_2' and I' is negligibly slow, but at p_H 9, the reaction between NO, I', and O_2 is rapid, indicating direct reaction between I' and NO_2. Iodide is determined by decomp. with $0{\cdot}2N$-H_2SO_4 and $NaNO_2$ in presence of excess of carbamide in a closed vessel. The solution is titrated with $Na_2S_2O_3$ in presence of KI. Br' at high concentrations interferes. Fresenius' method is improved by adding carbamide. NO_2' is determined by the I liberated in the presence of KI, AcOH, H_2SO_4, and $NaHCO_3$ which affords CO_2 to exclude air. 2—3% of EtOH and amyl alcohol do not interfere. J. G. A. GRIFFITHS.

Determination of phosphorus in steel etc. N. D. RIDSDALE.—See B., 1931, 845.

Removal of phosphate ions from solution in analysis. J. BOUGAULT and E. CATTELAIN (J. Pharm. Chim., 1931, [viii], **14**, 97—98).—Metals precipitable by H_2S are removed, NH_3 solution is added until no further ppt. is dissolved, followed by much AcOH, and a slight excess of $Pb(OAc)_2$. After filtration a few drops of HCl are added and H_2S is passed into the boiling solution to remove Pb. T. MCLACHLAN.

Titrimetric determination of arsenic [in insecticides]. A. TERENYI and J. PASKUJ.—See B., 1931, 908.

Separation and determination of boric acid and alumina. MALAPRADE and SCHNOUTKA.—See B., 1931, 841.

Colorimetric determination of carbon dioxide. E. M. EMMERT (J. Assoc. Off. Agric. Chem., 1931, **14**, 386—389).—The CO_2 is passed through 1% H_2SO_4, and absorbed in an EtOH solution of Na phenolphthalein (wt. of salt $100 \times CO_2$ approx.). The diminution in colour is a measure of the amount of $NaHCO_3$ formed. T. MCLACHLAN.

Titration of sodium hydroxide and carbonate by Winkler's and by Warder's method.—A. SUCHIER.—See B., 1931, 839.

Gravimetric determination of beryllium. H. FISCHER and G. LEOPOLDI.—See B., 1931, 845.

Determination of magnesium by means of 8-hydroxyquinoline. K. NEHRING (Z. Pflanz. Düng., 1931, **21A**, 300—305).—Methods based on the precipitation of Mg, in the presence of Ca, by 8-hydroxyquinoline (cf. A., 1927, 639) are described. Results are in close agreement with those obtained by the pyrophosphate method. A. G. POLLARD.

Alkalimetric titration of magnesium and determination of magnesium chloride in carnallite. A. RAUCH.—See B., 1931, 802.

Determination of mixtures of mercury, copper, and arsenic in the presence of iron salts. M. FŒRSTER (Ann. Chim. analyt., 1931, [ii], **13**, 225—228).—NaCl is added to a solution of the substance in acid until only free HCl (about 12 c.c.) is present, followed by H_2O_2 and 10—15 c.c. of 10% NaH_2PO_2 (the last gradually and with shaking). After 25 min. the ppt. is collected and weighed, or is extracted with aqua regia and titrated with $AgNO_3$ in presence of KCN, NH_3, and KI. The filtrate is made alkaline with KOH, boiled with H_2O_2, and the black ppt. collected in the cold, dissolved in H_2SO_4, and electrolysed for Cu in presence of HNO_3 and (if necessary) $Fe_2(SO_4)_3$. The residual liquid and the alkaline filtrate are combined and saturated with H_2S; HCl is added to dissolve the Fe, and the residue washed and dissolved in NH_3 solution. As is then determined after oxidation with H_2O_2 by Bailly's $MgNH_4AsO_4$ method. Accurate results were obtained for about 0·2 g. each of Hg and As in the presence of Fe and about 0·87 g. of Cu. J. GRANT.

Volumetric determination of manganese in ferrosilicon. J. H. D. BRADSHAW (Foundry Trade J., 1931, **44**, 311).—With Si up to 18% the alloy is heated to fuming with HCl (30 c.c.), HNO_3 (15 c.c.), and H_2SO_4 (5 c.c.) and Mn is determined by the persulphate method in the filtrate from the SiO_2. With a higher Si content fusion with alkali carbonate is necessary. CHEMICAL ABSTRACTS.

Precipitation of manganese as manganous ammonium phosphate. P. NUKA (Latvij. Univ. Raksti, 1931, **2**, 1—23).—A hot 1% solution of $(NH_4)_2HPO_4$ is the most suitable liquid for washing precipitated $MnNH_4PO_4$, 60% EtOH being used for the final washing. Other NH_4 salts, and NH_3 solution, dissolve more of the ppt. than does H_2O. Precipitation in the cold, or in a colloidal form which has to be heated to give the cryst. form, yields high results. NaCl is adsorbed by the ppt. and in addition it hinders the conversion of $Mn_3(PO_4)_2$ into $MnNH_4PO_4$; AcOH

is without influence, but SO_4'', if present, is always retained in the ppt. H. F. GILLBE.

Analytical chemistry of rhenium. VI. Separation of molybdenum and rhenium. W. GEILMANN and F. WEIBKE (Z. anorg. Chem., 1931, **199**, 347—352; cf. this vol., 1025).—From a mixed solution of alkali molybdate and per-rhenate the Mo may be precipitated quantitatively as $MoO_2(C_9H_6ON)_2$ by means of 8-hydroxyquinoline in presence of AcOH, the Re in the filtrate then being precipitated with nitron. In determining a very small amount of Re in presence of a large amount of Mo, however, the Re should be separated from the bulk of the Mo by the distillation method before this procedure is followed. R. CUTHILL.

Colorimetric determination of iron in drinking water and [pharmaceutical] iron preparations. K. SCHERINGA.—See B., 1931, 908.

Spectroscopic identification of traces of nickel and chromium. A. J. DE A. GOUVEIA (Rev. Chim. Pura Appl., 1930, **5**, 41—43).—In a mixture of $NiSO_4$ and SiO_2 0·05% of Ni may be detected by visual observation of the line at 5476·9 Å.; in a mixture of $K_2Cr_2O_7$ and SiO_2 0·005% of Cr may be detected by observation of the triplet at 5204·5—5208·4 Å. The dimethylglyoxime method for Ni is therefore more sensitive than the spectroscopic, but the latter method is more sensitive for Cr than are any of the chemical reactions commonly employed. H. F. GILLBE.

Analysis of cassiterite. S. TAMARU and N. ANDÔ.—See B., 1931, 802.

Precision thermostat for temperatures from − 25° to 500°. J. A. BEATTIE (Rev. Sci. Instr., 1931, [ii], **2**, 458—465).—Details of construction are given. The variation in temp. is ±0·001°. C. W. GIBBY.

Thermostat. IV. Relation between sensibility of toluene thermoregulator and its shape and the volume of toluene. S. KAMBARA and M. MATSUI (J. Soc. Chem. Ind. Japan, 1931, **34**, 273—277B).—The sensibility of a thermoregulator is defined as the amplitude of temp. variation in a thermostat controlled by it; it is the combined effect of lack of perfect sensitiveness and time lag. The action of the Pt wire carrying the relay current on the surface of Hg causes the former; it increases with the square of the diam. of the tube, which should therefore be as narrow as possible. It cannot, however, be reduced below about 0·9 mm. The time lag of various bulbs was determined. If convection is neglected it increases linearly with the vol. The rate of temp. variation of the thermostat in which the regulator is set should be as small as possible, which is best produced by perfect insulation using 2 heaters, one only being controlled by the regulator. The limit of sensibility of a PhMe regulator is estimated to be 0·002°. C. IRWIN.

Methods and apparatus used in the Cryogenic Laboratory. XXIV. Cryostat for temperatures between 20·3° and 27·5° abs. W. H. KEESOM and J. H. C. LISMAN (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 602—604).—The design and manipulation of a cryostat used in determining the melting curve of H_2 (this vol., 1004) are discussed. W. R. ANGUS.

Copper–constantan thermocouple calibration below 0°. R. WIEBE and M. J. BREVOORT (Rev. Sci. Instr., 1931, [ii], **2**, 450—457).—A Cu–constantan couple can be calibrated between 0° and −193° with an accuracy of about 0·05° by determining the e.m.f. at the normal sublimation point of CO_2 and the normal b. p. of O_2, and applying the equation: deviation $=ae+be^2$, where a and b are consts. and e is the e.m.f. of the standard thermocouple. C. W. GIBBY.

Thermocouples. C. MÜLLER (Naturwiss., 1931, **19**, 416—419).—New sensitive radiation thermoelements are described. W. GOOD.

Calorimeter for measurement of heat effects in liquefied gases. P. CHALL and O. DOEPKE (Z. Elektrochem., 1931, **37**, 357—359).—A calorimeter in which a liquefied gas under a pressure of up to 10 atm. is the calorimetric liquid is described. By means of this apparatus the integral heat of dissolution of NaCl in NH_3 at room temp. has been determined, the mean val. being 2·7 kg.-cal. per mol. R. CUTHILL.

Quantitative spectrum analysis. A. IWAMURA (Mem. Coll. Sci. Kyoto, 1931, **A**, **14**, 43—54).—Various forms of electrodes when the sample to be analysed is in the form of (1) a solution, or (2) a sol. or an insol. non-conducting solid or powder are considered. The method and results of a quant. emission-spectrum determination of Pb contained in ZnO are given. W. GOOD.

Calibration of Abbé refractometer with compensating prisms, to measure refractive index for any wave-length. L. E. DODD (Rev. Sci. Instr., 1931, [ii], **2**, 466—501).—The error in dispersion measurements made with the Abbé refractometer varies with n, from 5% for $n=1·627$ to 30% for $n=1·330$. More accurate vals. can be obtained by calibrating the instrument to read for any wave-length, the average deviation over the above range being less than 5%. A method of calibrating the instrument for any wave-length if described. C. W. GIBBY.

Glass electrode. Various characteristics. H. KAHLER and F. DE EDS (J. Amer. Chem. Soc., 1931, **53**, 2998—3012; cf. A., 1930, 50, 423).—Specific resistances of glasses have been determined and a 100-fold decrease with a rise of temp. from 5° to 55° has been observed. With cells of thick glass, the zero correction (asymmetry potential) varies greatly with p_H, and this correction is higher if the outside of the bulb is immersed only to the top of the bulb. The correction decreases with rise of temp. Before the attainment (frequently slow) of complete equilibrium, glasses give deviations from the theoretical calibration (voltage–p_H) curve for the side of smallest fluid immersion and these are approx. proportional to the thickness (resistance) of the glass. For the side of greater immersion, the calibration agrees with theory. The results show that the deviation occurs only when the inner and outer surfaces are not immersed equally and to the same level, and the effect is due to a hygroscopic film on the glass surface above the liquid line. It is suggested that the observed potential is the val.

of the spurious film potential and the true potential for the immersed glass connected in parallel. The potentials given by an electrode exhibiting deviations are changed by varying the character of the film above the liquid line, but the deviations are eliminated by suppressing the film with insulating substances. The potential on the side of a glass bulb coated with semi-conducting material depends only slightly on the p_H and exhibits large salt effects. The uncoated side behaves normally. Salt effects in the p_H range 3·97—12·55 only become large at $p_H > 11{\cdot}4$ (cf. A., 1928, 370).

J. G. A. GRIFFITHS.

Use of thermionic valves for potential measurements. F. MÜLLER (Z. angew. Chem., 1931, **44**, 698—701).—A critical survey. Measurements of the e.m.f. of elements of high internal resistance are readily falsified by even small stray grid currents, and the ordinary arrangements of apparatus are unsatisfactory. Suggestions for suitable apparatus are made.

H. F. GILLBE.

Accurate form of copper coulometer. H. P. MATTHEWS and I. W. WARK (J. Physical Chem., 1931, **35**, 2345—2356).—Marshall's Cu coulometer (Trans. Faraday Soc., 1925, **21**, 297) is accurate for high current densities. The modifications required to keep the error less than 0·2% with low current densities are described.

L. S. THEOBALD.

Preparation of "distilled water" by electro-osmosis. R. DIETZEL and G. MÜLLER (Pharm. Ztg., 1931, **76**, 926—927).—The performance of an apparatus for the prep. of H_2O having a purity complying with the D.A.B. VI standards is described.

E. H. SHARPLES.

Depolarisation current in the capillary electrometer. F. O. KOENIG (Z. physikal. Chem., 1931, **156**, 38—40).—Calculation shows that the depolarisation current is carried by electrolytically deposited $H^{\cdot}$ which, however, do not form an amalgam with the Hg, but enter the electrolyte, form H mols., and as such diffuse through the capillary into the bulk of the solution.

H. F. GILLBE.

Oxometer for the determination of hydrogen peroxide etc. CHEM. FABR. PYRGOS, G.M.B.H.—See B., 1931, 880.

Accurate form of Huygens manometer adapted as a tensimeter. B. TOPLEY and M. L. SMITH (J. Sci. Instr., 1931, **8**, 194—196).—The oil column which balances the greater part of the gas pressure is separated from the gas by a barrier of Hg. The instrument is calibrated against the saturated v. p. of ice or H_2O, and is sensitive to 0·001 mm. Hg.

C. W. GIBBY.

Glass tap for pressure apparatus. T. FLEITMANN (Chem. Fabr., 1931, 351—352).—The tap described is suitable for work at pressures up to 3 atm.

E. S. HEDGES.

"Point-pyknometer" with measuring screw. G. HOFFMANN (Chem. Fabr., 1931, 325—326).—Two glass beakers with plane upper and lower edges, of 100 c.c. and 50 c.c. capacity, are clamped on a level bed plate. Each bears a graduation mark on the side and the interval between this mark and the liquid surface is measured by a metal point connected to a cap having a screw adjustment and scale. The content of distilled H_2O at 15° to the level and the calibration of the scale are determined once for each glass. Actual determinations are then made at any suitable temp., corrections being applied. The two beakers are alternative according to the mass of the sample.

C. IRWIN.

Gas pipette for the absorption of unsaturated hydrocarbons. J. PLANK (Chem. Fabr., 1931, 343).—In order to permit the use of Br as absorbent in conjunction with Hg as confining liquid a double pipette is used. One pipette is charged with Br-H_2O, the other with NaOH solution. They are connected both directly and through a 3-way cock with connexion to the gas burette. Air connexions from each pipette allow the capillaries to be cleared of Br vapour by blowing and no contact between Br and Hg is possible.

C. IRWIN.

Sputtering of quartz fibres. G. M. JONES (J. Sci. Instr., 1931, **8**, 155—159).—The fibres are kept under tension during sputtering to prevent breakage of the metal coating by straining during use. To prevent vibration during sputtering they are surrounded by an open Al cage.

C. W. GIBBY.

Humidity control. W. H. APTHORPE and M. C. MARSH (J. Sci. Instr., 1931, **8**, 152—154).—An instrument previously described has been improved (cf. B., 1928, 111).

C. W. GIBBY.

Maintaining constant humidity in a closed chamber. R. H. STOUGHTON (J. Sci. Instr., 1931, **8**, 164—166).—A stream of air is blown over muslin kept wet by a supply of H_2O entering through a carburettor float chamber.

C. W. GIBBY.

Theory of extraction and washing. R. G. C. DA COSTA (Rev. Chim. Pura Appl., 1930, **5**, 34—38).—Various equations are derived.

H. F. GILLBE.

General principle of condistillation. B. RASSOW and H. SCHULTZKY (Z. angew. Chem., 1931, **44**, 669—670).—Steam-distillation is a special case of a generally applicable principle which the authors designate as "condistillation." A satisfactory condistillation substance should have (*a*) a v. p. about the same as the substance to be distilled and (*b*) a mol. wt. at least not greater than this substance; further it should have no, or only a slight, solubility for the substance to be distilled. In the nitration of PhOH in glacial AcOH the constituents of the reaction mixture can be separated as follows: the *o*-nitrophenol is removed by condistillation with H_2O, the H_2O by condistillation with C_6H_6, the AcOH by condistillation with a petroleum fraction b. p. 120°, and *p*-nitrophenol by condistillation with a petroleum fraction b. p. 260—270° under 16 mm. pressure (130—160°). The *p*-compound can be further purified by crystallisation from CCl_4.

A. R. POWELL.

Sensitive membrane manometer. K. SOMMERMEYER (Z. physikal. Chem., 1931, **155**, 208—210).—The membrane forms part of a condenser and its movements are determined from capacity measurements. A sensitivity of 0·01 mm. is attainable.

R. CUTHILL.

Filter tubes with removable filter plug. H. MAISTER (Chem.-Ztg., 1931, **55**, 590).—The tube is of the usual shape, but the lower, narrower portion is made wider and carries a glass rod provided at its upper end with a porous glass filter plate which fits closely into the wide part of the tube and serves as support for the asbestos filtering layer, which can thus be readily and cleanly pushed out of the tube after use. The apparatus is especially designed for collecting Cu_2O in sugar determinations.

A. R. POWELL.

Behaviour of organic nitrogen compounds on fusion with potassium hydroxide. Apparatus for determining volatile bases produced during the fusion. R. KAPELLER-ADLER (Biochem. Z., 1931, **235**, 375—389).—The N in coniine, morphine, glucosamine, NMe_3 derivatives, and in most NH_2-acids is quantitatively eliminated as NH_3 or as volatile alkylamine when the substance is fused at 220—280° with KOH–NaOH. From many compounds containing N in the ring and many substances which can undergo ring-closure elimination is not complete, but can sometimes be made so or nearly so by addition of $KHSO_3$, Zn dust, or Fe powder. An apparatus for the rapid determination of N by fusion of 20—100 mg. of substance with KOH and NaOH is described. The volatile base is trapped in acid and can be recovered. The melt can likewise be quantitatively recovered.

W. MCCARTNEY.

Theory and construction of a circular mass-spectrograph. H. MURAWKIN (Ann. Physik, 1931, [v], **9**, 974—976).—Supplementary and a correction (cf. this vol., 546). W. GOOD.

Circulating pump for liquids. D. R. BARBER (J. Sci. Instr., 1931, **8**, 183—188).—A rubber bulb is compressed periodically by means of a motor-driven cam and operates a simple type of all-glass force-pump. C. W. GIBBY.

X-Ray apparatus for powder analysis. G. GRIME (J. Sci. Instr., 1931, **8**, 197—199).—The relative positions of tube and camera cannot be disturbed accidentally; the tube can be removed without destroying alinement, and fine adjustment and finding the best position are simplified. C. W. GIBBY.

Rapid analysis by phase separation with the centrifuge. W. KUNITZ (Z. angew. Chem., 1931, **44**, 742—745).—Details are given of the apparatus and method, and some of the applications and the results obtainable are described. H. F. GILLBE.

Weight-%-mol.-% nomograph. H. WATERMAN.—See B., 1931, 785.

B. p. nomograph. D. S. DAVIS (Chemist-Analyst, 1931, **20**, No. 3, 7—8).—From the nomograph the b. p. at atm. pressure is determined from that at another pressure. CHEMICAL ABSTRACTS.

Geochemistry.

Ammonia content of sea water. H. R. SEIWELL (Ecology, 1931, **12**, 485—488).—Variations from 0 to 48 mg. NH_3 per cu. m. of surface H_2O were observed in the vicinity of Mt. Desert Is., Maine, and up to 350 mg. at 25 m. depth. The bottom mud is probably the source of considerable amounts of NH_3-N. A. G. POLLARD.

Salt water of petroleum beds. P. PETRESCU (Petroleum, 1931, **27**, 653—655).—The composition is discussed and Palmer's method of interpreting the analytical results is criticised. Analyses of some Rumanian waters are give. N. H. HARTSHORNE.

Petroleum salt springs rich in radium and the problem of the origin of their radium. W. SALOMON-CALVI (Petroleum, 1931, **27**, 652—653).—Petroleum well H_2O, when free from SO_4'' and so far as studied, contains 10^{-11} to 10^{-8} g. Ra per litre. The Ra may have been derived from the surrounding strata or from Ra-accumulating plants. It is suggested that, in prospecting for oil, borehole H_2O showing a high radioactivity might be a useful indication of the presence of oil. N. H. HARTSHORNE.

Actinium problem. III. G. ELSEN (Chem. Weekblad, 1931, **28**, 486—491).—A survey. The problem of the calculation of the age of radioactive minerals from the Pb content is discussed on the basis of the hypothetical existence of several Th elements.

H. F. GILLBE.

Abundance of elements in the earth's crust and in meteorites. G. I. POKROVSKI and W. K. KORSUNSKI (Naturwiss., 1931, **19**, 421—422).—The curve representing the log. of the ratio of the no. of atoms in the earth's crust to the no. of atoms in meteorites as a function of the at. no. is similar to that for at. vol. as a function of at. no. W. GOOD.

Ilmenite and titaniferous iron ore from Nellore district, Madras. V. S. SWAMIMATHAN (Proc. XV Indian Sci. Cong., 1928, 287).—The ilmenite contains 49·82% TiO_2. The titaniferous ore contains SiO_2 0·65, TiO_2 28·71 Al_2O_3 0·48, Fe_2O_3 0, FeO 67·71, MnO 1·89, MgO 0·90, CaO 0, P_2O_5 0, total 100·34%.

CHEMICAL ABSTRACTS.

Iron ore of Mandi State. S. K. ROY (Proc. XV Indian Sci. Cong., 1928, 288).—A magnetite–hæmatite–quartz schist is described. The magnetite contains 73·28% Fe; Maroti ore contains about 61% Fe. CHEMICAL ABSTRACTS.

Absorption spectra of certain Belgian and Congo minerals. F. CORIN (Ann. Soc. Sci. Bruxelles, 1931, **B**, **51** 148—153).—Four monazite minerals from different sources each give similar absorption spectra, having two regions of intense absorption at 5800—5900 and 5270 A., due to Na and Pr. Er and Sa give rise to intense absorption at 6670 and 5250 Å. in each of four xenotime minerals. In monazites there is a large amount of absorption in the yellow, whilst in xenotimes there is none. Yttrocrastite gave two weak absorption bands at 5200—5300 and 4900 Å. Absorption data on the U-containing minerals, torbernite, kasolite, sklo-

dowskite, curite, and gummite, are given. Muscovite, fuchsite, and several garnets have also been examined.
W. R. ANGUS.

X-Ray analysis of slate. H. V. ANDERSON and K. G. CHESLEY (Amer. J. Sci., 1931, [v], **22**, 103—112).—Seven samples of slate contain predominantly quartz and corundum in submicroscopic particles, some cyanite (but no kaolin or andalusite), hydromicas (but no leverrierite or mica proper; cf. A., 1925, ii, 997), and chlorite, with small amounts of $CaCO_3$, $MgCO_3$, pyrite, hæmatite, and magnetite. The cleavage is due to oriented mica.
C. A. SILBERRAD.

Manganese in a mineral from Mirando do Corvo [Portugal]. A. J. DE A. GOUVEIA (Rev. Chim. Pura Appl., 1930, **5**, 44—45).—The mineral contained 0·11% Mn, in agreement with the limits determined spectroscopically. H. F. GILLBE.

Nickeliferous mineral. E. F. P. BASTO (Rev. Chim. Pura Appl., 1930, **5**, 23—29).—A specimen of mineral from Mirando do Corvo, Portugal, contained Fe_2O_3 6·26%, Al_2O_3 3·85%, Cr_2O_3 0·22%, NiO 0·16%, the residue being principally alkali (trace) and alkaline-earth metals, SiO_2, and CO_2. H. F. GILLBE.

Absorption spectra of rock-forming minerals. B. LANGE and W. EITEL (Tsch. Min. Petr. Mitt., 1931, **41**, 435—452).—Curves of light absorption, determined with a photo-cell, in micro-sections of minerals are given for rays of different vibration-directions. Such curves will be an aid in the identification of rock-forming minerals. L. J. SPENCER.

Felspars in the syenite of the Gröba type. L. DOLAR-MANTUANI (Tsch. Min. Petr. Mitt., 1931, **41**, 272—307).—Optical determinations were made with the Fedorov universal microscope-stage of the felspars (anorthoclase and basic andesine to labradorite). The composition of the rock as calc. from the micrometric measurements of the various constituents differs somewhat from the chemical analysis, owing to the presence of phenocrysts. L. J. SPENCER.

Pyroxene-andesite from Cserhát Mts., Hungary. R. REICHERT (Tsch. Min. Petr. Mitt., 1931, **41**, 265—271).—Optical determinations of the felspars were made, and a chemical analysis of the rock is given. L. J. SPENCER.

Radioactive fluorspar from Wilberforce, Ontario. F. L. HESS (Amer. J. Sci., 1931, [v], **22**, 215—221).—Deep purple fluorite was found to be as strongly radioactive as pitchblende (as shown by the action on a photographic plate). The material is free from microscopic inclusions, and Ra is perhaps present in isomorphous mixture $(Ca,Ra)F_2$. The name radiofluorite is suggested. L. J. SPENCER.

Rôle of water in tremolite. E. POSNJAK and N. L. BOWEN (Amer. J. Sci., 1931, [v], **22**, 203—214).—The tremolite formula $H_2Ca_2Mg_5(SiO_3)_8$ of Schaller (1916) and Warren (A., 1930, 844), which requires 2·22% H_2O, is substantiated. This H_2O is lost at about 900°, and, as shown by X-ray and optical examination, the material is converted into a mixture of pyroxene and cristobalite: $H_2Ca_2Mg_5(SiO_3)_8 \longrightarrow 2CaSiO_3,5MgSiO_3+SiO_2+H_2O$. Any excess of H_2O (in one case the total H_2O being 3·37%) is adsorbed and is given off gradually on heating.
L. J. SPENCER.

Magnesian amphibole from the dry melt: a correction. N. L. BOWEN and E. POSNJAK (Amer. J. Sci., 1931, [v], **22**, 193—202).—Allen, Wright, and Clement (A., 1906, ii, 865) described two forms of pyroxene and two of amphibole from $MgSiO_3$ melts. The latter are too minutely cryst. for satisfactory optical determination, and it is now shown by X-ray methods that the material is really forsterite mixed with some glass: $2MgSiO_3 \leftarrow Mg_2SiO_4+SiO_2$. A difficulty in accepting the recent view that H_2O is an essential constituent of amphiboles is thus removed.
L. J. SPENCER.

Tectites of the Philippines. A. LACROIX (Compt. rend., 1931, **193**, 265—267).—The rizalites of Rosario (Batangas, Luzon) are quite similar to the tectites of Indo-China (cf. this vol., 1028), Malay, and North Borneo, and, save for subsequent change, the billitonites of Billiton. Analyses of a rizalite, and of a tectite from Dan-Kia (Annam) give (in this order): SiO_2 71·64, 72·26; Al_2O_3 12·53, 13·18; FeO 5·32, 5·32; MgO 2·79, 2·15; CaO 3·42, 2·42; Na_2O 1·21, 1·42; K_2O 2·28, 2·15; TiO_2 0·98, 0·99; H_2O (+) 0·19; 0·14; H_2O (−) trace, 0·06; MnO 0·10, 0·10; total 100·46, 100·40%; d 2·447—2·451, 2·440. A common meteoric origin for all is inferred.
C. A. SILBERRAD.

Types of humus layer in forests of N.E. United States. L. G. ROMELL and S. O. HEIBERG (Ecology, 1931, **12**, 567—607).—A general classification into "mull" and "duff" types is adopted. The distribution of humus types is largely governed by H_2O conditions and by the texture and CaO content of the soil. Nitrification is fairly general in all types, but is more characteristic of mull-humus. Acidity is not the limiting factor in non-nitrifying types, some samples of p_H 2·9 showing definite nitrification. In the duff type there is a positive correlation between p_H and nitrification during storage.
A. G. POLLARD.

Radioactivity of the coal and anthracite of the Donezky basin. E. S. BURKSER, M. J. SCHAPIRO, and V. V. KONDOGURI (Biochem. Z., 1931, **237**, 276—281).—Tables summarise the Ra contents of the ash, and the Ra and Th contents of a number of samples, of coal, anthracite, etc., details being given of the position from which the samples were drawn. The Ra content of the samples is of the order 10^{-12} to 10^{-11}% and the Th content 10^{-4} to 10^{-3}%.
P. W. CLUTTERBUCK.

Organic Chemistry.

Number of isomeric hydrocarbons of the methane series. H. R. HENZE and C. M. BLAIR (J. Amer. Chem. Soc., 1931, **53**, 3077—3085).—Theoretical. No simple relationship exists between the total no. of isomerides and the C content. A relationship is established between the no. of isomerides and alkyl groups composing the hydrocarbons, and formulæ are advanced for calculating the no. of isomeric hydrocarbons of various structural types from the C content. H. BURTON.

Slow combustion of methane and ethane. E. MARDLES (Nature, 1931, **128**, 304—305).—A reply to Bone (this vol., 1030). L. S. THEOBALD.

Significant temperatures in the pyrolysis of pentanes and pentenes. J. F. NORRIS and G. THOMSON (J. Amer. Chem. Soc., 1931, **53**, 3108—3115).—The temp. quoted in parentheses after the following hydrocarbons are those at which decomp. begins in pyrex glass vessels: *n*-pentane (391°), *iso*pentane (383°), Δ^{α}-pentene (389±1·4°), Δ^{β}-pentene (400±2·4°), β-methyl-Δ^{β}-butene (433±0·6°). Δ^{α}-and Δ^{β}-Pentenes decompose 3 times as rapidly as *n*-pentane when heated 10° above the initial decomp. temp., but only at one half the rate of β-methyl-Δ^{β}-butene. The increase in the rate of decomp. of the hydrocarbons per 10° is const. within certain limits. The rate of decomp. of Δ^{β}-pentene is doubled by the presence of a trace of H_2O. H. BURTON.

Decomposition of ethylene by heating under high pressure. H. I. WATERMAN and A. J. TULLENERS (J. Inst. Petroleum Tech., 1931, **17**, 506—510).—When heated in an autoclave at 350° and 175 kg. per sq. cm. C_2H_4 decomposes explosively with considerable evolution of heat and formation of C, CH_4, and H_2. H. A. PIGGOTT.

Factors affecting the catalytic activity of cobalt oleate in the autoxidation of Δ^{β}-pentene. J. HYMAN and C. R. WAGNER (J. Amer. Chem. Soc., 1931, **53**, 3019—3027).—Oxidation of Δ^{β}-pentene by O_2 in presence of Co oleate (cf. this vol., 61) is retarded by NH_3 or NEt_3 and accelerated by stearic acid. The active catalyst is a Co''' derivative (assumed to be a complex cobaltic acid), probably formed by oxidation of the Co oleate. H. BURTON.

Allene hydrocarbons. M. BOUIS (Ann. Chim., 1928, [x], **9**, 402—465).—A general method for the prep. in good yields of allenes, R·CH:C:CH$_2$, where R is an alkyl group, is described and the physical and chemical properties of these derivatives are investigated. The starting point is the appropriate substituted allyl alcohol, R·CH(OH)·CH:CH$_2$, prepared by the action of the appropriate Grignard reagent on acraldehyde, the essential experimental conditions of the reaction being described in detail, and thus is obtained *δ-methyl-Δ^{α}-penten-γ-ol*, b. p. 125°/760 mm.; ε-methyl-Δ^{α}-hexen-γ-ol has b. p. 146° (corr.)/760 mm. These by the action of PBr_3 with cooling in presence of pyridine yield the pure allyl bromides, R·CH:CH·CH$_2$Br, the isomeric change being complete in each case (cf. this vol., 634) and thus are obtained *α-bromo-Δ^{β}-pentene*, b. p. 35°/25 mm.; *α-bromo-Δ^{β}-hexene*, b. p. 42—44°/10 mm.; *α-bromo-δ-methyl-Δ^{β}-pentene*, b. p. 46°/18 mm.; *α-bromo-Δ^{β}-heptene*, b. p. 62—64°/10 mm.; *α-bromo-ε-methyl-Δ^{β}-hexene*, b. p. 60°/15 mm. These by boiling with anhyd. NaOAc in AcOH yield the corresponding acetates, and thus are obtained Δ^{β}-pentenyl acetate; *Δ^{β}-hexenyl acetate*, b. p. 171—173°; *δ-methyl-Δ^{β}-pentenyl acetate*, b. p. 163°; *Δ^{β}-heptenyl acetate*, b. p. 192—194° (corr.); *ε-methyl-Δ^{β}-hexenyl acetate*, b. p. 180—182°. Hydrolysis of these acetates with aq. MeOH–NaOH yields the corresponding alcohols, CHR:CH·CH$_2$·OH, and thus are obtained Δ^{β}-penten-α-ol, b. p. 138—139°; *Δ^{β}-hexen-α-ol*, b. p. 158—160° (*naphthylurethane*, m. p. 76°); *δ-methyl-Δ^{β}-penten-α-ol*, b. p. 150°; *Δ^{β}-hepten-α-ol*, b. p. 177—179° (corr.); *ε-methyl-Δ^{β}-hexen-α-ol*, b. p. 169° (corr.). Addition of Br at 0° to the allyl bromides (above) yields the tribromides, CHRBr·CHBr·CH$_2$Br, and thus are obtained: αβγ-tribromopentane, 122—124°/18 mm.; αβγ-tribromohexane, b. p. 127—129°/11 mm.; *αβγ-tribromo-δ-methylpentane*, b. p. 131—132°/18 mm., m. p. 35°; αβγ-tribromoheptane, b. p. 142—143°/12 mm.; *αβγ-tribromo-ε-methylhexane*, b. p. 134—135°/12 mm. Fusion with 75—80% KOH converts these into allene dibromides, CHRBr·CBr.CH$_2$, and thus are obtained; *βγ-dibromo-Δ^{α}-pentene*, b. p. 173°/760 mm.; *βγ-dibromo-Δ^{α}-hexene*, b. p. 83—85°/9 mm.; *βγ-dibromo-δ-methyl-Δ^{α}-pentene*, b. p. 81°/14 mm.; *βγ-dibromo-Δ^{α}-heptene*, b. p. 108—110°/12 mm.; *βγ-dibromo-ε-methyl-Δ^{α}-hexene*, b. p. 100—101°/12 mm. The allenes CHR:CH:CH$_2$ are obtained (yield 50—60% on the original allyl alcohols) by dropwise addition of these dibromides to Zn dust and boiling EtOH, and thus are prepared: *ethylallene*, b. p. 45°; *n-propylallene*, b. p. 78°; iso*propylallene*, b. p. 70°; *n-butylallene*, b. p. 106° (corr.); iso*butylallene*, b. p. 96° (corr.). These all show a slight mol. optical exaltation (about 0·5) which increases with the mol. wt. of the derivatives and is greater with branched chains than with straight chains. Addition of 1 mol. of Br in CCl_4 solution to propylallene occurs mainly at the βγ double linking, a little of the αβ-compound being obtained as a by-product. Further addition of Br yields, with the appropriate allene, *αββγ-tetrabromopentane*, b. p. 120°/3 mm.; *αββγ-tetrabromohexane*, b. p. 130°/3 mm.; *αββγ-tetrabromoheptane*, b. p. 140°/3 mm. The action of a 35% AcOH solution of HBr on ethylallene at 0° yields a mixture of products from which were isolated a mixture which probably contains β-bromo-Δ^{α}-pentene (yields an acetylene which forms a Cu derivative on treatment with alkali) and β-bromo-Δ^{β}-pentene (yields propionic acid on oxidation) and *ββ-dibromopentane*, b. p. 62—63°/18 mm. Hydration of the allenes with conc. H_2SO_4 at −10° and subsequent treatment with H_2O yields the corresponding methyl ketones CH$_2$R·CO·Me, whilst by the action of $NaNH_2$ the Na derivatives of the isomeric acetylenes CH$_2$R·C:CNa are obtained. J. W. BAKER.

Raman effect and chemistry. Sensitiveness of organic spectrum analysis. R. LESPIEAU, M. BOURGUEL, and R. L. WAKEMAN (Compt. rend., 1931, **193**, 238—240).—The presence of an isomeric Δ^{α}-hydrocarbon in a cyclic paraffin, *e.g.*, of Δ^{α}-hexene or

Δ^{α}-heptene in methylethyl- or methylpropyl-*cyclo*propane, respectively, is detectable by the presence of the Raman line 1642, that of an Δ^{β}- or Δ^{γ}-isomeride by that of 1665. Of the first 1·4% can in this way scarcely, of 2·4% with certainty, be detected, of the two last " a very small quantity."

C. A. SILBERRAD.

Isomerides in "di*iso*butylene." F. C. WHITMORE and S. N. WRENN (J. Amer. Chem. Soc., 1931, **53**, 3136—3142).—" Di*iso*butylene " is separated by fractional distillation into ββδ-trimethyl-Δ^{α}-, b. p. 101·2—101·3° (corr.)/760 mm., and -Δ^{β}-pentenes, b. p. 104·1—104·5° (corr)/760 mm., the former predominating (cf. A., 1930, 1018). H. BURTON.

Detection of the nitro-group in organic compounds. P. K. BOSE (Analyst, 1931, **56**, 504—507).—When 0·01—0·05 g. of the substance is hydrolysed with 1 c.c. of KOH (10 g. in 6 c.c. of H_2O) part of the NO_2 group is hydrolysed to HNO_2. On dilution and addition of AcOH a straw-yellow colour may be formed, but, if not, HNO_2 is tested for by the Griess–Ilosvay reagent. Aliphatic NO_2-compounds and nitrites react in the cold, aromatic NO_2-compounds are unaffected, and aromatic polynitro-compounds are hydrolysed by boiling for not more than 2 min. Nitroso-derivatives of phenols and amines do not give the reaction. T. MCLACHLAN.

Number of structurally isomeric alcohols of the methanol series. H. R. HENZE and C. M. BLAIR (J. Amer. Chem. Soc., 1931, **53**, 3042—3046).—Theoretical. No simple relationship exists between the total no. of isomerides and the C content. Recursion formulæ are advanced for calculating the no. of isomeric alcohols of a given C content, but their use involves the knowledge of the total no. of isomerides of every smaller C content. H. BURTON.

Diastereoisomerides of αα'ββ'-tetrabromodiethyl ether. W. L. RUIGH and R. T. MAJOR (J. Amer. Chem. Soc., 1931, **53**, 3131—3135).—Divinyl ether and Br in presence of CCl_4 and $CaCO_3$ give two diastereoisomeric αα'ββ'-tetrabromodiethyl ethers, m. p. 65—66° (I) (cf. A., 1929, 791) and 62—63° (II). (I) and Zn dust in AcOH or Na in xylene afford MeCHO, whilst (I) and *p*-nitrophenylhydrazine in AcOH furnish glyoxal-*p*-nitrophenylosazone, also obtained similarly from (II). These results confirm the view (*loc. cit.*; cf. A., 1923, i, 439; 1927, 42) that the tetrabromobutaldehyde of Freundler (A., 1907, i, 285) is really (I). When (II) is heated above the m. p. or a solution in Et_2O is kept, (I) is produced.

H. BURTON.

Hexosemonophosphates. Synthetic Robison ester. Galactose-6-phosphate. P. A. LEVENE and A. L. RAYMOND (J. Biol. Chem., 1931, **92**, 757—763, 765—768).—Further examination of the glucose-6-phosphate previously described (this vol., 63) has shown it to be identical with Robison's ester. It is also obtained in small yield by the action of $POCl_3$ on 1 : 2 : 3 : 4-tetra-acetylglucose in dry pyridine, being isolated as Ba salt. An improved method of prep. of di*iso*propylideneglucose is described.

Phosphorylation of di*iso*propylidenegalactose gives *Ba galactose-6-phosphate*, $[\alpha]_D^{25}$ +24·5°, which is not fermented by zymin, and does not reduce the period of induction with this enzyme. H. A. PIGGOTT.

Conjugated systems. IX. Addition of hypochlorous and hypobromous acids to β-vinylacrylic acid. I. E. MUSKAT and L. HUDSON (J. Amer. Chem. Soc., 1931, **53**, 3178—3183).—β-Vinylacrylic acid in $CHCl_3$ and aq. HClO afford (probably) *γ-chloro-δ-hydroxy-Δ^{α}-pentenoic acid* (I), m. p. 71—74° (ozonolysis product oxalic acid), which adds a further mol. of HClO, yielding a *dichlorohydrin*, m. p. 143°. Distillation of (I) in a vac. gives unidentified products, whilst dehydration with P_2O_5 in Et_2O affords probably a polymeric γ-chloro-β-vinylacrylic acid. β-Vinylacrylic acid and HBrO give a *monobromohydrin*, m. p. 92—93°, converted by HBrO into a *dibromohydrin*, m. p. 148—149°. H. BURTON.

[Hydrogenation of linolenic acid.] H. VAN DER VEEN (Chem. Umschau, 1931, **38**, 219; cf. this vol., 712).—A corrected graph is given.

E. LEWKOWITSCH.

C_4-Saccharinic acids. V. Preparation of βγ-dihydroxybutyrolactone. γ-Hydroxy*iso*crotonolactone. Attempt to prepare ββ'-dihydroxy*iso*butyric acid. J. W. E. GLATTFELD, G. LEAVELL, G. E. SPIETH, and D. HUTTON (J. Amer. Chem. Soc., 1931, **53**, 3164—3171).—Details of an improved method of prep. of βγ-dihydroxybutyrolactone (I), b. p. 150—151°/5 mm., m. p. 22·5—26°, from glycerol-α-chlorohydrin are given. γ-Hydroxy*iso*crotonolactone (II), m. p. 5°, produced as a by-product in the prep. of (I), and NH_2·NHPh give a *compound*, m. p. 183°. (I) and (II) are also produced when the nitrile from glycerol-β-chlorohydrin and NaCN is hydrolysed; no ββ'-dihydroxy*iso*butyric acid is formed. βγ-Dihydroxybutyrphenylhydrazide has m. p. 109° (lit. 99—101°). H. BURTON.

Bismuth tartrate. S. G. STEVENSON (Quart. J. Pharm., 1931, **4**, 178—182).—$Bi_2(C_4H_4O_6)_3$ is the normal salt, but the composition of the final product is regulated by the washing. H_2O containing 0·375% of tartaric acid should be used. There are no complex Bi tartrates. T. MCLACHLAN.

Electrometric studies of complex-formation. III. Fehling's solution and the scale preparations. C. MORTON (Quart. J. Pharm., 1931, **4**, 161—174).—Fehling's solution contains a blue basic colloid complex, $3CuC_4H_4O_6,5Cu(OH)_2$, peptised, not by excess of alkali, but by tartrate ions. The colloidal nature of $BiC_6H_5O_7,3Bi(OH)_3$ and $Bi(OH)C_4H_4O_6,2Bi(OH)_3$ is demonstrated by dialysis, these basic complexes being distributed in alkali citrate or tartrate in pharmaceutical preps. In preps. of Fe and NH_4 citrate the basic colloid complex present is $FeC_6H_5O_7,2Fe(OH)_3$, which is green in colour; there is no reduction of $Fe^{\cdots}$ to $Fe^{\cdot\cdot}$, and the red colour of commercial preps. is due to the presence of peptised uncombined $Fe(OH)_3$. T. MCLACHLAN.

M. p. of mucic acid. G. TANRET (Bull. Soc. Chim. biol., 1931, **13**, 710—711).—Mucic acid has m. p. 255° (decomp.) on the Maquenne block.

C. C. N. VASS.

Determination of the humic acid content of dilute solutions by means of potassium per-

manganate. D. J. W. Kreulen (Brennstoff-Chem., 1931, 12, 265—266).—2—3 c.c. of the humic acid solution, previously diluted to contain approx. 0·4 mg. per c.c., 50 c.c. of H_2O, 20 c.c. of dil. H_2SO_4 (1 vol. 96% H_2SO_4, 3 vols. of H_2O), and 20 c.c. of 0·01N-$KMnO_4$ solution are heated in a 300-c.c. flask in such a manner that after 4 min. the liquid boils gently, and is kept at this temp. for a further 6 min. It is then cooled rapidly to about 70°, 20 c.c. of 0·10N-oxalic acid are added, and the excess is titrated with the $KMnO_4$ solution. From the $KMnO_4$ used the humic acid is determined by reference to standard curves obtained with known concentrations of Merck's humic acid. Reproducible results are obtained, but the humic acid solution must be freshly prepared.

A. B. Manning.

Determination of the carbonyl and aldehyde content of organic compounds. Determination of phenylhydrazine. S. Marks and R. S. Morrell (Analyst, 1931, 56, 508—514).—Ellis' modification of Smith's method (cf. A., 1906, ii, 312) for the determination of ·CO· and ·CHO groups is the most trustworthy of those previously described and may be used for the determination of NH_2·NHPh. The precipitated hydrazone is filtered off before adding to Fehling's solution and the addition made gradually from a funnel. The N_2 collected is saturated with C_6H_6 vapour before measurement and a correction allowed. Glacial AcOH is employed as a solvent where H_2O or EtOH is unsuitable.

T. McLachlan.

Condensation products of dextrose with *o*-phenetidine, *o*-anisidine, and *o*-toluidine. I. Glucosidic compounds. M. Amadori (Atti R. Accad. Lincei, 1931, [vi], 13, 195—199; cf. this vol., 1039).—In EtOH, these bases (1 mol.) condense with dextrose (1 mol.) giving *compounds* of glucoside type with the characters: with *o*-phenetidine, $C_{14}H_{21}O_6N$, m. p. 157°; $[\alpha]_D^{20}$ −7° to −62° in H_2O; +31° to −15° in EtOH. With *o*-anisidine, m. p. 146°; $[\alpha]^{20}$ −15° to −70° in H_2O; +10° to −12° in EtOH. With *o*-toluidine, m. p. 97° $[\alpha]_D^{15}$ −96° in H_2O; −96° to −40° in EtOH. Compounds of the Schiff's base type are obtainable by fusing the bases with dextrose.

T. H. Pope.

Velocity of ether formation between α-methyl-*d*-glucoside and triphenylmethyl chloride in pyridine. B. Helferich and N. M. Bigelow (J. pr. Chem., 1931, [ii], 131, 259—265).—The reaction between CPh_3Cl and α-methyl-*d*-glucoside in pyridine is very slow at 0°, but proceeds with measurable velocity at 30°, being complete within 48 hr. at this temp. Measurement of the change of rotation of the solution did not give a satisfactory bimol. equilibrium const., partly because of errors of observation, increased by decomp. of the chloride by moist air, but mostly because of complex formation. A satisfactory const. was obtained when the chloride and glucoside were in the mol. ratio 2 : 1 (but not when the ratio was 1 : 1), by hydrolysis of the excess of chloride with a little H_2O, subsequent removal of most of the CPh_3·OH and $(CPh_3)_2O$ by dilution with H_2O to a 20% pyridine solution, and determination of the rotation of this solution. A slight rise in K in the intermediate stages of the reaction is due to complex formation. Ether formation is almost complete at equilibrium, but for preparative purposes an excess of chloride is advisable. No indication of secondary groups of the glucoside reacting was obtained.

R. S. Cahn.

γ-Glucoside of 3-methyl-*d*-glucose. P. A. Levene and R. T. Dillon (J. Biol. Chem., 1931, 92, 769—776).—By the action of HCl in MeOH 3-methyl-*d*-glucose is readily converted into its *-γ-methylglucoside*, the structure of which is confirmed by its further methylation (MeI and Ag_2O) to tetramethyl-γ-methylglucoside (identified by hydrolysis and oxidation of the resulting tetramethyl-γ-glucose to 2 : 3 : 5 : 6 - tetramethylgluconic acid). Glucoside formation occurs at the same rate as with dextrose; it is therefore considered that the propylene oxide structure is excluded for the γ-glucosides.

H. A. Piggott.

Constitution of melezitose and turanose. E. Pacsu (J. Amer. Chem. Soc., 1931, 53, 3099—3104).—Turanose (A., 1930, 1024) and CPh_3Cl in pyridine give *tri(triphenylmethyl)turanose*, m. p. 105—115° (*Ac_5* derivative, m. p. 95—105° after sintering at 85°), indicating that the glucose residue is not attached to C_6 of the fructose residue. The structures assigned to turanose and melezitose by Zemplén and Braun (A., 1926, 1229) are probably correct.

H. Burton.

Lignin and related compounds. VIII. Action of sulphurous acid on lignin and related compounds. C. A. Sankey and H. Hibbert (Canad. J. Res., 1931, 5, 1—47).—Conductivity measurements over the range 18—145° and in some cases equilibrium, hydrolysis, and stability measurements show that the sulphonic acids of PhCHO, vanillin, dextrose (the free aldehydic form appears to be present in very small amount), and furfuraldehyde are typically unstable, but less so than those of COMeEt and *cyclo*hexanone; that the sulphonic acid of CHPh:CH·COMe is formed by 1 : 4 addition followed by H migration; that H_2SO_3 is added only very slowly and at high temps. to CHPh:CH·CH_2·OH and tetrahydrobenzene; that sulphonic acids of $COBz_2$, CH_2Bz_2, and quinone (reduction occurs) are not formed and $C_6H_4(OH)_3$ gives a small percentage of unstable derivative; and that furfuryl alcohol and glucal form intermediate oxonium derivatives. Similar studies of lignosulphonic acids from various sources indicate that ring O and an ethylenic linking are present in the same ring of the lignin mol. and that ligninsulphonic acid is formed first through an oxonium additive product and finally by direct ethylenic addition. This mechanism explains the conditions involved in the manufacture of sulphite pulp.

A. Renfrew.

Constitution of pine lignin, humic acids, and humins. W. Fuchs and R. Daur (Brennstoff-Chem., 1931, 12, 266—268).—The recent results of Fuchs and others are summarised.

A. B. Manning.

Amino-derivatives of dodecoic acid. D. M. Birosel (J. Amer. Chem. Soc., 1931. 53. 3039—3041).—α-*Aminododecoic acid*, m. p. 263° (decomp.) [*picrate*, m. p. 255—256° (decomp.); *Ac* derivative, m. p. 93—94°; *Me*, m. p. 241—242° (decomp.), *Prᵅ*, m. p. 246° (decomp.), *Prᵝ*, m. p. 250—252° (decomp.), and *Buᵝ*, m. p. 248—249° (decomp.), esters], is prepared

from dodecoic acid by Adams and Marvel's method (A., 1920, i, 283). The above esters are obtained from the requisite alkyl α-bromododecoate and conc. NH_3 at 58°. *Dodeco*-m- and -p-*nitroanilides* have m. 78° and 80°, respectively. H. BURTON.

Elimination of halogen by dilute alkali from stereoisomeric halogenoacylamino-acids. E. ABDERHALDEN and F. SCHWEITZER (Fermentforsch., 1931, **12**, 532—541, 601—607).—The four isomerides l-*α-bromopropionyl*-l-*leucine* (I) m. p. 88—90°, $[\alpha]_D^{20}$ −35·4°, l-d- (II) m. p. 83° $[\alpha]_D^{20}$ +1·8°, d-d- (III), $[\alpha]_D^{20}$ +35·8°, d-l- (IV), m. p. 68—70°, $[\alpha]_D^{20}$ −1·4°, were prepared. Of the racemates, (I), (III) corresponds with A and (II), (IV) with B (cf. A., 1930, 816). Halogen was more rapidly removed from (I) in presence of trypsin; the rate of halogen elimination from (II) was unaltered.

The following were also prepared: *d*-α-bromohexoyl-*l*-tyrosine, m. p. 144—145°, $[\alpha]_D^{20}$ +44°, *l*-*l*-, m. p. 141—142°, $[\alpha]_D^{20}$ +29; *l*-α-bromopropionyl-*l*-tyrosine, $[\alpha]_D^{20}$ +33°, *d*-*l*-, m. p. 148—151°, $[\alpha]_D^{20}$ +29·7°. Halogen was eliminated more rapidly from the *d*-*l*-compounds than from the *l*-*l*-compounds. The latter type are more readily hydrolysed by trypsin-kinase.

J. H. BIRKINSHAW.

Preparation of α-amino-acid amides. P. S. YANG and M. M. RISING (J. Amer. Chem. Soc., 1931, **53**, 3183—3184).—Glycine, *d*-alanine, and *dl*-leucine Me esters are treated with a solution of NH_3 in MeOH (saturated at 0°) at room temp. for 20—80 hr., and the resulting amides isolated by evaporating the excess of NH_3 and MeOH in a vac. H. BURTON.

Reactivity of fused bases. II. Action of fused potassamide on aliphatic nitriles. R. A. FULTON and F. W. BERGSTROM (J. Amer. Chem. Soc., 1931, **53**, 3092—3099).—Aliphatic nitriles (MeCN, EtCN, PrCN, BuCN, and *iso*amyl cyanide) are passed through KNH_2 at 300—400°, whereby the following changes occur: $RCN+KNH_2 \longrightarrow NH{:}CR{\cdot}NHK \longrightarrow RH+K_2CN_2+NH_3$. These reactions are followed by decomp. of RH to H_2 and simpler hydrocarbons. The yield of RH diminishes, and the amount of H_2 increases, with rise in temp. and length of the C chain.

H. BURTON.

ψ-Halogens. XV. Reactions of fulminic acid and its salts with halogens. L. BIRCKENBACH and K. SENNEWALD (Annalen, 1931, **489**, 7—30).—Addition of halogens to free fulminic acid (prepared *in situ*) affords the additive products $CX_2{:}NOH$ in good yields and thus are obtained: *dichloro*-, $+H_2O$ and anhyd., b. p. 45°/12 mm., *dibromo*-, $+H_2O$, m. p. 40°, and anhyd., m. p. 68—69°, b. p. 75—85°/3 mm. (*Me* ester, b. p. 139—141° by action of diazomethane), and *di-iodo*-, $+H_2O$, m. p. 52°, and anhyd., m. p. 69° (decomp.), -*formoxime*, the stability decreasing in this order. The initial products of thermal decomp. of these substances (at 130°, 80°, and room temp., respectively) are the halogenocyanogen and hypohalous acid, subsequent reactions yielding Cl_2O Cl_2, $COCl_2$, NH_4Cl, CO_2, $(ClCN)_3$, and CCl_3NO_2 in the case of the chloro-compound, whilst dissociation into I and polymerised CNOH occurs with the I compound. Dichloroformoxime with fuming HNO_3 affords *dichlorodinitromethane*, b. p. 46°/20 mm. [$CBr_2(NO_2)_2$, b. p. 77°/21 mm., obtained similarly from the Br compound], whilst $KMnO_4$ in H_2SO_4 solution causes extensive decomp., some dichlorofuroxan being obtained. Dibromoformoxime is quantitatively hydrolysed by dil. H_2SO_4: $CBr_2{:}NOH+2H_2O=NH_2OH+2HBr+CO_2$, and is converted into dibromofuroxan by HgO, MgO, or NH_3. In agreement with Wieland (A., 1909, i, 892) additive halogen products of metallic fulminates cannot be isolated, but decompose, giving dichloro-, b. p. 67°/17 mm. and di-iodo-, m. p. 93·5° (decomp. 89°: lit., m. p. 90—91°), -furoxan. On keeping, an aq. suspension of $Hg(CNO)_2$ after treatment with excess of Cl_2 deposits *trichloronitrosomethane* as a blue oil. Di-iodofuroxan is reduced with H_2S or H_2SO_3, in the latter case with the formation of HI and *iodofurazan*, $\begin{matrix}CH{:}N\\CI{=}N\end{matrix}{>}O$, m. p. 111—112° (decomp., in bath at 105°) (60% yield). J. W. BAKER.

Action of hydrogen chloride on stannanes of the type $SnR_2R'_2$. R. H. BULLARD and F. R. HOLDEN (J. Amer. Chem. Soc., 1931, **53**, 3150—3153) —MgMeI and $SnEt_2Cl_2$ give *Sn dimethyldiethyl*, b. p. 132°, 32°/14 mm., converted by dry HCl into *Sn methylethyl dichloride*, m. p. 52° (corresponding *oxide*), which with Na and MeI in liquid NH_3 gives Sn trimethylethyl. *Sn diethyldi*-n-*propyl*, b. p. 84·5°/10—11 mm. (from MgPrBr and $SnEt_2Cl_2$), and *Sn diphenyldiethyl*, b. p. 155—157°/4 mm. (from MgEtBr and $SnPh_2Cl_2$), yield similarly *Sn ethyl*-n-*propyl*, m. p. 53°, and diethyl *dichloride*, respectively.

H. BURTON.

Mechanism of the oxidation of double linkings by peracetic and perbenzoic acids. J. BOESEKEN and G. C. C. C. SCHNEIDER (J. pr. Chem., 1931, [ii], **131**, 285—288).—The authors accept the view (A., 1930, 1175, 1294) that peracetic acid and perbenzoic acid form primarily cyclic oxides with unsaturated substances; the formation of the monoacetate of the diol with AcO_2H in AcOH is due to fission of the ring by the solvent. The following new evidence supports this view. Only cyclic oxides are obtained on treatment of *cyclo*hexene, stilbene, or *iso*stilbene with AcO_2H in $CHCl_3$, or of *cyclo*hexene with AcO_2H in dry Et_2O. Stilbene and *iso*stilbene oxides in AcOH pass in several days into the acetylhydrobenzoins. PhI with AcO_2H in $CHCl_3$, or BzO_2H in AcOH gives a mixture of PhOI and iodosodiacetylbenzene.

R. S. CAHN.

Friedel–Crafts reaction. A. WOHL and E. WERTYPOROCH (Ber., 1931, **64**, [*B*], 1357—1369).—The following conclusions are based on the experimental results of Wertyporoch (this vol., 913). In the Friedel–Crafts reaction, the union of the reactants to a ternary compound depends on solvate formation of the Al ψ-salt with the halogen compound and conversion of this feeble salt into a strongly conducting compound by addition of the unsaturated or aromatic hydrocarbon. The union of the reactants to a single mol. is the first essential for a possible reaction. The pre-dissociation of the original linkings of the org. halogeno-compound during this arrangement or, thermodynamically expressed, the heat of activation diminished by the energy of addition, fulfils

the second condition for reaction and the separation of the volatile H halide from the equilibrium conditions the stabilisation. The reaction corresponds with the general scheme of org. chemical reactions the incidence of which is governed by key atoms, halogen, O, S, N, C:C and usually occurs in the three phases, primary addition, transformation to a main valency compound, and stabilisation. The external similarity of the course of the Al salt action and a typical C_6H_6 reaction such as nitration is shown by the primary formation in each case of a deeply coloured compound which, during stabilisation, becomes lighter or decolorised with respective separation of HBr, or HNO_3 or H_2SO_4. H. WREN.

Decomposition of phenyl iodide dichloride. IV. Action of solid phenyl iodide dichloride on magnesium methyl iodide. E. V. ZAPPI and H. DEGIORGI (Bull. Soc. chim., 1931, [iv], **49**, 1035—1041).—The reaction between solid $PhICl_2$ and MgMeI solution affords mainly PhI, $MgCl_2$, and MeI, about 70% of MeI being obtained. The reaction $PhICl_2 + 2MgMeI = PhI + 2MgClI + C_2H_6$ is secondary and only about 28% of C_2H_6 is formed on an average. The yield of C_2H_6 is very variable, depending on the proportions of the reactants, the state of aggregation of the $PhICl_2$, and other factors. The fact that the formation of C_2H_6 is not quant. supports the view of the non-equivalence of the two Cl atoms in $PhICl_2$ (cf. A., 1930, 79, 758). R. BRIGHTMAN.

Quaternary arylsulphonylalkylammonium salts. D. VORLANDER (Ber., 1931, **64**, [B], 1736—1739).—The production of benzenesulphonyltrimethylammonium chloroplatinate, $SO_2Ph{\cdot}NMe_3PtCl_6$, from $Ph{\cdot}SO_2Cl$ and NMe_3 in H_2O or aq. EtOH is confirmed (cf. A., 1913, i, 1321). *Benzenesulphonyltrimethylammonium chloride*, m. p. 184—186° (decomp.), and *chloroaurate*, m. p. 194° (decomp.), are described. The failure of Jones and Whalen (A., 1925, i, 801) to obtain the compounds is due to the absence of H_2O. Under similar conditions, benzenesulphonic esters and NMe_3 yield the benzenesulphonates of tetra-alkylammonium bases free from S. H. WREN.

Dissociable organic oxides. Hydrocarbon formed by elimination of one phenyl group from rubrene. C. DUFRAISSE and M. BADOCHE (Compt. rend., 1931, **193**, 242—245).—Under the prolonged action of excess of MgMeI, MgEtBr, or MgPhBr at room temp. in absence of air *iso*rubrene dioxide (A., 1930, 1173) loses one Ph group as PhOH, giving a *hydrocarbon*, $C_{36}H_{24}$, m. p. 236—237° ($+C_6H_6$, m. p. 177—178°), in 90% yield. This is yellower than rubrene and has a greater fluorescence in solution, the characteristic absorption spectra of rubrene being slightly displaced towards the violet. The irradiated solution readily absorbs O_2 and becomes decolorised. The reaction mixture itself does not show the characteristic rubrene absorption spectrum and the first product is probably the Mg derivative, treatment of which with I prior to decomp. with H_2O affords the *iodo*-derivative, $C_{36}H_{23}I$, m. p. 270°. R. BRIGHTMAN.

Steric hindrance: application to the study of *cis-trans* isomerism in cyclic compounds. G. VAVON (Bull. Soc. chim., 1931, [iv], **49**, 937—1025).—A lecture.

Tetra- and hexa-sulphides of substituted thiurams. T. G. LEVI (Gazzetta, 1931, **61**, 373—382).—Treatment of the NH_4 or Zn salts of the phenylalkyldithiocarbamic acids with S_2Cl_2 gives the tetrasulphides, m. p. 131° and 138°, respectively, of diphenyldimethyl- and diphenyldiethyl-thiuram. The use of SCl_2 gives a trisulphide. This confirms the results of Whitby (cf. B., 1928, 203). The NH_4 or K salt of pentamethylenedithiocarbamic acid gives with S_2Cl_2 a mixture of the *hexasulphide*, m. p. 129°, and *tetrasulphide*, m. p. 96—98°, of dipentamethylenethiuram, and with SCl_2 a mixture of hexa-, tetra-, and di-sulphides. With the NH_4 salt of dimethyldithiocarbamic acid S_2Cl_2 gives a disulphide and free S and with the Zn salt a mixture of the di- and *hexasulphide*, m. p. 102—104°, of tetramethylthiuram. E. E. J. MARLER.

***p*-Nitrophenylcarbamyl chloride and *p*-nitrophenylcarbimide. Correction.** W. H. HORNE and R. L. SHRINER (J. Amer. Chem. Soc., 1931, **53**, 3186).—The compound previously described (this vol., 709) as *p*-nitrophenylcarbamyl chloride is *p-nitrophenylcarbimide*, m. p. 57°, formed by loss of HCl from the chloride during crystallisation. H. BURTON.

Nitration of acylanilines. L. C. RAIFORD and J. N. WICKERT (J. Amer. Chem. Soc., 1931, **53**, 3143—3147).—Benz-2 : 4 : 6-tribromoanilide is nitrated by Borelli's method (A., 1888, 1292) to a mixture of o-, m. p. 266°, and m-, m. p. 242°, *-nitrobenz-*2 : 4 : 6-*tribromoanilides*, both hydrolysed to *s*-tribromoaniline. 2 : 4-Dibromoacetanilide with fuming HNO_3 and conc. H_2SO_4 gives a mixture of 5- and 6-NO_2-derivatives; with HNO_3 alone, only the 6-NO_2-derivative is produced. The following are prepared from the requisite benzoyl chloride and substituted aniline: o-, m-, and p-, m. p. 246—247°, *-nitrobenz-*2 : 4 : 6-*tribromoanilides*; 2 : 3-, m. p. 282—283°, 2 : 4-, m. p. 307—308°, 2 : 5-, m. p. 286—287°, 2 : 6-, m. p. 334—336°, 3 : 4-, m. p. 263—264°, and 3 : 5-, m. p. 288°, *-dinitrobenz-*2 : 4 : 6-*tribromoanilides*; o-, m. p. 269—270°, m-, m. p. 236—237°, and p-, m. p. 299—300°, *-nitrobenz-*2 : 4 : 6-*tribromo-3-nitroanilides*; *benz-*2 : 5-*dibromoanilide*, m. p. 152°, -2 : 6-*dibromo-4-nitroanilide*, m. p. 190—191°, -4 : 6-*dibromo-2-methylanilide*, m. p. 181—182°, -2 : 4 : 6-*tribromo-3-nitroanilide*, m. p. 234—235°, and -2 : 4 : 6-*tribromo-*3 : 5-*dinitroanilide*, m. p. 271—272°. 3 : 4-*Dinitrobenzoyl chloride* has m. p. 45—47°. H. BURTON.

5-Bromo- and 5 : 4′-dibromo-3-nitro-4-acetamidodiphenyls. Correction. F. BELL (J.C.S., 1931, 2227).—Bromination of 3-nitro-4-acetamidodiphenyl gives 5-bromo- (*Ac* derivative, m. p. 223°) and 5 : 4′-dibromo-3-nitro-4-aminodiphenyls (*Ac* derivative, m. p. 251°) and not their Ac derivatives as stated in A., 1927, 657. The Ac derivatives of Hinkel and Hey (A., 1928, 996) are the above amines. H. BURTON.

Manufacture of monoacyl-*m*- and -*p*-diamines of the benzene series. I. G. FARBENIND. A.-G.—See B., 1931, 711.

Reduction of aromatic mono- and poly-nitrocompounds. XII. K. BRAND and J. MAHR (J. pr.

Chem., 1931, [ii], **131**, 97—131).—A kinetic study of the formation of azoxy-compounds by interaction of similarly substituted nitroso-compounds and β-arylhydroxylamines in EtOH solution. The reaction is bimol. and (in the case of azoxybenzene) is accelerated by traces of acid or alkali, but much more so by the latter; it is more rapid in dil. EtOH, and is not affected by colloidal Pt. *o*-Me groups exert a considerable retarding influence, but *m*- and *p*-Me groups are practically without effect (cf. A., 1901, i, 529). The *m*-NO_2-group, on the other hand, causes a very considerable increase in reaction velocity, more than sufficient to counterbalance the effect of an *o*-Me group; *m*- and *p*-Cl-groups have a similar, but somewhat less, accelerating effect, but in the *o*-position Cl exerts a marked retarding influence. The apparently anomalous behaviour of polynitro-compounds on chemical or electrochemical reduction in neutral or only slightly acid solution is therefore a consequence of acceleration of the "azoxy-condensation" by the additional NO_2-group; with this reservation the course of reduction still conforms to Haber's scheme (cf. A., 1901, i, 281, 282). The formation of NH_2-compounds in more strongly acidic solutions is a result of the increased velocity of reduction of arylhydroxylamines with increasing acidity, and in view of the acceleration of the azoxy-condensation by traces of acid cannot be due, as suggested by Flurscheim (J.C.S., 1908, **93**, 1463), to salt-formation on their part. The isolation of *o*-chloro-β-phenylhydroxylamine in a cryst. form, m. p. 53—54°, is described. 6-Nitro-2-nitrosotoluene has m. p. 121—122° (lit. 117°) and *o*-chloronitrosobenzene 65·5—66·5° (lit. 56—57°).

H. A. PIGGOTT.

Disazoxyphenols. Z. JOLLES (Gazzetta, 1931, **61**, 543—550).—Four isomeric *op*-disazoxyphenols are obtained from the α- (I) and β- (II) -*o*-azo-*p*-benzeneazoxyphenols: Ph·NO:N·C_6H_3(OH)·N_2·Ph (I), Ph·N:NO·C_6H_3(OH)·N_2·Ph (II). On oxidation with AcO_2H (I) gives p-α : o-β′-*disazoxyphenol*, Ph·NO:N·C_6·H_3(OH)·NO:NPh, m. p. 136°, and (II) gives p-β : o-β′-*disazoxyphenol*, m. p. 121—122°. Oxidation of the *Ac* derivative, m. p. 138—140°, of (I) gives the *Ac* derivative, m. p. 152° of p-α : o-α′-*disazoxyphenol*, m. p. 140° (*Br*-derivative, m. p. 177°; *NO_2*-derivative, m. p. 175°). The *Ac* derivative, m. p. 123—124°, of (II) gives the *Ac* derivative, m. p. 124°, of p-β : o-α -*disazoxyphenol*, m. p. 145—148° (crude).

E. E. J. MARLER.

Basic character of 3-chloro-4-nitrosophenol and acidic nature of 3-chlorobenzoquinone-4-oxime. H. H. HODGSON (J.C.S., 1931, 2227—2228).—3-Chloro-4-nitrosophenol (I) forms additive *compounds* (1 : 1) with 2 : 4 : 6-trinitro-*m*-cresol, m. p. 160° (decomp.), 3-fluoro-, m. p. 147—150° (decomp.), 3-chloro-, m. p. 163° (decomp.), 3-bromo-, m. p. 172—175° (decomp.), and 3-iodo-, m. p. 177° (decomp.), -2 : 4 : 6-trinitrophenols, whilst 3-chlorobenzoquinone-4-oxime (II) forms *compounds* (1 : 1) with carbamide, m. p. 160° (decomp.), and acridine, m. p. 174°. The compounds are largely dissociated in PhOH, $PhNO_2$, $C_{10}H_8$, and *o*-cresol. (I) and (II) unite to give an additive compound, decomp. 145°.

H. BURTON.

Electrolytic preparation of *m*-amino-*p*-cresol. W. E. BRADT and E. J. HART (Trans. Amer. Electrochem. Soc., 1931, **60**, 211—222).—The best yield of *m*-amino-*p*-cresol by electrolytic reduction of the corresponding NO_2-compound is obtained by using 6 amp. per sq. dm. at a Cu-gauze cathode in a vigorously stirred solution of 5 g. of the NO_2-compound in 300 c.c. of 10% Na_2CO_3 containing 1 g. of $CaCl_2$ at 95°. The anode is a Pb plate dipping into 10% Na_2CO_3 separated from the catholyte by a porous cup. The passage of the theoretical quantity of electricity gives a 96·1% yield of the amine. Addition of salts of Ca, Al, Ce, Fe, and Sr increases the yield, but Cu, Ag, V, As, and Te salts cause a marked decrease. H. J. T. ELLINGHAM.

Constitution of butyl-*m*-tolyl methyl ether and its dinitro-derivative, "musc ambrette." G. DARZENS and A. LÉVY (Compt. rend., 1931, **193**, 321—324).—On condensation of *m*-tolyl Me ether with *tert*.-butyl chloride at a low temp. and in presence of only a little $AlCl_3$, 6-*tert*.-butyl-*m*-tolyl Me ether is obtained cryst., m. p. 23·4°. This is the pure progenitor of the perfume (the 2 : 4-dinitro-derivative), which it affords in better yield than the oily material; it gives also the same acetophenone derivative on treatment with AcCl and $AlCl_3$. The high m. p. suggests the configurations given above (contrast A., 1928, 291; 1929, 439), which are confirmed by synthesis of the ether by the Grignard reaction from 6-bromo-*m*-tolyl Me ether and *tert*.-butyl bromide, identity being confirmed by the prep. of the dinitro- and acetophenone derivatives. The new formula explains the odour (due to 2 NO_2-groups *o*- to the MeO group), the necessity for the use of HNO_3 in Ac_2O for nitration, and the ready elimination of the *tert*.-butyl group during nitration. R. S. CAHN.

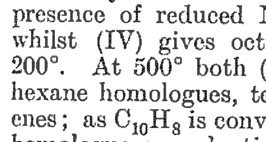
Thermal decomposition of aromatic ethers under high hydrogen pressure. T. OGAWA (Bull. Chem. Soc. Japan, 1931, **6**, 174—195).—In all the reactions quoted below the substances were heated electrically in an autoclave with H_2 at 100 atm. pressure (measured at 0°). When Ph_2O (I), diphenylene oxide (II), α- or β-dinaphthylene oxide (III and IV, respectively) is thus heated, the primary reaction is reductive fission of a C·O linking, followed by disruption of the diphenyl linking; when, however, a reduced Ni catalyst (10%) is added, hydrogenation of the aromatic nucleus is the primary action, followed by disruption of the C·O linking and other secondary reactions. (I), when heated at 500° for 1 hr., decomposes to the extent of 90% into C_6H_6, PhOH, and H_2O in the mol. ratios 1 : 0·4 : 0·3, whence it is concluded that reaction takes place mostly by formation of (*a*) PhOH+C_6H_6 and (*b*) $2C_6H_6$+H_2O, and partly by (*c*) reduction of PhOH to C_6H_6 and H_2O. Reaction (*b*) is not new, and reaction (*c*) has been observed experimentally at 460—490°, in spite of statements to the contrary (A., 1908, i, 342; 1930, 1428). (I) with reduced Ni at 250° gives *cyclo*hexane (0·65 mol.) and *cyclo*hexanol (0·65 mol.) produced by reduction of the primary product, di*cyclo*hexyl ether; at 500° CH_4, *cyclo*pentane, methyl*cyclo*pentane, and H_2O in the mol. ratios 2 : 0·2 : 0·4 : 1 are produced, *cyclo*hexene being here assumed to be precursor. (II), when heated at 500° for 5 hr., gives *o*-hydroxydi-

phenyl (0·2 mol.), m. p. 58°, b. p. 283° (cf. A., 1901, i, 700), C_6H_6 (0·14 mol.), PhOH (0·13 mol.), and unchanged (II) (0·33 mol.). At this temp. (III) gives CH_4, benzene homologues, $C_{10}H_8$, and a little ββ′-dinaphthyl, whereas (IV) gives CH_4, benzene homologues, αα′-dinaphthyl, and perylene, but no naphthol in either case. Thus (II), but not (III) or (IV), behaves similarly to (I). This is explained by the assumption that the bivalent naphthylene radical, formed by disruption of the C·O linking and of the linking joining the naphthalene radicals, will decompose more readily than the C_6H_4 radical formed by similar decomp. of (II).

In the presence of reduced Ni (II) gives at 200° *o*-hydroxydi*cyclo*hexyl (0·47 mol.), di*cyclo*hexyl (0·33 mol.), and H_2O (0·15 mol.), and at 280° the same products in the mol. proportions 0·25 : 0·54 : 0·69, indicating that the formation of di*cyclo*hexyl is a secondary reaction favoured by high temp. In the presence of reduced Ni (III) is unaffected at 225°, whilst (IV) gives octahydrodinaphthylene oxide at 200°. At 500° both (III) and (IV) give CH_4, *cyclo*hexane homologues, tetra-, and deca-hydronaphthalenes; as $C_{10}H_8$ is converted into CH_4 and *cyclo*hexane homologue on reduction at high temp. and pressure, it is assumed that the primary reactions are reduction to the octahydro-oxide, and dehydration to a bivalent hydronaphthylene radical.

With a Cu catalyst at 500° (II) gives 3·4% of H_2O with C_6H_6 and PhOH in the mol. ratio 2·1 : 1; with Fe_2O_3 as catalyst the corresponding figures are 5·4%, and 2·7 : 1, and with Japanese acid clay 6·0%, and 4·1 : 1. In all three cases large amounts of *o*-hydroxydiphenyl and diphenyl are also formed. R. S. CAHN.

Interaction of 2 : 6-dichloro-4-methylquinitrol with methyl and ethyl alcohols. E. C. S. JONES and J. KENNER (J.C.S., 1931, 1943—1950).—The compound $C_{15}H_9O_3Cl_3$, obtained by Zincke (A., 1903, i, 756; cf. Suhl, Diss., Marburg, 1906) from 2 : 6-dichloro-4-methylquinitrol and boiling MeOH is 6 : 3′ : 5′-*trichloro*-2-p-*tolyloxy*-2-*methoxy*-4-*methyl*-$\Delta^{3:5}$-cyclo*hexadienone* (I), m. p. 157°; 2 : 6-dichloro-4-nitrophenol (II), 2 : 6-dichloro-4-methyl-ψ-quinol (III), and 3 : 5-*dichloro*-4-*hydroxybenzyl Me ether*, m. p. 68—71°, are also formed in addition to (I). (I) and aq. HI in CO_2 at 80° give MeI, I, 3 : 5-dichloro-*p*-cresol, and 3 : 3′ : 5′-*trichloro*-5-p-*tolyloxy*-p-*cresol*, m. p. 98—100° (*Bz* derivative, m. p. 173°). Decomp. of the quinitrol in boiling EtOH (cf. *loc. cit.*) affords Et nitrite, (II), (III), 3 : 5-dichloro-4-hydroxybenzyl Et ether, and 6 : 3′ : 5′-*trichloro*-2-p-*tolyloxy*-2-*ethoxy*-4-*methyl*-$\Delta^{3:5}$-cyclo*hexadienone*, m. p. 125° (also decomposed by aq. HI to the above cresols). The compounds obtained similarly by Suhl (*loc. cit.*) from 2 : 3 : 6-trichloroquinitrol are assigned analogous constitutions.



(I.)

H. BURTON.

Nitrosation of phenols. XII. Resorcinol mono-*n*-propyl ether. H. H. HODGSON and H. CLAY (J.C.S., 1931, 2097—2104).—Nitrosation of resorcinol Pr^α ether gives 20·5% of the 4-*nitroso*- (I), decomp. 170—175° after darkening above 150°, in addition to the 6-*nitroso*-derivative (II), m. p. 93° after darkening at 70—80°; this supports the views previously expressed (A., 1930, 209, 910). Oxidation of (I) with alkaline $K_3Fe(CN)_6$ and (II) with dil. HNO_3 affords 4-*nitro*- (III), m. p. 86°, and 6-*nitro*- (IV), m. p. 34°, -3-n-*propoxyphenols*, respectively; (III) and (IV) are also formed during the nitration of resorcinol Pr^α ether. Na *m*-nitrophenoxide and PrI give m-*nitrophenyl Pr^α ether*, m. p. 28°, reduced by Fe powder and 50% AcOH to m-*aminophenyl Pr^α ether*, b. p. 257—258°/752 mm. (*hydrochloride*, m. p. 155°; *picrate*, m. p. 147—148°), the *Ac* derivative, m. p. 71°, of which is nitrated to the *Ac* derivatives, m. p. 97° and 120—121°, respectively, of 4- and 6-*nitro*-3-*aminophenyl Pr^α ethers*, m. p. 98—99° and 117°, respectively. Replacement of the NH_2 group by OH in these nitroamines yields (IV) and (III), respectively. 3-n-*Propoxydimethylaniline*, b. p. 262—263°/747 mm. [*picrate*, m. p. 150—152° (decomp.)], and HNO_2 give the 4-*nitroso*-derivative, m. p. 98° (*hydrochloride*, m. p. 151—152°), converted by boiling alkali into (I). 6-*Nitroresorcinol* 1-*Et* 3-*Pr^α ether*, m. p. 39°, from the Ag salt of 4-nitro-3-ethoxyphenol and PrI, is also formed by ethylation of (IV). Depropylation occurs during the nitration of *resorcinol Pr^α_2 ether*, m. p. 50°; a mixture of (IV) and a little (III) is produced. H. BURTON.

Condensation products of phenols and aldehydes. XVI. Isolation and identification of 2 : 4′-dihydroxydiphenylmethane. T. SHONO, K. KIZAWA, and T. DOHA (J. Soc. Chem. Ind. Japan, 1931, 34, 262—263B).—By heating equal quantities of PhOH and CH_2O (35%) in a quartz flask under a quartz condenser for 50—60 hr. on a water-bath, a large amount of 4 : 4′-dihydroxydiphenylmethane is obtained and also the 2 : 4′-derivative, m. p. 117—118° (Ac_2 derivative, m. p. 69—70°; Bz_2 derivative, m. p. 113—114°). E. H. SHARPLES.

Rearrangement of β-naphthol-1-sulphone. L. A. WARREN and S. SMILES (J.C.S., 1931, 2207—2211).—A development of the interpretation given (this vol., 723) to the conversion of *iso*-β-naphthol sulphide into β-naphthol 1-sulphide is that β-naphthol-1-sulphone (I) should be convertible into *iso*-β-naphtholsulphone (2-hydroxy-1 : 2′-dinaphthyl ether-1′-sulphinic acid) (II), owing to the relative polarities of the O and S atoms in (I) being reversed. The change (I⟶II) can be effected with *N*-NaOH at 150°, but owing to the ready loss of SO_2 from (II), 2-hydroxy-1 : 2′-dinaphthyl oxide is isolated. Similarly, 6-*bromo*-β-*naphthol*-1-*sulphone*, m. p. 227° (decomp.), yields 6 : 6′-*dibromo*-2-*hydroxy*-1 : 2′-*dinaphthyl oxide*, m. p. 166°; the Me_2 ether of (I) is hydrolysed to 2-methoxynaphthalene, whilst the *Me ether*, m. p. 201° (decomp.) [*Ac* derivative, m. p. 211° (decomp.)], of (I), prepared from the corresponding sulphide (*loc. cit.*) and H_2O_2 in AcOH, is converted by loss of MeOH into αβα′β′-dinaphthathioxin dioxide.

4 : 4′-Dihydroxydi-*m*-tolylsulphone is unaffected by *N*-NaOH at 250°, showing that the character of the α-C atom (cf. *loc. cit.*) has an important influence on the above type of rearrangement. The chlorothiol from 2-acetoxynaphthalene 1-disulphide and Cl in $CHCl_3$ is treated with *p*-cresol, and the resulting pro-

duct oxidised by H_2O_2 in AcOH to 4 : 2'-*dihydroxy*-m-*tolyl*-1'-*naphthylsulphone*, m. p. 203° (Bz_2 derivative, m. p. 249—250°), which with N-NaOH at 250° gives a phenol and Na_2SO_3. H. BURTON.

Manufacture of chloromethyl derivatives of aryl alkyl ethers. I. G. FARBENIND. A.-G.—See B., 1931, 711.

Constitution of cholesterol. I. R. DE FAZI (Gazzetta, 1931, **61**, 369—373).—Evidence concerning the structure of cholesterol is sought by examination of cholesterylene, derived from it by elimination of 1 mol. H_2O. When the dehydrating agent is anhyd. $CuSO_4$ coprostene and coprostane are formed in addition to cholesterylene, indicating that the latter is derived from *allo*-cholesterol (A., 1927, 557). Comparison of absorption spectra (A., 1928, 219, 459) and of colour reactions with $CCl_3{\cdot}CO_2H$ suggests that *allo*-cholesterol and cholesterylene have a double linking in the same position as ergosterol. The stability of cholesterylene towards *Bacterium aliphaticum* shows it to be cyclic, whence it is inferred that cholesterol has a cyclic structure. E. E. J. MARLER.

Yeast sterols. III. H. WIELAND and W. M. STANLEY (Annalen, 1931, **489**, 31—42).—Fractional distillation of the amorphous residue of the first crystallisation of ergosterol of yeast gives a cryst. fraction, b. p. 230—255°/0·1—0·08 mm., from which by treatment with BzCl and pyridine is obtained the *benzoate*, m. p. 185—187°, $[\alpha]^{20}$ +68·8° in $CHCl_3$, of *cryptosterol* $C_{27}H_{44}O,0{\cdot}5H_2O$ (2 double linkings), m. p. 134—135°, $[\alpha]^{20}_{D}$ +63·4° in $CHCl_3$ (absorption spectra and colour reactions given), a further quantity being isolated from the non-distillable residue. Fractional crystallisation of the original material with MeOH, precipitation of the various fractions with digitonin, and benzoylation of the products obtained gave, in addition to cryptosterol, the following cryst. products: a *sterol*, m. p. 109—111°, $[\alpha]_D$ +18·7° (a mixture from which a single Bz derivative, m. p. 162—163°, $[\alpha]^{0}_{D}$ −6·6°, is obtained); a mixture of sterols, m. p. 152—154°, $[\alpha]^{20}_{D}$ −32·2° (Bz derivative, m. p. 170—172°, $[\alpha]^{20}_{D}$ −16·9°) (probably not a mixture of ergosterol and dihydroergosterol; cf. this vol., 618). J. W. BAKER.

Autoxidation of α-n-amylcinnamaldehyde. cis- and trans-α-n-Amylcinnamic acids. M. T. BOGERT and D. DAVIDSON (J. Amer. Chem. Soc., 1931, **53**, 3122—3130).—When air is passed through α-n-amylcinnamaldehyde (I), b. p. 161—163°/16 mm., at room temp. in the dark, PhCHO, BzOH, hexoic acid, unidentified substances, and cis-α-n-*amylcinnamic acid*, m. p. 40°, are produced. (I) is the *trans*-form since it is oxidised by Ag_2O to trans-α-n-*amylcinnamic acid*, m. p. 80° (*amide*, m. p. 117°, also formed by hydrolysis of α-n-*amylcinnamonitrile*, b. p. 173°/18 mm., 135°/3 mm., which is obtained from the oxime of (I), Ac_2O, and NaOAc), which is synthesised by the following methods: (*a*) from PhCHO, heptoic acid, and Na heptoate, (*b*) from PhCHO and Me heptoate with subsequent hydrolysis, (*c*) from $CHPhCl_2$, heptoic acid, and Na, (*d*) oxidation of α-amylstyryl Me ketone by NaOCl. Inversion during the passage of (I) into the *cis*-acid is assumed to result from a chemiluminescent reaction. The *trans*-acid is converted into the *cis*-form by ultra-violet irradiation, whilst the *cis*-acid can be converted into the *trans*-form by the action of KI in EtOH on the *dibromide*, m. p. 143—144°, obtained from either acid. The *trans*-acid is not affected by conc. H_2SO_4, whereas the *cis*-form is converted into 2-n-*amylindone*, m. p. 4° (*oxime*, m. p. 75°), also obtained when the *trans*-acid is distilled with P_2O_5. H. BURTON.

Partial dehydrogenation of ursolic acid. W. A. JACOBS and E. E. FLECK (J. Biol. Chem., 1931, **92**, 487—494).—Interaction of ursolic acid with diazomethane in Et_2O gives its Me ester and an unidentified substance, m. p. 221—222°. The *benzoate*, m. p. 212—213° (solidifies and re-melts at 235—236°), of the Me ester when heated with S in N_2 gives a *dehydro*-derivative, m. p. 210—212°. Oxidation of the Me ester with CrO_3 and AcOH gives *Me ursonate*, m. p. 192—193° (*oxime*, m. p. 243—244°), by attack of the ·CH(OH)· group; with an excess of Kiliani's chromic acid mixture the corresponding *diketone*, $C_{31}H_{46}O_4$, m. p. 176—177° (*monoxime*, m. p. 210—211°), is formed. Reduction of Me ursonate by Clemmensen's method gives the *Me* ester, m. p. 117—118°, of *ursanic acid*, $C_{30}H_{48}O_2$ (hydrolysis with MeOH–KOH), m. p. 223—225°, by dehydrogenation of which with S at 230—240° *Me dehydroursanate*, m. p. 110—111°, is obtained, and this is hydrolysed to *dehydroursanic acid*, $C_{30}H_{46}O_2$, m. p. 174—176°, with 20% EtOH–KOH. Ultimate analysis, and the composition of the above derivatives, agree with the formula $C_{30}H_{48}O_3$ for ursolic acid. H. A. PIGGOTT.

Reaction between α-oxides and amino-acid esters. VI. cycloHexene oxide and ethyl aminoacetate. A. I. KIPRIANOV and G. I. KIPRIANOV (Ukrain. Chem. J., 1931, **6**, [Sci.], 93—103).—2-*Hydroxy*cyclo*hexylglycine* (I), m. p. 196—197°, is prepared by condensing *cyclo*hexene oxide with $NH_2{\cdot}CH_2{\cdot}CO_2Et$, or $ClCH_2{\cdot}CO_2H$ with 2-amino*cyclo*hexanol. *cyclo*-Hexene oxide and Et α-aminopropionate do not under similar conditions undergo condensation. At 200°, (I) undergoes further condensation with the production of a *diketopiperazine* derivative, $C_8H_{13}O_2N$, m. p. above 240°. N-β-*Hydroxyethyldiketopiperazine*, m. p. 137—157°, is obtained from ethylene oxide and $NH_2{\cdot}CH_2{\cdot}CO_2Et$. Ethylene oxide does not react with diketopiperazine. R. TRUSZKOWSKI.

Asymmetric syntheses. X. Optically active substituted glycollic acids. A. MCKENZIE and P. D. RITCHIE (Biochem. Z., 1931, **237**, 1—19).—When dry HCl is passed into a mixture of *l*-β-octanol (1 mol.) and benzoylformic acid (1⅓ mols.), *l*-β-*octyl benzoylformate*, b. p. 182—186°/13 mm., is formed, which reacts with MgMeI to give *l*-atrolactinic acid (K salt, $[\alpha]^{20}_{5461}$ −2·6°; Et ester, −6·6°); crystallised from C_6H_6 this yields the *dl*-compound, m. p. 88—90° (cf. J.C.S., 1925, **127**, 522). *d*-β-Octanol similarly yields *d*-β-octyl benzoylformate, b. p. 179—180°/16 mm., $[\alpha]^{20}_{5461}$ +7·56°, which reacts with $C_{10}H_7(\alpha)MgBr$ to give, after hydrolysis, phenyl-α-naphthylglycollic acid as a mixture of the *dl*- (isolated, m. p. 140—145°) and the *l*-isomeride. *l*-β-Octanol (1 mol.) and pyruvic acid (6 mols.) at 100° for 13 hr. with dry HCl yield *l*-β-*octyl pyruvate*, b. p. 114°/14 mm., α^{20}_{5461} −7·46° (0·5 dm. tube), which with MgPhBr gives atrolactinic

acid, $[\alpha]_{5461}^{20}$ $+1{\cdot}8°$ in EtOH. The *d*-isomeride, b. p. 109—111°/17 mm., $[\alpha]_{5461}^{20}$ $+7{\cdot}57°$ (0·5 dm. tube), with $C_{10}H_7(\alpha)MgBr$ (4 mols.) yields naphthyl-α-methylglycollic acid, α_{5461}^{20} $-0{\cdot}06°$ (5·952% EtOH solution in 2 dm. tube), which when recrystallised from C_6H_6 gives the *dl*-acid, m. p. 145—148°.

The mutarotation of these and previously described compounds and the mechanism of their asymmetric synthesis are explained by formation of a semipolar double linking occurring through "polar activation."

F. O. HOWITT.

Benzylidenepyruvic acid dibromide. M. REIMER (J. Amer. Chem. Soc., 1931, **53**, 3147—3149). Improved methods of prep. of benzylidenepyruvic acid (*K* salt) and its dibromide, m. p. 150—151° (decomp.), (+H_2O) m. p. about 140° (decomp.) when heated rapidly, (+MeOH) m. p. about 125° (decomp.) after softening at 70—80° (*Et* ester, m. p. 61—62°), are given. The compound, m. p. 147—150°, described by Musajo (this vol., 221), is probably the above dibromide.

H. BURTON.

N-Arylhomophthalimides. A. MEYER and R. VITTENET (Compt. rend., 1931, **193**, 400—402).—*N*-Arylhomophthalimides are obtained when 1 mol. of homophthalic acid is heated with a slight excess of NH_2Ar; the following are prepared: *N*-phenyl-, m. p. 191° (lit. 188°); N-p-*tolyl*-, m. p. 173°; N-α-*naphthyl*-, m. p. 212°, and N-β-*naphthyl*-, m. p. 220°, -*homophthalimides*. The *benzylidene* derivatives of these have m. p. 193—194°, 185—186°, 225°, and 204°, respectively, and the p-*dimethylaminobenzylidene* derivatives have m. p. 224—225°, 245—246°, 141°, and 159—160°, respectively.

H. BURTON.

Stereochemistry of diphenyl compounds. Resolution of 1 : 1′-dinaphthyl-8 : 8′-dicarboxylic acid. W. M. STANLEY (J. Amer. Chem. Soc., 1931, **53**, 3104—3108).—1 : 1′-*Dinaphthyl*-8 : 8′-*dicarboxylic acid* (I), m. p. 306—307°, obtained by hydrolysis of its Et ester (II) (A., 1914, i, 849), is resolved by quinine into d-, m. p. 305—306°, and l-, m. p. 304·5—305·5° *forms*, which racemise readily. The *l*-acid and Ac_2O in pyridine give an inactive *anhydride*, m. p. 179—180° [derived from 1 mol. of (I) and 2 mols. of AcOH], which passes above its m. p. into the anthanthrone obtained from (II) and conc. H_2SO_4 (*loc. cit.*).

H. BURTON.

Rotenone. XIII. Oxidation of methylderritolic acid and synthesis of 2 : 3 : 5- and 2 : 3 : 6-trimethoxybenzoic acids and their derivatives. L. E. SMITH and F. B. LAFORGE (J. Amer. Chem. Soc., 1931, **53**, 3072—3077).—The trimethoxybenzoic acid, m. p. 78—80°, previously obtained (this vol., 227) from methylderritolic acid, is impure 2 : 4 : 5-trimethoxybenzoic acid (I). Et 2 : 4 : 5-trimethoxyphenylacetate (*loc. cit.*) and MgPhBr give *diphenyl-2 : 4 : 5-trimethoxybenzylcarbinol*, m. p. 130—131°, which at 138° in presence of I passes into ββ-*diphenyl-2 : 4 : 5-trimethoxyphenylethylene*, m. p. 101—103°. This is oxidised by $KMnO_4$ in $COMe_2$ to (I), also formed by similar oxidation of dihydroderritol Me ether. Oxidation of derritol gives a hydroxydimethoxybenzoic acid identical with that obtained from hydrodeguelin (this vol., 841).

5-Nitro-*o*-vanillin Me ether is converted through the 5-NH_2-derivative into 5-*hydroxy*-2 : 3-*dimethoxybenzaldehyde*, m. p. 152°, methylated to 2 : 3 : 5-*trimethoxybenzaldehyde*, m. p. 71° (*azlactone*, m. p. 181—183°, converted by successive hydrolysis and oxidation into 2 : 3 : 5-*trimethoxyphenylacetic acid*, m. p. 83°), which is oxidised by $KMnO_4$ to 2 : 3 : 5-*trimethoxybenzoic acid*, m. p. 105°. 6-*Hydroxy*-2 : 3-*dimethoxybenzoic acid*, m. p. 82°, obtained by way of the 6-NO_2- and 6-NH_2-derivatives, is methylated to 2 : 3 : 6-*trimethoxybenzoic acid*, m. p. 145—146°. 2 : 4 : 5-*Trimethoxyphenylacetamide* has m. p. 169°.

H. BURTON.

Friedel–Crafts reaction with maleic anhydride and resorcinol dimethyl ether. Addition of aromatic ethers to unsaturated substances. G. P. RICE (J. Amer. Chem. Soc., 1931, **53**, 3153—3159).—Maleic anhydride and resorcinol Me_2 ether in presence of $AlCl_3$ and CS_2 give the *anhydride* (I), m. p. 147°, of α-2 : 4-*dimethoxyphenylsuccinic acid*, m. p. 160° [α-*Me*, m. p. 117°, β-*Me*, m. p. 142·5°, and *Me*$_2$, b. p. 231°/31 mm., m. p. 60°, esters; 5-*bromo*-derivative, m. p. 219° (*Me* ester, m. p. 90°)], together with β-2 : 4-*dimethoxybenzoylacrylic acid* (II), yellow, m. p. 189° (decomp.) after becoming colourless at 180° (*Me* ester, m. p. 85°), β-2 : 4-*dimethoxybenzoyl*-α-2 : 4-*dimethoxyphenylpropionic acid* (III), m. p. 160° [*Me* ester (IV), m. p. 140°; *semicarbazone*, m. p. 204°], and an *acid*, $C_{18}H_{18}O_7$, m. p. 185—187°. The production of (I) involves a 1 : 4-addition of the ether to maleic anhydride. The Friedel–Crafts reaction with resorcinol Me_2 ether and (I) or (II) also gives (III); in the former case, β-2 : 4-*dimethoxybenzoyl*-β-2 : 4-*dimethoxyphenylpropionic acid*, m. p. 157° (*Me* ester, m. p. 104°), is produced also. (III) and Br in CS_2 give β-*bromo*-β-5-*bromo*-2 : 4-*dimethoxybenzoyl*-α-5-*bromo*-2 : 4-*dimethoxyphenylpropionic acid*, m. p. 213° (decomp.) [*Me* esters, m. p. 210° and 165—173°, obtained from Br and (IV)].

H. BURTON.

Condensation of aromatic aldehydes with malonanilic acid and its derivatives. G. S. AHLUWALIA, M. A. HAQ, and J. N. RAY (J.C.S., 1931, 2059—2062).—Malonanilic acid condenses with various benzaldehydes in pyridine, forming benzylidenemalonanilic acids (sometimes accompanied by cinnamanilides), which are reduced by Na–Hg to benzylmalonanilic acids. None of these products could be dehydrated to quinolones, indenoquinolones, *iso*indenoquinolones, or hydrindonecarboxyanilides. The following are described: 3 : 4-*methylenedioxy*-, m. p. 158°, 3 : 4-*dimethoxy*-, m. p. 111°, and p-*methoxy*-, m. p. 140°, -*cinnamanilides*; 3 : 4-*methylenedioxy*-, m. p. 181°, and p-*methoxy*-, m. p. 177°, -*cinnam-o-toluidides*; 3 : 4-*methylenedioxy*-, m. p. 202° (decomp.), 3 : 4-*dimethoxy*-, m. p. 222° (decomp.) (*Ag* salt), p-*methoxy*-, m. p. 213° (decomp.), and o-*nitro*- (I), m. p. 172° (decomp.), -*benzylidenemalonanilic acids*; 3 : 4-*methylenedioxy*-, m. p. 213°, 3 : 4-*dimethoxy*-, m. p. 219°, p-*methoxy*-, m. p. 217°, and o-*nitro*-, m. p. 221° (decomp.), -*benzylidenemalon-o-toluidic acids*; 3 : 4-*methylenedioxy*-, m. p. 172° (decomp.), and 3 : 4-*dimethoxy*-, m. p. 173°, -*benzylmalonanilic acids*; 3 : 4-*methylenedioxy*,- m. p. 163° (decomp.), and 3 : 4-*dimethoxy*-, m. p. 128°, -*benzylmalon-o-toluidic acids*; *o-nitropiperonylidenemalonanilic acid*, m. p. 230°.

Salicylaldehyde and malonanilic acid give *coumarin-3-carboxyanilide*, m. p. 247° (corresponding o-, m. p. 226°, and m-, m. p. 200°, *-toluidides*). 2-Anilinoquinoline is formed when (I) is reduced with Zn dust or $SnCl_2$ and AcOH. H. BURTON.

Oxidation of organic compounds [methyl derivatives to aldehydes and carboxylic acids] with selenium dioxide etc. I. G. FARBENIND. A.-G.—See B., 1931, 712.

Manufacture of condensation products [acid wool dyes] of the benzanthrone series. I. G. FARBENIND. A.-G.—See B., 1931, 712.

Manufacture of alkoxybenzophenone-di- and -tri-carboxylic acids. I. G. FARBENIND. A.-G.—See B., 1931, 797.

Action of chlorine on chloro-substituted hydrazones. F. D. CHATTAWAY, T. DEIGHTON, and A. ADAIR (J.C.S., 1931, 1925—1928).—2 : 4 : 5-Tri- and 2 : 3 : 4 : 6-tetra-chloroanilines (convenient methods of prep. given) are diazotised and then reduced by $SnCl_2$ and conc. HCl to 2 : 4 : 5-*tri-* and 2 : 3 : 4 : 6-*tetra-chlorophenylhydrazines*, m. p. 132° and 162°, respectively. Chlorination of o-, polymorphic forms both with m. p. 156°, m-, m. p. 172°, and p-, m. p. 221°, *-nitrobenzaldehyde-*2 : 5-*dichlorophenylhydrazones* in AcOH below 20° gives o- (too soluble for ready isolation), m-, m. p. 195°, and p-, m. p. 252°, *-nitrobenzaldehyde-ω-chloro-*2 : 4 : 5-*trichlorophenylhydrazones*, whilst in hot AcOH, o-, m. p. 129°, m-, m. p. 174°, and p-, m. p. 165°, *-nitrobenzaldehyde-ω-chloro-*2 : 3 : 4 : 6-*tetrachlorophenylhydrazones* result. These ω-chloro-*m*- and *-p*-nitro-compounds are converted by alcoholic NH_3 into hydrazidines, NHR·N:CR'·NH_2, whilst the *o*-NO_2-isomerides give explosive *iso*diazole oxides. The following are described: o-, m. p. 184°, m-, m. p. 211°, and p-, m. p. 219°, *-nitrobenzaldehyde -*2 : 3 : 4 : 6-*tetrachlorophenylhydrazones*; m-, m. p. 234°, and p-, m. p. 268°, *-nitrobenzaldehyde-*2 : 4 : 5-*trichlorophenylhydrazones*; m-, m. p. 210° (decomp.), and p-, m. p. 250° (decomp.), *-nitrobenzaldehyde-*2 : 4 : 5-*trichlorophenylhydrazidines*; m-, m. p. 175° (decomp.), and p-, m. p. 230° (decomp.), *-nitrobenzaldehyde-*2 : 3 : 4 : 6-*tetrachlorophenylhydrazidines*. H. BURTON.

Coupling reactions between aldehydehydrazones and diazo-compounds. Formazyl formation. M. BUSCH and R. SCHMIDT (J. pr. Chem., 1931, [ii], **131**, 182—192).—The interaction of benzenediazonium chloride with benzaldehydephenylhydrazone in aq. EtOH in presence of NaOAc results in coupling at the ·NH· group of the hydrazone with formation of 1-*benzylidene-*2 : 4-*diphenyltetrazene*, CHPh:N·NPh·N:NPh, decomp. 50—55°, which is readily isomerised into formazylbenzene by evaporation of its solution in Et_2O. In EtOH–C_6H_6 coupling occurs in the *p*-position of the phenylhydrazino-nucleus; *p*-nitrobenzenediazonium chloride gives the same azo-compound (benzaldehyde-*p*-benzeneazophenylhydrazone) and benzaldehyde-*p*-nitrophenylhydrazone. Isomeric p-*bromoformazylbenzenes*, m. p. 189° and 191°, are obtained by interaction of benzaldehydephenylhydrazone with K *p*-bromophenyldiazotate, and of benzaldehyde-*p*-bromophenylhydrazone with K phenyldiazotate, respectively (cf. A., 1894, i, 456); these isomerides are apparently non-interconvertible by action of solvents. Diazonium salts react with benzaldehydephenylmethylhydrazone and similar compounds much more readily than the corresponding diazotates, but give the same products; thus benzenediazonium chloride in $COMe_2$–EtOH gives benzaldehyde-*p*-benzeneazophenylmethylhydrazone, and *p*-nitrobenzenediazonium chloride couples normally to give the corresponding NO_2-derivative. H. A. PIGGOTT.

Reaction of acetophenone derivatives with sodium hypochlorite. A. M. VANARENDONK and M. E. CUPERY (J. Amer. Chem. Soc., 1931, **53**, 3184—3186).—Acetophenone derivatives are oxidised by NaOCl to the corresponding benzoic acids in 85—96% yield provided OH and NO_2-groups are absent; 8 examples are given. H. BURTON

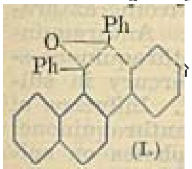
Ketones of naphthalene group. Three isomeric bromonaphthyl methyl ketones. K. DZIEWOŃSKI and L. STERNBACH (Bull. Acad. Polonaise, 1931, **A**, 59—68).—1-Bromonaphthalene and AcCl in presence of $AlCl_3$ and CS_2 (cf. A., 1891, 684) give 1-*bromo-*4-*acetylnaphthalene*, b. p. 193—196°/18 mm. (*oxime*, m. p. 142°; *semicarbazone*, m. p. 216—218°), oxidised by dil. HNO_3 to 4-bromo-α-naphthoic acid. Similarly, 2-bromonaphthalene and AcCl afford 2-*bromo-*1-*acetylnaphthalene*, m. p. 64—65° (*semicarbazone*, m. p. 186—187°; *oxime*, m. p. 117°, converted by HCl in AcOH and Ac_2O into the *Ac* derivative of 2-*bromo-α-naphthylamine*, m. p. 59—60°), and 2-*bromo-*6-*acetylnaphthalene*, m. p. 96° [*semicarbazone*, m. p. 228°; *phenylhydrazone*, m. p. 187—188° (decomp.); *oxime*, m. p. 154°, convertible into 6-bromoacet-β-naphthalide]. 2-*Bromo-α-naphthoic acid* has m. p. 233°. H. BURTON.

Configurations of oximes from measurements of electric dipole moment. L. E. SUTTON and T. W. J. TAYLOR (J.C.S., 1931, 2190—2195).—Oximation of *p*-nitrobenzophenone gives α- (I), m. p. 159°, and β-oximes (II), m. p. 136° [the β-oxime described by Brady and Mehta (A., 1925, i, 43) is a mixture of the α- and β-forms]; the Beckmann rearrangement with (II) affords benz-*p*-nitroanilide, the groups involved in the transformation being in the *anti*-position to one another. The *N*-Me ether of (I) has an electric moment of $6{\cdot}60\times10^{-18}$ and is the *syn*-form, whilst the N-*Me ether*, m. p. 186°, of (II) (moment $1{\cdot}09\times10^{-18}$) is the *anti*-modification. *N*-Methyl-*p*-nitrobenzaldoxime (moment $6{\cdot}4\pm0{\cdot}1\times10^{-18}$) is the *syn*-compound; the Beckmann transformation with this also involves groups in the *anti*-position to one another. H. BURTON.

Mechanism of sulphur lability in cysteine and its derivatives. I. Thio-ethers readily cleaved by alkali. B. H. NICOLET (J. Amer. Chem. Soc., 1931, **53**, 3066—3072).—The keto-sulphides R'S·CHR·CH_2·COR'', prepared from a mercaptan and an αβ-unsaturated ketone in presence of NaOEt in EtOH or C_6H_6, are decomposed readily by aq. alkali into the starting materials. Thus, β-*benzoyl-α-phenylethylthiolacetic acid*, m. p. 129°, gives thiolacetic acid and Ph styryl ketone; *Ph* β-p-*tolylthiol-*β-*phenylethyl ketone*, m. p. 113°, affords *p*-thiocresol and Ph

styryl ketone, and β-p-*tolylthiol*-β-*phenylethyl Me ketone*, m. p. 64°, yields *p*-thiocresol and styryl Me ketone. The above ketones are analogous to cysteine; a mechanism for the elimination of S from cysteine by alkali is suggested. H. BURTON.

Polycyclic aromatic hydrocarbons. V. Synthesis of chrysene homologues. J. W. COOK and (in part) R. A. E. GALLEY (J.C.S., 1931, 2012—2018).—Chrysenequinone and MgPhBr in C_6H_6 give 1 : 2-*dihydroxy*-1 : 2-*diphenyl*-1 : 2-*dihydrochrysene*, m. p. 219—220°, dehydrated by conc. HCl in AcOH to 1 : 2-*diphenyl*-1 : 2-*dihydro*-α-*chrysapinacolin* (I),



m. p. 218·5—219·5°, which is reduced by red P and HI (*d* 1·9) at 190—200° to 1 : 2-*diphenylchrysene*, m. p. 208—209°. The α-*pinacolin*, m. p. 162—163°, from 1 : 2-*dihydroxy*-1 : 2-*dibenzyl*-1 : 2-*dihydrochrysene*, m. p. 184—185°, is reduced similarly to chrysene. When 1-phenylacetylnaphthalene (II) is boiled for 3 hr., 2-*phenylacetylnaphthalene*, m. p. 99—100° (oxidised by $Na_2Cr_2O_7$ and AcOH to β-naphthoic acid), is produced. Similar pyrolysis of 1-*phenylacetyl*-4-*methylnaphthalene* (III), m. p. 59—61°, prepared from 1-methylnaphthalene and phenylacetyl chloride in presence of $AlCl_3$ and CS_2, causes dehydrogenation to 7-*phenyl*-3-*methyl*-8-*acenaphthenone* (IV), m. p. 162—163° [*oxime*, m. p. 195—197° (decomp.); enol *acetate*, m. p. 113°]. Oxidation of (IV) with $Na_2Cr_2O_7$ and AcOH gives 8-*benzoyl*-4-*methyl*-1-*naphthoic acid*, m. p. 194°, which with KOH at 260° yields BzOH and 4-methyl-1-naphthoic acid. The carbinol from (II) and MgMeI is dehydrated by HCl in AcOH to ω-1-*naphthyl*-ω-*methylstyrene*, m. p. 139°.

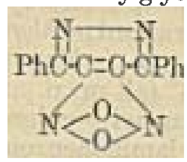
[With R. A. E. GALLEY.] Amyl nitrite and (III) in alcoholic NaOEt give the α-*monoxime*, m. p. 160—161°, of α-*phenyl*-β-(4-*methyl*-1-*naphthyl*)*glyoxal*, m. p. 111·5—112·5° (*quinoxaline*, m. p. 132—133°, from *o*-phenylenediamine), together with the *anil*, m. p. 258—259° (decomp.), from 1 mol. of the oxime and 1 mol. of (III). The glyoxal and $AlCl_3$ at 150° yield a minute amount of a chrysenequinone derivative, m. p. 217—218°. H. BURTON.

Dioximes. LXXVII. G. PONZIO (Gazzetta, 1931, 61, 561—575; cf. A., 1930, 1409).—Treatment of the 2-Bz derivative of phenylchloroglyoxime with Na_2CO_3 gives the *Bz* derivative, m. p. 109—110°, of oximinophenylacetonitrile oxide, giving, when boiled in xylene, a *dimeride*, m. p. 139°. The *Bz* derivative, m. p. 140° (*dimeride*, m. p. 174—175°), of oximino-*p*-tolylacetonitrile oxide is similarly obtained and on treatment with NH_3 gives the *Bz* derivative, m. p. 178—179°, of α-*p*-tolylaminoglyoxime. A nitroso-oximic structure CAr(N·OBz)·CHCl·NO is suggested for the 2-Bz derivatives of phenyl- and *p*-tolylchloroglyoximes. Wieland's views on the formation of glyoxime peroxides are shown to be incompatible with the results of this work. E. E. J. MARLER.

Dioximes. LXXIX. M. MILONE (Gazzetta, 1931, 61, 584—589).—The velocities of hydrolysis of the Ac and Bz derivatives of the α-, β-, and γ-forms of benzildioxime have been measured.

E. E. J. MARLER.

Dioximes. LXXX. E. DURIO (Gazzetta, 1931, 61, 589—596).—The peroxide $(C_2O_2N_2)Bz_2$ (I) of dibenzoylglyoxime is converted by the action of bases into benzoylmetazonic acid, CBz(NOH)·CH:NO·OH (Ac_3 derivative, m. p. 145—146°; Bz_2 derivative, m. p. 151—152°; *K* salt), and by PCl_5 into the peroxide, m. p. 126—127°, of benzoyldichlorobenzylglyoxime. This reacts with NH_2OH,HCl,



giving the *azine*, m. p. 190°, of dibenzoylfurazan. This *azine* is similarly obtained from dibenzoyl- or benzoyldichlorobenzyl-glyoxime, also from the azine (A., 1909, i, 656) of (I), to which the annexed formula is therefore assigned. The *azine*, m. p. 207°, of the peroxide of di-*p*-toluoylglyoxime and the *azine*, m. p. 298°, of di-*p*-toluoylfurazan are described. E. E. J. MARLER.

Configurations of α-oximinoketones. T. W. J. TAYLOR (J.C.S., 1931, 2018—2027).—Indications regarding the configurations of oximinoketones, COR·CR':N·OH, which are consistent with the result deduced from the Beckmann transformation, are obtained from a study of the following properties: (1) formation of co-ordination complexes with Cu and Co (cf. A., 1928, 291), which is typical of the α-configuration, (2) reactivity of the CO group and solubility relationships (cf. A., 1927, 58), (3) the coupling of compounds containing the CO·CH:N·OH group with aromatic diazo-compounds (cf. A., 1907, i, 326). Two oximes exist (the β being the more stable) when R is aryl and R' is attached to the rest of the mol. by a *tert.*-C atom. Where only one oxime is known (in the cases studied), this has the α-structure and is stable; an exception is Et oximinobenzoylacetate, which is a β-oxime. The stable oximinocamphor (m. p. 152°) has the α-configuration and not the β [as stated by Forster (J.C.S., 1905, 87, 232)]. Oximinobenzyl Me ketone (*phenylhydrazone*, m. p. 146—147°) yields a *Co* salt, R_3Co (R=1 mol. of oxime−1H); the β-configuration assigned to this oxime by Orekhov and Tiffeneau (A., 1927, 872) is based on evidence of no stereochemical value, since both α- and β-benzilmonoximes react with MgMeI, yielding the same (probably α) *methylbenzoinoxime*, m. p. 124°. Oximino-*p*-methoxybenzyl Me ketone (I) gives a *Co* salt, R_3Co. The pyruvylanisidine of Borsche (A., 1907, i, 326) is the oxime p-MeO·C_6H_4·CO·CMe:N·OH (cf. A., 1903, i, 837), which is formed by hydrolysis of (I) to the diketone and NH_2OH (followed by recombination) and not as the result of a Beckmann change. p-*Methoxyphenyl* α-*oximinoethyl ketone*, m. p. 128° (*Co* salt, R_3Co), is obtained from *p*-methoxypropiophenone, amyl nitrite, and NaOEt, and *oximinodibenzyl ketone*, m. p. 114° (*Cu* complex, probably RCuOH; *Co* salt, R_2Co), is prepared similarly from dibenzyl ketone.

[With N. J. MAWBY.] Methoxydeoxybenzoin, amyl nitrite, and NaOEt give a mixture of the α-, m. p. 95·5° (lit. 87·5—89°) (*Co* salt, R_3Co), and β-, m. p. 130°, forms of 4'-methoxybenzil-α-oxime; the former is converted into the latter by animal charcoal in boiling C_6H_6.

[With N. J MAWBY and G. M. PRICE.] 4-Methyl-

deoxybenzoin is similarly converted into α-4-*methylbenzil-α-oxime*, m. p. 111·5° (*phenylhydrazone*, m. p. 183°; *Co* salt, R_3Co), transformed as above into the β-*oxime* $+C_6H_6$, begins to melt at 90°, m. p. (C_6H_6-free) 123·5°. H. BURTON.

Structure and derivatives of *p'*-chloro-*p*-dimethylaminobenzoin. S. S. JENKINS (J. Amer. Chem. Soc., 1931, **53**, 3115—3122).—*p*-Dimethylaminomandelamide and *p*-ClC_6H_4·MgBr afford p-*chlorobenzoyl*-p-*dimethylaminophenylcarbinol* (α-p'-*chloro*-p-*dimethylaminobenzoin*) (I), m. p. 104·5° (all m. p. are corr.), whilst *p*-dimethylaminobenzoyl-*p*-chlorophenylcarbinol (β-*p'*-chloro-*p*-dimethylaminobenzoin) (II), m. p. 128° (cf. A., 1913, i, 1354), is obtained from *p*-chloromandelamide and *p*-NMe_2·C_6H_4·MgBr. (I) and (II) are oxidised by Fehling's solution to 4-*chloro*-4'-*dimethylaminobenzil*, m. p. 144·5°. When (I) is heated with KCN in 70% EtOH, (II) is produced. Reduction of (II) with Na–Hg and aq. EtOH gives p'-*chloro*-p-*dimethylaminohydrobenzoin*, m. p. 180°, converted by conc. HCl in AcOH into p-*chlorophenyl* p-*dimethylaminobenzyl ketone* (α-p'-*chloro*-p-*dimethylaminodeoxybenzoin*) (III), m. p. 140° (*oxime*, m. p. 150·5°), also formed when (I) is reduced with Sn and conc. HCl in EtOH containing a little $CuSO_4$. When (II) is reduced with Sn [as for (I)] a mixture of (III) and p-*dimethylaminophenyl* p-*chlorobenzyl ketone* (β-p'-*chloro*-p-*dimethylaminodeoxybenzoin*) (IV), m. p. 170° (*oxime*, m. p. 152°), is produced. Reduction of (IV) with Na–Hg and 90% EtOH gives β-p-*chlorophenyl*-α-p-*dimethylaminophenylethyl alcohol*, m. p. 112° (also prepared from *p*-NMe_2·C_6H_4·CHO and Mg *p*-chlorobenzyl bromide), dehydrated by conc. HCl in AcOH to 4-*chloro*-4'-*dimethylaminostilbene*, m. p. 229°. This is prepared similarly from (III). H. BURTON.

Constitution and synthesis of embelic acid (embelin), the active principle of *Embelia Ribes*. K. H. HASAN and E. STEDMAN (J.C.S., 1931, 2112—2123).—Oxidation of embelic acid (embelin) (I) with alkaline $KMnO_4$ or HNO_3 gives dodecoic (as stated in A., 1900, i, 498) and not *iso*dodecoic acid (A., 1929, 1306). (I) is shown to be 2 : 5-dihydroxy-3-*n*-dodecyl-*p*-benzoquinone and not 2 : 5-dihydroxy-4-*n*-undecyl-*p*-toluquinone (A., 1900, i, 498).

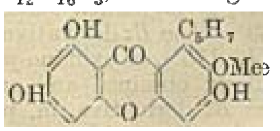
Nonyl chloride and PhMe in presence of $AlCl_3$ give p-*tolyl* n-*octyl ketone*, b. p. 183—184°/12 mm., m. p. 37°, reduced (Clemmensen) to p-n-*nonyltoluene*, b. p. 160—161°/12 mm., which is nitrated to a mixture (*A*) of the 2- and 3-nitro-derivatives. The mixed amines (individual *sulphates*, m. p. 144° and 178°, are described), obtained by reducing *A* with Fe powder and 50% AcOH, are oxidised by $Na_2Cr_2O_7$ and dil. H_2SO_4 to 4-n-*nonyl*-p-*toluquinone*, m. p. 53°, which with NH_2Me in EtOH gives 2 : 5-*di*(*methylamino*)-4-n-*nonyl*-p-*toluquinone*, m. p. 167°. This is hydrolysed by 40% H_2SO_4 to 2 : 5-*dihydroxy*-4-n-*nonyl*-p-*toluquinone*, m. p. 154°. p-*Tolyl* n-*decyl ketone*, b. p. 196—197°, m. p. 32°, is similarly converted through the mixed nitro- and amino-derivatives (a *sulphate*, m. p. 177°, is described) of p-*undecyltoluene*, b. p. 171—172°/12 mm., into 4-n-*undecyl*-p-*toluquinone*, m. p. 64°. 2 : 5-*Di*(*methylamino*)-4-n-*undecyl*-p-*toluquinone*, m. p. 158°, is hydrolysed by 70% H_2SO_4 to 2 : 5-*dihydroxy*-4-n-*undecyl*-p-*toluquinone*, m. p. 150°.

Quinol and dodecoyl chloride in presence of $ZnCl_2$ at 130—140° give *didodecoylquinol*, m. p. 68°, which on reduction (Clemmensen) affords quinol, dodecoic acid, and *dodecylquinol*, m. p. 109°. This is oxidised by $Na_2Cr_2O_7$ and dil. H_2SO_4 to 3-*dodecyl*-p-*benzoquinone*, m. p. 81°, the 2 : 5-*di*(*methylamino*)-derivative, m. p. 147°, of which is hydrolysed by 80% H_2SO_4 in EtOH to 2 : 5-*dihydroxy*-3-n-*dodecyl*-p-*benzoquinone*, m. p. 143°. H. BURTON.

Anthraquinonesulphonic acids. I. Their separation, identification, and determination. II. Fission of sulpho-groups from anthraquinone-α-sulphonic acids. III. Anthraquinone-β-sulphonic acids. IV. Anthraquinone-α-sulphonic acids. V. Use of mercury in sulphonation of anthraquinone. VI. Influence of impurities in sulphonation of anthraquinone. VII. Influence of inorganic sulphates on sulphonation of anthraquinone. K. LAUER.—See B., 1931, 751.

Paprika colouring matter. VI. Pigment of Japanese paprika. L. ZECHMEISTER and L. VON CHOLNOKY (Annalen, 1931, **489**, 1—6).—Contrary to Bilger (this vol., 847), after repeated purification the pigment isolated from Japan red pepper (*Capsicum frutescens japonicum*) is physically and chemically identical with capsanthin from paprika. Carotene is also isolated. The yellow alcoholic component obtained (with capsanthin) by hydrolysis of the ester fraction of *C. annuum* (this vol., 1066) is identical with zeaxanthin (50 mg. per kg. dried material). J. W. BAKER.

Constitution of mangostin. I. M. MURAKAMI (Proc. Imp. Acad. Tokyo, 1931, **7**, 254—257).—Mangostin, $C_{23}H_{24}O_6$, yields a Me derivative, m. p. 172°, *Me*₂ derivative, m. p. 123°, and a Me_3 derivative, m. p. 100°. With HCl the Me_3 derivative loses Me to give $C_{25}H_{29}O_6Cl,2H_2O$. With Br dimethylmangostin forms an unstable *heptabromide*, $C_{25}H_{25}O_6Br_7$, which loses Br in aq. solution, giving *tetrabromodimethylmangostin*, $C_{25}H_{24}O_6Br_4,H_2O$, m. p. 174° (decomp.), which with KOH in EtOH gives *dibromodimethylmangostin*, $C_{25}H_{24}O_6Br_2,2H_2O$, m. p. 165°. When mangostin is heated with KOH in EtOH at 170—180°, *iso*amyl alcohol, AcOH, methylheptenol, b. p. 80—83°/14·8 mm., and a phenolic substance, $C_{12}H_{16}O_3$, containing one OMe and two OH groups, which on oxidation of its *Me*₂ derivative, b. p. 176—180°/14 mm., gives 2 : 3 : 5-*trimethoxybenzoic acid*, m. p. 99—100°, are formed. Oxidation of the *dihydro*-derivative of the phenolic substance gives *iso*hexanilide. The phenolic substance, $C_{19}H_{18}O_6$, obtained by alkali fusion of mangostin is formulated as annexed. C. C. N. VASS.



Quinovic acid. III. H. WIELAND and S. UTZINO (Annalen, 1931, **488**, 242—258).—Quinovic acid at 340—350°/12 mm. passes by way of pyroquinovic acid into *anhydropyroquinovic acid* (I), $C_{29}H_{44}O_2$, m. p. 227—228° (*Me*, m. p. 150°, and *Et*, m. p. 203°, esters), which is isomeric with that pre-

viously described (A., 1927, 562) and probably differs only in the position of a double linking; (I) is isomerised by $ZnCl_2$ in AcOH to a *lactone*, m. p. 200°. The CO_2H group eliminated as CO_2 during thermal decomp. of quinovic acid is the one which lactonises during the formation of novic acid (*loc. cit.*); the last-named acid [*chloride*, m. p. 208° (decomp.)] can be distilled unchanged. The OH group in quinovic acid is not in the α-position to the second CO_2H group since CO is not produced from pyroquinovic acid and conc. H_2SO_4. Oxidation of (I) with CrO_3 in AcOH gives a *lactone*, $C_{29}H_{40}O_3$, m. p. 277°, and a yellow *acid*, $C_{29}H_{40}O_4$, m. p. 283° (decomp.) (*Me* ester, m. p. 245°); the acid is oxidised further by $KMnO_4$ to a neutral *compound*, $C_{29}H_{42}O_5$, m. p. 317°, and a yellow *acid*, $C_{29}H_{40}O_5$, m. p. 302° (decomp.). The yellow acids are probably *o*-quinones; they are unaffected by alkali. Decomp. of the ozonide from (I) with H_2O gives a *lactone*, $C_{28}H_{44}O_3$, m. p. 256—257° (decomp.), and an *acid*, $C_{26}H_{38}O_4$, m. p. 313° (decomp.). (I) and Br in AcOH afford a *bromolactone*, $C_{29}H_{43}O_2Br$, m. p. 168—169° (decomp.), converted by pyridine into a *compound*, $C_{29}H_{42}O_2$.

The ozonide from pyroquinovic acid is decomposed by H_2O mainly to a *lactone*, $C_{29}H_{44}O_4$, m. p. 275° (*Ac* derivative, m. p. 300°), and oxidised by CrO_3 in AcOH to a *lactone*, $C_{29}H_{42}O_4$, m. p. 293°, which when dissolved in alkali and then acidified yields *acids*, $C_{26}H_{38}O_4$, m. p. 284°, and $C_{26}H_{40}O_3$, m. p. 184° (decomp.). Triacetylquinovic acid (*loc. cit.*) and CrO_3 in AcOH give an *acid*, $C_{32}H_{44}O_7$, m. p. 278° (decomp.), hydrolysed by cold MeOH–KOH to an *acid*, $C_{30}H_{42}O_6$, m. p. 257° (decomp.), which is similarly oxidised to a dicarboxylic *acid*, $C_{30}H_{40}O_8$, m. p. 244° (decomp.), probably formed thus: $\cdot\underbrace{CO\cdot CHR}\cdot \longrightarrow \cdot\underbrace{CO_2H \quad COR}\cdot$.

Anhydroquinovic acid is converted into novic acid by treatment with Zn–Hg and HCl (or $ZnCl_2$) in AcOH, and oxidised by O_3 to an *acid*, $C_{30}H_{44}O_5$, m. p. 306—307° (decomp.), and an isomeric *substance*, m. p. 310°. The dibasic acid $C_{29}H_{38}O_9$, previously obtained (A., 1930, 600) from tribenzoylquinovic acid by way of a quinone and a glycollic acid, loses CO_2 and H_2O at 280—300° forming a neutral *substance*, $C_{28}H_{36}O_6$, m. p. 287°. H. BURTON.

Saponin group. I. Saponin of horse-chestnuts. A. WINTERSTEIN. **II. Saponin of soap-nuts.** A. WINTERSTEIN and J. MEYER. **III. Detection of a double linking in sapogenins.** A. WINTERSTEIN and W. WIEGAND. **IV. Sapogenin from *Viscum album*.** A. WINTERSTEIN and W. HAMMERLE. **V. Guaiacum saponin and a saponin from *Calendula officinalis*.** A. WINTERSTEIN and G. STEIN. **VI. Catalytic hydrogenation of the double linking in hederagenin.** A. WINTERSTEIN and G. STEIN (Z. physiol. Chem., 1931, **199**, 25—37, 37—46, 46—56, 56—64, 64—74, 75—80).—I. Mild hydrolysis of the saponin of horse-chestnuts yields a prosapogenin *B*, $C_{53}H_{88}O_{27}$, m. p. 220—230° (decomp.) [*Br*-derivative, browns at 160°, m. p. 220° (decomp.)], which on prolonged acid hydrolysis gives ascigenin, $C_{35}H_{58}O_7$, m. p. 309° (corr.), $[\alpha]_D^{17}$ +26·8° in EtOH, [*Br*-derivative, m. p. 196—197° (corr.)]. Ascigenin contains 5 OH groups and with HCl in EtOH yields Et tiglate, indicating that it is an ester of tiglic or β-hydroxy-α-methylbutyric acid.

II. Mild hydrolysis of the saponin of soap-nuts yields hederagenin, $C_{30}H_{47}(OH)_2\cdot CO_2H$, m. p. 327—329 (corr.). The *Br*-derivative, m. p. 226—228°, on hydrolysis gives a *product*, $C_{31}H_{50}O_5$, m. p. 338°. Hydrolysis of the *diformyl* derivative, m. p. 258—259°, furnishes a substance, m. p. 354°. Hederagenin is decarboxylated in high vac. at 300° yielding a *product*, m. p. 275—277° (corr.). The hæmolytic activity of the saponin and prosaponin is lost on bromination.

III. Hederagenin is a βγ- or γδ-unsaturated pentacyclic acid. The *Br*-derivative (a bromolactone) [*Ac*, m. p. 235° (corr.) (decomp.), and *acetonyl*, m. p. 172° (decomp.), derivatives] with Zn dust and AcOH gives diacetylhederagenin, with Zn dust in $COMe_2$ hederagenin. Conc. HCl converts hederagenin into the lactone, m. p. 354°; H_2SO_4, or HBr in AcOH, yields the *diacetyl-lactone*, m. p. 244°. The lactone yields the Na salt of the hydroxy-acid with NaOEt.

IV. Oleanolic acid, a sapogenin of mistletoe, identical with sugar-beet sapogenin, $C_{31}H_{50}O_3$, $[\alpha]_D^{18}$ +76·1° [*Ac* derivative, m. p. 258—260° (corr.), $[\alpha]_D^{18}$ +72·8; *Me* ester, m. p. 196—198°], is an unsaturated, pentacyclic hydroxycarboxylic acid. The *bromolactone*, m. p. 242·2—242·4° (corr.), with Zn dust and AcOH regenerates oleanolic acid. From the latter H_2SO_4 liberates CO.

V. The aglucone of guaiacum saponin prepared by hydrolysis of the latter with H_2SO_4 in EtOH in two stages is identical with oleanolic acid. With HCl in AcOH it gives the *acetyl-lactone*, m. p. 354—355°. *Calendula* saponin contains the same aglucone.

VI. *Diacetylhederabetulin*, m. p. 190°, and hederabetulin take up O with BzO_2H and H in presence of Pt [*dihydro*-derivatives, m. p. 131—132° (corr.) and 235—239° (corr.), respectively] in contrast to hederagenin, in which the CO_2H group inhibits. Betulin and hederabetulin (and the dihydro-derivatives) are not identical. J. H. BIRKINSHAW.

Oxidation–reduction of pyocyanine. I. Biochemical preparation of pyocyanine. B. ELEMA and A. C. SANDERS (Rec. trav. chim., 1931, **50**, 796—806).—Good yields of pyocyanine are obtained when *Pseudomonas pyocyanea* is cultivated in a liquid medium containing peptone (1%), NaCl (0·5%), and gelatin (12%) at 25°. H. BURTON.

Optical activity and the polarity of substituent groups. XX. Aliphatic and aromatic ethers of *l*-menthol. H. G. RULE and H. TOD (J.C.S., 1931, 1929—1936; cf. this vol., 961).—The influence of X on the rotatory power of *l*-menthoxy-ethers $C_{10}H_{19}O\cdot CH_2X$ is in the order $Cl > CO_2Pr > CO_2Me > CO_2H > CO\cdot NH_2 >$ allyl > Et > Me > H > COO′, in agreement with the polarity deduced from dipole moments, or dissociation consts. of the correspondingly substituted acetic acids. The rotatory power of *l*-menthoxyacetic acid (improved prep.; cf. J.C.S., 1911, **99**, 2329) in EtOH is raised by addition of HCl, whilst that of its Na salt is lower than that of *l*-menthyl Me ether. The chloride of this acid gives the *Me* ester, b. p. 131°/8 mm., l-*menthyl* ester, and *amide*, m. p. 93°. K menthoxide (improved prep.; cf. A., 1897, i, 248) gives with picryl chloride in PhMe a complex of

menthyl picryl ether and K menthoxide, from which l-*menthyl picryl ether*, m. p. 133° (violent decomp. at 150°), is obtained; with chlorodinitrobenzene in C_6H_6 l-*menthyl* 2 : 4-*dinitrophenyl ether*, m. p. 88°, which shows anomalous dispersion and low rotatory power; and with PhI l-*menthyl Ph ether*, m. p. 49·5°, b. p. 144°/12 mm. The NO_2-ethers are unstable to light. The rotatory power of the Ph and picryl ethers is depressed, and that of the 2 : 4-dinitrophenyl ether is raised, in polar solvents. A. A. LEVI.

Optical activity and polarity of substituent groups. XXI. Growing chain effects among the *l*-menthyl esters of *n*-aliphatic acids. J. HARROWER (J.C.S., 1931, 2048—2056).—A study of the optical rotations of *l*-menthyl esters of the type $OMe\cdot[CH_2]_n\cdot CO_2C_{10}H_{19}$ alone and in EtOH and C_6H_6. In the latter solvent they are roughly parallel to those of the *l*-menthyl H dicarboxylates (cf. A., 1928, 765). l-*Menthyl* β-*methoxypropionate*, b.p. 135—137°/10 mm., is prepared from the corresponding *Me* ester, b. p. 142—144°/760 mm. (from Me β-iodopropionate), by the Na menthoxide process (A., 1930, 1558). γ-*Methoxybutyric acid*, b. p. 216—220° (l-*menthyl* ester, b. p. 143—145°/10 mm.), is prepared by alkaline hydrolysis of the corresponding nitrile. δ-*Methoxyvaleric acid*, b. p. 124—128°/12 mm. (l-*menthyl* ester, b. p. 155—165°/12 mm.), is obtained by methods parallel to those used by Noyes (A., 1898, i, 60) for the δ-ethoxy-acid. From pentamethylene dibromide ε-*bromo*-, b. p. 125—135°/14 mm., and ε-*methoxy*-n-*hexonitrile*, b. p. 98—102°/23 mm., and ε-*methoxy*-n-*hexoic acid*, b. p. 140—142°/15 mm. (l-*menthyl* ester, b. p. 181—182°/16 mm.), were successively prepared. Interaction of pentamethylene dibromide with NaOMe gives *Me* ε-*bromo*-n-*amyl ether*, b. p. 70·5°/10 mm., from which, by condensation with Et sodiomalonate, hydrolysis, and decarboxylation of the product, ξ-*methoxy*-n-*heptoic acid*, b. p. 155—160°/12 mm. (l-*menthyl* ester, b. p. 183—184°/10 mm.), is obtained. Except in the case of the first-named, all the menthyl esters are prepared by way of the acid chloride. H. A. PIGGOTT.

Constitution of *l*-menthyl esters of maleic acid. A. WASSERMANN (Annalen, 1931, 488, 211—241).—*l*-Menthol (1 mol.) and maleic anhydride (1 mol.) at 145—150° for 2·5 hr. give a l-*menthyl H maleate* (I). m. p. 85°, $[\alpha]_D^{19}$ −74·6° in EtOH, $[\alpha]_D^{100}$ −68·3° (*Ag* and *Ba* salts), whilst at 150—155° for 6 hr. a l-*menthyl H maleate* (II), m. p. 56°, $[\alpha]_D^{19}$ −76·6° in EtOH, $[\alpha]^{100}$ −79·2° (*Ag* and *Ba* salts), is produced. l-*Menthyl H fumarate* (*Ag* salt) has b. p. 177°/3 mm., m. p. 49°, $[\alpha]_D^{19}$ −76·2 in EtOH, $[\alpha]_D^{100}$ −76·9°. All these esters are unimol. in camphor but are associated in C_6H_6. The rates of hydrolysis and catalytic reduction of (I) and (II) differ appreciably, whilst the ultra-violet absorption curves for solutions in hexane are identical. It is suggested that (I) and (II) are diastereoisomerides formed by addition of the menthol to a ·CO· group in maleic anhydride. Other physical data are recorded for (I) and (II).

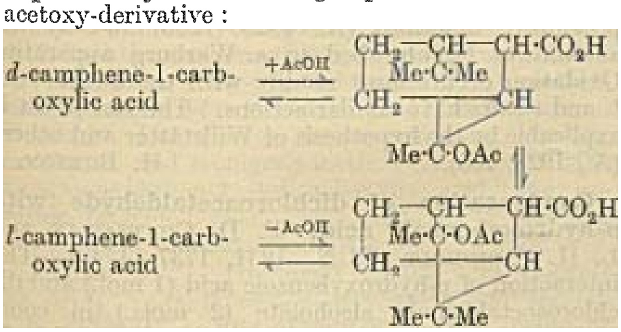
Only one l-*menthyl maleate*, m. p. 98·3°, could be prepared. H. BURTON.

Dependence of optical rotatory power on chemical constitution. XII. Rotatory dispersion of stereoisomeric anilino-, toluidino-, and naphthylamino-methylenecamphors. B. K. SINGH, B. BHADURI, and T. BARAT (J. Indian Chem. Soc., 1931, 8, 345—371; cf. this vol., 962).—The following data are recorded. Anilinomethylene-*d*- and -*l*-camphor (I), m. p. 158—160°; *dl*-compound, m. p. 135—136°. *m*- and p-Toluidinomethylene-*d*- and -*l*-camphor (II) and (III), m. p. 149—150° and 179—180°, respectively; *dl*-compounds, m. p. 120° and 186°, respectively (the corresponding *o*-compound is an oil). α-Naphthylaminomethylene-*d*- and -*l*-camphor (IV), dimorphous, α-forms, m. p. 152—154° and 151—153°, respectively β-forms, m. p. 76—78°; *dl*-compound, dimorphous, α-form, m. p. 140—142°, β-form, m. p. 88—90°. β-Naphthylaminomethylene-*d*- and -*l*-camphor (V), m. p. 184—187°; *dl*-compound, m. p. 187—189°. The α-forms of the dimorphous compounds pass irreversibly into the β-forms on prolonged digestion with hot MeOH; both forms have the same rotatory dispersion in all solvents. The difference of the m. p. of (I) and (II) from published data (A., 1895, i, 62) is possibly due to dimorphism. The rotatory dispersion of the above compounds in C_6H_6, $CHCl_3$, pyridine, $COMe_2$, EtOH, and MeOH, using 10 lines from Hg_{4358} to Li_{6708}, can be expressed by the one-term equation of Drude. Mutarotation was observed only for (I), (II), (III), (IV, α-form), and (V) in C_6H_6, (III) in MeOH and $CHCl_3$, and (V) in $CHCl_3$. [α] increases as the solvent is changed in the above order [except that the order is reversed for (IV) in $CHCl_3$ and pyridine, and for (II) in $COMe_2$ and EtOH], as also does ε for the solvent. The graphs of rotatory dispersion do not intersect, except for (IV) in pyridine and $CHCl_3$, showing the relation between [α] and ε to hold also for other solvents. λ for the hypothetical absorption band in the ultra-violet varies with the solvent [except for (III) in $CHCl_3$ and pyridine], the variation being of the same order as ε for (I) and (III), and lowest in C_6H_6, but otherwise unrelated to ε. Previous hypotheses (J.C.S., 1896, 69, 1583; A., 1924, ii, 645) are not in agreement with the following results: (*a*) the exceptions mentioned above; (*b*) the sequence of [α] for position isomerides is $H>p>m$ in C_6H_6, $CHCl_3$, and MeOH, but $H>m>p$ in the other solvents; (*c*) the sequence of [α] for (II) and (III) is (II)>(III) below 5893 Å., but (III)>(II) above this λ. Comparison of $[M]_D$ for the above compounds with results previously recorded shows that $[M]_D$ is increased by conjugation and by the PhN. grouping, and that the effects of C:C and C.N linkings are nearly equal. The numerical identity of [α] for optical isomerides is confirmed within experimental error by 283 out of 297 observations, discrepancies being ascribed to errors of reading. R. S. CAHN.

Action of light on a chloroform solution of α-naphthylaminocamphor. B. N. MITRA (J. Physical Chem., 1931, 35, 2371—2376; cf. A., 1925, ii, 195).—The changes observed when α-naphthylaminocamphor in $CHCl_3$ is exposed to sunlight for periods up to 100 hr. are described. Green substitution compounds with the $CHCl_3$ are probably formed. Prolonged exposure ppts. α-naphthylamine hydrochloride. Oxidation also occurs on insolation and in other solvents. L. S. THEOBALD.

***rac.*-Camphorcarboxylic acid, *rac.*-borneolcarboxylic acid, *rac.*-bornylenecarboxylic acid, and *rac.*-epicamphor, also *rac.*-epicamphormono- and -di-bromides.** J. BREDT [with E. DROUVEN, L. SCHUMANN, and P. SCHOLL] (J. pr. Chem., 1931, [ii], **131**, 132—136).—rac.-*Camphorcarboxylic acid,* m. p. 124°, is prepared from inactive camphor by the method used for *d*-camphor (cf. A., 1922, i, 937), and converted by electrolytic reduction into cis-, m. p. 129—130°, and cis-trans-dl-*borneolcarboxylic acid,* m. p. 144—145°, which are separated by crystallisation from EtOAc. The former is dehydrated by AcCl to bornylenecarboxylic acid and anhydride, and the latter converted into its *acetate,* m. p. 124°; the *cis*-acid alone is oxidised by $KMnO_4$ and gives *dl*-camphoric acid. *dl*-Bornylenecarboxylic acid is converted by means of its *hydrazide,* m. p. 108—109° into *dl*-epicamphor (*dibromo*-derivative, m. p. 130°). When heated with excess of Br, *l*-epicamphor gives, in addition to the known Br-derivative, an *isomeride,* m. p. 144—145°, which increases in amount with the excess of Br and the time of heating, and passes into the known compound, m. p. 134°, on keeping. H. A. PIGGOTT.

***cis-* and *cis-trans*-Camphene hydrate-*meso*-carboxylic acid, and *rac.*-*o*- and -*p*-*iso*borneolcarboxylic acids.** J. BREDT (J. pr. Chem., 1931, [ii], **131**, 137—145; cf. A., 1909, i, 498; 1922, i, 936). —The racemisation that occurs in the series of reactions leading to the formation from *d*- or *l*-bornylenecarboxylic acids of the acetates of *iso*borneol-*cis-trans-o-* and -*p*-carboxylic acids may occur partly during formation of the camphenecarboxylic acid but is certainly completed during the succeeding Bertram–Walbaum reaction under the influence of AcOH and H_2SO_4. It may be explained by mutual interchange of position by Me and OAc groups in the intermediate acetoxy-derivative:



The (apparent) partial racemisation at the camphenecarboxylic acid stage may be due to a similar change of the intermediate Br-derivative under the influence of HBr. This mechanism requires alterations in some structures previously assigned. The hydroxy-acid, $C_{11}H_{18}O_3$, m. p. 171° (A., 1909, i, 498), is proved by purification to be "camphenehydrate-*cis-trans-meso*-carboxylic acid," and the acid, $C_{11}H_{16}O_2$, m. p. 55° (A., 1912, i, 112), the corresponding camphene derivative. The non-occurrence of *dl-iso*borneol-*trans-o*-carboxylic acid amongst the reduction products of camphorcarboxylic acid (cf. preceding abstract) suggests that this is a chemical individual and has the CO_2H group in the *iso*borneol position. H. A. PIGGOTT.

5-Chlorofurfuraldehyde. H. GILMAN and G. F. WRIGHT (Rec. trav. chim., 1931, **50**, 833—836).—Furfurylidene acetate (prepared in 70—75% yield from furfuraldehyde and Ac_2O in presence of a little $SnCl_2,2H_2O$) and SO_2Cl_2 in CS_2 give 30% of 5-*chlorofurfuraldehyde* (I), b. p. 92°/30 mm., 70°/10 mm., m. p. 36° (*oxime,* m. p. 84°), oxidised by aq. $KMnO_4$ to 5-chlorofuroic acid. (I) is also obtained in small yield from the acetate and Cl_2 or from furfuraldehyde and SO_2Cl_2 in CS_2. H. BURTON.

Hydroxy-carbonyl compounds. IV. Coumarins and 1 : 4-benzopyrones from pyrogallol. F. W. CANTER, A. R. MARTIN, and A. ROBERTSON (J.C.S., 1931, 1877—1881; cf. this vol., 962).—Pyrogallol condensed with Et acetoacetate, α-methylacetoacetate, and benzoylacetate gives 4-methyl-, 3 : 4-*dimethyl*-, m. p. 272—273° (*diacetate,* m. p. 202°), and 4-phenyl-7 : 8-dihydroxycoumarin (*Me, ether,* m. p. 138°), respectively. Gallacetophenone, NaOAc, and Ac_2O give triacetylgallacetophenone and 7 : 8-*diacetoxy-3-acetyl-2-methyl*-1 : 4-*benzopyrone,* m. p. 132°, hydrolysed by acid or alkali to the *dihydroxy*-compound, m. p. 247° (*Me_2 ether,* m. p. 148°). Gallopropiophenone by similar treatment gives 7 : 8-*diacetoxy*-2 : 3-*dimethyl*-1 : 4-*benzopyrone,* m. p. 150°, hydrolysed to the *dihydroxy*-compound, m. p. 234°. Gallobenzophenone treated similarly at 170—180° gives the triacetate, but at 215° gives the diacetylcoumarin (A., 1911, i, 901). A. A. LEVI.

Coumaryl 6-*iso*cyanate [coumarinyl-6-carbimide] and its reactions. B. B. DEY and T. R. SESHADRI (J. Indian Chem. Soc., 1931, **8**, 293—300).—6-Aminocoumarin (I), suspended in dry C_6H_6, and $COCl_2$ in PhMe yield *coumarinyl-6-carbimide* (II), m. p. 163°, the hydrochloride of (I), and a little s-6-*dicoumarinylcarbamide* (III), m. p. 326° (decomp.). (II) is stabler and less reactive than PhNCO. Thus, it is stable in dry air, although it changes slowly in moist air, and rapidly in hot H_2O into (III) and CO_2. With boiling abs. EtOH it yields *Et coumarinyl-6-carbamate* (IV), m. p. 156° [together with a little (III)], also obtained from (I) and $ClCO_2Et$ in *N*-Na_2CO_3 solution at 60°. *Me, Pr,* and *Bu*$^{\beta}$ *coumarinyl-6-carbamate,* m. p. 200—201°, 129—130°, and 155—156°, respectively, were similarly prepared. (IV), when heated at 200—250°, yields (III), is unaffected by H_2O or conc. HCl at 100°, but yields (I) with H_2O at 180—200° or conc. HCl at 120°, (III) not being formed in the latter reactions (cf. J.C.S., 1918, **113**, 622). (IV) does not react with NH_2Ph below 150°; with 1 mol. of NH_2Ph at 200—220° it yields (III), and with 4 mols. it gives $CO(NHPh)_2$. (IV) and (I) at 200—220° form only (III), s-6-*coumarinylphenylcarbamide* (V), m. p. 225—226° (decomp.), being assumed to be an intermediate product. (II) and PhOH in boiling, dry C_6H_6 give *Ph coumarinyl-6-carbamate,* m. p. 186—187°. Good yields of (III) were obtained from (*a*) (I) and (II) in boiling, dry C_6H_6, (*b*) (I) and $COCl_2$ (4 mols.) in C_6H_6, and (*c*) carbamide (1 mol.) and (I) (2 mols.) in boiling AcOH. *Coumarinyl-6-carbamide* (VI), m. p. 245° (decomp.), was prepared (*a*) by passing dry NH_3 into a solution of (II) in C_6H_6, and (*b*) by gradual addition of KCNO to the hydrochloride of (I) in H_2O. (V) was obtained on boiling (II) and

NH_2Ph, or PhNCO and (I) in C_6H_6. Werner's formula for carbamide is thus inapplicable to (V) or (VI) in the static condition. On melting (VI) gives only (III), and at 220—240° (V) gives a mixture of (III) and $CO(NHPh)_2$. It is assumed that decomp. of (VI) yields simultaneously (*a*) (II) and NH_3, and (*b*) (I) and HCNO, whilst that of (V) yields (*a*) (II) and NH_2Ph, and (*b*) (I) and (II); these products subsequently condense together, but NH_3 and HCNO escape as formed. (II) with NH_2·NHPh and CMe_2:N·OH in boiling, dry C_6H_6 yields *phenyl-6-coumarinylsemicarbazide*, m. p. 236°, and the *compound* $C_9H_5O_2$·NH·CO_2·N:CMe_2, m. p. 187°. *Et* 4 : 7-*dimethylcoumarinyl*-6-*carbamate*, m. p. 196°, was prepared from (*a*) the corresponding carbimide (VIII) and EtOH, and (*b*) the corresponding aminocoumarin (IX) and $ClCO_2Et$ in warm *N*-Na_2CO_3 solution. Passage of NH_3 into a solution of (VIII) in C_6H_6 yielded 4 : 7-*dimethylcoumarinyl*-6-*carbamide*, m. p. 250° (decomp.), which on melting gave *bis*-(4 : 7-*dimethylcoumarinyl*)*carbamide*, m. p. 320—330°, also prepared by the methods described for (III). s-*Phenyl*-4 : 7-*dimethylcoumarinyl*-6-*carbamide*, m. p. 265—266° (decomp.), was obtained from (VIII) and NH_2Ph, or (IX) and PhNCO. R. S. CAHN.

Synthesis of polyhydroxychalkones, polyhydroxyhydrochalkones, and polyhydroxyflavanones. VIII. Synthesis of 3′ : 4′ : 5′-trimethoxy-5 : 7-dihydroxyflavanone, and 3′ : 4′ : 5′ : 5 : 7-pentahydroxyflavanone. J. SHINODA, M. KAWAGOYE, and D. SATO (J. Pharm. Soc. Japan, 1931, **51**, 23—25).—The method previously described (A., 1929, 189) leads normally to 3′ : 4′ : 5′-*trimethoxy*-5 : 7-*dihydroxyflavanone* (I), but when applied to phloroglucinol and *tricarbomethoxy* - 3 : 4 : 5 - *trihydroxy* - *cinnamoyl chloride* (II), appears to give a chalkone. 3 : 4 : 5-Trimethoxycinnamic acid (III) (from 3 : 4 : 5-trimethoxybenzaldehyde, malonic acid, pyridine, and 2 drops of piperidine) has m. p. 127—128° (lit. 123—124°). Addition of $AlCl_3$ to the chloride of (III) and anhyd. phloroglucinol in $PhNO_2$ affords (I), m. p. 225—226° (*oxime*, m. p. 222—223°), which with Mg and HCl gives a yellowish-red colour, and with diazomethane yields 3′ : 4′ : 5′ : 5 : 7-pentamethoxyflavanone. Gallaldehyde, Ac_2O, and NaOAc, heated at 150—160° for 8 hr., yield penta-acetylgallaldehyde, but heating for 18 hr. leads to 3 : 4 : 5-triacetoxycinnamic acid. 3 : 4 : 5-Trihydroxycinnamic acid with NaOH and $ClCO_2Me$ gives *tricarbomethoxy*-3 : 4 : 5-*trihydroxycinnamic acid*, m. p. 166—167°, which with $SOCl_2$ gives (II). Condensation of this with phloroglucinol and $AlCl_3$ in $PhNO_2$ and Et_2O was slow and led to a product, giving a red colour with Mg and HCl only after hydrolysis with alcoholic HCl, which produced a yellow *substance*, decomp. 250° after darkening at 230°. R. S. CAHN.

Polyhydroxy-chalkones, -hydrochalkones, and -flavanones. IX. Synthesis of citronetin and analogous flavanones. J. SHINODA and S. SATO (J. Pharm. Soc. Japan, 1931, **51**, 78—82).—Phloroglucinol and *o*-methoxycinnamoyl chloride in presence of $AlCl_3$ and $PhNO_2$ give an unidentified substance, m. p. 229°, *di-o-methoxycinnamoylphloroglucinol*, m. p. 214°, and 5 : 7-*dihydroxy*-2′-*methoxyflavanone* [citronetin], m. p. 224—225° (*oxime*, m. p. 234—235°; *Me ether*, m. p. 92°, prepared by the action of diazomethane in Et_2O; *Ac* derivative, m. p. 118—119°). Prolonged acetylation of citronetin affords 2 : 4 : 6-*triacetoxyphenyl* o-*methoxystyryl ketone*, m. p. 192—195°. 5 : 7 - *Dihydroxy* - 3′- *methoxyflavanone*, m. p. 179—180° (*oxime*, m. p. 194—195°; *Me ether*, m. p. 96°; *Ac* derivative, m. p. 106°), is prepared from *m*-methoxycinnamoyl chloride. *o*- and *m*-Coumaric acids are converted by $ClCO_2Et$ into their *o-carbethoxy*-derivatives, m. p. 163° and 136°, respectively, the chlorides of which with phloroglucinol give 5 : 7 : 2′-, m. p. 185—187° (*Me ether*, m. p. 192°), and 5 : 7 : 3′-*trihydroxyflavanone*, m. p. 240—241° (*Me ether*, m. p. 182°), respectively. H. BURTON.

Constitution of cyanidin chloride. M. NIERENSTEIN (J. Indian Chem. Soc., 1931, **8**, 329—335).—A lecture. From evidence already published it is concluded that cyanidin chloride is not 3 : 5 : 7 : 3′ : 4′-pentahydroxyflavylium chloride. R. S. CAHN.

Constitution of anthocyanins. G. M. ROBINSON and R. ROBINSON (Nature, 1931, **128**, 413).—It is suggested that pelargonin, pæonin, cyanin, and malvin are not biosides but are di-monosides with separate glucose residues attached to positions 3 and 5 in the anthocyanidin nucleus. Mecocyanin, prunicyanin, keracyanin, etc. are biosides, however, with the biose group in position 3. The anthocyanins are considered to be related as follows: 3-bioside⟵3-monoside (chrysanthemin, œnin)—— : 5-dimonoside⟶complex diglucoside (monardæin etc.). L. S. THEOBALD.

Asymmetric oxidation. II. Y. SHIBATA, Y. TANAKA, and S. GODA (Bull. Chem. Soc. Japan, 1931, **6**, 210—216).—The catalytic oxidation of *d*-catechin by *d*-, *l*-, and *r*-amminochlorodiethylenediaminecobaltic bromide at p_H 7·5 is studied by the method previously described (A., 1929, 1296) and by the amount of O_2 absorbed in a Warburg apparatus. Oxidation occurs most readily with the *d*-salt; the *l*- and *r*-salts have similar actions. The last result is explicable by the hypothesis of Willstätter and others (A., 1928, 755). H. BURTON.

Condensation of dichloroacetaldehyde with *p*-hydroxybenzoic acid. F. D. CHATTAWAY and L. H. FARINHOLT (J.C.S., 1931, 1737—1740).—The interaction of *p*-hydroxybenzoic acid (1 mol.) and dichloroacetaldehyde alcoholate (2 mols.) in conc. H_2SO_4 gives 6-*carboxy*-2 : 4-*bisdichloromethyl*-1 : 3-*benzdioxin*, m. p. 181—183° (*chloride*, m. p. 110°; *amide*, m. p. 177°; *anilide*, m. p. 145°; *Et*, m. p. 114—115°, and *Me* ester, m. p. 113°), converted by aq. NaOH or KOH in EtOH into 2-*dichloromethyl*-4-*chloromethylene*-1 : 3-*benzdioxin*-6-*carboxylic acid*, m. p. 183° (*Et* ester, m. p. 102°, by alkaline hydrolysis of the bisdichloromethyl ester, m. p. 114—115°), which forms a normal *dibromide*, m. p. 116°, but with Cl_2 in AcOH gives ωω-dichloro-2-hydroxyacetophenone-5-carboxylic acid. H. A. PIGGOTT.

2 : 3-Dichloro-1 : 4-dioxan and two stereoisomeric naphtho-1 : 4 : 5 : 8-dioxans. J. BOESEKEN, F. TELLEGEN, and P. C. HENRIQUEZ (Rec. trav. chim., 1931, **50**, 909—914, and Proc. K. Akad.

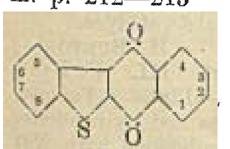
Wetensch. Amsterdam, 1931, **34**, 631—635).—Dioxan and Cl_2 at about 90° give 2 : 3-*dichlorodioxan*, b. p. 82·4°/14 mm., hydrolysed by H_2O to glyoxal and ethylene glycol, and converted by NaOEt into 2 : 3-*diethoxydioxan*, b. p. 96—97°/15 mm. 2 : 3-Dichlorodioxan and ethylene glycol in C_6H_6 afford two (cis and trans) *naphtho*-1 : 4 : 5 : 8-*dioxans*,
$\begin{matrix} CH_2\cdot O\cdot CH\cdot O\cdot CH_2 \\ CH_2\cdot O\cdot CH\cdot O\cdot CH_2 \end{matrix}$, m. p. 109—112° and 133—136°.

H. Burton.

Penthian series. IV. Four stereoisomeric oxides of benzamidobenzpenthiene. G. M. Bennett and W. B. Waddington (J.C.S., 1931, 1692—1697).—*Thiachromanoneoxime*, m. p. 98—100°, is reduced by Zn and glacial AcOH to dl-4-*aminobenzpenthiene* [liquid; *picrate*, m. p. 220° (decomp.); *hydrochloride*; *Ac* derivative, m. p. 157—159° (*dioxide*, m. p. 238·5—240°); *Bz* derivative, m. p. 158° (*dioxide*, m. p. 201—202·5°)]. The *dl*-Bz derivative is converted into a mixture of dl-α-*oxide*, m. p. 210·5°, and dl-β-*oxide*, m. p. 180·5°, by H_2O_2 in AcOH. Resolution of the oily base with *d*-α-bromocamphor-π-sulphonic acid gives l-4-*aminobenzpenthiene* [d- and l-*bromocamphorsulphonates*; *Bz*, m. p. 170°, $[\alpha]_D$ −99·6° in $CHCl_3$ (α-*oxide*, m. p. 220·5°, $[\alpha]_D$ −177° in $CHCl_3$; β-*oxide*, $[\alpha]_D$ +105·5° in $CHCl_3$; *dioxide*, m. p. 237°), and *Ac*, m. p. 199° (*dioxide*, m. p. 239°), derivatives] and d-4-*aminobenzpenthiene* [l-*bromocamphorsulphonate*; *Bz* derivative, m. p. 190° (α-*oxide*, m. p. 220·5°; β-*oxide*, m. p. 204°; *dioxide*, m. p. 237°)]. Attempts to convert thiachromanone into its cyanohydrin by various methods failed.

H. A. Piggott.

Dyes of the thionaphthen series. F. Mayer [with A. Mombour, W. Lassmann, W. Werner, P. Landmann, and E. Schneider] (Annalen, 1931, **488**, 259—296).—3-Hydroxythionaphthen and *p*-nitrosodimethylaniline in dil. alkali at 50° give thionaphthenquinone-2-*p*-dimethylaminoanil, hydrolysed by HCl to thionaphthenquinone (2-p-*hydroxyanil*, m. p. 251—252°, formed as a by-product together with o-*thiolphenylglyoxylic acid* +MeOH, m. p. 172° after previous softening). The quinone is converted by Bezdrik, Friedländer, and Königer's method (A., 1908, i, 200) into thionaphthen-2 : 3-dicarboxylic acid, the anhydride of which reacts with C_6H_6 in presence of $AlCl_3$ forming 3-*benzoylthionaphthen-2-carboxylic acid*, m. p. 215—216°. Treatment of the acid chloride with $AlCl_3$ in CS_2 gives *benzthiophanthrenquinone* (I), m. p. 212—213° ring closure with 20% oleum at room temp. affords a sulpho-derivative (*Na* salt) of (I). Similarly, 3-p-*toluoyl*-, m. p. 199°, 3-p-*bromobenzoyl*-, m. p. 220°, and 3-p-*chlorobenzoyl*-, m. p. 198—199°, -*thionaphthen-2-carboxylic acids* are converted into 2-*methyl*-, m. p. 216°, 2-*bromo*-, m. p. 225°, and 2-*chloro*- m. p. 215—220°, -*benzthiophanthrenquinones*, respectively. Ring closure of 3-*anisoylthionaphthen-2-carboxylic acid*, m. p. 195°, could not be effected. 1-*Chloro*-*dimethylbenzthiophanthrenquinone* has m. p. 254—255°. Thionaphthen-2 : 3-dicarboxylic anhydride and $C_{10}H_8$ in $PhNO_2$ with $AlCl_3$ give a mixture of acids convertible into two (1 : 2- and 3 : 4-) *benzobenzthiophanthrenquinones*, m. p. 157° and 257°. The following are prepared by the above methods: 6-*chloro-4-methyl*-, m. p. 129—130° (2-p-*dimethylaminoanil*, m. p. 232—233°; *phenylhydrazone*, m. p. 169°), 5-*chloro-7-methyl*-, m. p. 135° (2-p-*dimethylaminoanil*, m. p. 206°; *phenylhydrazone*, m. p. 183°), 6-*ethoxy*-, m. p. 162° (2-p-*dimethylaminoanil*, m. p. 157°; *phenylhydrazone*, m. p. 142°), 4 : 5-*benzo*-, m. p. 157—158° (2-p-*dimethylaminoanil*, m. p. 229—230°; *phenylhydrazone*, m. p. 184°), and 5 : 6-*benzo*-, m. p. 166° (2-p-*dimethylaminoanil*, m. p. 191°; *phenylhydrazone*, m. p. 212—213°), -*thionaphthenquinones*; 3-*chlorotoluene-ω-thioglycollic-6-glyoxylic*, m. p. 131°, and -6-*thioglycollic-5-glyoxylic acids*, m. p. 169°; *phenetole-3-thioglycollic-4-glyoxylic acid*, m. p. 169°; *naphthalene-2-thioglycollic-1-glyoxylic*, m. p. 193—194°, and -3-*thioglycollic-2-glyoxylic acids*, m. p. 280—285° (decomp.); 6-*chloro-4-methyl*-, m. p. 259—260° (*anhydride*, m. p. 188—189°), ω-*chloro-7-methyl*-, m. p. 253—254° or 267°, according to rate of heating (*anhydride*, m. p. 190°), 6-*ethoxy*-, m. p. 226° (*anhydride*, m. p. 177°), 4 : 5-*benzo*-, m. p. 276° (*anhydride*, m. p. 283°), and 5 : 6-*benzo*-, m. p. 264—265° (*anhydride*, m. p. 273—274°), -*thionaphthen-2 : 3-dicarboxylic acids*; 6-*chloro-3-benzoyl-4-methyl*-, m. p. 256—257°, 5-*chloro-3-benzoyl-7-methyl*-, m. p. 252°, 5-*chloro*-3-p-*toluoyl-7-methyl*-, m. p. 244°, and 3-*benzoyl*-4 : 5-*benzo*-, m. p. 275—276°, -*thionaphthen-2-carboxylic acids*; 7-*chloro-5-methyl*- (II), m. p. 272°, 6-*chloro-8-methyl*-, m. p. 304—305°, and 6-*chloro*-2 : 8-*dimethyl*-, m. p. 262—263°, -*benzthiophanthrenquinones*.


(I.)

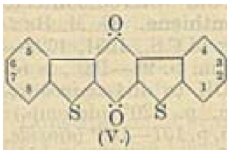
Phthalic anhydride, thionaphthen, and $AlCl_3$ in $PhNO_2$ give 2-*benzoylthionaphthen-2′-carboxylic acid*, m. p. 175° (*Me* ester, m. p. 97°), convertible through the chloride into (I). Similarly, 6-*chloro-2-benzoyl-4-methylthionaphthen-2′-carboxylic acid*, m. p. 227—228°, yields (II). Naphthalene-2 : 3-dicarboxylic anhydride and thionaphthen afford 2-β-naphthoylthionaphthen-3′-carboxylic acid, converted by warm conc. H_2SO_4 into 2 : 3-*benzobenzthiophanthrenquinone*, m. p. 301° (7-*chloro-5-methyl* derivative, m. p. 298—299°, obtained similarly from 6-*chloro-2-β-naphthoyl-4-methylthionaphthen-3′-carboxylic acid*, m. p. 244°). Thionaphthenquinone and phenacyl bromide in dil. NaOH give 2-*benzoylthionaphthen-3-carboxylic acid*, m. p. 240—241° (6-*ethoxy*-derivative, m. p. 233—234°), also convertible through its chloride into (I). 3-*Methylbenzthiophanthrenquinone*, m. p. 207—208°, is obtained similarly from 2-p-*toluoylthionaphthen-3-carboxylic acid*, m. p. 208—209°. 2-*Benzoyl*-5 : 6-*benzothionaphthen-3-carboxylic acid* has m. p. 281—282°. *o*-Thiolbenzaldehyde and ω-bromoacetophenone-*o*-carboxylic acid in dil. NaOH afford 2-benzoylthionaphthen-2′-carboxylic acid, m. p. 179—180° (cf. above). o-*Benzylthiolphenylglyoxylic acid* has m. p. 133—134°. Thionaphthen-2 : 3-dicarboxylic anhydride and resorcinol in presence of $ZnCl_2$ at 210° yield, after bromination, an eosin *dye*, $C_{22}H_8O_5Br_4S$.

(I) is reduced by alkaline hyposulphite to benzthiophanthrenquinol (*dibenzoate*, m. p. 257—258°), by Al-bronze in conc. H_2SO_4 below 40° to *benzthiophanthrone*, and by Zn dust and aq. NH_3 to *benzthiophanthracene*, m. p. 154—155° [oxidised by CrO_3 in AcOH to (I)]. 4 : ω-*Benzthionaphthen*, m. p. 108—109° (NO_2-derivative, m. p. 92°), and its 5 : 6-*isomeride*,

m. p. 189° (oxidised by CrO_3 in AcOH to thiophanthrenquinone), are prepared by reduction of their 3-OH-derivatives. (I), glycerol, aniline sulphate, and 82% H_2SO_4 at 130—140° give a benzanthrone-like *compound*, $C_{19}H_{10}OS$, m. p. 172—173° (*CN*-derivative, m. p. above 360°, prepared by way of the NO_2- and NH_2-derivatives); similar *compounds*, m. p. 183°, 217—218°, and 305—306°, are obtained from the 2- and 3-methyl and 6-chloro-8-methyl derivatives of (I), respectively. 2-Methylbenzthiophanthrenquinone and Br in $PhNO_2$ at 145—160° afford a mixture of *ωω-dibromo-*, m. p. 284°, and *tribromo*-derivatives, m. p. 239°; the former of these with Cu powder in $PhNO_2$ yields *αβ-di(benzthiophanthrenquinonyl)ethylene*, m. p. above 350°. 1(or 4)-*Methylbenzthiophanthrenquinone*, m. p. 165—166°, is obtained from its 4(or 1)-Cl-derivative, Cu powder, and KOAc in $PhNO_2$.

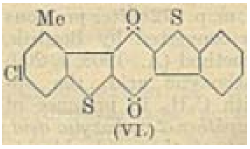
Thionaphthen-2 : 3-dicarboxylic anhydride and quinol in presence of $AlCl_3$ and NaCl at 160—190° give 1 : 4-*dihydroxybenzthiophanthrenquinone* (III), m. p. 253—254° (6-*chloro*-8-*methyl* derivative, m. p. 291—292°), oxidised by $Pb(OAc)_4$ in AcOH to the 1 : 2(or 3) : 4-*trihydroxy*-derivative (IV), m. p. 241—242°, also formed as above using hydroxyquinol. Reduction of (IV) with NH_3 and $Na_2S_2O_4$ at room temp. affords the 1 : 3- or 2 : 4-*dihydroxy*-derivative, m. p. 292—293°, whilst similar reduction of (III) at 70—90° and 135—140° yields 4(or 1)-*amino*-1(or 4)-*hydroxy*-, m. p. 275—276°, and 1 : 4-*diamino-benzthiophanthrenquinone*, m. p. 305—306°, respectively. *p*-Toluidine, (III), conc. HCl, Zn dust, and H_3BO_3 at 100° give the 1 : 4-*di*-p-*toluidino*-derivative, m. p. 232°, converted by 20% oleum into a trisulphonic acid (*Na* salt). (I) is formed from its 2-Br-derivative, NH_3, and Cu_2Cl_2 at 210°. The compound $C_{19}H_{10}OS$ (above) is oxidised by CrO_3 in dil. H_2SO_4 to *benzthiophanthrenquinone*-1(or 4)-*carboxylic acid*, m. p. 278° (*chloride*, m. p. 225°; *amide*, m. p. 297°), converted by the Hofmann method into 1(or 4)-*aminobenzthiophanthrenquinone*, m. p. 255°. Thionaphthenquinone and *m*-nitrophenacyl bromide in dil. NaOH give 2-m-*nitrobenzoylthionaphthen*-3-*carboxylic acid*, m. p. 204—205°, reduced by $Fe(OH)_2$ to the NH_2-*acid*, m. p. 202—203° (*Ac* derivative, m. p. 270—271°), which is converted by Ac_2O and conc. H_2SO_4 into the *Ac* derivative, m. p. 343—345°, of 2-*aminobenzthiophanthrenquinone*, m. p. 302—304° after softening at 275°. 2-p-*Nitro*-, m. p. 251—252°, 2-p-*amino*-, m. p. 217° (*Ac* derivative, m. p. 277°), 2-o-*nitro*-, m. p. 180—181°, and 2-o-*amino-benzoylthionaphthen*-3-*carboxylic acids* (*lactam*, m. p. 312—313°) are described. *Azomethines*, m. p. 203—204° and 227°, respectively, are formed when 2- and 3-methylbenzthiophanthrenquinones are heated with NH_2Ph, $PhNO_2$, and K_2CO_3; the latter is hydrolysed to *benzthiophanthrenquinone*-3-*aldehyde*, m. p. 257—258° (*azine*, m. p. above 355°).

Thionaphthenquinone and chloroacetone in dil. NaOH give 2-*acetylthionaphthen*-3-*carboxylic acid*, m.p. 129—130° (ω-*bromo*-derivative, m. p. 166—167°), reduced (Clemmensen) to 2-*ethylthionaphthen*-3-*carboxylic acid*, m. p. 124—125°, and converted by isatin in aq. EtOH–KOH into 2-(2′-*thionaphthenyl*)*quinoline*-4 : 3′-*dicarboxylic acid*, m. p. 282—283°. 2-*Acetylthionaphthen* has m. p. 88—89°. Thionaphthenquinone and *s*-dichloroacetone furnish 2 : 2′-*dithionaphthenyl ketone*-3 : 3′-*dicarboxylic acid*, m. p. 228—229° (*phenylhydrazone*, m. p. 180—181°; 6 : 6′-*diethoxy*-, m. p. 164—165°, 4 : 5 : 4′ : 5′-*dibenzo*-, m. p. 323—324°, 5 : 6 : 5′ : 6′-*dibenzo*-, m. p. 282—283°, 6 : 6′-*dichloro*-4 : 4′-*dimethyl*, m. p. above 340°, 6-*chloro*-4-*methyl*, m. p. 287—288°, and 6-*OEt*-, m. p. 247—248°, derivatives), converted by boiling Ac_2O into the *dilactone*, m. p. 272—273°, which when heated at 270—290° in N_2 or with $AlCl_3$ and NaCl at 140° passes into m-(S)-*dithionaphthenylquinone* (V), m. p. 310—312° (3 : 4 : 5 : 6-*dibenzo*-, m. p. 307—308°, 2 : 7-*dichloro*-4 : 5-*dimethyl*, m. p. 332°, 2-*chloro*-4-*methyl*, m. p. 290°, 2-*OEt*-, m. p. above 300°, and 2-*OH*-, decomp. 220—230°, derivatives).


(V.)

The dilactone of benzophenone-2 : 2′-dicarboxylic acid is similarly converted into anthraquinone. Thionaphthenquinone and ω-bromoacetophenone-*o*-carboxylic acid give *phenyl 2′-thionaphthenyl ketone*-2 : 3′-*dicarboxylic acid*, m. p. 234—235°, and 2 : 2′-*dithionaphthenyl ketone*-3-*carboxylic acid*, m. p. 268—269°, is obtained from *o*-thiolbenzaldehyde and 2-bromoacetylthionaphthen-3-carboxylic acid. The following are prepared similarly: 2-*acetyl*-, m. p. 216°, and 2-*bromoacetyl*-, m. p. 168°, -4 : 5-*benzthionaphthen*-3-*carboxylic acids*; *phenyl* 2′-(5 : 6-*benzthionaphthenyl*)-*ketone*-2 : 2′-*dicarboxylic acid*, m. p. 228°; 2-*acetyl*-5 : 6-*benzthionaphthen*-3-*carboxylic acid*, m. p. 209—210° (Br_2-derivative, m. p. 223—224°); 6-*chloro*-2-*acetyl*-4-*methylthionaphthen*-3-*carboxylic acid*, m. p. 180—181° (ω-*Br*-derivative, m. p. 217—218°).

6-*Chloro*-4-*methyl*-2 : 3′-*dithionaphthenyl ketone*-2′-*carboxylic acid*, m. p. 277—278°, from 6-chloro-4-methylthionaphthen and thionaphthen-2 : 3-dicarboxylic anhydride in presence of $AlCl_3$ and $PhNO_2$, is converted into the acid chloride, which with $AlCl_3$ in $PhNO_2$ gives p-(S)-4-*chloro*-2-*methyldithionaphthenylquinone* (VI), m. p. 260—262°. 1 : 5-*Di*(*bromoacetyl*)-*naphthalene*, m. p. 181—182°, and thionaphthenquinone in dil. NaOH give 1 : 5-*di*-(2-*thionaphthenyl*)-*naphthalene*-3′ : 3″-*dicarboxylic acid*, m. p. 299—300°, the chloride of which with $AlCl_3$ in $PhNO_2$ furnishes 1 : 2-*bisbenzthiophanthrenquinone*, m. p. above 350°. Many of the compounds prepared are vat dyes.


(VI.)

H. BURTON.

β-Diketones in ring formation. III. U. BASU (J. Indian Chem. Soc., 1931, 8, 119—128).—p-*Toluoylacetone* (I), b. p. 132°/15 mm. (obtained by condensation of AcOEt and *p*-methylacetophenone with Na) (*Cu* salt), condenses with NH_2OH to give 5-p-*tolyl*-3-*methyl*isooxazole, m. p. 92°, with N_2H_4 to form the corresponding *pyrazole*, m. p. 125°, and with NH_3 and NH_2Ph to yield p-*tolyl* β-*amino*-, m. p. 93°, and β-*anilino*-, m. p. 136—137°, -Δ^{α}-*propenyl ketone*, respectively. The former condenses with cyanoacetamide in the presence of $NHEt_2$ to yield 2-*keto*-3-*cyano*-6-p-*tolyl*-4-*methyl*-1 : 2-*dihydropyridine* (II), m. p. 330°, methylated to the corresponding 1 : 4-*Me*₂

compound (III), m. p. 248° [also by condensation of (I) with cyanoacetmethylamide], and hydrolysed to 2-*keto*-6-p-*tolyl*-4-*methyl*-1 : 2-*dihydropyridine*, m. p. 183°. Similar condensation of (I) itself with cyanoacetamide or -methylamide affords mainly (>90%) (II) or (III), respectively, together with a trace of 2-*keto*-3-*cyano*-4-p-*tolyl*-6-*methyl*-, m. p. indefinite, 275°, or -1 : 6-*dimethyl*-, m. p. 175—176°, -1 : 2-*dihydropyridine*, respectively. p-*Tolyl* β-*ethoxy*-Δ^{α}-*propenyl ketone*, OEt·CMe.CH·CO·C_6H_4·Me, b. p. 163°/15 mm. [obtained from (I) and ethyl orthoformate with $FeCl_3$ in EtOH], also condenses with sodiocyanoacetamide to give (II), whilst with NH_2OH, 3-p-*tolyl*-5-*methyl*iso*oxazole*, m. p. 73—74°, is obtained. Similarly, ethyl benzoylpyruvate and cyanoacetamide afford *Et* 2-*keto*-3-*cyano*-6-*phenyl*-1 : 2-*dihydropyridine*-4-*carboxylate*, m. p. 229—230° (*acid*, m. p. 350°; N-*Me* derivative, m. p. 150°). Phenyl β*p*-dimethoxystyryl ketone (A., 1928, 291) and cyanoacetamide afford 2-*keto*-3-*cyano*-6-*phenyl*-4-*anisyl*-1 : 2-*dihydropyridine*, m. p. 314°, also obtained by dehydrogenation of the corresponding 1 : 2 : 3 : 4-*tetrahydropyridine*, m. p. 204—205° (from Ph *p*-methoxystyryl ketone and sodiocyanoacetamide) with HNO_2.

J. W. BAKER.

β-Diketones in ring-formation. IV. U. BASU (J. Indian Chem. Soc., 1931, **8**, 319—328; cf. preceding abstract).—β-Diketones react in the enolic form with cyanoacetamide (I) (cf. J.C.S., 1905, **87**, 1688; Proc. C.S., 1912, 51), since Et ethoxycrotonate (II) condenses with this substance. Similarly, for a substance containing the grouping CO·C:C·NH_2 to condense with benzylidenebenzoylacetone, it must contain a labile methine H atom, since neither 3 : 4 : 5 : 6-tetrahydroanthranilate (IV) nor methylacetylacetonamine (V) undergoes this condensation. Et diacetoacetate (VI), b. p. 82°/6 mm. (*Cu* salt, m. p. 150—151°), (I), and a little piperidine in EtOH at 50° give AcOEt and 6-*hydroxy*-2-*keto*-3-*cyano*-4-*methyl*-1 : 2-*dihydropyridine* (VII), m. p. 304° (decomp.) after sintering, the constitution of which is proved because it is sol. in NaOH, and in Na_2CO_3 with evolution of CO_2, is hydrolysed by conc. HCl at 150—160° to 2 : 6-dihydroxy-4-methylpyridine, and is also obtained from (I) and Et acetoacetate. 6-*Hydroxy*-2-*keto*-3-*cyano*-1 : 4-*dimethyl*-1 : 2-*dihydropyridine*, m. p. 274°, was similarly prepared from (VI) and cyanoacetmethylamide. (VII) was also obtained from (II) and sodiocyanoacetamide, and by heating (I) with Et β-aminocrotonate at 130° for 15 min. (I), NaOEt, and Et *cyclo*hexanone-2-carboxylate (VIII) in EtOH give 1-*hydroxy*-3-*keto*-4-*cyano*-2 : 3 : 5 : 6 : 7 : 8-*hexahydro*iso*quinoline* (IX), m. p. 278° (decomp.) [*K* salt; NH_4 salt, m. p. 320° (decomp.)], sol. in NaOH and Na_2CO_3; this is hydrolysed by fuming HCl at 180° to 1 : 3-*dihydroxy*-5 : 6 : 7 : 8-*tetrahydro*iso*quinoline*, m. p. 205° (*hydrochloride*), sol. in NaOH and Na_2CO_3. Sodiocyanoacetmethylamide yields similarly 1-*hydroxy*-3-*keto*-4-*cyano*-2-*methyl*-2 : 3 : 5 : 6 : 7 : 8-*hexahydro*iso*quinoline*, +H_2O m. p. 199°, anhydrous m. p. 202—203° (*Ag* salt), sol. in Na_2CO_3. 3-Methyl*cyclo*hexanone yields similarly Et 5-methyl*cyclo*hexanone-2-carboxylate, b. p. 137—140°/25 mm., 1-*hydroxy*-3-*keto*-4-*cyano*-6-*methyl*-2 : 3 : 5 : 6 : 7 : 8-*hexahydro*iso*quinoline*, m. p. 271—272° (decomp.), sol. in Na_2CO_3, and 1 : 3-*dihydroxy*-6-*methyl*-5 : 6 : 7 : 8-*tetrahydro*iso*quinoline*, m. p. 200°, sol. in NaOH and Na_2CO_3. (IV) [prepared by passing NH_3 into (VIII)], when heated with (I) at 120° for 25 min., gives (IX), but with (III) in EtOH at 50° gives PhCHO and (VIII). Benzoylacetonamine and (I) at 150° give NH_3 and 3-cyano-6-phenyl-4-methyl-2-pyridone, the Na salt of which with MeI in MeOH yields 3-*cyano*-6-*phenyl*-1 : 4-*dimethyl*-2-*pyridone*, m. p. 265° (insol. in NaOH), which is hydrolysed by HCl to 6-*phenyl*-1 : 4-*dimethyl*-2-*pyridone*, an oil (*hydrochloride*, m. p. 163° after sintering). (V), m. p. 112°, with (I) yields 3-cyano-4 : 5 : 6-trimethyl-2-pyridone, but with (III) at 120—125° gives no definite product. (III), m. p. 99°, and *p*-toluoylacetonamine at 120° give 5-*acetyl*-3-p-*toluoyl*-4 : 6-*diphenyl*-2-*methyl*-1 : 4-*dihydropyridine*, m. p. 183°.

R. S. CAHN.

2-o-Aminobenzylpyridine. R. H. WILSON (J.C.S., 1931, 1936—1937).—2-(2′ : 4′-Dinitrobenzyl)-pyridine reduced with NH_3 and H_2S in EtOH gives 2-o-*nitro*-p-*aminobenzylpyridine*, m. p. 118·5°, also obtained by nitration of 2-*p*-aminobenzylpyridine. It is converted by diazotisation and treatment with NaH_2PO_2 into 2-o-*nitrobenzylpyridine*, m. p. 29·5°, b. p. 165—185°/0·06 mm. (*hydrochloride*, m. p. 204°), oxidised by $KMnO_4$ to 2-o-*nitrobenzoylpyridine*, m. p. 118°, and by more prolonged action to *o*-nitrobenzoic acid, whilst it is reduced by $SnCl_2$ and HCl to 2-o-*aminobenzylpyridine*, m. p. 69—70°, b. p. 138—165°/0·1 mm., 185—210°/10 mm. (*dihydrochloride*, decomp. 280°). 2-(2′ : 4′-Dinitrobenzyl)pyridine reduced with $SnCl_2$ gives 2-(2′ : 4′-*diaminobenzyl*)-*pyridine*, m. p. 161°.

A. A. LEVI.

Polymerisation of indole. II. Action of aqueous halogen acids on indole. O. SCHMITZ-DUMONT, B. NICOLOJANNIS, E. SCHNORRENBERG, and H. H. SAENGER (J. pr. Chem., 1931, [ii], **131**, 146—181).—By measuring the progressive change in the ratio of di- to tri-indoles as the polymerisation of indole in aq. HCl proceeds it is shown that the former is an intermediate in the formation of the latter. Conditions which reduce or retard the formation of tri-indole, *e.g.*, an increase of acid concentration or diminution of its vol., low temps., or short reaction periods, therefore, favour the production of di-indole, and conversely. Except in the case of the first-named these factors also retard the overall velocity of polymerisation. The use of HBr in the place of HCl reduces the tendency to formation of tri-indole, whilst HF has the opposite effect. Optimum experimental conditions for the prep. of the two polymerides are given. The apparent polymerisation of di- to tri-indole under the influence of alkali during liberation from its hydrochloride observed by Oddo (A., 1924, i, 427; cf. A., 1930, 618) is regarded as due to acid produced by hydrolytic dissociation during dissolution of this salt in H_2O under the conditions employed.

H. A. PIGGOTT.

Action of nitric acid on polycyclic indole derivatives. X. Further derivatives of dihydropentindole. XI. Combined addition and substitution. J. P. MASSEY and S. G. P. PLANT (J.C.S., 1931, 1990—1997, 2218—2225).—X (cf. A., 1930, 93).

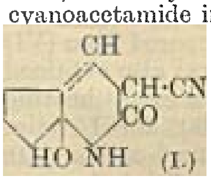
8-*Cinnamoyldihydropentindole*, m. p. 156°, prepared by acylation with cinnamoyl chloride and aq. KOH in $COMe_2$, is converted by slightly more than an equimol. proportion of HNO_3 (*d* 1·42) in AcOH at 40—70° into its 4 (or 6)-NO_2-derivative, m. p. 230° (identified by hydrolysis by aq.-EtOH–KOH into cinnamic acid and 4[or 6]-nitrodihydropentindole). At higher temps. (90°) or with acid of *d* 1·5 this is accompanied by 10-*nitro*-9-*hydroxy*-8-*cinnamoyltetrahydropentindole*, m. p. 187° (decomp.), formed by addition of HNO_3 to the double linking in the partly-hydrogenated ring; this is not affected by boiling EtOH, but is dissolved by aq. KOH with hydrolysis to γ-*o*-*cinnamamidobenzoylbutyric acid*, m. p. 162°.

Cyclisation of *cyclo*pentanone-*p*-chlorophenylhydrazone with dil. H_2SO_4 gives 5-*chlorodihydropentindole*, m. p. 132° (*Ac*, m. p. 142°, *cinnamoyl*, m. p. 185°, and 8-CO_2Et, m. p. 103—104°, derivatives). 5-*Chloro*-4(or 6)-*nitro*-, m. p. 167°, and 5-*chloro*-6(or 4)-*nitro-dihydropentindole*, m. p. 182°, are similarly prepared, but cyclo*pentanone*-4-*chloro*-2-*nitrophenylhydrazone*, m. p. 128°, could not be converted into the corresponding indole. By nitration of the appropriate acyl derivatives in glacial AcOH 5-*chloro*-4(or 6)-*nitro*-8-*acetyldihydropentindole*, m. p. 222° (identified by hydrolysis), 5-*chloro*-10-*nitro*-9-*hydroxy*-8-*acetyltetrahydropentindole*, m. p. 197° (decomp.), and *Et* 5-*chloro*-4(or 6)-*nitrodihydro*-, m. p. 152—153°, and *Et* 5-*chloro*-10-*nitro*-9-*hydroxytetrahydro*-, m. p. 163—164°, -*pentindole*-8-*carboxylates* are obtained, in proportions depending on the concentration of HNO_3 and temp.; the compounds of the latter type were not changed by boiling EtOH, and did not give definite products with aq. KOH. From 5-chloro-8-cinnamoyldihydropentindole the crude 4(or 6)-nitro-derivative, and 5-*chloro*-10-*nitro*-9-*hydroxy*-8-*cinnamoyltetrahydropentindole*, m. p. 221° (decomp.), and its (9)-*Ac* derivative, m. p. 169°, are obtained; the OH-derivative is unchanged by boiling EtOH, but both it and the OAc-compound are hydrolysed by aq.-EtOH–KOH to 5-*chloro*-2-*cinnamamidobenzoylbutyric acid*, m. p. 146°.

XI. The action of excess of HNO_3 in AcOH on the acyldihydropentindoles gives products in which both addition and nuclear substitution have taken place, the occurrence of the latter in the 5-position being an indication that 9 : 10-addition precedes substitution. 5 : 10-*Dinitro*-9-*hydroxy*-8-*cinnamoyltetrahydropentindole*, m. p. 234°, is prepared both from 8-cinnamoyldihydropentindole and 5-*nitro*-8-*cinnamoyldihydropentindole*, m. p. 231° (made by acylation); it is not affected by EtOH at its b. p., but is converted by aq. KOH successively into γ-5-*nitro*-2-*cinnamamidobenzoylbutyric acid*, m. p. 233—234° (room temp.), and β-6-*nitro*-2-*styryl*-4-*quinolone*-3-*propionic acid*, m. p. 306° (decomp.). The isomeric 4(or 6) : 10-*dinitro*-compound, m. p. 244° (decomp.), which results from the nitration of 4(or 6)-nitro-8-cinnamoyldihydropentindole, is decomposed by aq. KOH to γ-2-*nitro*-6-*cinnamamidobenzoylbutyric acid*, m. p. 217°. 5 : 10-*Dinitro*-9-*hydroxy*-8-*acetyltetrahydropentindole*, m. p. 187° (decomp.), is prepared by both of the methods employed for its cinnamoyl analogue (5-*nitro*-8-*acetyldihydropentindole* has m. p. 218°) and also by nitration of 10-nitro-9-hydroxy-8-acetyltetrahydropentindole in boiling AcOH, and is converted as before into γ-5-*nitro*-2-*acetamidobenzoylbutyric acid*, m. p. 166°, and β-6-*nitro*-2-*methyl*-4-*quinolone*-3-*propionic acid*, m. p. 213—214°, but contact for a short time only with very dil. aq.-EtOH–KOH results in hydrolysis to 5-*nitro*-9 : 10-*dihydroxy*-8-*acetyltetrahydropentindole*, m. p. 111°. *Et* 5 : 10-*dinitro*-9-*hydroxytetrahydropentindole*-8-*carboxylate*, m. p. 222° (decomp.), prepared by the first of these methods, did not give definite products with alkali. 6-*Nitro*-10 : 11-*dihydroxy*-9-*acetylhexahydrocarbazole*, m. p. 238° (decomp.), results from the energetic nitration of 9-acetyltetrahydrocarbazole, its 6-nitro-derivative, or 10 : 11-dihydroxy-9-acetylhexahydrocarbazole: it dissolves unchanged in aq.-EtOH–KOH, but is dehydrated to 6-*nitro*-11-*hydroxytetrahydrocarbazolenine*, m. p. 192°, on boiling the solution; on boiling with Ac_2O and subsequent hydrolysis 9-nitro-ψ-indoxyl*spirocyclo*pentane (J.C.S., 1923, **123**, 676) is formed. H. A. Piggott.

Stereoisomerism in polycyclic systems. VIII. (Miss) M. M. Cartwright and S. G. P. Plant (J.C.S., 1931, 1898—1904; cf. A., 1930, 1297).—2 : 3 : 4 : 5-Tetrahydroheptindole (A., 1928, 1258) reduced with Sn and HCl in EtOH gives, besides *cis*-, a little trans-2 : 3 : 4 : 5 : 11 : 12-*hexahydroheptindole*, m. p. 92° (*picrate*, m. p. 190—191°), separated by means of the Bz derivatives. Similar treatment of 5 : 6-dihydro-αβ-naphthacarbazole (this vol., 366) gives cis-5 : 6 : 12 : 13-*tetrahydro*-αβ-*naphthacarbazole*, m. p. 47—48° [*Ac* derivative, m. p. 118°: *Bz* derivative, m. p. 135° (cloudy liquid, clearing at 142°); *picrate*, m. p. 158°; *nitroso*-derivative, m. p. 83°], and a smaller amount of trans-5 : 6 : 12 : 13-*tetrahydro*-αβ-*naphthacarbazole*, m. p. 102° (*Ac* derivative, m. p. 140°; *Bz* derivative, m. p. 150—151°; *nitroso*-derivative, m. p. 87°), separated by means of the Ac derivatives. The stereoisomerides A and B of octahydroacridine (A., 1928, 1258) yield *nitroso*-derivatives, m. p. 125° and 95°, and *Bz* derivatives, m. p. 185° and 86°, respectively. A. A. Levi.

Synthesis of 5 : 6-dihydropyrindine. W. C. Thompson (J. Amer. Chem. Soc., 1931, **53**, 3160—3164).—2-Hydroxymethylene*cyclo*pentanone and cyanoacetamide in presence of aq. EtOH and a little piperidine give 2-*keto*-3-*cyano*-8-*hydroxy*-1 : 2 : 3 : 5 : 6 : 8-*hexahydropyrindine* (I), not melted at 310°, converted by conc. HCl at 120—130° into 2-*hydroxy*-5 : 6-*dihydropyrindine*-3-*carboxylic acid*, m. p. 272° (decomp.), and at 150—160° into 2-*hydroxy*-5 : 6-*dihydropyrindine*, m. p. 187—188°. This with PCl_5 and $POCl_3$ at 120—130° affords 2-*chloro*-5 : 6-*dihydropyrindine*, m. p. 70—71°, reduced by Zn dust and conc. HCl to 5 : 6-dihydropyrindine (II), b. p. 199°/750 mm. (*picrate*, m. p. 181°), which is oxidised by $KMnO_4$ to quinolinic acid. (II) is probably identical with the base obtained by Eguchi (B., 1929, 6) from shale oil. H. Burton.



(I.)

Salts of the ammono-enolic modification of 2-methylquinoline. F. W. Bergstrom (J. Amer. Chem. Soc., 1931, **53**, 3027—3038).—2-Methylquinoline (I) and $NaNH_2$ in liquid NH_3 or Et_2O give the

N-*Na* derivative of the enamic form of (I). The *K* derivative (II) (Li and *Ba* derivatives also described) reacts with MeI, EtBr, PrBr, BuBr, and CH_2PhBr in liquid NH_3 or Et_2O forming 2-ethyl-, -*n*-propyl- [methiodide, m. p. 181·7—182·7° (corr.) (lit. 180—184°)], -*n*-butyl-, -*n*-amyl- [*picrate*, m. p. 108·5—109·5° (corr.)], and -β-phenylethyl-quinoline, respectively. (II) does not react with PhBr or PhI, whilst treatment with $CHCl_3$, CH_2Cl_2, CH_2I_2, and ethylene or trimethylene dibromide regenerates (I). *cyclo*-Hexyl bromide and (II) give mainly (I) and a little 2-*cyclo*hexylmethylquinoline (?) [*picrate*, m. p. 146·5—147·8° (corr.)], whilst (II) and I afford tarry material instead of the expected products. (I) can be regarded as a cyclic ammonoketone.

Fe_2O_3 and Co_3O_4 are good catalysts for the prep. of KNH_2; the oxides, however, react slowly with KNH_2 in liquid NH_3 forming K_2O or KOH and compounds containing Fe (or Co), K, and N. H. BURTON.

Optically active tetrammine salts of bivalent platinum and palladium. H. REIHLEN and W. HUHN (Annalen, 1931, **489**, 42—62; cf. this vol., 924).—K_2PdCl_4 reacts with αβ-*iso*butylenediamine in aq. solution to give *di*-αβ-iso*butylenediaminepalladium chloride*, $[Pd\{C_4H_4(NH_2)_2\}_2]Cl_2$, resolved by fractional crystallisation of its dl-α-*bromo*-d-*camphor*-π-*sulphonate*, $+H_2O$ and anhyd., from EtOH into l-, $[M]_D$ +502° (least sol.), and d-, $[M]_D$ +582° in H_2O, -*di*-αβ-iso*butylenediaminepalladium* α-*bromo*-d-*camphor*-π-*sulphonate*, from which the val. $[M]_D$ −44° and +36° is calc. for the complex Pd ion, since attempted conversion into the active chloride causes fission of 1 mol. of the diamine. dl-*Di*-αβ-iso*butylenediamineplatinum chloride* and α-*bromo*-d-*camphor*-π-*sulphonate*, and l-*di*-αβ-iso*butylenediamineplatinum* α-*bromo*-d-*camphor*-π-*sulphonate*, $[M]_D$ +517° in H_2O (whence $[M]_D$ −29° for the ion is calc.), are similarly prepared. The *d*-salt could not be isolated in this case. 3-Methyl-2-aminomethyl-4-ethylquinoline and K_2PtCl_4 form the chloroplatoate, converted by heating with H_2O into *di*-3-*methyl*-2-*aminomethyl*-4-*ethylquinolineplatinum chloride*, $[Pt::(NH_2{\cdot}CH_2{\cdot}C_9H_4NMeEt)_2]Cl_2$, converted into its α-*bromo*-d-*camphor*-π-*sulphonate*, $+4H_2O$, which is not a true racemate but contains an excess of the l-*salt*, $[M]_D$ +492° in EtOH, whence the val. $[M]_D$ −144° is obtained for the ion. The *complex* $Cl_2Pt::(C_9H_6N)_2CO$ is obtained from K_2PtCl_4 and 2-quinolyl 1-*iso*quinolyl ketone, steric factors apparently preventing the co-ordination of a second mol. of ketone. The optical activity of these derivatives shows that the 4 linkings do not lie in a plane. The configuration of bivalent Pt- and Pd-tetrammines is discussed, an irregular tetrahedral model being favoured. The following are described: αβ-*iso*-butylenediamine gives the *compounds*,

$H_2PtCl_6,[C_4H_8(NH_3)_2]Cl_2,4H_2O$;
$[C_4H_8(NH_3)_2PtCl_6],HCl,2H_2O$;
$[C_4H_8(NH_2)_2PdCl_2]$; $[C_4H_8(NH_3)_2][PdCl_4]$;
$[Pt\{C_4H_8(NH_2)_2\}_2][PtCl_4]$, and
$[Pd\{C_4H_8(NH_2)_2\}][Pt(\text{or } Pd)Cl_4]$: 3-methyl-2-aminomethyl-4-ethylquinoline gives the *compounds* $[C_{13}H_{14}N{\cdot}NH_3]_2[PtCl_4]$; $[C_{13}H_{14}NH{\cdot}NH_3][PtCl_4]+4H_2O$, and $[Pt(C_{13}H_{14}N{\cdot}NH_2)_2][PtCl_4]$.

J. W. BAKER.

Aminoethanol derivatives of substituted cinchonic acids. H. WOJAHN (Arch. Pharm., 1931, **269**, 422—427).—Of four possible methods of preparing diethylaminoethyl 2-alkoxycinchonates, viz., (*a*) interaction of alkoxycinchonoyl chlorides and diethylaminoethyl alcohol, (*b*) decomp. of the Et ester with diethylaminoethyl alcohol (Swiss P. 131,926), (*c*) interaction of diethylaminoethyl 2-chlorocinchonate with alkoxides, and (*d*) treatment of β-chloroethyl 2-alkoxycinchonates with $NHEt_2$, only (*a*) is practicable.

The following 2-*alkoxyquinoline*-4-*carboxylic acids* are obtained from the 2-chloro-acid by heating with the Na alkoxide in the corresponding alcohol: 2-*propoxy*-, m. p. 136°; 2-iso*propoxy*-, m. p. 150°; 2-*butoxy*-, m. p. 111°; 2-iso*butoxy*-, m. p. 140—141°; 2-iso*amyloxy*-, m. p. 122°. 2-*Diethylaminoethylquinoline*-4-*carboxylic acid*, liquid (*hydrochloride*, m. p. 185°), is formed from chlorocinchonic acid and Na in diethylaminoethyl alcohol. The unstable 2-alkoxyquinoline-4-carboxyl chlorides are prepared from the acids and $SOCl_2$ in C_6H_6 and are not isolated. β-*Chloroethyl* 2-*hydroxyquinoline*-4-*carboxylate*, m. p. 205°, is obtained by heating the acid with $Cl{\cdot}C_2H_4{\cdot}OH$ and 5% of H_2SO_4. It is also formed by loss of the Et group when ethoxycinchonic acid is esterified with $Cl{\cdot}C_2H_4{\cdot}OH$ or when the acid chloride reacts with $Cl{\cdot}C_2H_4{\cdot}OH$. The following *diethylaminoethyl alkoxyquinoline*-4-*carboxylates* are prepared by addition of the acid chloride in C_6H_6 to aq. diethylaminoethyl alcohol and Na_2CO_3: 2-*ethoxy*-, b. p. 225—227°/2 mm. (*hydrochloride*, m. p. 185°); 2-*propoxy*-, b. p. 230/2 mm. (*hydrochloride*, m. p. 165°); 2-iso*propoxy*-, b. p. 232°/2 mm. (*hydrochloride*, m. p. 173°); 2-*butoxy*, b. p. 242—245°/2 mm. (*hydrochloride*, m. p. 149°); 2-iso*butoxy*-, b. p. 245°/2 mm.; 2-iso*amyloxy*-, b. p. 256°/2·5 mm. These esters exert local anæsthetic action. R. K. CALLOW.

Quinoline derivatives. XXVI. 2-Phenylquinoline-3-carboxylic acid and 2-phenylquinoline-4′-carboxylic acid. H. JOHN (J. pr. Chem., 1931, [ii], **131**, 266—274; cf. this vol., 1073).—The effect of adding MnO_2 and otherwise altering details of the prep. of 2-phenylquinoline-3- and -4′-carboxylic acids (I and II) (A., 1927, 675) is described. The yields can be raised to 66 and 70%, respectively. 29 inorg. salts of (I), 26 of (II), 25 of 2-phenyl-3-methylquinoline-4-carboxylic acid, and 26 of 2-*p*-tolylquinoline-4-carboxylic acid are described, and the data (*loc. cit.*) concerning these and related compounds are confirmed. R. S. CAHN.

Quinoline compounds. IV. U. N. BRAHMACHARI, J. M. DAS-GUPTA, and T. BHATTACHARJEE (J. Indian Chem. Soc., 1931, **8**, 313—317; cf. this vol., 970).—8-Aminoquinoline hydrochloride, when treated successively in aq. EtOH with CH_2O and $NaHSO_3$ and heated on the water-bath for 30—60 min., gives *Na* 8-*aminoquinoline*-N-*methylenesulphonate*. *Na* 6-*amino*- and 6-*methoxy*-8-*amino*-*quinoline*-N-*methylenesulphonate* were similarly prepared. *Na* 8-*amino*-, 6-*amino*-, and 6-*methoxy*-8-*amino*-*quinoline*-N-*methylenesulphonate*, m. p. above 300°, were prepared by warming the appropriate aminoquinoline with Na formaldehydesulphoxylate in H_2O. 8-*Carbamido*-, 6-

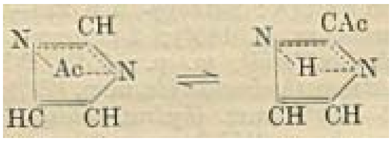
carbamido-, and 6-*methoxy-8-carbamido-quinoline*, m. p. 206°, 208°, and 218°, respectively, were prepared by treating the appropriate aminoquinoline (*a*) with carbamide at 170°, and (*b*) with KCNO.

R. S. CAHN.

Synthesis of *iso*quinoline derivatives. G. S. AHLUWALIA, K. S. NARANG, and J. N. RAY (J.C.S., 1931, 2057—2059).—The condensation of 6 : 7-dimethoxy-3 : 4-dihydro*iso*quinoline methiodide (I) with resorcinol in presence of alkali gives the 2′ : 4′-*dihydroxyl-1-phenyl* derivative, m. p. 188°. A *substance*, m. p. 137° (decomp.), probably similar in structure, is obtained by condensation of cotarnine with PhOMe in presence of NaOEt (cf. A., 1904, i, 765). *Anis-β-3 : 4-dimethoxyphenylethylamide*, m. p. 126°, prepared by interaction of the appropriate base with anisoyl chloride in C_6H_6–pyridine, is cyclised by $POCl_3$ in PhMe to 6 : 7 : 4′-*trimethoxy-1-phenyl-3 : 4-dihydro*iso*quinoline*, m. p. 107°, the *methiodide*, m. p. 194—195°, of which is reduced by Al–Hg in MeOH to 6 : 7 : 4′-*trimethoxy-1-phenyl-2-methyltetrahydro*iso*quinoline*, m. p. 96—97°, identical with the product of condensation of (I) with PhOMe.

H. A. PIGGOTT.

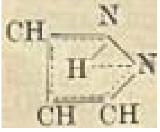
Glyoxaline. IV. Acetylation of glyoxaline. B. ODDO and F. INGRAFFIA (Gazzetta, 1931, **61**, 446—449).—The conception of the mesohydric formula for glyoxaline (A., 1907, ii, 15) is extended to derivatives with a simple substituent group, *e.g.*, magnesyl or Ac, the Ac group in (I) being on account of its position

(I.)  (II.)

easily hydrolysed. This explains the failure to acetylate glyoxaline by treatment of its magnesyl derivative with AcCl under ordinary pressure (A., 1928, 1381). By carrying out the reaction in a sealed tube the above equilibrium is displaced in the direction —— and the stable *Me 2-glyoxalinyl ketone* (II), m. p. 80° (*picrate*, m. p. 204°), is obtained.

E. E. J. MARLER.

Pyrazole and its magnesyl derivative. Q. MINGOIA (Gazzetta, 1931, **61**, 449—458).—Pyrazole reacts with MgEtBr giving *magnesylpyrazole*, which reacts with BzCl giving *benzoylpyrazole*, b. p. 220—225°/60 mm.; with $COCl_2$ giving N-*dipyrazolyl ketone* (*picrate*, m. p. 166°); and with Et chloroformate giving *ethyl*-N-*pyrazolecarboxylate*, b. p. 120—123°/42 mm. (*acid*, m. p. 102—103°). Under ordinary pressure acetylation of magnesylpyrazole does not occur, but heating in a sealed tube with AcCl gives N-*acetylpyrazole*, b. p. 138—140°/52 mm. (*picrate*, m. p. 170—171°). This is explained as in the case of glyoxaline (preceding abstract) on the annexed mesohydric formula.



E. E. J. MARLER.

Pyrroketones from fission products of blood-colouring matter and their conversion into chloropyrromethenes. H. FISCHER and H. ORTH (Annalen, 1931, **489**, 62—86).—$COCl_2$ in PhMe converts the product of the interaction of MgEtBr on crypto-, hæmo-, and 2 : 4-dimethyl-pyrroles, respectively, into *di-(3 : 5-dimethyl-4-ethylpyrryl)* (I), m. p. 207° (reduced by Wolff's method to cryptopyrrole) [*hydrazone*, m. p. 126° (*Ac* derivative, m. p. 200°); *thiocarbohydrazide*, m. p. 239°; *ketazine*, m. p. 209 (*Cu* derivative, m. p. 240—242°)], *di-(4 : 5-dimethyl-3-ethylpyrryl)* (II), m. p. 179° (*hydrazone*, m. p. 104°; *ketazine*, m. p. 226°), and *di-(3 : 5-dimethylpyrryl)* (III), m. p. 238° [*hydrobromide*; *hydrazone*, m. p. 118° (*Ac* derivative, m. p. 196—197°); *thiocarbohydrazide*, m. p. 242°; *ketazine*, m. p. 234°], *ketone*. This procedure is not applicable to pyrrolecarboxylic esters, but Et 3 : 5-dimethylpyrrole-4 carboxylate is converted by a boiling 5% solution of $COCl_2$ in PhMe into *di-(4-carbethoxy-3 : 5-dimethylpyrryl) ketone* (IV), m. p. 221 [*hydrobromide*, m. p. 197°; *hydrazone*, m. p. 197°; free *acid*, m. p. 254° (decomp.)]; excess of $COCl_2$ in the cold affords mainly the acid chloride, and thus Et 3 : 5-dimethylpyrrole-4-propionate (V) is converted into the acid chloride, which with MeOH affords *Me 2-carbomethoxy-3 : 5-dimethylpyrrole-4-propionate*, m. p. 108°, or by heating with another equiv. of (V) and $AlCl_3$ in CS_2 gives *di-(4-β-carbomethoxyethyl-3 : 5-dimethylpyrryl) ketone* (VI), m. p. 137° (free *acid*, m. p. 217—218°). $SOCl_2$ in Et_2O converts (I) into the corresponding 5 : 5′-trichloromethyl compound, readily hydrolysed to *di-(5-carboxy-3-methyl-4-ethylpyrryl) ketone*, decomp. 246° (*Me* ester, m. p. 192°), converted by Br in AcOH into 3-*methyl-4-ethylpyrrole-2 : 5-dicarboxylic acid*, decomp. 230°. (I) is converted by 20% $COCl_2$ in PhMe into the *hydrochloride*, m. p. 157—158°, of 3 : 3′ : 5 : 5′-*tetramethyl-4 : 4′-diethylpyrrochloromethene*, sinters at 240°, hydrolysed by H_2O at 100° to (I). Similarly, (II) and (III) give, respectively, 4 : 4′ : 5 : 5′-*tetramethyl-3 : 3′-diethyl-* (*hydrochloride*, sinters 180°), and 3 : 3′ : 5 : 5′-*tetramethyl-* (*hydrochloride*, m. p. 171°) *-pyrrochloromethene*, whilst (VI) gives *Me* 3 : 3′ : 5 : 5′-*tetramethylpyrrochloromethene-4 : 4′-dipropionate* [*hydrochloride*, m. p. 139° (decomp.)]. Opsopyrrole is converted by $COCl_2$ followed by NH_2Ph into 3-*methyl-4-ethylpyrrole-2-carboxyanilide*, m. p. 17[illegible] (*Et* ester, b. p. 130°/12 mm.). Br in AcOH converts (I) and (IV) into the corresponding bromomethenes.

J. W. BAKER.

Residual affinity and co-ordination. XXXIII. Optical activity dependent on co-ordinated nickel. G. T. MORGAN and F. H. BURSTALL (J.C.S., 1931, 2213—2218).—The interaction of αα′-dipyridyl with $NiCl_2$ in warm aq. solution gives *tris-αα′-dipyridylnickelous chloride* [Ni dipy$_3$]Cl_2,$6H_2O$ ($+3H_2O$ above 110°), red; it is decomposed into its constituents by dil. HCl, but cold 50% aq. KOH precipitates the base, which is stable in the cold. By double decomp. the *bromide* ($+6H_2O$), *iodide* ($+6H_2O$), *nitrate* ($+6H_2O$), *thiocyanate* ($+3H_2O$), *tartrate* ($+6H_2O$), and *hydroxide* (Ag_2O) are prepared: passage of CO_2 into an aq. solution of the hydroxide gives the *carbonate* ($+6H_2O$). Resolution into optical isomerides was effected by means of the tartrates, d-*tris-αα′-dipyridylnickelous* d-*tartrate* ($+6H_2O$) and *chloride* ($+6H_2O$), $[\alpha]_{5461}^{17}$ +529°, and l-*tris-αα′-dipyridylnickelous chloride* ($+6H_2O$) being isolated. The enantiomorphism is similar to that of the corresponding Fe″ complexes (cf. A., 1912, i, 298), and the active forms are rapidly racemised in aq. solution.

H. A. PIGGOTT.

Reaction of certain diazosulphonates derived from β-naphthol-1-sulphonic acid. VII. 3-Nitro- and 3′-amino-derivatives of 3-phenyl-4-methylphthalaz-1-one and the nitro-3-phenyl-1-methylphthalaz-4-ones. F. M. ROWE and A. T. PETERS (J.C.S., 1931, 1918—1925).—Oxidation of 1-hydroxy-3-*m*-nitrophenyl-1 : 3-dihydrophthalazine-4-acetic acid (A., 1928, 1262) with $K_2Cr_2O_7$ and cold dil. H_2SO_4 gives 3-m-*nitrophenyl-4-methylphthalaz-1-one*, m. p. 249° (*picrate*, m. p. 197°), reduced by aq. Na_2S to 3-m-*aminophenyl-4-methylphthalaz-1-one* (I), m. p. 271° (*Ac* derivative, m. p. 274°), also formed when 1-hydroxy-3-*m*-aminophenyltetrahydrophthalazine-4-acetic acid is oxidised with $Na_2Cr_2O_7$ (cf. this vol., 835) or heated with KOH in EtOH. Reduction of (I) with Zn dust and dil. HCl affords 1-*keto*-3-m-*aminophenyl-4-methyltetrahydrophthalazine*, m. p. 188°, reduced further by Zn dust and dil. H_2SO_4 to N-m-*aminophenyl-3-methylphthalimidine*, m. p. 165° (*Ac* derivative, m. p. 181°). 3-*m*-Aminophenylphthalaz-1-one is reduced by alkaline hyposulphite to (probably) 1-*keto*-3-m-*aminophenyltetrahydrophthalazine* (containing variable amounts of EtOH), m. p. 225°, reducible to *N*-*m*-aminophenylphthalimidine.

o-*Carboxyacetophenone*-p-*nitrophenylhydrazone* is converted when heated with AcOH or alone at 160—170° into 3-p-*nitrophenyl*-1-*methylphthalaz-4-one* (II), m. p. 214°, also formed in small amount from *p*-chloronitrobenzene and 1-methylphthalaz-4-one in presence of EtOH, NaOAc, and a little aq. $CuSO_4$ at 180°. o-*Carboxyacetophenone*-o-*nitrophenylhydrazone*, m. p. 184°, is best converted into 3-o-*nitrophenyl*-1-*methylphthalaz-4-one*, m. p. 202°, by Aggarwal, Darbari, and Ray's method (A., 1929, 1314). Acetophenone-*o*-carboxylic acid with phenyl- and *m*-nitrophenylhydrazine yields 3-*phenyl*-, m. p. 102° (nitrated to II), and 3-m-*nitrophenyl*-1-*methylphthalaz-4-one*, m. p. 167°, respectively; the intermediate hydrazones exist only momentarily. H. BURTON.

Transformation of 3-phenylnaphthoquinoxaline into 3 : 6-diphenylpyrazine. G. B. CRIPPA and M. LONG (Gazzetta, 1931, **61**, 388—391).—The 5 : 6-quinone obtained by oxidation of 3-phenylnaphthoquinoxaline with CrO_3 gives, on further oxidation with $KMnO_4$, 5-*phenyl-2-o-carboxyphenylpyrazine-3-carboxylic acid*, m. p. 197°, and this when distilled with lime gives 3 : 6-diphenylpyrazine. E. E. J. MARLER.

Murexide reaction. L. EKKERT (Pharm. Zentr., 1931, **72**, 481—484).—0·05 mg. of either caffeine, theophylline, or theobromine can be detected by modifications of the di- and tetra-methylmurexide reactions and they can be distinguished by the colour differences obtained when the reaction is carried out in the presence of conc. H_2SO_4 and either morphine, codeine, or ethylmorphine. Reactions obtained when different oxidising agent are used are described. E. H. SHARPLES.

Chlorophyll series. VI. Mechanism of the phase test. C. C. STEELE (J. Amer. Chem. Soc., 1931, **53**, 3171—3177).—Phase test saponification of chlorophyll *a* derivatives involves atm. oxidation; the amounts of O_2 absorbed are determined for chlorin *e* Me_3 ester and methyl phæophorbide *a* in a modified Warburg apparatus. Oxidation is suppressed when hydrolysis is carried out in presence of $Sn(ONa)_2$ and N_2. The rates of hydrolysis of 10 esters of the chlorophyll *a* series are determined under phase test conditions. Partial formulæ are suggested for chlorin *e* Me_3 ester and phæopurpurin 7. H. BURTON.

Iron compounds of the chlorophyll series with properties resembling those of blood-pigment. I. Iron phæophytin *a*. K. KUNZ, W. MORNEWEG, and H. MULLER (Z. physiol. Chem., 1931, **199**, 93—111).—Phæophytin *a* with $Fe(OAc)_2$ in pyridine and AcOH gives the hæmochromogen (Fe-phæophytin+$2C_5H_5N$) (I). Pyridine inhibits oxidation with molecular O_2 and absorption of CO; in other solvents (I) absorbs $\frac{1}{2}$ mol. of O [yielding the hæmatin (FeOH-phæophytin *a*) (II)], and 1 mol. of CO. In pyridine, it undergoes slow autoxidation on keeping in air. Reduction of (II) regenerates (I); the change occurs more readily in pyridine. In pyridine under N_2, (II) gives a substance resembling (I). With HCl, (II) yields FeCl-phæophytin (phæophytin-*a*-hæmin) (III). Phæophytin *a* gives (III) with $FeCl_3$ and NaOAc. These changes were followed spectroscopically. J. H. BIRKINSHAW.

Action of hydrazine hydrate on ω-bromoacetophenone. R. STOLLE [with I. FRENKEL, F. HANUSCH, and F. POLLECOFF] (J. pr. Chem., 1931, [ii], **131**, 275—284).—Phenacyl bromide (1 mol.) and N_2H_4,H_2O (3 mols.) in EtOH, when boiled for 70—80 hr., form NH_3 (1·68 mols.), N_2H_4,HBr, a little diphenylpyrazine, and a basic *substance* (I), $C_{16}H_{16}N_6$, m. p. 208°. The presence of an NH_2 group in (I) is shown by formation of *benzylidene*, iso*propylidene*, and *phenylglyoxylidene* compounds, m. p. 212°, 202° (yellow), and 246° (depending on the rate of heating) (yellow), respectively. With Ac_2O (I) rapidly forms an *Ac* derivative (+EtOH, $CHCl_3$, or C_6H_6), m. p. 175°, and slowly at room temp., or more rapidly under reflux an Ac_3 derivative (+$\frac{1}{2}C_6H_6$), m. p. 273°, the latter being transformed into the former by long boiling with dil. aq.-alcoholic Na_2CO_3. With hot 1·6% aq.-alcoholic (5 : 3) HCl (I) is partly hydrolysed to N_2H_4 and Bz·CHO, which last unites with unchanged (I) to yield the phenylglyoxylidene compound. The formula $\begin{matrix}N{:}CPh{\cdot}CH_2{-}N{\cdot}NH_2\\ N{:}CPh{\cdot}CH{-}N{\cdot}NH\end{matrix}$, therefore, assigned (I). With conc. HCl at 120° (I) gives tars, and with cold dil. aq.-alcoholic HCl slowly a small amount of a *substance*, $C_{16}H_{16}N_4$, m. p. 262°, also obtained together with a *substance*, $C_{16}H_{12}N_2$, m. p. 166°, by treatment with HgO in C_6H_6. With hot conc. alcoholic KOH (I) gives a little NH_3, some N_2, and a *substance*, $C_6H_{14}N_2O$ (?), m. p. 121°, b. p. about 130°/high vac. Addition of HNO_2 to (I) in EtOH yields N_2O and a yellow *substance*, m. p. 90°. Prolonged heating of N_2H_4,H_2O with Bz·CHO affords *phenylglyoxalhydrazone*, yellow, m. p. 118°, and with benzoylcarbinol in EtOH a *substance*, m. p. 102°, probably $OH{\cdot}CH_2{\cdot}CPh{:}N{\cdot}NH_2$. R. S. CAHN.

Action of nitric acid on acetylene. V. A. QUILICO and M. FRERI (Gazzetta, 1931, **61**, 484—500; cf. this vol., 194).—Decomp. of the product, $C_4H_2O_7N_6$, of the action of HNO_3 on C_2H_2 gives a

compound $C_4H_2O_3N_4$. This on treatment with saponifying agents or with conc. H_2SO_4, or on treatment with $NaNO_2$ of the product, $C_3H_5ON_3,HCl$, of its reduction with $SnCl_2$, yields a *diazoimide* $(C_3H_2ON)N_3$, b. p. 146·5°/752 mm., which is reduced by $SnCl_2$ to a *compound*, $C_3H_4ON_2$ (*Bz* derivative, m. p. 149°), and condenses with Et acetoacetate giving 1-(*C_3H_2ON*)-5-*methyltriazole-4-carboxylic acid*, m. p. 155°, with loss of CO_2 and formation of 1-(*C_3H_2ON*)-5-*methyltriazole*, m. p. 110°. Oxidation of the *acid* with $KMnO_4$ or saponification with KOH gives 5-methyltriazole-4-carboxylic acid, identical with that obtained by Wolff (A., 1903, i, 206), m. p. 234—235° (decomp.). $C_4H_2O_3N_4$ forms a piperidine *derivative*, m. p. 185°, and with aniline gives *s*-diphenylcarbamide. On the above evidence the structure $(C_3H_2ON)N(NO)·N:CO$ is proposed for $C_4H_2O_3N_4$, the group (C_3H_2ON) being probably an *iso*oxazole residue.

E. E. J. Marler.

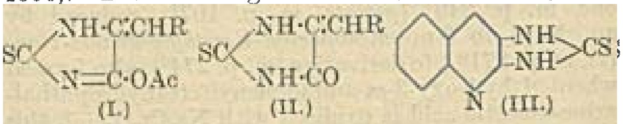
Rhodanines. I. Derivatives of β-phenylethylamine. J. S. Buck and C. S. Leonard (J. Amer. Chem. Soc., 1931, **53**, 2688—2692).—β-Phenylethylamines with CS_2 and NH_3 in EtOH give NH_4 β-phenylethyldithiocarbamates, converted by $CH_2Cl·CO_2K$ and dil. AcOH into the dithiocarbamineglycollic acids, $CH_2Ph·CH_2·NH·CS_2·CH_2·CO_2H$. These are transformed by warm dil. AcOH into 4-keto-2-thion-3-β-phenylethyltetrahydrothiazoles (rhodanines), also formed when β-phenylethylammonium β-phenylethyldithiocarbamates (from the amine and CS_2) are warmed with dil. AcOH and $CH_2Cl·CO_2K$. The following are new: *NH_4*, m. p. 132° (decomp.), and β-*phenylethylammonium*, m. p. 130° (decomp.), β-*phenylethyldithiocarbamates*; *NH_4* m. p. 138° (decomp.), and β-3 : 4-*dimethoxyphenylethylammonium*, m. p. 124° (decomp.), β-3 : 4-*dimethoxyphenylethyldithiocarbamates*; *NH_4*, m. p. 139° (decomp.), and β-p-*methoxyphenylethylammonium*, m. p. 135° (decomp.), β-p-*methoxyphenylethyldithiocarbamates*; *NH_4*, m. p. 138° (decomp.), and β-3 : 4-*methylenedioxyphenylethylammonium*, m. p. 133° (decomp.), β-3 : 4-*methylenedioxyphenylethyldithiocarbamates*; β-*phenyl-*, m. p. 125° (decomp.), β-p-*methoxyphenyl-*, m. p. 128° (decomp.), and β-3 : 4-*methylenedioxyphenyl-*, m. p. 132° (decomp.), -*ethyldithiocarbamineglycollic acids*; 3-β-*phenylethyl-*, m. p. 107°, 3-β-3′ : 4′-*dimethoxyphenylethyl-*, m. p. 154°, 3-β-p-*methoxyphenylethyl-*, m. p. 106°, and 3-β-3′ : 4′-*methylenedioxyphenylethyl-*, m. p. 126°, -4-*keto-2-thiontetrahydrothiazoles*.

H. Burton.

Polysulphides and esters of mercaptobenzthiazole. T. G. Levi (Gazzetta, 1931, **61**, 383—387).—Treatment of the Zn salt of 1-thiolbenzthiazole (I) with S_2Cl_2 gives *tetra-2-benzthiazolyl tetrasulphide*, $\left(C_6H_4{<}\genfrac{}{}{0pt}{}{N}{S}{>}C\cdot\right)_2S_4$, m. p. 108—110°, which when heated in MeOH or EtOH with KCN gives, besides KCNS and the K salt of (I), the Me ether, m. p. 46° [obtained by Hofmann by the action of MeI on (I)] or the *Et ether*, m. p. 26°, of (I). Alkyl ethers are similarly obtained from the disulphide of (I).

E. E. J. Marler.

Dyes derived from thiohydantoin. II. V. G. Namjoshi and S. Dutt (J. Indian Chem. Soc., 1931, **8**, 241—246; cf. this vol., 495).—Condensation of thiohydantoin with aromatic aldehydes in boiling Ac_2O gives Ac acylidene compounds, readily deacetylated by warm 20% NaOH, the reaction proceeding more readily than in AcOH with NaOAc (J.C.S., 1900, **77**, 246; A., 1913, i, 1237). The constitutions I and II are assigned to these compounds on the basis of the theory of colour previously advanced (A., 1927, 1006). The following substances, which are yellow



(I.) (II.) (III.)

unless otherwise stated (T=thiohydantoin) were prepared, the absorption maxima in wave-lengths (in EtOH, or for the Ac derivatives in AcOH), and the shades obtained on wool and silk from an acid bath being given after the m. p.: o-*nitrobenzylidene-T*, orange-yellow, m. p. 249°, 4960, orange (*Ac* derivative, m. p. 241°, 5060); m- and p-*nitrobenzylidene-T*, m. p. 257° and 266°, 4860 and 4961, respectively, bright yellow (*Ac* derivatives, m. p. 263° and 270°, 4930 and 4950, respectively); o-, m-, and p-*hydroxybenzylidene-T*, m. p. 231°, 256°, and 270°, 4740, 4680, and 4730, respectively (*Ac_2* derivatives, m. p. 237°, 250°, and 265°, 4820 4710 and 4810, respectively); 2 : 3-*thiocarbamidoquinoline* (III) (from *o*-aminobenzaldehyde), m. p. 213°; m- and p-*aminobenzylidene-T*, m. p. above 285°, 4670 and 4710, respectively, bright yellow (*Ac_2* derivatives, m. p. above 285°, 4710 and 4750, respectively); 3 : 5-*dihydroxybenzylidene-T*, m. p. 210°, 4760, brownish-yellow (*Ac_3* derivative, orange-yellow, m. p. 240°, 4880); p-*methoxybenzylidene-T*, m. p. 255°, 4680, canary-yellow (*Ac* derivative, brownish-yellow, m. p. 265°, 4720); 3 : 4-*methylenedioxybenzylidene-T*, m. p. 283°, 4740, deep yellow (*Ac* derivative, brownish-yellow, m. p. 275°, 4790); *vanillylidene-T*, m. p. 240°, 4750, deep yellow (*Ac_2* derivative, m. p. 261°, 4800); *cinammylidene-T*, m. p. 260°, 4760, deep yellow (*Ac* derivative, m. p. 267°, 4820); p-*dimethylaminobenzylidene-T*, light red, m. p. 252°, 4980, orange-red (*Ac* derivative, bright red, m. p. 272°, 5110); *acetylbenzylidene-T*, m. p. 260°, 4540, gives on hydrolysis the *enolic* form of *benzylidene-T*, m. p. 220° after 2 days in vac., changing in 24 days in vac., or on crystallisation and drying at 120° for 1 day into the *ketonic* form, m. p. 259°, 4450, lemon-yellow. The other compounds are the ketonic forms, having been recrystallised and dried at 120°. The deacetylated compounds are sol. in NaOH, and dye cotton from a Na_2CO_3 bath in shades which are only slightly lighter than those on wool. Alkaline solutions decompose by oxidation and hydrolysis on keeping, and in strongly acid solutions the thiohydantoin ring is ruptured with formation of phenylalanine or its derivatives.

R. S. Cahn.

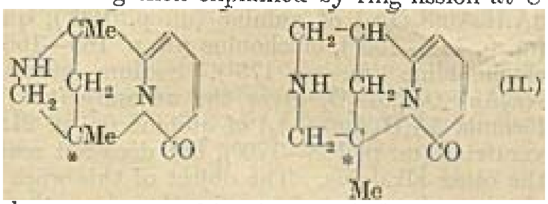
Thiodiazines. VIII. Action of ethyl α-chloroacetoacetate on thiosemicarbazides. P. K. Bose and B. K. Nandi (J. Indian Chem. Soc., 1931, **8**, 311—313; cf. this vol., 634).—4-Substituted thiosemicarbazides and Et α-chloroacetoacetate in dry EtOH yield substances of the general formula (I), showing that the ester grouping takes part in the reaction (cf. thiocarbamide, A., 1889, 725). The

products are sol. in NaOH, but insol. in Na_2CO_3, are basic, yield Ac derivatives which are hydrolysed to the original substances by aq.-alcoholic HCl, and do not condense with $NH_2 \cdot NHPh$, semicarbazide, aldehydes, or ketones. The structure

R·N—C:N·N
| >S ||
OH·CMe·CH—C·OH

is, therefore, assigned to them. The following compounds were prepared, the radical named being the substituent R in (I): *Me*, m. p. 156° (*Ac* derivative, m. p. 65°; *hydrochloride*, m. p. 197°); *Bu*$^{\beta}$, m. p. 145° (*hydrochloride*, m. p. 158°; *Ac* derivative, m. p. 240°); *Ph*, m. p. 166° (*hydrochloride*, m. p. 149°; *Ac* derivative, m. p. 118°); o-*tolyl*, m. p. 165° (*hydrochloride*, m. p. 147°; *Ac* derivative, m. p. 175°); p-*tolyl*, m. p. 181° (*Ac* derivative, m. p. 124°). R. S. CAHN.

Cytisine. I. H. R. ING (J.C.S., 1931, 2195—2203).—The amorphous methiodide of de-*N*-dimethylcytisine is converted into the hydroxide in MeOH, and this when boiled with amyl alcohol is decomposed into NMe_3, a weak *base*, $C_{22}H_{22}O_2N_2$, m. p. 300° (previous sintering), and a small amount of an unidentified sol. base. The alternative formulæ (I) and (II) are suggested to account for the formation of this bimol. degradation product, the production of a 6 : 8-dimethylquinoline derivative by reduction with P and HI being then explained by ring-fission at C*

(I)  (II.)

and subsequent re-combination. p-*Toluenesulphonylcytisine*, m. p. 207—208°, and a cryst. *methiodide*, m. p. 276° (decomp.), of methylcytisine are described.

Oxidation of 8-*nitro*-6-*methylquinoline methiodide*, m. p. 164° (decomp.), with alkaline H_2O_2 gives 8-*nitro*-1 : 6-*dimethyl*-α-*quinolone*, m. p. 165—166°, converted by PCl_5 at 170—180° into 2-*chloro*-8-*nitro*-6-*methylquinoline*, which with Fe and aq. AcOH at 40—50° gives 8-*amino*-2-*hydroxy*-6-*methylquinoline*, m. p. above 300° (*hydrochloride*; *formyl*, m. p. 263—264°, and *Ac*, m. p. 300°, derivatives). In contrast to the last-named NH_2-compound, 8-amino-6-methyl-1 : 2 : 3 : 4-tetrahydroquinoline readily yields 6-*methyl*-1 : 2 : 3 : 4-*tetrahydroquiniminazole*, m. p. 82—83°, b. p. 210—220°/18 mm. [*perchlorate*, m. p. 240° (decomp.)], when boiled with HCO_2H.

H. A. PIGGOTT.

Cocaine and allylcocaine in narcotic poisons. H. EMDE (Chem.-Ztg., 1931, 55, 537—539).—Methylcocaine can be detected in presence of allylcocaine by treating the H_2SO_4 solution of the two bases with 2% $KMnO_4$ below 5° until the pink colour persists for 1 min., filtering, treating the filtrate with aq. NH_3, and extracting with Et_2O. The methylcocaine in the ethereal layer is detected by the usual m. p. and refractometer tests. Directions for detecting and distinguishing between cocaine, novocaine, and allylcocaine are also given. A. R. POWELL.

Physiologically active constituents of yew (*Taxus baccata*). I. Taxine. R. K. CALLOW, J. M. GULLAND, and C. J. VIRDEN (J.C.S., 1931, 2138—2148).—The isolation of taxine in a cryst. state, m. p. 121—124° (softens 115°), $[\alpha]_D^{17}$ +95·7° [$+xC_6H_6$, m. p. 80° (decomp.)], is described: it is accompanied by a carbonyl compound, after removal of which it no longer reduces Fehling's solution. Even when pure it decomposes in a dry atm., an ill-defined, practically N-free substance, m. p. 122—124°, being isolated. Decomp. of taxine with boiling 5% H_2SO_4 gives cinnamic acid, β-diethylamino-β-phenylpropionic acid, *anhydroxatine*, $C_{24}H_{32}O_7$, m. p. 155—165° (the name "xatine" is proposed for the group $[OH]_2C_{24}H_{34}O_6$; cf. A., 1923, i, 942), and a trace of carbonyl compound (? semicarbazone, m. p. 259°). Anhydroxatine has the properties of an unsaturated lactone, and all the O in taxine, which is shown to contain 4 OH groups (Zerevitinov), can therefore be accounted for. The action of p-nitrobenzoyl chloride and aq. NaOH on taxine gave *acetylxatine* (?), m. p. 125 130° (decomp.), in a single non-reproducible instance. H. A. PIGGOTT.

Alkaloids of ergot. II. Ergotinine and ψ-ergotinine. S. SMITH and G. M. TIMMIS (J.C.S. 1931, 1888—1891; cf. A., 1930, 1050).—The more sol. fractions from crude ergotinine yield *ψ-ergotinine*, converted by H_3PO_4 in boiling EtOH into ergotoxine, and by boiling MeOH into ergotinine. Discrepancies in the sp. rotation of ergotinine are attributed to this substance, which is probably isomeric with ergotoxine.

A. A. LEVI.

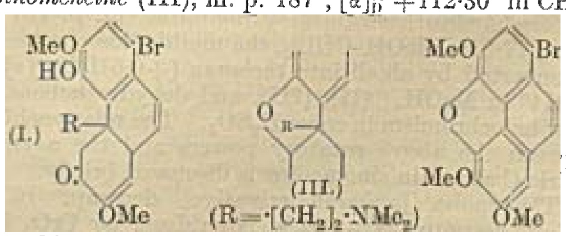
Behaviour of solanine on micro-sublimation R. FISCHER (Pharm. Zentr., 1931, 72, 545—547).—The fine needles obtained by microsublimation of solanine consist only of solanidine, m. p. 206—207°.

E. H. SHARPLES.

Spectrographic examination of yohimbine. M. KARSCHULIN (Arh. Hemiju, 1931, 5, 227—232).—The absorption spectra of yohimbine and of yohimboic acid are similar to that of indole, but not to that of quinoline. Yohimbine on dry distillation in vac. gives 7-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline, b. p. 190°, and a *methyldihydroindole*, m. p. 41°.

R. TRUSZKOWSKI.

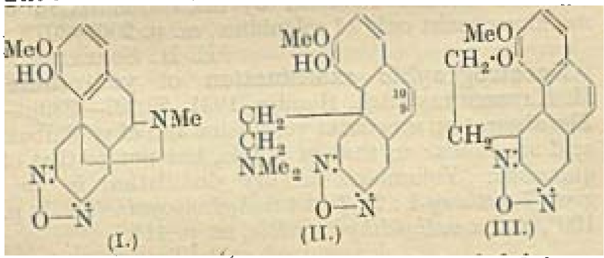
Bromination of sinomenine and its derivatives. d-Dehydrocodeinone from sinomenine. K. GOTO [with K. TAKUBO and S. MITSUI] (Annalen, 1931, 489, 86—96).—The methiodide of 1-bromosinomenine (cf. Schopf and Pfeifer, this vol., 104) is converted by 2% NaOH into 1-*bromo-de*-N-*methylsinomenine* (I), m. p. 185° (decomp.), $[\alpha]_D^{24}$ +15·92° in $CHCl_3$, and by Me_2SO_4 and 10% NaOH into 1-*bromo*-4 : 6-*dimethylsinomenol* (II), m. p. 143·5°. 1-Bromosinomeneine methiodide with 5% KOH affords 1-*bromode*-N-*methylsinomeneine* (III), m. p. 187°, $[\alpha]_D^{24}$ +112·30° in $CHCl_3$



(*methiodide*, m. p. 213—214°), and with Me_2SO_4 and 10% NaOH gives 1-*bromo*-6 : 7-*dimethoxy*-3-*methyl*-

morphenol (IV), m. p. 143°, prolonged treatment giving (II). Dihydrosinomenine with 2 mols. of Br gives 1-bromosinomeninone, whilst 3 mols. of Br followed by successive treatment with Na_2CO_3 and 5% KO at 80° converts it into 1-bromosinomeneine. Hence Br enters successively positions 1, 7, and 5, that in C_7 being concerned in the formation of the double linking (between C_7 and C_8), and that at C_5 in the oxide-ring closure. Bromination of demethoxydihydrosinomenine (*d*-dihydrothebainone) with 1 mol. of Br gives the 1-Br derivative (A., 1930, 795), but with 2 mols. the oxide ring is closed giving *hydrosinomeneine*, m. p. 206 , $[\alpha]_D$ +161·0 in $CHCl_3$, identical with *d*-1-bromodihydrocodeinone, since it is racemised by the corresponding *l*-derivative (Schopf, *loc cit.*), giving the *dl*-compound, m. p. 190 5 . Catalytic reduction of 1-bromodemethoxydihydrosinomeneine with Pd and AcOH gives *demethoxydihydrosinomeneine*, m. p. 193°, $[\alpha]_D^{23}$ +207·42° in $CHCl_3$ (*oxime*, 264—265°), identical with *d*-dihydrocodeinone and racemised by the corresponding pared from *l*-dihydrothebainone. J. W. BAKER.

Sinomenine. XXVII. Hofmann degradation of sinomenine hydrate dioxime K. GOTO and S. MITSUI (Bull. Chem. Soc. Japan, 1931, 6, 197 .—Sinomenine hydrate dioxime (A., 1930, 353) when heated with 16·5% KOH gives *si* m p 223—225°, decomp. 240 , $[\alpha]_D$ +136 2 in $CHCl_3$, whilst its *methiodide*, m. p. 218—220° (decomp.), similarly affords *sinomeninonefurazanmethine* (II), m p 226—227° (decomp.), $[\alpha]_D$ +49·9° in $CHCl_3$. The methiodide (not characterised) of (II) is converted



by 16·5% KOH into NMe_3 and *dehydro*-l-*thebenoneketone-(7)-furazan* (III), m. p. 200° (sinters from 197°), $[\alpha]_D^{19}$ −458 2° in $CHCl_3$. Catalytic reduction (Pd–charcoal) of (II) in 1% AcOH gives the 9 : 10-*dihydro*-derivative m p 205—207 after darkening at 203 , $[\alpha]_D$ +91·9° in $CHCl_3$, the methiodide of which is converted by alkali into l-*thebenoneketone-(7)-furazan* m. p. 148 (sinters from 140°), $[\alpha]_D^{19}$ −120·4 in $CHCl_3$. Similar reduction of deoxodemethoxydihydrosinomeninemeth- (this vol , 635) (methiodide degraded to dehydrothebenan, $[\alpha]_D^{19}$ −175·7° in MeOH) affords *deoxodemethoxydihydrosinomeninedihydromethine*, m. p. 161 , $[\alpha]_D^{19}$ +77·9° in MeOH–$CHCl_3$, the methiodide of which is converted y alkali into thebenan +0·5H_2O), $[\alpha]_D^{19}$ 3 1° in MeOH (II), (III), and dehydrothebenan show halochromism in conc. H_2SO_4. The relationship between the above rotatory powers and the asymmetric C atoms in sinomenine is discussed briefly.

l-Thebenone [*oximino*-derivative, decomp. 165° (*oxime*, decomp. 241—242°)] is oxidised by CrO_3 in AcOH to l-*thebenoneketone*, m. p. 187° (*dioxime*, decomp. 255—260° after softening at 160°). H. BURTON.

Action of soluble iodides on strychnine sulphate. G. W. HARGREAVES (J. Amer. Pharm. Assoc., 1931, 20, 763—766).—Strychnine hydriodide (sol. in 345 pts. H_2O at 25°) is formed by treatment of the sulphate solutions with alkali iodides or HI. The solubility is greatly decreased by the presence of excess of sol. iodide. A very dil. solution of I converts the hydriodide into the periodide, which is sparingly sol. in both H_2O and EtOH.

E. H. SHARPLES.

Alkaloids of gelsemium. II. Sempervine and an amorphous alkaloid. T. Q. CHOU (Chinese J. Physiol., 1931, 5, 295—299).—From the rhizome and roots of American gelsemium, a cryst. alkaloid *sempervine*, m. p. 223° (from $CHCl_3$), 254 (from EtOH) [*nitrate*, m. p. 282° (decomp.); *hydrochloride*, m. p. 300°], has been isolated which closely resembles sempervirine (A., 1915, i, 85). An amorphous alkaloid (hydrochloride, $[\alpha]_D^{25}$ +35° in H_2O), possibly impure, and some physiological properties of these two compounds are also described. W. O. KERMACK.

Aurosulphites and aurothiosulphates of organic bases. Q. MINGOIA (Gazzetta, 1931, 61, 458—466 · cf. A., 1928, 140).—Sodium aurothiosulphate, $Na_3Au(S_2O_3)_2,2H_2O$, reacts with the common alkaloids, giving the *aurothiosulphates* [general formula $3A,H_3Au(S_2O_3)_2$] of quinine (m. p. 182°), quinidine (m. p. 148—150°), cinchonine (m. p. 165—166), and cinchonidine (m. p. 175°). Sodium aurosulphite $Na_5Au(SO_3)_4,5H_2O$, gives the *aurosulphites* [general formula $5A,H_5Au(SO_3)_4$] of quinine (m. p. 212°) and veratrine (m. p. 168—170°), but does not react with the other alkaloids. The object of this work was to obtain substances of use in the chemotherapy of tuberculosis. E. E. J. MARLER.

Organic gold compounds. III. Direct duction of gold into the aromatic nucleus. IV. Gold imide compounds. M. S. KHARASCH and H. S. ISBELL (J. Amer. Chem. Soc., 1931, 53, 3053—3059, 3059—3065).—III. Slow addition of C_6H to anhyd. $AuCl_3$ results in the formation of HCl, AuCl, and 1 : 2 : 4 : 5-tetrachlorobenzene, whilst addition of anhyd. $AuCl_3$ to an excess of C_6H_6 gives, if reaction goes to completion, AuCl, HCl, and PhC ; in the last case, intermediate formation of $AuPh_2Cl$ is probable. When reaction is stopped by addition of a little Et_2O, AcOH or EtOH, *gold phenyl dichloride*, decomp. 73 75°, is obtained. *Gold tolyl, diphenylyl*, decomp. about 65°, *hydroxycarbomethoxyphenyl*, m. p. 107° (decomp.) (from Me salicylate), and *nitroanisyl dichlorides* (from *o*-nitroanisole) are also described. These dichlorides are readily reduced by $SnCl_2$ or quinol to Au; they are insol. in H_2O, but dissolve in aq. NaCl probably forming complexes of the type $Na(ArAuCl_3)$.

IV Imides react with AuO,OH, usually in presence of a little HCl or $AuCl_3$, forming imidoauric acids $H[Au(imide)_4]$, or, in some cases, the NH_4 imidoaurate. *Succinimidoauric acid*, decomp. 210—240 according to rate of heating (NH_4, decomp. 270 280°, and *Ba*, decomp. 268—270 , salts), *Na phthalimidoaurate*, and the *imidoauric acids* (+3H_2O), decomp. 200° and from 135°, respectively, from 5 : 5-diethylbarbituric acid and *o*-benzoicsulphinide, respect-

ively, are described. These acids are very stable towards reducing agents (cf. G.P. 347,139, 348,070).
H. BURTON.

Influence of the arsino-group on the activity of nuclear chlorine. R. E. ETZELMILLER and C. S. HAMILTON (J. Amer. Chem. Soc., 1931, **53**, 3085—3091).—*o*-Chlorophenylarsinic acid (I) reacts with primary alkylamines in presence of K_2CO_3, a little Cu_2I_2, and amyl alcohol at 130—135° forming *o*-alkylaminophenylarsinic acids. The following are described: o-n-*propyl-*, m. p. 128° (all m. p. are corr.); o-n-*butyl-*, m. p. 126° [*nitroso*-derivative, m. p. 147° (decomp.)]; o-n-*amyl-*, m. p. 98°; o-iso*amyl-*, m. p. 115°, and o-β-*hydroxyethyl-*, m. p. 141—143°, *-aminophenylarsinic acids*. *Phenylglycine-*o*-arsinic acid* has m. p. 178° (decomp.). (I) and $(NH_4)_2CO_3$ in presence of K_2CO_3, $Cu(OAc)_2$, and amyl alcohol at 135° give a little *o*-aminophenylarsinic acid and *diphenylamine-2 : 2′-diarsinic acid*, m. p. 198—200°, whilst (I) and NHPhMe in presence of K_2CO_3 and Cu powder at 140—150° afford 2 : 2′-*diarsinodiphenyl ether*, softens and darkens at 240°. o-n-*Butoxy-*, m. p. 200°, o-iso*amyloxy-*, m. p. 201°, and o-*phenoxy-*, m. p. 174°, *-phenylarsinic acids* are prepared from (I) and the appropriate Na alkoxide in presence of K_2CO_3 and Cu powder at 130—135°. The effects of temp., time, solvent, and catalysts on the reaction between (I) and NH_2Ph are investigated. H. BURTON.

Quinoline compounds containing arsenic. III. *o*-5′-Nitro-8′-quinolylaminophenylarsinic acid, 12-chloro-10-nitro-5 : 12-dihydroquinbenzarsazine, and 10-nitroquinbenzarsazinic acid. R. H. SLATER (J.C.S., 1931, 1938—1943; cf. this vol., 372).—8-Bromo-5-nitroquinoline (improved prep.; cf. A., 1929, 825) with *o*-aminophenylarsinic acid gives unchanged starting materials, 5-nitro-8-hydroxyquinoline, and a *substance*, m. p. about 200°. 8-Bromo-5-nitroquinoline with NH_3 in MeOH gives 5-nitro-8-aminoquinoline (A., 1929, 825), which condenses with *o*-bromophenylarsinic acid in amyl alcohol with a little Cu and I to give o-5′-*nitro-8′-quinolylaminophenylarsinic acid*, m. p. 264—265° (decomp.) (*Na*, NH_4, *Ca*, *Ba*, *Mg*, *Zn*, *Ag*, *Pb*, *Hg*, *Fe*, *Cu*, *Ni*, and *Co* salts). This in HCl and EtOH with SO_2 and a little I gives 12-*chloro*-10-*nitro*-5 : 12-*dihydroquinbenzarsazine hydrochloride*, m. p. 258—260° (decomp., previous colour change at 200°), oxidised by H_2O_2 in AcOH to 10-*nitroquinbenzarsazinic acid*, m. p. 310° (darkens 300°) (*K*, *Na*, NH_4, *Mg*, *Ba*, *Ca*, *Ag*, *Hg*, *Pb*, *Cu*, *Fe*, *Zn*, *Ni*, and *Co* salts), reduced by SO_2 in HCl and EtOH to the above arsazine hydrochloride. A. A. LEVI.

Meriquinonoid derivatives of 5 : 10-dihydrophenarsazine. V. G. RAZUBAIEV (Rec. trav. chim., 1931, **50**, 900—908; cf. A., 1929, 585, 834).—The velocities of reduction of 10 : 10′-oxybis-(5 : 10-dihydrophenarsazine) (I), 10 : 10′-oxybis-(2-methyl-5 : 10-dihydrophenarsazine), and 12 : 12′-oxybis-(7 : 12-dihydrobenzophenarsazine) by formic acid at 30° are determined conductimetrically. The structure assigned to the red compound from (I) and formic acid by Gibson, Johnson, and Vining (A., 1930, 1601) is held to be invalid.

10-Iodo-5 : 10-dihydrophenarsazine and Hg in xylene and O_2 give an oxide, converted by alkali into phenarsazinic acid. H. BURTON.

Alleged existence of triphenyldialkylpentaphosphines. B. K. BLOUNT (J.C.S., 1931, 1891—1894).—Treatment of triphenylphosphine oxide with PCl_5 in toluene gave the original substance (cf. this vol., 502). Triphenylphosphine dichloride (improved prep.; cf. A., 1885, 1134) is hydrolysed by atm. moisture. With MgEtI in C_6H_6 it gives triphenylphosphine oxide, a *substance*, m. p. 129°, and a *substance*, m. p. 162—163°. Triphenylphosphine oxide is unattacked by MgEtI. A. A. LEVI.

Action of neutral salts on the optical activity of gelatin. J. M. JOHLIN (J. Biol. Chem., 1931, **92**, 751—755).—Addition of neutral salts to a solution of ash- and electrolyte-free gelatin, in addition to increasing the $[H^{\cdot}]$ of the solution (cf. A., 1930, 693), reduces its optical activity. The latter effect is not produced by addition of small amounts of HCl. Both phenomena are explained by a displacement of the enol–keto-equilibrium decreasing the no. of asymmetric C atoms and increasing the no. of OH groups.
F. O. HOWITT.

Preparation of globin and gliadin. N. TROENSEGAARD (Z. physiol. Chem., 1931, **199**, 129—132).—Large-scale laboratory preps. are described.
J. H. BIRKINSHAW.

Fission products of hydrogenated proteins. N. TROENSEGAARD and H. G. MYGIND (Z. physiol. Chem., 1931, **199**, 133—134; cf. this vol., 245).—The fraction from hydrogenated acetylcaseinogen and acetylglobin containing the base $C_{11}H_{22}O_2$ contains another *base*, $C_7H_{16}N_2$ [*chloroaurate*, $B(HAuCl_4)_2$, decomp. 240—244°; *chloroplatinate*, $B(H_2PtCl_6)$, unchanged at 290°; *hydrochloride*, m. p. 280°; *picrate*, browns at 230°, decomp. 260—270°; *Bz* derivative, $C_7H_{14}N_2Bz_2$, m. p. 225° (uncorr.)], containing neither NH_2-N nor :NMe groups. J. H. BIRKINSHAW.

Reactions of silk fibroin with solutions of stannic chloride and disodium hydrogen phosphate. W. E. COUGHLIN (J. Physical Chem., 1931, **35**, 2434—2445).—The adsorption of $SnCl_4$ by silk fibroin after the first immersion is complete in 10 min., and the relation between the increase in wt. per g. of silk and concentration of $SnCl_4$ conforms to Freundlich's adsorption equation. Adsorption is apolar, since the ratio Sn : Cl removed from the bath is 0·82 (Sn : Cl in $SnCl_4$=0·837). At 40° adsorption is slightly greater than at 15°; at 80°, deterioration of the silk commences, and at 100° it is far advanced. At all the temps. used the p_H of the $SnCl_4$ was 3 both before and after immersion of the silk, and a lowering of p_H by addition of HCl results in a slight increase in adsorption. Silk containing small amounts of Sn decreases in wt. when immersed in Na_2HPO_4 for 1 hr. at 40°, but that containing larger amounts increases in wt. independently of the concentration of Na_2HPO_4. No increase in wt. occurs with fibroin which contains no Sn. Further immersion in $SnCl_4$ of silk treated successively with $SnCl_4$ and Na_2HPO_4 results in an increase in wt. which depends on the concentration of $SnCl_4$, but the adsorption in this case is different from that first observed. L. S. THEOBALD.

Kjeldahl–Ronchese method applied to bromatological analysis. V. COLOBRARO (Anal. Farm. Bioquim., 1931, **2**, 45—55).—The accuracy of this method (cf. A., 1907, ii, 651) is confirmed.

H. POPE.

Detection of organic compounds. VI. L. ROSENTHALER (Pharm. Ztg., 1931, **76**, 888—890; cf. this vol., 971).—The colorations obtained on addition of Co salts and NaOH to solutions of hydroxyl compounds are tabulated. Lilac colours are ascribed to complex Co^{II}, subsequent green coloration to Co^{III} compounds. The behaviour of various phenols towards $Hg(OAc)_2$, ICl_4, and $CPhCl_3$ is tabulated.

I. VY

Apparatus for the determination of small quantities of aminonitrogen. J. C. HARRAL (Analyst, 1931, **56**, 527—528).—An apparatus is described by which the NH_2-N liberated by treatment with alkaline $KMnO_4$ may be collected and measured.

M. L.

Functional analytical study of dulcine. J. A. SANCHEZ (Anal. Farm. Bioquim., 1931, **2**, 63—67).—Reactions are given for characterising the NH_2-, phenolic, and OEt-groups and the carbamic function of *p*-phenetolecarbamide. The Bellier, Morpurgo, Ruggeri, and Jorissen reactions for this compound are given, and a method for isolating it is described.

T. H. POPE.

Narceine: new reactions and interpretation of Wangerin's reaction. J. A. SANCHEZ (Anal. Farm. Bioquim., 1931, **2**, 68—74).—The presence of the $O·CH_2·O$ group in narceine and narcotine may be shown (1) by heating 0·05 g. of the alkaloid, 10 drops of H_2SO_4, and 2 c.c. of H_2O for 2—3 min. and collecting the gas in a little H_2O in a cooled test-tube, the liquid gives a deep red coloration with Schryver's reagent (1 c.c. 1% $NH_2·NHPh,HCl$, 2 drops 5% $K_3Fe(CN)_6$, and 1—2 c.c. conc. HCl); (2) by gently heating a few mg. with about 0·01 g. of carbazole and 10 drops of conc. H_2SO_4, a deep violet-blue colour gradually developing. The emerald-green colour obtained with tannin and H_2SO_4 is also due to the $O·CH_2·O$ group. The presence of OMe-, NMe_2-, CO_2H, and ·CO· groups may also be demonstrated by suitably hydrolysing or decomposing the narceine.

T. H. POPE.

Action of the emetics on gallic and tannic compounds. M. N. A. DE CELSI and S. A. CELSI (Anal. Farm. Bioquim., 1931, **2**, 56—62).—The reactions of tannin, gallic acid, and pyrogallol with mixtures of Rochelle salt and a number of salts are described. With Rochelle salt and NH_4 metavanadate, tannin gives a bluish-black ppt. and gallic acid or pyrogallol an intense green coloration. Tannin gives an amorphous, and pyrogallol or gallic acid a microcryst., ppt. with tartar emetic.

T. H. POPE.

Simplification of the Okey method for determination of cholesterol by oxidation of the digitonide. M. E. TURNER (J. Biol. Chem., 1931, **92**, 495—498).—The method (A., 1930, 1303) is simplified by carrying out the precipitation, washing, and oxidation in a single centrifuge tube. Applied to 0·5—1·5 mg. of free cholesterol the error is less than that with the colorimetric method.

F. O. HOWITT.

Biochemistry.

Blood traces in forensic practice. W. F. HESSELINK (Z. angew. Chem., 1931, **44**, 653—655).—Modern methods of detecting blood and of determining its age are described with reference to a number of special cases.

Enzymes and blood groups. I. F. SCHIFF and G. WEILER (Biochem. Z., 1931, **235**, 454—465).—Even in very dil. solution pepsin inhibited the hæmolysis of sheep's blood by the *A*-immune serum, whereas the same pepsin solution even when conc. had no effect on the hæmolysis by a homologous immune serum from sheep's blood, by a serum immune to guinea-pig kidney, or by one immune to Shiga Kruse bacillus. The amount of solution which was just active contained 5×10^{-6} g. of pepsin, that which completely inhibited hæmolysis contained $0·25\times10^{-5}$. Pepsin therefore contains the "sheep portion" of the *A*-substance. Trypsin, although only in much greater amounts, inhibited the action of *A*-specific sheep hæmolysin. The inhibitory effects of pepsin and trypsin have no connexion with their enzyme contents. The substance A_1 was not attacked by many species of bacillus, but was rendered inactive by extracts of fresh human fæces. The inactivating agent in the fæces was destroyed by heat. It also inactivated the group substances *A* and *B* and was found also both in human saliva and in the placenta. Possibly it is an enzyme produced by the body.

W. MCCARTNEY.

Tryptase of leucocytes. K. G. STERN (Z. physiol. Chem., 1931, **199**, 169—183).—Leucocytes from the peritoneal exudate of the guinea-pig contain in addition to catheptic proteinase, a tryptase, optimum p_H 8, attacking native protein. This tryptase was not found in the liver or kidneys. It was not activated by kinase nor could it be separated by means of $Al(OH)_3$ into inactive trypsin and kinase. The tryptases of the leucocytes and of the pancreas behave similarly towards Cu, Zn, and Hg ions, but differently towards Mn, Fe, and selenite ions. The catheptic proteinases of the leucocytes, liver, and kidney behave similarly towards the heavy metals, but differently towards selenite ions.

J. H. BIRKINSHAW.

State of carbon dioxide in blood. W. C. STADIE and H. O'BRIEN (Biochem. Z., 1931, **237**, 290—302).—CO_2 is most probably present in blood only as H_2CO_3 and HCO_3', electrometric and osmotic measurements with hæmoglobin solutions and blood giving no evidence for the existence of carbhæmoglobin.

P. W. CLUTTERBUCK.

Vital staining of reticulocytes. M. J. MIKULIČIC, jun. (Arh. Hemiju, 1931, **5**, 216—227).—Brilliant-

cresol-blue (0·024 g.) is added to 20 c.c. of Fleisch's solutions I and II, this solution is mixed with blood in the pipette, and the blood count is made 20 min. later. The optimal p_H for staining is 6·04—6·8.

R. TRUSZKOWSKI.

Activation of carbohydrate in red blood-cells. O. WARBURG and W. CHRISTIAN (Biochem. Z., 1931, **238**, 131—134).—From cytolysed blood after shaking with $CHCl_3$ a substance can be precipitated by EtOH and Et_2O which activates the biological oxidation of carbohydrates. A second activator can be obtained from oxyhæmoglobin crystals, together with which it separates, by washing with H_2O. Both activators are adsorbed by $Al(OH)_3$. The first is almost completely destroyed in 10 min. when heated at 50°. The second can be dialysed, but the first disappears when subjected to dialysis. Both activate carbohydrates in presence of methylene-blue and enable them to react directly with mol. O_2. It is concluded that even in the absence of Fe as O-carrier respiration may occur and that according to the conditions the two methods (with and without Fe) may compete with each other or one method may predominate over or exclude the other. W. McCARTNEY.

Determination of hæmoglobin in minute amounts of blood by Wu's method. F. C. BING and R. W. BAKER (J. Biol. Chem., 1931, **92**, 589—600). —The benzidine–H_2O_2 technique of Wu (J. Biochem. Japan, 1923, **2**, 189) has been improved and applied to the determination of hæmoglobin in 0·001—0·005 c.c. of blood. The max. error is $\pm 4\%$.

F. O. HOWITT.

Oxidation of hæmoglobin to methæmoglobin by oxygen. J. BROOKS (Proc. Roy. Soc., 1931, B, **109**, 35—50).—Laked ox-blood diluted in phosphate buffer was oxidised by a slow current of air passing over the solution. At intervals determinations were made of (*a*) the hæmoglobin by the CO-combining capacity (A., 1928, 1149), (*b*) the total pigment by the CO-combining capacity after reduction by hyposulphite (A., 1929, 1476), and (*c*) the undenatured pigment by the O-combining capacity after reduction by Ti tartrate (A., 1928, 315). The methæmoglobin concentration is given by *c*—*a* and the denatured hæmoglobin and hæmatin by *b*—*c*. Decrease of hæmoglobin in diluted blood containing O_2 is due to formation of methæmoglobin, the oxidation being a unimol. reaction. The rate of oxidation varies with different samples of blood and is directly proportional to a power (0·54—0·61) of $[H^{\cdot}]$. The uncorr. temp. coeff. is approx. 4 for a p_H range of 5·72—7·06. Increase of PO_4''' at p_H 6·29 from 0·2 to 0·6M increases the rate of oxidation by 19%, due partly to decrease in dissolved O_2, whilst an increase from 0·6 to 1·0M has no effect. Dissolved PhMe has no influence on the reaction, the course of which, however, is changed by the presence of considerable amounts.

F. O. HOWITT.

Alleged reduction in the oxygen capacity of the hæmoglobin of the blood of splenectomised animals. B. DEUTSCH (Biochem. Z., 1931, **238**, 136—147).—No reduction in the O_2 capacity of the hæmoglobin occurs as a result of the splenectomy (cf. A., 1930, 366). W. McCARTNEY.

Combination of globin with hæmatins from various sources. J. ROCHE and A. BENDRIHEM (Compt. rend., 1931, **193**, 324—326).—Hæmatins from helicorubin, yeast, and cytochrome have each been combined with globin from horse hæmoglobin to give a pigment, spectroscopically identical with that of blood and from which oxy-, met-, fluoromet-, and carboxy-hæmoglobin have been prepared.

C. C. N. VASS.

Carbohydrate complex of the serum-proteins. II. Isolation and redetermination of structure. Isolation of glucosaminodimannose from proteins of ox-blood. C. RIMINGTON (Biochem. J., 1931, **25**, 1062—1071; cf. A., 1929, 837).—The carbohydrate is composed of an association of 1 mol. of glucosamine with 2 mols. of mannose. The impurity in the original preps. consisted largely of histidine, which is united chemically to the complex. Glucosaminodimannose has been isolated from the mixed serum-proteins of both horse- and ox-blood. The carbohydrate content of serum-proteins has been determined colorimetrically. Serum-globulin contains approx. 3·7% of carbohydrate. This figure is not decreased by thorough washing of the coagulated protein. S. S. ZILVA.

Examination by means of the ultra-centrifuge of the protein fractions obtained by electrodialysis of serum. P. VON MUTZENBECHER (Biochem. Z., 1931, **235**, 425—437).—Both the H_2O-sol. and insol. fractions obtained from serum by electrodialysis (method of Ettisch and Ewig, A., 1929, 110) are polydisperse. The sp. rate of sedimentation of the H_2O-sol. fraction varies greatly, but lies between those found for globulin and serum-albumin prepared by salting out with $(NH_4)_2SO_4$. The variations are independent of the serum used, but apparently dependent on the course of the electrodialysis. The insol. fraction contains several components of high mol. wt., and the results obtained for this fraction agree well with those found by Svedberg and Sjogren (A., 1930, 1197) for euglobulin prepared in another way. From the sol. fraction, after pseudoglobulin has been precipitated by half-saturation with $(NH_4)_2SO_4$ slightly impure cryst. albumin can be obtained. Both the sol. fraction and the pseudoglobulin have higher rates of sedimentation in electrolyte-free solutions than in solutions containing electrolytes, and both contain appreciable amounts of components of high mol. wt. Fractionation of the proteins by removal of electrolytes does not lead to production of monodisperse systems, but to irreversible changes causing the appearance of smaller mols. and larger mol. aggregates. Only in a solution containing salts is a homogeneous globulin mol. stable. It is concluded that for the fractionation of the proteins of serum electrodialysis is not a sufficiently protective method.

W. McCARTNEY.

Characteristic variations in the refractive index of the blood-serum of the dog. P. WEINSTEIN (Biochem. Z., 1931, **235**, 303—310).—The n of the blood-serum of fasting dogs determined in samples taken, first hourly, then at 2 hr. intervals during 24 hr., first falls slowly for about 5 hr., then rises suddenly at about the 7th hr., and finally falls

slowly until, after 24 hr., a val. close to that obtained at the first test is found. The changes are to be attributed to phenomena of "fatigue" and "recovery" depending on the condition of the dogs and on the effects of the taking of the blood-samples.

W. McCartney.

Refractometric investigation of serum-proteins. V. Determination of the protein content of horse-serum. VI. Relation between refractive index, specific gravity, and concentration of ammonium sulphate solutions. D. von Deseö (Biochem. Z., 1931, **238**, 104—115, 116—124; cf. this vol., 505).—V. The sp. increment in the n of horse-serum is now found to be 0·00187. Because of its simplicity the refractometric method acquires special val. as a control procedure in the determination of proteins.

VI. Results of refractometric determination of $(NH_4)_2SO_4$ agree very well with those of gravimetric determination, and the latter are not influenced by the presence of usual amounts of protein. Since a vol. change occurs when conc. solutions of $(NH_4)_2SO_4$ are diluted, corresponding changes take place in the sp. gr. and concentration of the solutions. A table showing the relation at 17·5° between the n, sp. gr., and concentration of $(NH_4)_2SO_4$ solutions (from 0·23 to 53·01 g. in 100 c.c. of solution) is given.

W. McCartney.

Determination of blood-sugar in highly-concentrated solutions by the method of Hagedorn and Jensen. L. Mosonyi (Biochem. Z., 1931, **238**, 95—100).—When the following changes are made the method of Hagedorn and Jensen can be used for the determination of sugar contents up to 0·7%: 4 c.c. of $K_3Fe(CN)_6$ solution are used; 2 c.c. of N-NaOH solution replace the Na_2CO_3 solution; 3 c.c. of 10% AcOH replace 2 c.c. of 3%. The $K_3Fe(CN)_6$ and NaOH solutions are kept separate. A table constructed from results obtained and from vals. calc. according to certain formulæ is given.

W. McCartney.

Periodic variation of the blood-sugar content of fowls during 24 hrs. L. Krasnianski and V. Dsikovski (Biochem. Z., 1931, **237**, 282—289).—The blood-sugar vals. show wave-like variations during the 24 hr. both for fasting and fed animals. After 45 hr. fasting, the max. amplitude of variation of the blood-sugar level in 13 experiments is from 109 to 232 mg. per 100 c.c. P. W. Clutterbuck.

Influence of the blood-gases on the distribution of cholesterol between blood-corpuscles and -plasma. J. Scheffer (Biochem. Z., 1931, **235**, 451—453).—The cholesterol content of the plasma from blood which has been saturated with CO_2 does not differ from that of the plasma from blood which has been saturated with O_2 except in cases of lactæmia. In the case of corpuscles from blood saturated with these gases the apparent difference in the cholesterol content is due to swelling of the corpuscles.

W. McCartney.

Distribution of amino-acids in the blood in health and disease. A. Simon and B. Zemplén (Arch. exp. Path. Pharm., 1931, **161**, 478—484).—In women the NH_2-acid content of the blood-corpuscles and the ratio blood-corpuscles NH_2-N/plasma NH_2-N are on the average higher than in men. The high vals. of the ratio noted in cases of anæmia (cf. this vol., 1082) are also found in many other diseases.

W. O. Kermack.

Determination of uric acid in blood-serum. A. Blankenstein (Biochem. Z., 1931, **238**, 461—475).—Parallel determinations of uric acid in serum were carried out by the methods of Thannhauser, Folin, Flatow, Folin and Svedberg, Benedict, Morris and Vladescu, concordant results being obtained only by the first three, and all methods showing considerable loss during deproteinisation. Combining the deproteinisation by Folin's method with the colorimetric determination by Thannhauser's method, the mean of 10 experiments gave a 101% recovery of added acid, and this arrangement is recommended.

P. W. Clutterbuck.

Titrimetric determination of the alkali reserve of serum. F. Ellinger (Biochem. Z., 1931, **238**, 80—94).—A colorimetric method for the direct titration of serum with 0·1N-HCl is described. Titration is continued until p_H 6·0 is reached, so that the Na salts of intermediate products of metabolism are not titrated and only the alkali reserve which is of importance for the buffering of the blood is measured. The acid which combines with the proteins, however, is determined together with the HCO_3'. For double determinations 4 c.c. of serum (15—20 c.c. of blood) are required. The method is not designed to give very accurate results, but distinguishes between normal and pathological sera. W. McCartney.

Lack of relationship between the calcium, protein, and inorganic phosphorus of the serum of non-nephritic children. G. Stearns and G. C. Knowlton (J. Biol. Chem., 1931, **92**, 639—649).—Contrary to the findings in nephritis in childhood, no const. relation is observed between the level of serum-Ca and that of serum-protein or -inorg. P in normal infants and children. F. O. Howitt.

Chlorine content of blood from denervated tissue. W. F. Sternberg (Biochem. Z., 1931, **235**, 466—468).—The Cl content of the blood from the denervated rabbit ear does not differ from that of the blood from the normal ear. W. McCartney.

Determination of iron in blood. I. T. Laszló. **II.** L. Klein (Biochem. Z., 1931, **237**, 483—491, 492—496).—I. With pure hæmoglobin solutions, the Willstatter colorimetric method for determination of Fe gives low results and the parallel determinations do not agree very well, but the Ti method gives results of sufficient accuracy. With blood, however, the former gives results of even less accuracy than with hæmoglobin, and the latter gives results considerably lower than would be expected either from the hæmoglobin content or the O_2 capacity.

II. Wong's method (A., 1928, 785) gives somewhat high results with pure hæmoglobin, and the results with blood are considerably higher than would be expected from the hæmocolorimetric determination.

P. W. Clutterbuck.

Determination of inorganic sulphate in human blood-plasma by microtitration. C. L. Cope (Biochem. J., 1931, **25**, 1183—1189).—A modified

benzidine technique in which the colorimetric determination is replaced by micro-titration with NaOH. The max. error with 1 c.c. of plasma or serum is 5%.
S. S. Zilva.

Inorganic sulphate content of the blood: method for its determination. D. P. Cuthbertson and S. L. Tompsett (Biochem. J., 1931, **25**, 1237—1243).—The precipitated benzidine is diazotised and coupled with thymol in alkaline solution, yielding a red colour which is compared with a standard. The method requires 2 c.c. of fluid. Concentrations of phosphate, chloride, and oxalate in the blood of the respective orders 20 mg. P, 1 g. NaCl, and 1 g. $K_2C_2O_4$ per 100 c.c. do not affect the reaction. There is very little inorg. S in the cellular constituents of the blood. Plasma from healthy adults contains 0·5 mg. S per 100 c.c. In cases of nephritis and cardio-renal disease there is usually an increased retention of inorg. S coincident with the increased retention of urea- and non-protein-N. Relative to N, inorg. S is retained in proportionately greater amount in the minor degrees of retention than in the more severe types where relative to N it is less prominent. The coeff. of correlation is $r_{\text{urea-N inorg S}} = +0{\cdot}85 \pm 0{\cdot}028$.
S. S. Zilva.

Micro-determination of sulphur in blood. Total sulphur in the filtrate from deproteinised human blood. I. S. Lorant and L. Kopetz (Biochem. Z., 1931, **238**, 67—79; cf. this vol., 55).—After prep. of the material, destruction of org. matter, conversion of S into sulphate, and reduction of the sulphate to H_2S by improvements of methods previously described, the S is colorimetrically determined as methylene-blue. On the average human blood contains the practically const. amount of 6·8 mg. per 100 c.c. Determinations can be made with 2 c.c. of deproteinised blood.
W. McCartney.

Sensitisation of red blood-corpuscles in hæmolysis. K. C. Sen (Biochem. J., 1931, **25**, 1244—1251).—According to experimental conditions there can be both inhibition and acceleration of hæmolysis by normal serum of corpuscles sensitised by bile salts. The effect of serum can be imitated by many substances which yield OH′ in solutions. Erythrocytes can be highly sensitised towards acids by previous treatment with bile salt or saponin. The acceleration of hæmolysis of corpuscles sensitised by bile salts due to the addition of serum or other acid or alkaline substances is not entirely dependent on the p_H change of the solution. The time allowed for the sensitisation to take place has a great influence on the effect of p_H change and acceleration of hæmolysis. Normal serum acts both as hæmolytic agent and an antihæmolyte, depending on conditions.
S. S. Zilva.

Use of protozoa in measuring the neutralising value of cobra anti-serum. C. H. Philpott (Science, 1931, **74**, 157—158).—*Paramecium multinucleatum* can be used to determine the strength of cobra anti-serum.
L. S. Theobald.

Technique of Kahn's reaction. R. Demanche (J. Pharm. Chim., 1931, [viii], **14**, 246—259).

Photographs of the chief absorption bands of MacMunn's histohæmatin. O. Warburg and E. Negelein (Biochem. Z., 1931, **238**, 135).—Spectrophotographs are given (cf. this vol., 860).
W. McCartney.

Osmotic equilibrium between yolk and white in hen's eggs. A. Grollman (Biochem. Z., 1931, **238**, 408—417).—The f. p. of the yolk, especially the measurement of the Δ-val. of the dialysate, is the same as for the egg-white, a physical equilibrium existing between the yolk and white through the yolk membrane.
P. W. Clutterbuck.

Free and bound water determinations by the heat of fusion of ice method. W. Robinson (J Biol. Chem., 1931, **92**, 699—709).—The total H_2O content of a tissue is determined by drying to const. wt. and the bound H_2O of the colloid system by freezing to −20° followed by calorimetric determination of the amount of H_2O present as ice. A detailed description of the latter technique is given (cf A., 1925, i, 718).
F. O. Howitt.

Calcium salts as skeletal material of invertebrates, in connexion with the passage of animals from salt to fresh water. J. Hadzi (Arh. Hemiju, 1931, **5**, 173—184).—Theoretical.
R. Truszkowski.

Mineral content of eyes. H. Ramage and J. H. Sheldon (Nature, 1931, **128**, 376—377).—Spectrographic analysis shows that the choroids of man, sheep, pigs, horses, and dogs generally contain traces of Sr, whilst those of the common sea fishes contain more Sr than the land animals. No Ba was found. Cattle choroids contain Ba in amounts which increase with the age of the animal, whilst those of Na, K, Mg, Ca, Fe, and Cu appear to decrease. Ba has also been detected in smaller amounts in the irises, but not in the retinas freed from the back pigmented layer.
L. S. Theobald.

"Black gut" [in pig carcases]. D. J. Anthony, F. W. Jackson, and T. G. Joyce (Veterinary Rec., 1931, **11**, 801).—The stain ("black gut") sometimes found in the cæcum and parts of the colon of pigs consists of FeS, which can be removed with dil. HCl. Probably the FeS is deposited when, because of the type of food consumed or for any other reason, the contents of the intestine cease to be acid.
W. McCartney.

Relation between total sulphur and cystine content of certain samples of rabbit fur. J. Barritt and C. Rimington (Biochem. J., 1931, **25**, 1072—1074).—The increased S vals. previously observed in the keratin of rabbit fur (A., 1930, 1313) can be accounted for within narrow limits as cystine.
S. S. Zilva.

Sulphur-free nature of medulla in blackface wool. J. Barritt and A. T. King (Biochem. J., 1931, **25**, 1075—1076).—The average content of actual medulla substance is approx. 5·5%. From the S content of medullated and unmedullated fibres and other data it is deduced that the medulla substance does not contain S.
S. S. Zilva.

Sulphur distribution in the component structures of wool and porcupine quills. J. G. Bekker and A. T. King (Biochem. J., 1931, **25**, 1077—1080).—Analytical data and results of differential staining both of wool and porcupine quill sections

confirm the view that medulla cells are substantially devoid of S and that keratinisation so far as sclero-proteins such as wool-keratin are concerned is the result of incorporation of the cystine nucleus.

S. S. ZILVA.

Chemistry of leather. I. Shifting of the isoelectric point of collagen by the action of trypsin. N. J. GAVRILOV and A. SEMSKAYA. **II. Isolation of some diketopiperazines from the collagen of skin.** N. J. GAVRILOV and E. STACHEYEVA (Biochem. Z., 1931, **238**, 44—52, 53—59).—I. The isoelectric point of collagen is not const. and depends on the treatment to which the collagen has been subjected. It is shifted to the acid side by the action of trypsin and reaches p_H 3·4, but since this change occurs, although more slowly, in the absence of trypsin it is probably due to the action of an enolase which isomerises the peptide linking from the keto- to the enol form.

II. When collagen is hydrolysed by the method previously adopted for gelatin (A., 1928, 189) and the product is extracted with solvents, various mixed NH_2-acid anhydrides (*e.g.*, glycyl-*l*-leucyl, glycyl-*l*-prolyl) are obtained. During the hydrolysis the amount of NH_3 produced is about 4 times that obtained from gelatin by the same treatment. It is concluded that in the collagen, as in the gelatin mol., there are two anhydride rings composed of phenylalanine, proline, and glycine residues. W. MCCARTNEY.

Glyceride structure of beef tallows. A. BANKS and T. P. HILDITCH (Biochem. J., 1931, **25**, 1168—1182).—In the whole fats of tallows of N. and S. American sources the total of stearic, oleic, and linoleic acids tends towards 62 or 69 mols.-%, a relation characteristic of a number of other tallows. The proportion of fully-saturated glycerides varies according to the relative total amounts of saturated and unsaturated acid in the whole fats, but the composition of the acids present is in all cases about 60% of palmitic (with myristic) and about 40% of stearic acid. S. S. ZILVA.

Animal adenine nucleotides. U. MROCZKIEWICZ (Biochem. Z., 1931, **235**, 267—270).—As far as the action of nucleotide deaminases from frog muscle is concerned, the adenine nucleotide from rabbit muscle is identical with that from pig's blood, but not with that from yeast-nucleic acid. Hence it is concluded that the adenine nucleotide of Hoffman (A., 1925, i, 711) is the same substance as that of Embden and Zimmermann (A., 1927, 749), but that the adenine nucleotide from yeast-nucleic acid (Jones, "Nucleic Acids," 1920, p. 35) is a separate individual.

W. MCCARTNEY.

Trimethylammonium bases. I. Reaction of trimethylammonium bases with permanganate. II. Determination of lecithin in organs. W. LINTZEL and S. FOMIN (Biochem. Z., 1931, **238**, 438—451, 452—458).—I. The behaviour of choline, acetylcholine, neurine, betainealdehyde, betaine, γ-butyrobetaine, carnitine, and NMe_3 to acid and alkaline $KMnO_4$ is investigated and a table summarises the products.

II. A method is described for determination of lecithin depending on the determination of choline in terms of the titration of the NMe_3 liberated from it on treatment with $KMnO_4$. For a determination, 1 mg. of lecithin-N or 50 mg. of lecithin are necessary.

P. W. CLUTTERBUCK.

Alternative occurrence of creat(in)ine and arginine in vertebrates and invertebrates. F. KUTSCHER and D. ACKERMANN (Z. physiol. Chem., 1931, **199**, 266—272).—Arginine was isolated [as the $Cu(NO_3)_2$ salt] from *Lumbricus terrestris*, *Holothuria tubulosa*, and *Arca Noæ*, but could not be detected in horse muscle, although creat(in)ine was present.

J. H. BIRKINSHAW.

Arcaine, a previously unknown animal base. F. KUTSCHER, D. ACKERMANN, and O. FLOSSNER (Z. physiol. Chem., 1931, **199**, 273—276).—From the arginine fraction obtained from *Arca Noæ*, a base *arcaine*, $C_6H_{16}N_6$ [*sulphate* (AB), decomp. 291°; *picrate* (A_2B), decomp. 251—254°; *chloroaurate* ($B,2HAuCl_4$), m. p. 170·5°; *chloroplatinate* (B,H_2PtCl_6), m. p. 222°; *picrolonate* (A_2B), decomp. 303°; *rufianate* ($B,2C_{14}H_8O$-S), decomp. 306—311°], was isolated as the picrate. It gives a positive Sakaguchi reaction.

J. H. BIRKINSHAW.

Constitution of arcaine. F. KUTSCHER, D. ACKERMANN, and F. A. HOPPE-SEYLER (Z. physiol. Chem., 1931, **199**, 277—280).—On boiling with aq. $Ba(OH)_2$, arcaine gives carbamide and agmatine. It is identical with tetramethylenediguanidine (A., 1922, i, 531). J. H. BIRKINSHAW.

Isolation of *d*-3 : 5-di-iodotyrosine from the thyroid gland by the action of proteolytic enzymes. C. R. HARINGTON and S. S. RANDALL (Biochem. J., 1931, **25**, 1032—1036).—The filtrate from the peptic or tryptic digestion of crude iodothyreoglobulin (A., 1930, 820) after fractionation with $AgNO_3$, tryptic digestion, and further fractionation is digested with erepsin. The pure compound is obtained from this digest by fractionation with $AgNO_3$. It therefore actually occurs as a constituent of the characteristic protein of the thyroid and is not artificially produced (A., 1930, 504). S. S. ZILVA.

Iodine method for the determination of glutathione. N. GAVRILESCU (Biochem. J., 1931, **25**, 1190—1194).—Compared with the nitroprusside end-point, starch without KI used as an indicator in acid samples yields very high figures. In the presence of excess of KI lower results are obtained. The use of starch and excess of KI in neutral (litmus) pure solutions or tissue extracts gives results in agreement with those obtained when nitroprusside is used.

S. S. ZILVA.

Reduction of oxyluciferin by atomic hydrogen. E. N. HARVEY and G. I. LAVIN (Science, 1931, **74**, 150).—Dry oxyluciferin is reduced to luciferin by at. H. Luminescence then appears when an aq. solution of luciferase is added. Dry luciferase and luciferin often give a faint blue glow when exposed to at. H.; this increases to incandescence with an increase in concentration of at. H. Dry ovalbumin and dry, powdered *Oniscus* behave similarly.

L. S. THEOBALD.

Ruthenium tetroxide as a fixative in cytology. D. C. CARPENTER and B. R. NEBEL (Science, 1931, **74**, 154—155).—RuO_4 has certain advantages and dis-

advantages when compared with OsO_4. Details for use are given. L. S. THEOBALD.

Comparison of the chloride and bicarbonate concentrations between plasma and cerebrospinal fluid and plasma and ascitic fluid in reference to the Donnan equilibrium. E. MUNTWYLER, C. T. WAY, and E. POMERENE (J. Biol. Chem., 1931, **92**, 733—742).—The Cl′ and HCO_3' distributions between human plasma (venous) and cerebrospinal fluid and between plasma and ascitic transudate were determined, the results indicating a concentration and distribution of electrolytes in agreement with the Donnan theory. F. O. HOWITT.

Alcohol-soluble proteins from milk products. L. A. ALLEN (Biochem. J., 1931, **25**, 1045—1050).—EtOH-sol. proteins have been isolated from ripe and unripe Cheddar cheese and from a peptic digest of caseinogen. The proteins differ appreciably among themselves and considerably from caseinogen in their composition. They have a very low P content. They are possibly decomp. products of caseinogen or casein. S. S. ZILVA.

Content of substances stimulating secretion in human gastric juice. N. HENNING and E. BACH (Arch. exp. Path. Pharm., 1931, **161**, 511—522).—Normal human gastric juice obtained fasting or after a meal, when injected intravenously into a dog, causes a marked flow of the gastric juice of the animal. The active substance is thermostabile and is destroyed by treatment with pepsin in NaCl solution; it is contained in normal fasting non-acid juices. Gastric juice from a human stomach with an organically diseased mucous membrane contains the substance only in so far as it is secreted at an acid reaction. W. O. KERMACK.

Solubility of iron in acids as basis for resorption in the organism. (Solubility of metallic iron in gastric juice.) F. BAUER (Arch. exp. Path. Pharm., 1931, **161**, 400—418).—The rate at which Fe powder dissolves in HCl increases with the amount of Fe present and with the concentration of the acid, but less quickly than in direct proportion. The rate increases by 50% when the temp. is raised from 20° to 37°. Similar observations hold for H_2SO_4 and org. acids, but the abs. rate of dissolution does not depend solely on the p_H, the rates for the org. acids being higher at the same p_H vals. than those for the inorg. acids. Solutions of $FeCl_3$ dissolve Fe much more rapidly than corresponds with the p_H. The dissolution of Fe by human gastric juice is regulated chiefly by the concentration of HCl, but under certain conditions, *e.g.*, at low concentrations of mineral acid and in presence of large quantities of Fe, the org. acids present may also assist. Fe_2O_3 is at most only very slightly sol. in HCl. W. O. KERMACK.

Determination of tetraiodophenolphthalein in duodenal fluids. M. CHIRAY and L. CUNY (J. Pharm. Chim., 1931, [viii], **14**, 123—129).—The I may be converted into the inorg. state by refluxing with Zn and N-H_2SO_4. On neutralisation $Zn(OH)_2$ carries down protein and colouring matter, giving a clear filtrate. The I is liberated by the addition of H_2SO_4 and $NaNO_3$, excess of carbamide being added to decompose NO_3' and CS_2 to extract I, which is titrated with $0{\cdot}01N$-$Na_2S_2O_3$. Alternatively, and more accurately when only traces of I are present, reduction is carried out in presence of N-NaOH instead of H_2SO_4. The solution is neutralised with H_2SO_4 and filtered, and NaOH and $KMnO_4$ are added to oxidise to $NaIO_3$, which is determined in the usual manner. T. MCLACHLAN.

Glycocholeic acid from rabbit-bile. T. SEKITOO (Z. physiol. Chem., 1931, **199**, 225—230).—The winter bile of rabbits contains principally glycocholeic acid (I), m. p. 183—184° (decomp.), $[\alpha]_D^{20}$ $+51{\cdot}3°$, yielding deoxycholic acid and glycine on hydrolysis. The glycine is attached by an amide linking. With xylene, (I) forms *xyleneglycocholeic acid*, m. p. 185—186°, $[\alpha]^{20}$ $+55{\cdot}0°$, and a fatty acid (probably margaric acid), m. p. 58°, giving with deoxycholic acid *margarincholeic acid*, m. p. 183—184°. (I) is a compound of glycodeoxycholic and margaric acids in the ratio 8 : 1. Glycodeoxycholic acid, m. p. 186—188°, $[\alpha]_D^{20}$ $+55{\cdot}25°$, was obtained from summer bile. J. H. BIRKINSHAW.

Appearance of protein in bile. II. Hetero-albuminocholia. T. MATSUDA (Japan. J. Gastroenterol., 1931, **3**, 14—17).—Egg-albumin, injected intravenously into rabbits, is excreted into the bile by the parenchymatous cells of the liver. Injury of the liver by CCl_4 decreases the ability to excrete foreign protein. CHEMICAL ABSTRACTS.

Properties of bile pigments. I. Agglutinating and hæmolytic power of bilirubin. A. CLEMENTI and F. CONDORELLI (Biochem. Z., 1931, **238**, 278—286).—Bilirubin possesses considerable agglutinating and hæmolytic power, the former being obtained down to concentrations of 1/20,000 immediately after addition to suspensions of red cells and the latter appearing only later, and not persisting to such great dilutions. Biliverdin has these properties to a much smaller extent. P. W. CLUTTERBUCK.

Use of the Molisch reactions in the study of sugars in biological fluids. J. H. FOULGER (J. Biol. Chem., 1931, **92**, 345—353).—A modification of the Molisch test is described in which 75 vol.-% H_2SO_4 replaces the conc. acid. The colorations produced by aldoses (red) and ketoses (reddish-violet) possess max. absorption at 480—510 and 550—580 mμ, respectively. Ketoses are present in urine, normal and diabetic blood, and normal and pathological cerebrospinal fluid. The relatively high aldose content of cerebrospinal fluid in meningococcic meningitis returns to normal during recovery. A. COHEN.

Precipitation reagent for the determination of urinary dextrose. P. FLEURY and G. BOYELDIEU (J. Pharm. Chim., 1931, [viii], **14**, 168—170).—Basic Pb acetate precipitation of urine results in a loss of part of the dextrose present. This loss is smaller when $HgSO_4$ or $Hg(NO_3)_2$ is used. F. O. HOWITT.

Detection and determination of lactose in urine. M. KUROYA (Biochem. Z., 1931, **235**, 447—450).—A method by which lactose in urine can be determined is described. The error varies from 2 to 10%. In the solution used the sugar can be identified by several known methods. W. MCCARTNEY.

Clinical method for determination of urea in urine by the use of mercuric chloride. B. Lustig and H. Bromberg (Biochem. Z., 1931, **238**, 321—324).—A rapid method for the determination of urea depends on the titration of the urine–phosphotungstic acid filtrate with $HgCl_2$, the accuracy claimed being $\pm 4\%$. P. W. Clutterbuck.

Nutritional anæmia. Quantitative variations in iron, copper, and manganese supplements. H. S. Mitchell and L. Miller (J. Biol. Chem., 1931, **92**, 421—434).—Rats with a uniformly low blood-hæmoglobin (3—4·5 g. per 100 c.c.) recover slowly on pure Fe salts added to a milk diet. Hæmoglobin regeneration is much more rapid when Fe is supplemented by 0·1—1·0 mg. of Cu daily. The optimum daily metal ration is 0·25 mg. of Fe and 0·1 mg. of Cu. 0·01—0·1 mg. of Mn added daily to Fe and Cu has an insignificant supplementary action, and salts of Al, Sn, Sb, and Zn give negative results. A. Cohen.

Fuchs' reaction for the serological diagnosis of carcinoma. II. B. H. E. Cadness and C. G. L. Wolf (Biochem. Z., 1931, **238**, 287—306).—All of the 18 malignant cases examined gave either a positive Fuchs reaction or an immunity reaction. Of 16 non-malignant cases, 11 gave no reaction. In one case (carcinoma of rectum) insertion of Ra completely inhibited the Fuchs reaction in 3 hr. and the proteolytic action did not return in 20 days. Cold-storage for more than 5 days decreased the proteolytic activity of the cancerous serum against normal fibrin. Addition of heparin did not inhibit the reaction. Heating the fibrin for 2 min. reduced the reaction with normal and cancerous serum and heating for 2—5 min. completely destroyed its suitability for proteolytic experiments with nephritic serum. Washing fibrin with 90% EtOH did not affect its suitability for the Fuchs reaction. Attempts to reactivate the heated fibrin by enterokinase and $CaCl_2$ were unsuccessful. Certain buffer solutions, especially at 37°, had a dissolving action on the fibrin. Heating fibrin inhibited the enzymic formation from it of substances giving the ninhydrin test. Precipitation of the serum with C_γ-$Al(OH)_3$ does not ppt. the Fuchs enzyme, which is of tryptic nature or identical with cathepsin, but such precipitation in presence of 0·5 vol. of EtOH gives a ppt. the Na_2HPO_4 eluate of which is proteolytically active against fibrin. P. W. Clutterbuck.

Globulin and albumin fractions of serum. IV. Amount, nitrogen, carboxyl, amino-, and carbohydrate content, carbonyl and amino-index of the lower protein fractions of puncture fluids in cirrhosis, sarcoma, and carcinoma. B. Lustig (Biochem. Z., 1931, **238**, 307—320).—The total albumin in the fluid in carcinoma is greatly increased as compared with that in sarcoma and cirrhosis. In carcinoma fluid, the amount of Na_2CO_3-sol. globulin is 3—4 times, and the amount of NaCl-sol. globulin one sixth, that in cirrhosis fluid. The carbohydrate content of the Na_2CO_3-sol. globulin is increased and the CO_2H and NH_2-content of the NaCl-sol. portion of the globulin is decreased in carcinoma fluid (cf. this vol., 505, 640). P. W. Clutterbuck.

Metabolism of tumours. II. S. Edlbacher and W. Kutscher (Z. physiol. Chem., 1931, **199**, 200—220; cf. A., 1928, 543).—Neither creatinine- nor arginine-phosphoric acid is present in mouse carcinoma. In tumour pulp digested in $NaHCO_3$, inorg. H_3PO_4 is liberated, addition of fluoride having no effect. In the muscle of healthy mice fluoride inhibits the hydrolysis. There is no lactic acid formation in carcinomatous tissue, indicating that the H_3PO_4 does not arise by glycolysis. Tumour tissue possesses in high degree the power of eliminating H_3PO_4 from added animal or plant nucleic acid. The enzyme responsible resembles the phosphatase found in the liver (A., 1930, 1065). J. H. Birkinshaw.

Proteolysis of tumours. H. A. Krebs (Biochem. Z., 1931, **238**, 174—196).—The proteolytic action of tumours does not differ in degree from that of normal tissues. Although tissues from different organs exert different degrees of proteolytic action, the order of magnitude remains the same. The best conditions for experiment are attained by grinding the tissues, extracting them with acid glycerol, adding protein to bring the concentration to 5%, and measuring at p_H 4·7. Cysteine is added in order to exclude the inhibition caused by heavy metals. W. McCartney.

Production of methylglyoxal by the water-soluble enzyme of rat sarcoma. M. Kuroya (Biochem. Z., 1931, **235**, 444—446).—Aq. extracts of rat sarcoma contain both phosphatase and glycolase and can produce methylglyoxal from hexosediphosphate. W. McCartney.

Inhibitor principle associated with the causative agent of a chicken tumour. J. B. Murphy and E. Sturm (Science, 1931, **74**, 180—181).—Additional tests and properties are described (cf. this vol., 645). Heating to 65° impairs the inhibiting action of the extract; this observation has been extended to mouse sarcomata. L. S. Theobald.

Hypothetical anti-cancer hormone. H. P. Teunissen (Chem. Weekblad, 1931, **28**, 505—507). A discussion. H. F. Gillbe.

Transformation of fats in diabetes mellitus. P. E. Verkade (Chem. Weekblad, 1931, **28**, 470 474, 477—484).—I. The grounds on which the conclusion that glycerides of acids containing uneven nos. of C atoms may be tolerated when ordinary fats cause ketonuria are set out. The poor results obtained by use of "Intarvin" may arise from its high m. p., content of mineral oil (17%), and free acid (acid val. 17), and the fact as found by vac. distillation of the Me esters that it contains a high proportion of acids with even nos. of C atoms; the taste and odour are repugnant. A more suitable fat for testing the conclusion is the glyceride of undecoic acid.

II. The catabolism of fats of which the acids contain both odd and even nos. of C atoms is discussed. S. I. Levy.

Artichokes in the diet of the diabetic patient. H. B. Stein, B. B. Longwell, and R. C. Lewis (Arch. Int. Med., 1931, **48**, 313—324).—The carbohydrates of the Jerusalem artichoke are absorbed and utilised by mild or moderate diabetics, but are no better

tolerated than carbohydrates from other sources. Decreased sugar excretion with such a diet is often due to bacterial fermentation in the intestine.

F. O. HOWITT.

Metabolism in experimental yellow fever in *Macacus rhesus*. IV. Tolerance for dextrose. A. M. WAKEMAN and C. A. MORRELL (Arch. Int. Med., 1931, **48**, 301—312; cf. this vol., 510).—The response of the blood-sugar of monkeys to oral administration of dextrose is irregular. When very ill with yellow fever no increase in the blood-sugar follows ingestion of dextrose (1 g. per kg.) owing to extremely slow absorption from the alimentary canal. With moderately ill monkeys intravenously injected dextrose is less rapidly removed from the blood and the sugar tolerance is below normal. Comparison of the venous and arterial blood-sugar curves of normal and diseased monkeys indicates a loss of hepatic function during yellow fever. F. O. HOWITT.

Jaundice in malarial diseases. I. S. SAIKI (Japan J. Gastroenterol., 1931, **3**, 46—53).—Hyperbilirubinæmia occurs in malaria.

CHEMICAL ABSTRACTS.

Phosphorus and total and diffusible calcium of the blood-serum of lepers in relation to bone changes. J. G. WOOLEY [with H. ROSS] (U.S. Publ. Health Rep., 1931, **46**, 641—658).—Total Ca and inorg. P in the serum of lepers were within normal limits, but the percentage of diffusible Ca was below normal. Bone atrophy occurred in 91% of the cases examined. P. G. MARSHALL.

Enzymes of the lymphocytes. H. A. OELKERS (Arch. exp. Path. Pharm., 1931, **161**, 344—351).—Lymphocytes from patients suffering from lymphatic leucæmia contain an erepsin, small quantities of trypsin, and a very small quantity of cathepsin. The glycerol extract of the lymphocytes contains a lipase acting on Et butyrate and to a smaller extent on tributyrin. W. O. KERMACK.

Blood in experimental disturbance of liver function. II. Liver function and protein metabolism. T. SAWADA (Japan. J. Gastroenterol., 1931, **3**, 38—45).—Injury by infection, ligation, or P poisoning increases the blood-NH_2-acids and serum-globulin, and decreases the fibrinogen and serum-albumin. CHEMICAL ABSTRACTS.

Urobilin substances. III. Urine-, bile-, and blood-urobilin substances in experimental hepatic disturbance. M. OSHIMA (Japan. J. Gastroenterol., 1931, **3**, 67—70).—A normal rabbit excretes 0·03—0·07 mg. of urobilin substances per day in the urine and 80 times as much in the bile. Injury of the liver increases the excretion of urobilin compounds. In the normal rabbit the proportion of urobilinogen to urobilin is 5 : 1.

CHEMICAL ABSTRACTS.

Chlorides and inorganic constituents of the serum and cerebrospinal fluid in nephritis and acidosis. G. C. LINDER and E. A. CARMICHAEL (Biochem. J., 1931, **25**, 1090—1094).—In moderate disturbances of acid–base balance due to nephritis or to NH_4Cl therapy the normal relationships of the cerebrospinal fluid and arterial blood-serum remain intact. In severe nephritis with great reduction in serum-HCO_3' and p_H and gross N retention a breakdown of these relationships may sometimes occur.

S. S. ZILVA.

Glycogen of the liver and muscle in the nephrectomised dog. F. RATHERY, S. GIBERT, and Y. LAURENT (Compt. rend., 1931, **193**, 326—327).—In the dog, after double nephrectomy, the blood-sugar is only slightly changed, usually the liver-glycogen falls, whilst the H_2O retention of the liver tissue is slightly diminished; injection of phloridzin does not modify these changes. C. C. N. VASS.

Physical properties of the proteins of serum and dropsical serous exudates in lipin nephrosis. C. ACHARD, A. BOUTARIC, and A. ARGAND (Compt. rend., 1931, **193**, 309—314).—The colloidal solutions of the serum-proteins precipitated by $COMe_2$ at 0°, like the sera and the serous exudates in lipin nephrosis, have lost the power of hydration on warming.

C. C. N. VASS.

Nitrogen balance during dietary corrections of obesity. J. M. STRANG, H. B. MCCLUGAGE, and F. A. EVANS (Amer. J. Med. Sci., 1931, **181**, 336—349).—The level of N metabolism is normal in obesity. The rapid reduction of wt. by a " maintenance protein diet " produces only a slight depression in the N level. CHEMICAL ABSTRACTS.

Creatinine excretion in abnormal states of nutrition. H. B. MCCLUGAGE, G. BOOTH, and F. A. EVANS (Amer. J. Med. Sci., 1931, **181**, 349—355).—The creatinine excretion in obesity differs little from the normal, and is little affected by dietary reduction. That of persons of subnormal wt. is low.

CHEMICAL ABSTRACTS.

Rice bran, a preventive of perosis (deforming leg weakness) in chickens. H. W. TITUS and W. M. GINN (Science, 1931, **74**, 249—250).—Perosis is prevented by the addition of 6—10% of rice-bran to the diet together with a Ca : P ratio of 2·5 : 1. An accessory food factor, or vitamin, in addition to vitamin-*D* appears to be necessary for the proper development of leg bones in chickens.

L. S. THEOBALD.

Rickets in rats. XII. Acid–base equilibrium of the blood in rickets and tetany. A. T. SHOHL, H. B. BROWN, C. S. ROSE, D. N. SMITH, and F. COZAD (J. Biol. Chem., 1931, **92**, 711—719).—In rats in which rickets had been developed by a high Ca–low P diet the acid–base equilibrium of the blood bordered on alkalosis. Such rats when fasted or fed on a diet with a Ca : P ratio of 2 or 1 developed tetany accompanied by an acidosis. Rickets and tetany, therefore, are not necessarily associated with acidosis or alkalosis respectively. F. O. HOWITT.

Curative properties of 45 elements in syphilis and trypanosomiasis. C. LEVADITI and P. LÉPINE (Compt. rend., 1931, **193**, 404—406).—Of the 45 elements examined (A., 1927, 587; 1928, 444; this vol., 865), only 10 (V, Ga, As, In, Sb, Te, Pt, Au, Hg, Bi) possess therapeutic activity.

H. BURTON.

Distribution of chloride and hydrogen carbonate between plasma and cells in the blood of various pathological conditions. E. MUNT-

WYLER, V. C. MYERS, and C. T. WAY (J. Biol. Chem., 1931, **92**, 721—731).—The distribution ratios of Cl′ and HCO_3' between plasma and cells in human subjects for a given plasma p_H are similar irrespective of the pathological condition, whilst their dependence on the p_H val. is in agreement with previous findings (A., 1923, i, 1249). F. O. HOWITT.

Kinetics of the cell reactions. II. J. WEICHHERZ (Biochem. Z., 1931, **238**, 325—334).—The author's earlier calculation of the degree of permeability of the membrane of the yeast cell (A., 1930, 168) is corrected and gives the val. $\alpha = 2{\cdot}016 \times 10^{-12} \sim 1{\cdot}334 \times 10^{-11} \cong 0{\cdot}77 \times 10^{-11}$. The described cell reaction is not periodic. The concentration of reaction products within and without the cell are determined. P. W. CLUTTERBUCK.

Growth and chemical composition of ovum of functioning fowl's ovary (*Gallus domesticus*). A. L. ROMANOFF (Biochem. J., 1931, **25**, 994—996).—The growth phases and particularly the maturation phase of the fowl's ovum are marked by a very rapid increase in the percentage of dry matter, reaching the highest point in a mature ovum. Ca and fat contents of the ovum increase proportionally with the advance of maturation. Density and p_H of ovum, I val. and n of the extracted fat show only slight changes during the maturation phase. S. S. ZILVA.

Effect of amino-acids on respiration of tissues. I. Glycine and alanine. B. KISCH (Biochem. Z., 1931, **238**, 351—363).—Glycine (optimal concentration, 0·01—0·003M) increases the respiration of heart, liver, and kidney when suspended in Ringer's solution, the action being greater with old than with fresh tissues. The increase is usually 15—30% of the initial val., the max. increase being 50%. Alanine (optimal concentration, 0·03—0·02M) has a similar but stronger action, the respiration being increased 4—7 times. Similar results were obtained with tissues of rats, guinea-pigs, rabbits, cats, dogs, pigs, and calves and the greatest increase was obtained with kidney tissue. P. W. CLUTTERBUCK.

Effect of sodium nitrite on tissue respiration. B. KISCH and K. CUPPERS (Biochem. Z., 1931, **238**, 364—369).—The respiration of kidney tissue is inhibited by 0·01M-$NaNO_2$ but is usually increased with concentrations of 0·002—0·0005M, the increase being 10—30% and with 0·00025M and older tissues may be more than 100%. The increase is obtained in Ca-containing and Ca-free solution. The respiration of Jensen sarcoma tissue (fresh or old) is not increased by $NaNO_2$. P. W. CLUTTERBUCK.

Respiration of tissues of mammalian embryos. B. KISCH (Biochem. Z., 1931, **238**, 370—376).—Tables summarise the influence of $AlCl_3$, H_3BO_3, "omega" and alanine on the respiration of kidney, liver, and heart tissue of guinea-pig, pig, and ox embryos of different ages. The effect of these substances on the respiration of embryonic tissues lies between that of tissues of adult animals and of tumour tissue, being smaller than the former and greater than the latter. The usual inhibition of respiration in normal and tumour tissue of adult animals by high concentrations of $AlCl_3$ (10^{-5}) is not obtained with embryonic tissue. P. W. CLUTTERBUCK.

Relation of glutathione to cell respiration with special reference to hepatic tissue. F. G. HOPKINS and K. A. C. ELLIOT (Proc. Roy. Soc., 1931, **B**, **109**, 58—88).—The tissue of initial glutathione content determined by Tunnicliffe's method (A., 1925, i, 752) is incubated at 37° (*a*) with oxidised glutathione in Thunberg tubes, (*b*) with frequent admittance of air, for varying periods and then extracted by 10% $CCl_3{\cdot}CO_2H$, the ·SH content of the filtered extract being determined. In well-fed animals the ·SH content of the excised liver slowly falls to zero, there being a preliminary delay or even rise which is due to survival respiration of thermolabile reducing processes in the tissue and is lessened or totally eliminated by starvation. The course of oxidation is linear. In the presence of added oxidised glutathione residual active H results in a well-marked increase in ·SH concentration. Oxidation of the ·SH group is inhibited by CN′ and P_2O_7'''' but not by CO and hence is catalysed by Fe in some association other than Fe-hæmatin. It proceeds after heating to 70° and hence is not enzymic. F. O. HOWITT.

Sulphur metabolism of the dog. VIII. Metabolism of glutathione compared with that of other cystine derivatives. T. S. HELE and N. W. PIRIE (Biochem. J., 1931, **25**, 1095—1101).—The dog can oxidise to the same degree *l*- and *r*-cystine, *l*- and *r*-cysteine, and glutathione, and less readily acetylcysteine and glycylcysteine, but not chloro- and dichloro-acetylcystine. Administration of glycylcysteine anhydride causes diuresis in dogs and rats but not in rabbits. *p*-Iodophenylcysteine upsets the dog and is not well absorbed. S. S. ZILVA.

Metabolism of normal and tumour tissue. III. A method for the measurement of respiratory quotient in serum. IV. Respiratory quotient in hydrogen carbonate-media. F. DICKENS and F. SIMER (Biochem. J., 1931, **25**, 973—984, 985—993).—III. A manometric method by means of which the pressure changes caused by the disappearance of O_2 consumed in respiration by respiratory CO_2, and by alteration in the amount of combined CO_2 during the experiment are determined. From these data and the total pressure change read on the manometer, the quantities of respired CO_2 and O_2 are obtained and hence the R.Q.

IV. No significant difference has been observed in the R.Q. and respiration measured in salt solutions buffered by $NaHCO_3$ under physiological tension of CO_2 or by phosphate in a CO_2-free atm. The R.Q. of the tissues of fed animals is in all cases within the limits corresponding with the oxidation of normal foodstuffs. In fasting animals the R.Q. of liver tissue in simple salt solutions containing dextrose falls below the physiological level. It is restored to the fat level when the measurement is made in serum. S. S. ZILVA.

Metabolism of iodobenzene and *p*-iodophenylmercapturic acid in the rat and the rabbit. N. R. LAWRIE (Biochem. J., 1931, **25**, 1037—1044).—The rat is able to synthesise *p*-iodophenylmercapturic

acid from PhI but is unable to oxidise the former to ethereal sulphate. It does not develop hæmoglobinuria after the administration of the mercapturic acid. The rabbit is able to convert a very small fraction of injected PhI into the mercapturic acid. It is also unable to oxidise the latter to ethereal sulphate and does not develop hæmoglobinuria after the administration of the mercapturic acid. S. S. ZILVA.

Influence of "acid" and "basic" food on the fate of aromatic substances in the organism. I. Oxidation and combination of phenol and benzene. A. E. BRAUNSTEIN, A. N. PARSCHIN, and O. D. CHALISOVA. **II. Oxidation of toluene.** I. S. EPSTEIN and A. E. BRAUNSTEIN. **III. Acid–base metabolism. Vegetative nervous system and the oxidation and combination of phenol.** A. E. BRAUNSTEIN and A. N. PARSCHIN. **IV. Influence of diuresis on the fate of phenol in the organism.** A. E. BRAUNSTEIN and A. N. PARSCHIN (Biochem. Z., 1931, **235**, 311—327, 328—333, 334—343, 344—352).—I. The conversion of injected PhOH into non-toxic compounds (chiefly esters) in the rabbit organism is favoured by administration of food in which acid radicals preponderate ("acid" food) and retarded by administration of food in which basic radicals preponderate ("basic" food). "Acid" food also favours the conversion in the organism of C_6H_6 into PhOH and of the latter into non-toxic compounds.

II. Quantitatively the oxidation of PhMe to BzOH in the rabbit is uninfluenced by the nature of the food consumed, but the rate of the oxidation is lower in the case of "acid" food than in that of "basic" food.

III. In the rabbit the oxidation of PhOH or its conversion into non-toxic compounds remains practically unaffected in the acidosis or alkalosis produced by administration of salts, but both processes are affected by changes in the tonus of the vegetative nervous system caused by administration of sympathetic or parasympathetic poisons. No direct relation could be found between the actions of "acid" and "basic" food on the tonus of the vegetative nervous system and the influence of such foods on the processes of oxidation of PhOH and its conversion into non-toxic compounds.

IV. The influence on the fate of PhOH in rabbits of the administration of "acid" or "basic" food is a result, not of the "acid" or "basic" character of the food as such, but chiefly, if not exclusively, of the different diuretic effects of the foods. It is concluded that a preponderance of acid or basic radicals in the food has no sp. influence on the synthetic or oxidative processes in the organism. W. McCARTNEY.

Effect of ingested cotton-seed oil on the composition of body-fat. N. R. ELLIS, C. S. ROTHWELL, and W. O. POOL (J. Biol. Chem., 1931, **92**, 385—398).—Addition of cotton-seed oil to pigs' rations increases the hardness and total saturated acid content of the body-fat to a max. at 4% of oil. Further addition of oil up to 12% of the diet increases the stearic acid content. The changes in fat composition are due to a precursor of stearic acid present in cotton-seed oil. Cotton-seed oil causes more softening of body-fat in rats than in pigs. A. COHEN.

Changes in the total fatty acids, phospholipin fatty acids, and cholesterol of the blood during the lactation cycle. L. A. MAYNARD, E. S. HARRISON, and C. M. McCAY (J. Biol. Chem., 1931, **92**, 263—272).—After parturition, the total fatty acids, phospholipin fatty acids, and cholesterol of the plasma of cows show sharp parallel increases, gradually returning to the original vals. towards the commencement of the next dry period. That these changes are due to lactation apart from changes in fat consumption is shown by similar rises in the blood lipins observed in the early lactation period of cows maintained on const. diet. A. COHEN.

Interrelationship between dietary fat and phosphorus distribution in the blood of lactating cows. C. M. McCAY and L. A. MAYNARD (J. Biol. Chem., 1931, **92**, 273—280).—Data are given for the P distribution and secretion of milk and fat of cows maintained on grain diets containing 1, 3, and 7% of fat, respectively. The change from high to low fat intake is accompanied by decreases in the secretion of milk and fat, and the total P and phospholipins of the plasma, although starch is given to compensate for low fat consumption. The phospholipins of the erythrocytes and other P-containing blood constituents are not affected by the change. A. COHEN.

Metabolism of phospholipins. III. Comparative influence of various fats on the degree of unsaturation of phospholipins and neutral fat in tissues of the rat. R. G. SINCLAIR (J. Biol. Chem., 1931, **92**, 245—256).—The degree of unsaturation (represented by I val.) of the phospholipins and neutral fats of the whole bodies, carcases, and livers of rats fed on a fat-containing diet is always greater than on fat-free or fat-poor diets. The I val. of the tissue phospholipins is not proportional to that of the food fat, but the latter has some influence on the I val. of the stored fat. A. COHEN.

Beneficial effects of fat in high sucrose diets when the requirements for vitamin-B_1 and the fat-soluble vitamin[s] are fully satisfied. H. M. EVANS and S. LEPKOVSKY (J. Biol. Chem., 1931, **92**, 615—622).—The growth of rats fed on a diet practically free from fat but very rich in vitamin-*B* by addition of yeast is improved by the feeding of vitamin-free fat (cf. A., 1929, 1203). F. O. HOWITT.

Relation of glycosuria to glycæmia and the determination of the renal threshold for dextrose. H. P. HIMSWORTH (Biochem. J., 1931, **25**, 1128—1146).—The concentration of urinary sugar is independent of the diuresis and is proportional to the excess of the blood-sugar concentration over the renal threshold. The concentration of the sugar reabsorbed is determined by the sugar content of the blood in the peritubule capillaries. S. S. ZILVA.

Consumption of dextrose by the isolated surviving central nervous system of *Bufo vulgaris*. M. MITOLO (Atti R. Accad. Lincei, 1931, [vi], **13**, 229—231).—The resting cerebrospinal axis of *B. vulgaris* consumes 3·8423 mg. of dextrose per g. of tissue in 2 hr., this amount being increased by a current of O_2 or by increase of the reflex excitability by neutral

strychnine sulphate. With the dead animal the consumption is less and with the living material narcotised with Et_2O less still. T. H. POPE.

Combustion of alcohol by the poikilotherm; value of the temperature quotient. M. NICLOUX (Compt. rend., 1931, **193**, 364—366).—In the frog between 1° and 29° the quantity of EtOH burnt in 24 hr. varies from 14 to 97% and the temp. quotient of the biochemical intraorg. reaction averages 2. C. C. N. VASS.

Utilisation of carbohydrate in the aerobic activity of muscle of cold-blooded animals. O. MEYERHOF (Biochem. Z., 1931, **237**, 427—436).—When the total carbohydrate content of frog's muscle is above 0·5%, the performance of work takes place almost exclusively at the cost of the carbohydrate, whereas when decreased to below 0·3% (by means of large doses of insulin) a considerable proportion (up to 500 kg. tension per g. muscle) is drawn from non-carbohydrate material. P. W. CLUTTERBUCK.

Oxidation quotient of lactic acid in muscle of warm-blooded animals. E. BOYLAND (Biochem. Z., 1931, **237**, 418—426).—The results of Hahn, Fischbach, and Niemer (this vol., 258) are examined and discredited in terms of further experimental evidence. P. W. CLUTTERBUCK.

Respiratory process of muscle poisoned with iodoacetic acid. O. MEYERHOF and E. BOYLAND (Biochem. Z., 1931, **237**, 406—417).—The slow appearance of poisoning in the muscle of cold-blooded animals is due in part to the slow penetration of the muscle by the acid. Poisoning is completed with a concentration of $0·25\times10^{-3}$ acting for 1 hr. without seriously inhibiting respiration. The respiration of pulped poisoned frog's sartorius muscle is more strongly increased by *d*-lactate and pyruvate (not by *l*-lactate) than in normal muscle, and lactate is simultaneously oxidised as in normal muscle, the effect resembling that on poisoning with fluoride. In all cases the disappearance of lactic acid is not greater than corresponds with the total respiration, synthesis of carbohydrate not being detected. The R.Q. is decreased to 0·7—0·8 both with the intact and the pulped muscle, but is increased to 0·95 on addition of lactate and again falls to 0·8 during recovery. P. W. CLUTTERBUCK.

The co-enzyme of lactic acid formation in muscle. O. MEYERHOF, K. LOHMANN, and K. MEYER (Biochem. Z., 1931, **237**, 437—444).—In the formation of lactic acid in muscle and in enzyme extracts of muscle a thermolabile enzyme and a thermostable dialysable co-enzyme take part as in yeast fermentation and the two co-enzymes are interchangeable. If the co-enzyme of boiled muscle juice is purified by the methods used for co-zymase, the system becomes incomplete and can be activated by adding the Ba salts containing readily hydrolysable phosphoric esters. If boiled muscle or yeast juice is autolysed it becomes inactive as a co-enzyme, but addition of adenylpyrophosphate reactivates it completely. P. W. CLUTTERBUCK.

Chemical nature of the co-enzyme of lactic acid formation. K. LOHMANN (Biochem. Z., 1931, **237**, 445—482).—Frog's muscle extract is unable after keeping 2—3 hr. at 20° to decompose added glycogen, but is completely reactivated by addition of adenylpyrophosphate. Both this and a Mg salt must be added to a dialysed extract for complete reactivation. Boiled muscle juice from which the Mg has been precipitated by aq. NH_3 is inactive as co-enzyme, but is reactivated by addition of Mg. The system inorg. phosphate—adenylpyrophosphate+Mg is designated the co-enzyme system of lactic acid formation. Similarly, fermentation with dialysed yeast maceration juice and with washed dried yeast on addition of purified co-enzyme occurs only in presence of Mg. The yeast must be washed with an acid medium (KH_2PO_4) to remove Mg. The respiration of washed frog's muscle on addition of adenylpyrophosphate+Mg attains only $\frac{1}{5}$ to $\frac{2}{5}$ of that on addition of boiled juice. The co-enzyme system for lactic acid formation is not identical with that for respiration. Adenylpyrophosphate is not the co-enzyme of methylglyoxalase. The activity of methylglyoxalase and carboxylase is not dependent on the presence of Mg, as is that of the enzymes of lactic acid formation and of alcoholic fermentation. P. W. CLUTTERBUCK.

"Non-irritable" muscle. D. R. MCCULLAGH and E. M. CASE (Biochem. J., 1931, **25**, 1220—1230).—No lactic acid is formed, no carbohydrate disappears, nor is there any heat production on electrical stimulation of "non-irritable" frog muscle. The resting anaerobic heat-rate of "non-irritable" muscle is normal. The oxidation mechanisms are intact. The caloric quotient of "non-irritable" muscle is much higher than that of normal muscle, being about 740 instead of 375. S. S. ZILVA.

Influence of yeast on the liver and muscle of trained dogs. H. AIDA (Biochem. Z., 1931, **237**, 347—357).—The substance in yeast which causes changes in carbohydrate metabolism (this vol., 117, 257) is destroyed by heating. The increase in liver-glycogen (this vol., 257) is very much greater when small amounts of sugar (1 g. per kg.) are given with the yeast. P. W. CLUTTERBUCK.

Occurrence of pyruvic acid and methylglyoxal in muscle metabolism. E. M. CASE and R. P. COOK (Biochem. J., 1931, **25**, 1319—1335).—Both compounds occur in frog and rabbit muscle in presence or absence of Na_2SO_3 and under aerobic or anaerobic conditions. They may both be intermediate compounds between carbohydrate and lactic acid. S. S. ZILVA.

Relation between lactic acid and the sympathetic nervous system. B. BASILIOU and F. ZELL (Biochem. Z., 1931, **238**, 418—426).—Injection of NH_2-acids causes an increase of blood-sugar and lactic acid which is inhibited by simultaneous injection of insulin. After extirpation of the suprarenals, the increase of blood-sugar and lactic acid on injection of NH_2-acids either does not appear or is much smaller; it is therefore concluded that the increase depends on the stimulation of the sympathetics. P. W. CLUTTERBUCK.

Effects of a large quantity of lactic acid in the diet. R. SASAKI (J. Agric. Chem. Soc. Japan, 1930,

6, 1144—1152).—Bone-Ca and -P and muscle-P were decreased. CHEMICAL ABSTRACTS.

Ammonia content of and production of ammonia in muscle: their connexion with function and change in condition. X. Production of ammonia during contraction of muscle poisoned with iodoacetic acid. C. LUTWAK (Biochem. Z., 1931, **235**, 485—489).—NH_3 is produced during the first stage (cf. this vol., 647) of the activity of frog muscle poisoned with iodoacetic acid. It is possible that the poisoned muscle produces more NH_3 than does normal muscle under the same conditions or that the excess of NH_3 results from unnoticed second stage activity. Less probably the accumulation of NH_3 may be due to the suppression by the poison of the supposed normal reversibility of the reaction. W. McCARTNEY.

Fate in the organism of alkylamines consumed with food. Supposed demethylation of the alkylamines in the organism. Occurrence of methylamine in normal urine. R. KAPELLER-ADLER and J. KRAEL (Biochem. Z., 1931, **235**, 394—406).—NMe_3 is decomposed (to the extent of 86—87%) in the organism of the dog. During the decomp. no intermediate formation of $NHMe_2$ or NH_2Me can be detected. NH_2Me is also destroyed. Normal human urine as well as that of the dog and cat contains NH_2Me. W. McCARTNEY.

Metabolism of amino-acids. IV. Phenylalanine and tyrosine. N. F. SHAMBAUGH, H. B. LEWIS, and D. TOURTELLOTTE (J. Biol. Chem., 1931, **92**, 499—511).—Oral or subcutaneous administration of the Na salt of phenylalanine to rabbits is followed by excretion of considerable amounts of phenylpyruvic acid, which if similarly administered is excreted unchanged. Blockage of the NH_2 group (*e.g.*, α-ureido-β-phenylpropionic acid) prevents oxidation in the organism, indicating oxidative deamination as a preliminary reaction. Administration of tyrosine is followed by excretion of *p*-hydroxyphenylpyruvic acid. The theory (A., 1913, i, 1279) that tyrosine formation is a primary reaction in the intermediary metabolism of phenylalanine is not upheld. Changes in the non-protein-N of the blood following administration of tyrosine and phenylalanine are described. F. O. HOWITT.

Replacement of proline by oxyproline in nutrition. M. ADELINE (Z. physiol. Chem., 1931, **199**, 184—188).—Oxyproline can replace proline as an NH_2-acid essential to growth in the diet of rats. J. H. BIRKINSHAW.

Resorption of protein substances in the digestive tract. K. SHIMA (Biochem. Z., 1931, **237**, 303—338).—The physiological importance of the whole and of various isolated sections of the digestive tract in resorption of protein can be followed in terms of changes of the HIO_3-reducing substances of blood as determined by Chikano's method (A., 1929, 474). Thus resorption of an aq. solution of Witte's peptone (5 g. per kg.) administered orally is at its height after - hr. (max. reducing substances) and complete after 10 hr. The stomach acts only as a regulator and has no resorptive power, resorption being quicker after its extirpation. In the small intestine, resorption is greatest in the duodenum, less active in the jejunum, and least in the upper portion of the ileum and the lower portion of the intestine. Resorption is very slow in the large intestine. P. W. CLUTTERBUCK.

Occurrence of phylloerythrin in the digestive system of herbivorous animals. O. L. INMAN and P. ROTHEMUND (Science, 1931, **74**, 221).—Phylloerythrin has been isolated from the omasum of cows and sheep fed on a normal winter diet containing chlorophyll. Spectroscopic traces also occur in the rumen of cows and sheep. L. S. THEOBALD.

Effect of lactose and the acid-base value of the diet on the p_H of the intestinal contents of the rat and their possible influence on calcium absorption. C. S. ROBINSON and C. W. DUNCAN (J. Biol. Chem., 1931, **92**, 435—447).—The effects of the ingestion of lactose on the reaction of the contents of different sections of the gastro-intestinal tract of rats fed on vegetable and meat diets are described. Ca absorption depends not only on the intestinal acidity, but also on the nature of the basal diet. A. COHEN.

Calcium-phosphorus ratio of the tibiæ of growing chicks. A. D. HOLMES and M. G. PIGOTT (J. Biol. Chem., 1931, **92**, 187—198).—The Ca : P ratio of the tibiæ of chicks up to 9 weeks of age (about 2 : 1) is independent of (*a*) the Ca : P ratio, the ash content, and the vitamin and protein content of their rations, and (*b*) the ash content of the tibiæ and the growth rate of the chicks. A. COHEN.

Feeding cotton-seed meal to cattle. J. O. HALVERSON and F. W. SHERWOOD (N. Carolina Agric. Exp. Sta. Tech. Bull., 1930, No. 39, 158 pp.).—"Cotton-seed meal poisoning" cannot be ascribed to the presence of toxic materials (*e.g.*, gossypol) in the meal, but is related to deficiencies of Ca and vitamin-*A*. Supplementary feeding with fresh grass or lucerne practically eliminated the disorder. Rations composed of maize products are deficient in vitamin-*A*, Ca, and possibly P. A. G. POLLARD.

Iodine metabolism of normal and thyroidectomised goats to which potassium iodide or iodised vegetable matter is administered. H. COURTH (Biochem. Z., 1931, **238**, 162—173).—In general the excretion of I in the milk, urine, and fæces of both normal and thyroidectomised she-goats to which daily doses of 10 mg. of I (as KI and as iodised radish leaves) are administered follows the same course. From 80 to 90% of the I given is excreted during the period of administration and the 8 days following. The form in which the I is given is immaterial. Of the I excreted most appears in the milk and urine and very little in the fæces. W. McCARTNEY.

Relation of manganese to the nutrition of the mouse. A. R. KEMMERER, C. A. ELVEHJEM, and E. B. HART (J. Biol. Chem., 1931, **92**, 623—630).—The growth of mice fed on a diet of cow's milk supplemented with Cu and Fe is improved and the abnormal œstrous cycle due to such a diet is corrected by the addition of Mn (0·01 mg. per mouse daily). F. O. HOWITT.

Effects of deprivation of manganese in the rat. E. R. ORENT and E. V. McCOLLUM (J. Biol. Chem.,

1931, **92**, 651—678).—Rats fed on a diet free from Mn as indicated by spectrographic analysis grow to maturity, the females reproducing normally when mated with normal males, but failing to suckle their young, which exhibit under-development. Male rats on the Mn-free diet show testicular degeneration and finally sterility. Mn is absent from the young of Mn-free mothers, whilst normal 15-day old rats contain Mn, which therefore passes through the placenta. Mn has no influence in blood regeneration. It is suggested that Mn is concerned with the hormone production of the anterior lobe of the pituitary gland. The Mn content of various vegetable and animal substances is investigated. F. O. HOWITT.

Inheritance of melanism in moths. A. W. McK. HUGHES (Nature, 1931, **128**, 496).—No signs of melanism appeared in *Selenia bilunaria* fed on foliage treated with Pb or Mn salts. L. S. THEOBALD.

Biochemical and physiological aspects of copper in animal nutrition. I. J. CUNNINGHAM (Biochem. J., 1931, **25**, 1267—1294).—Cu was determined in plants, foodstuffs, insects, marine animals, and in the organs of 12 species of land animals. Cu content of the skin and of the livers of rats increases in relatively small degree compared with additional Cu fed. Feeding additional Cu to the mother causes increased storage of Cu in the newly-born rat. There is a catalytic effect of Cu on the oxidation of "dopa" to melanin. Cu feeding has little or no effect on the storage or excretion of Fe by the rat. The stimulating effect of Cu on the formation of hæmoglobin in rats is confirmed. The use of milk diets for production of nutritional anæmia in rats is criticised. Feeding high amounts of $CuSO_4$ or $Cu(OAc)_2$ has no effect on the growth and reproduction of rats, whilst high amounts of verdigris stop reproduction. Rats receiving one fifth of the normal amount of Cu grow and reproduce normally. S. S. ZILVA.

Reversible coagulation in living tissue. IV. W. D. BANCROFT and G. H. RICHTER (Proc. Nat. Acad. Sci., 1931, **17**, 410—413).—When a coagulating solution is added to the nerve portion of a frog's muscle-nerve prep., the chronaxie at first decreases and then increases. The decrease corresponds with increasing irritability. These changes are qualitatively reversible when the coagulating agent is removed. The chronaxie of the frog's nerve passes through a max. at p_H 4·8, which is the isoelectric point of many proteins. The results indicate that anæsthesia is due primarily to reversible coagulation of the proteins of the brain and sensory nerves rather than to disturbance of the lipins. E. S. HEDGES.

Allergically active substance in ragweed pollen. A. STULL, R. A. COOKE, and R. CHOBOT (J. Biol. Chem., 1931, **92**, 569—588).—Desensitisation of passively sensitised sites affords a method superior to the direct skin test for the determination of allergically active substances. Successive extraction of the pollen of the giant ragweed (*Ambrosia trifida*) by cold abs., 95%, and 70% EtOH removes H_2O-sol. reducing substances, nitrogenous material, acidity, and inert gum, leaving an active prep. which by precipitation with $(NH_4)_2SO_4$ at p_H 4·6 followed by dialysis yields a protein substance responsible for all the activity of the pollen. F. O. HOWITT.

Action of saponins in pig feeding. K. SCHARRER and W. SCHROPP (Biochem. Z., 1931, **235**, 367—374).—Administration of saponin (0·25 g. per animal daily) during a period of 3 months had no unfavourable effects on the health of pigs, but the effect on the rate of increase in wt. and on the consumption of food was unfavourable. W. McCARTNEY.

Inherited taste deficiency. L. H. SNYDER (Science, 1931, **74**, 151—152).—Fox's observation (*ibid.*, **73**, 14) that certain persons independent of age, sex, or race cannot taste *p*-ethoxyphenylthiocarbamide is confirmed. This deficiency is apparently due to a single recessive gene. L. S. THEOBALD.

Nature of the biological action of alcohols. M. MITOLO.—See this vol., 1125.

Determination of alcoholic intoxication during life by cerebrospinal fluid analysis. A. O. GETTLER and A. W. FREIREICH (J. Biol. Chem., 1931, **92**, 199—209).—EtOH in blood and cerebrospinal fluid is steam-distilled, oxidised, and determined as AcOH. The EtOH contents of the blood, cerebrospinal fluid, and brain of alcoholic and non-alcoholic patients have been determined. The blood-EtOH varies irregularly, but the cerebrospinal fluid : brain ratio is 1·1—1·4 for intoxication, and increases as the brain-EtOH decreases. The vals. of this ratio at different levels of cerebrospinal fluid-EtOH are suggested as indices of the EtOH content of the brain, and therefore of intoxication. A. COHEN.

Toxicity of methyl alcohol following skin absorption and inhalation. C. P. McCORD (Ind. Eng. Chem., 1931, **23**, 931—936).—MeOH is toxic to animals either by absorption through the skin or by inhalation. There is no evidence of its oxidation to CH_2O in the body. H. A. PIGGOTT.

Pharmacology of ethylene glycol and its derivatives in relation to chemical constitution and physical-chemical properties. W. F. VON OETTINGEN and E. A. JIROUCH (J. Pharm. Exp. Ther., 1931, **42**, 355—372).—The antiseptic action, as judged by inhibition of yeast fermentation and formation of leuco-methylene-blue in milk, is only moderate in the unsubstituted glycols, but very marked with ethylene glycol Et ether and others, and runs parallel to decreased surface tension and an increased partition coeff. in an oil–water system. The irritant action runs parallel to the ability to precipitate proteins; the ability of 1 : 4-dioxan and ethylene glycol Bu ether to render muscle fibres opaque is also explained in this way. All the glycols have hæmolytic properties. 1 : 4-Dioxan is the least and ethylene glycol Bu ether the most toxic. P. G. MARSHALL.

Comparison of the toxicity of various heart-active pure compounds and fractions of *Digitalis purpurea* on the frog and cat. K. FROMHERZ and A. WELSCH (Arch. exp. Path. Pharm., 1931, **161**, 266—305).—An investigation of the pharmacological activities of 12 preps. including 5 glucoside preps., 4 pure glucosides, and 3 genins. The bearing of the results on the assay of *D. purpurea* is discussed.

W. O. KERMACK.

Action of "cinchophen." G. P. GRABFIELD and J. H. PRATT (J. Pharm. Exp. Ther., 1931, **42**, 407—439).—Administration of "cinchophen" (atophan) to non-gouty individuals does not cause a regular increase in the excretion of uric acid, nor does it appreciably alter the uric acid level in the blood, although it raises the concentration of uric acid in the urine. Some decomp. product, which gives a diazo-reaction, appears both in the blood and urine 2—21 hr. after administration of the drug, the mode of action of which is unknown. P. G. MARSHALL.

Therapeutic interference caused by isomerides of trypanocidal styrylquinoline derivatives. C. H. BROWNING, J. B. COHEN, K. E. COOPER, and R. GULBRANSEN (Proc. Roy. Soc., 1931, **B**, **109**, 51—57; cf. A., 1929, 1109).—6-*Acetamido*-2-p-*aminostyrylquinoline methosulphate* when prepared by condensation in presence of piperidine of the quaternary salt of the quinaldine derivative with the aldehyde (method I) is markedly greater in trypanocidal action and also different chemically and physically from the substance prepared by forming the quaternary salt by the addition of Me_2SO_4 or alkyl halide subsequent to condensation with the aldehyde, using $ZnCl_2$ as condensing agent (method II). Thus method I gives a substance, m. p. 270° (decomp.), which is unchanged on boiling with aq. NH_3, whilst one of m. p. 280° (decomp.) which yields the original base on boiling with aq. NH_3 is synthesised by method II as follows: *p*-nitrobenzaldehyde condensed with 6-acetamidoquinaldine in presence of $ZnCl_2$ gives 6-*acetamido*-2-p-*nitrostyrylquinoline*, m. p. 274—278°, reduced to 6-*acetamido*-2-p-*aminostyrylquinoline*, m. p. 224—226°, the *methosulphate* being formed on treatment with Me_2SO_4 in $PhNO_2$. This latter isomeride is not a true quaternary salt, but a loose mol. complex which, when administered with the former, produces therapeutic interference on testing for trypanocidal action in mice infected with *T. brucei*. That this complex formation is associated with a free NH_2-group in the quinoline nucleus is shown by its occurrence with 6-*amino*-2-p-*acetamidostyrylquinoline methochloride* (by method I, m. p. 299—300°) [A] and not with 6-*acetamido*-2-p-*acetamidostyrylquinoline methosulphate* [by method I or II, m. p. 295° (decomp.)] [B]. B is prepared by acetylation of the acetamidoaminostyrylquinoline and treatment of the 6-*acetamido*-2-p-*acetamidostyrylquinoline*, m. p. 312—314°, with Me_2SO_4 in $PhNO_2$, the product (by either method) yielding 6-*amino*-2-p-*aminostyrylquinoline methochloride*, m. p. 270—273° (decomp.), on hydrolysis with conc. HCl, the free *base*, m. p. 241—242°, of which is prepared by hydrolysis of 6-*amino*-2-p-*acetamidostyrylquinoline*, m. p. 216—218°, formed by condensation of *p*-acetamidobenzaldehyde and 6-aminoquinaldine. F. O. HOWITT.

Nature of chemotherapy. R. HILGERMANN (Arch. exp. Path. Pharm., 1931, **161**, 352—358).—Experiments are described in support of the view that chemotherapeutic agents act by destroying a fraction of the parasites and thereby liberating toxins which stimulate the production of antibodies. W. O. KERMACK.

Significance of liver-glycogen in liver function. III. Dextrose test. T. IKUSHIMA (Japan. J. Gastroenterol., 1931, **3**, 54—59).—The blood-sugar of rabbits was determined after injection of dextrose. After fasting, or after injection of adrenaline, strychnine, or phloridzin the blood-sugar rises to higher levels and persists longer after dextrose injections. Ligation of the bile duct has a similar effect. CHEMICAL ABSTRACTS.

Cytopathological study of acute and chronic morphinism in the albino rat. W. C. MA (Chinese J. Physiol., 1931, **5**, 251—278).—The effect of acute and chronic morphinism on muscular, epithelial, and nervous tissue has been examined. C. C. N. VASS.

[Failure of] potassium permanganate as a detoxicating agent in acute morphine, cocaine, and potassium cyanide poisoning. MUNTSCH (Arch. exp. Path. Pharm., 1931, **161**, 544—552).—In rabbits and rats $KMnO_4$ has no effect. W. O. KERMACK.

Action of sulphydryl, iron, and cyanide compounds on the oxygen consumption of living cells. S. M. ROSENTHAL and C. VOEGTLIN (U.S. Pub. Health Rep., 1931, **46**, 521—539).—Neither form of glutathione influences the inhibitory effect of cyanide on respiration, whilst methæmoglobin, Na Fe^{III} tartrate, and $Fe(NH_4)_2(SO_4)_2$ have a slight effect, although the last two compounds do not actually accelerate O_2 consumption, nor does glutathione alone. Glutathione and cysteine are slowly oxidised in presence of rat kidney, but not of liver, brain, or testicle tissue, whilst the rate of oxidation of the former is increased by blood-serum. Cyanide reacts with Fe compounds and S compounds of tissues as well as with the respiratory enzyme. P. G. MARSHALL.

Influence of poisonous gases on the pigment-excreting function of the liver and kidneys. II. Cyanogen. H. YAGATA (Japan. J. Gastroenterol., 1931, **3**, 80—84).—In rabbits the pigment-excreting function of the liver and kidneys is injured by HCN poisoning. Common liver poisons injure the kidneys so severely when acting with HCN that the liver pigment excretion increases. Kidney poisons alone increase the pigment excretion of the liver, but when accompanied by HCN they decrease the liver excretion. CHEMICAL ABSTRACTS.

Distribution of arsenic in the bones of the human body. H. POPP (Z. angew. Chem., 1931, **44**, 658—659).—In a fatal case of As poisoning in which death ensued 8 days after taking the poison 110·26 mg. of As were found in the bones of which about half was present in the tubular bones of the arms and legs and about 20% in the flat bones of the skull. In another case in which death occurred 12 hr. after taking the poison only 3·2 mg. of As out of 1907 mg. found in the body were found in the bones. A. R. POWELL.

Alleged caustic action of arsenious acid. P. ELLINGER (Arch. exp. Path. Pharm., 1931, **161**, 562—572).—The caustic action of H_3AsO_3 applied locally is not directly on the cells of the horny layer of the epithelium but primarily on the capillaries. W. O. KERMACK.

Acute poisoning by hydrogen arsenide. B. Kogan (Arch. exp. Path. Pharm., 1931, **161**, 310—324).—Clinical findings in patients are described.
W. O. Kermack.

Toxicity of acid lead arsenate to the larvæ of the Colorado potato beetle. C. H. Richardson and L. E. Haas (J. Econ. Entom., 1931, **54**, 732—736).—The lethal dose of acid Pb arsenate for *L. decemlineata* is 0·144 g. or 0·30 mg. per 1 g. body-wt. The val. for Paris green is approx. 0·10.
A. G. Pollard.

Behaviour of lead in the animal organism. II. Lead tetraethyl. R. A. Kehoe and F. Thamann (Amer. J. Hyg., 1931, **13**, 478—498).—The rate of absorption of $PbEt_4$ through the skin is rapid; from 0·1% in petrol such absorption is negligible. $PbEt_4$ is rapidly decomposed by tissue, so that after 1—2 weeks the Pb deposit resembles that of a H_2O-sol. Pb compound. Chemical Abstracts.

Detection of fluorine in chemico-toxicological analysis. A. Bruning and H. Quast (Z. angew. Chem., 1931, **44**. 656—658).—The material to be tested (25 g.) is thoroughly incorporated with 10 c.c. of 5% milk of $Ca(OH)_2$ and 10 c.c. of 10% $CuSO_4$ solution, the mixture is dried and calcined to remove org. matter. The residue is tested for F by the usual etching method. In cases of poisoning by fluorides the digestive organs, kidneys, and liver should be examined for F. A. Powell.

Industrial poisons. H. Gerbis (Z. angew. Chem., 1931, **44**, 640—645).—The effect of numerous industrial poisons is discussed. A. R. Powell.

Pharmacological action of iron: investigations on isolated organs. F. Hendrych (Arch. exp. Path. Pharm., 1931, **161**, 419—436).—Compounds containing Fe^{II} exert a paralytic action both on the whole animal and on isolated organs. Fe^{III} exerts a toxic effect which results from its precipitating action on protein. Stable complex Fe compounds such as hæmatin and ferrocyanide are without action on the animal organism, but compounds such as Na ferricitrate, although not toxic to the isolated organs, are highly toxic to the whole animal, presumably because in the latter case they give rise to Fe^{III}.
W. O. Kermack.

Comparison of the relative killing power of some colloidal metals on the schistosome *Cercariæ* of the human type. A. Hassan (J. Egypt. Med. Assoc., 1931, **14**, 405—414).—Fresh *Cercariæ* are killed in 1 hr. by the following dilutions of (Crookes') colloidal preps.; Bi, Fe, Ag, Mn, and Hg 1 in 4000; Cu and I 1 in 8000; As 1 in 20,000; Sb 1 in 40,000; Au 1 in 80,000, and Ca 1 in 100,000. $CaCl_2$ does not kill *Cercariæ* in 1 hr. at concentrations less than 1 in 20. W. O. Kermack.

Formation of sulphite and sulphide from sulphate in the intestine and their role in the purgative action of salts of sulphuric acids. W. Zorkendorfer (Arch. exp. Path. Pharm., 1931, **161**, 437—454).—The addition of sulphate to suspensions of fæces results in a partial reduction of the S to sulphide. An increase in the sulphide content of the fæces occurs after oral administration of sulphate. As, however, the purgative action of sulphates is not inhibited by the simultaneous administration of Fe salts, it is considered that the H_2S formed in the intestine plays only a subsidiary role in producing purgative action. Sulphite is present in the fæces, being formed partly by hydrolysis of org. compounds and partly by reduction of sulphates, but it is not the cause of the purgative action of the latter.
W. O. Kermack.

Measurement of the swelling power of swelling substances used in pharmacology. E. Klecker (Arch. exp. Path. Pharm., 1931, **161**, 5—608).—A simple apparatus is described whereby the swelling in H_2O of a substance is automatically registered, and swelling curves for various substances used as purgatives have been obtained. The losses of H_2O sustained as the result of filtration under 0·5 atm. pressure have also been determined. The results obtained give a measure of the efficiency of the substances as purgatives. W. O. Kermack.

Influence of X-rays on the acid–base equilibrium. D. H. Sprunt (J. Biol. Chem., 1931, **92**, 605—613).—X-Irradiation of the abdominal region of monkeys (*Macacus rhesus*) and dogs results in a decrease, sometimes preceded by a temporary increase, in total base of the blood and in acidic radicals other than HCO_3'. The Cl′, protein, P, and non-protein-N levels of the serum are unchanged. The decrease in total base is probably due to excretion of

Oxidative fermentation. K. Bernhauer (Oesterr. Chem.-Ztg., 1931, **34**, 159—164, 16[illegible]).—A lecture.

Honey catalase. C. C. Gillette (J. Econ. Entom. 1931, **24**, 605—606).—The presence of catalase in honey is confirmed. It is not produced by bees, but occurs in included pollen grains and arises from fermentation yeasts. Catalase is rapidly destroyed by heating 50% honey solutions at 75°, and less rapidly at lower temp. Catalase activity is directly correlated with the temp. to which honey samples have been exposed. A. G. Pollard.

Inactivation of catalase. III. Destruction of catalase by hydrogen peroxide. S. Morgulis (J. Biol. Chem., 1931, **92**, 377—383).—Catalase suffers loss of activity if insufficiently buffered. With adequate buffering, the catalase reaction is directly proportional to the enzyme concentration and independent of H_2O_2 concentration. With insufficient buffering, increasing H_2O_2 concentration lowers the rate of O_2 liberation, which also becomes less proportional to enzyme concentration. A. Cohen.

Trypanocidal action and toxicity to enzymes. J. H. Quastel (Biochem. J., 1931, **25**, 1121—11[illegible]).
Trypan-blue, trypan-red, and Bayer 205 are [illegible] fumarase. The free naphthylaminedisulphonic acids and their first s-carbamide derivatives are [illegible]. Toxicity, as in the case of trypanocidal action, begins to be apparent with the second, and is very marked with the third, carbamide derivatives (A., 1928, 10[illegible]). There is also a parallelism between substantivity to cotton and toxicity to fumarase. These derivatives are, however, not toxic to urease. Derivatives of the β-naphthylaminedisulphonic acids are much mor

toxic to fumarase than those of the α-acids. Fumarate "protects" fumarase from the toxic action of these derivatives. The presence of proteins diminishes or eliminates the toxic action of these derivatives.

S. S. ZILVA.

Role of the enzyme in the succinate–enzyme–fumarate equilibrium. H. BORSOOK and H. F. SCHOTT (J. Biol. Chem., 1931, **92**, 535—557).—The oxidation–reduction potential of the system was investigated by a Thunberg vac. micro-technique over a range of p_H 6·15—7·9, using a dehydrogenase prepared from ox-heart and -diaphragm. The molar potential is independent of the ratio of the two reacting substances, the reaction and the ionic strength of the solution: its val., —0·437 volt, is the same as that obtained with such catalysts as resting *B. coli* (A., 1924, i, 913) or enzymes from horse skeletal muscle (A., 1930, 1619). This potential corresponds with a standard free energy change at 25° for the reaction succinate'' $\longrightarrow$ fumarate'' $+2H^{\cdot}+2\epsilon$ of —20,140 g.-cal., agreeing with the theoretical val. of —20,460. Similar agreement is obtained between the theoretical and found val. for the heat of reaction. Hence the enzyme promoting the reaction functions as a perfect catalyst. For molar activity at 25° the standard free energy of succinate'' is —165,090 and that of fumarate'' is —144,630 g.-cal.

F. O. HOWITT.

Pyrrole as a catalyst for certain biological reactions. F. BERNHEIM and M. L. C. BERNHEIM (J. Biol. Chem., 1931, **92**, 461—469).—Washed liver tissue is able to oxidise lactic and citric acids when pyrrole is added, the pyrrole itself not being oxidised. Such a system oxidises lactic acid quantitatively to pyruvic acid; KCN and $K_4P_2O_7$ completely inhibit the reaction, indicating that, unlike methylene-blue, activation by an Fe complex is necessary. A latent period suggests a preliminary condensation of the pyrrole. F. O. HOWITT.

Respiration processes in plant organs. VIII. Dehydrogenating power of *Zea mais* in presence of plant acids as hydrogen donators and the antagonism between dehydrase and catalase. A. FODOR, L. FRANKENTHAL, and M. BILETZKY (Biochem. Z., 1931, **238**, 268—277).—The authors' previous results (A., 1930, 1064; this vol., 130) are extended, using enzyme extracts of three kinds of maize. All these extracts reduced methylene-blue in presence but not in absence of boiled yeast juice, without addition of donator. The amount of this self-reduction is increased by addition of methylglyoxal, K formate, malate, and succinate, is decreased by addition of citrate, lactate, tartrate, and oxalate, and is stimulated by addition of phosphate, the optimal p_H being 8·05. Phosphate at p_H 4—6 strongly inhibits. The same optimum is obtained in presence of donators. As considerable differences are obtained with different kinds of maize, the dehydrase action, catalase action, respiration, and germinating power of a number of different kinds of one and the same variety are studied and a theoretical explanation of the results is attempted. P. W. CLUTTERBUCK.

Plant oxidoreductases. III. Non-identity of plant aldehydrase and mutase. D. MICHLIN and B. SEVERIN (Biochem. Z., 1931, **237**, 339—342).—In vegetable enzyme preps. it is possible to obtain oxidoreductase entirely free from mutase (cf. A., 1929, 217). P. W. CLUTTERBUCK.

Oxidation of hexosediphosphoric acid by an enzyme from animal tissues. D. C. HARRISON (Biochem. J., 1931, **25**, 1011—1015).—An enzyme has been prepared from liver and muscle capable of oxidising hexosediphosphoric acid in presence of methylene-blue. It is distinct from the citric acid dehydrogenase of cucumber (A., 1929, 602) or of ox liver (A., 1928, 1281). S. S. ZILVA.

Dextrose dehydrogenase: an oxidising enzyme from animal tissues. D. C. HARRISON (Biochem. J., 1931, **25**, 1016—1027).—The enzyme can be obtained in clear cell-free solution, which can be filtered through a porcelain candle or through kieselguhr, by precipitation with $(NH_4)_2SO_4$ from aq. extract of "$COMe_2$-liver" (A., 1928, 1281) of the ox, sheep, cat, and dog. It oxidises dextrose in presence of methylene-blue to gluconic acid. The reaction is not inhibited by KCN, NaF, PhMe, or $CH_2I{\cdot}CO_2H$. Dextrose is not oxidised in presence of O_2 alone, but is when combined with Keilin's cytochrome–indophenol oxidase system. S. S. ZILVA.

Amylase from rice. D. V. KARMARKAR and V. N. PATWARDHAN (J. Indian Inst. Sci., 1931, **14A**, 47—50).—Rice-malt amylase is obtained by extracting the sun-dried malt powder, obtained after paddy has been steeped for 4 days at 24—25° and allowed to germinate, with 0·6% aq. $NaHCO_3$ and is precipitated with EtOH. It is less than $\frac{1}{4}$ as active as wheat-amylase and loses its activity after 15 days' continuous dialysis. The optimum temp. is 60°.

C. C. N. VASS.

Dialysis of some cereal amylases. V. N. PATWARDHAN and D. V. KARMARKAR (J. Indian Inst. Sci., 1931, **14A**, 51—57).—Prolonged dialysis of cereal amylases causes a decrease in activity. The amylases of wheat and rice, freed from electrolytes, retain their activities over several months. The enzymes are not adsorbed on the collodion membranes. On electro-dialysis through collodion membranes all amylases except wheat-amylase lose their activity.

C. C. N. VASS.

Protective substances for amylase. VIII. Takadiastase, malt-amylase, pancreatic amylase, and calcium. H. NAKAMURA (J. Soc. Chem. Ind. Japan, 1931, **34**, 265B—268B).—Inactivation of takadiastase, malt-amylase, and pancreatic amylase at 37—53° in KH_2PO_4 solution is prevented by the addition of small amounts of Ca at p_H 4·6—5·8, regardless of the particular salt used. This effect is not observed with any salt of K, Na, or Mg.

P. G. MARSHALL.

Determination and stability of urinary amylase. G. NØRBY (Compt. rend. Lab. Carlsberg, 1931, **18**, No. 7).—Urinary amylase is determined by determination of the maltose formed from starch under standard conditions by a modification of Hagedorn and Jensen's method. The amount of amylase excreted in 24 hr. is independent of the vol. of urine following controlled diuresis. Inactivation does not, as a rule, take place in the urinary passages, since

amylase is relatively stable between p_H 5·0 and 9·0. In acidosis or some types of kidney disease, when the urine is on the acid side of p_H 5·0, some inactivation may occur. Inactivation at temps. of 50·5—60·5° and [Cl′] of 0·079N does not follow a unimol. course. Dilution experiments with H_2O, saline, and inactivated urine indicate that the stability of urinary amylase is affected by other substances in the urine than NaCl. P. G. Marshall.

Validity of the viscosimetric and Wohlgemuth methods for the determination of amylase. L. C. Chesley (J. Biol. Chem., 1931, **92**, 171—176).—The activity of the same amylase solution measured on four different starches by the Wohlgemuth method varied from 100 to 2400%, and from 350 to 2100% when measured by the viscosimetric method. The discrepancies are attributed to the different digestibility of the starches caused by the variation in α- and β-amylose content. A. Cohen.

Activation and stabilisation of pancreas diastase by hæmatin. G. Cosack (Biochem. Z., 1931, **235**, 469—484; cf. Kollath, A., 1930, 963).—The activity of pancreas diastase is increased from about 6- to 10-fold by hæmatin and by other blood-pigments which contain iron. Hæmatin also extends the limits of reaction within which the diastase is active, the extension being moderate on the acid side but considerable on the alkaline. The influence of the hæmatin (which is not due to the substances which accompany it or only to the Fe which it contains) expresses itself chiefly as protection from destruction by O_2, but also as protection against the effects of heat. Such protection is given also, in a slight degree, by NaCl but not by hæmoglobin. W. McCartney.

Glutathione as activator of enzymic saccharification of starch. H. Pringsheim, H. Borchardt, and H. Hupfer (Biochem. Z., 1931, **238**, 476—477).—Pancreatic amylase (lipase-, trypsin-, and maltase-free) is activated equally by yeast complement and by glutathione (0·0001M). Cysteine also activates and analogous results were obtained with malt-amylase. P. W. Clutterbuck.

I. Sources of error in sugar determinations based on the reduction of solutions of cupric salts. II. Erroneous application of the method of Hagedorn and Jensen to the determination of sugar. III. Sources of error in the application of iodoacetic acid as an agent for the inhibition of fermentation. IV. Stability of glycolase. V. Activity of an invertase solution 19 years old. C. Neuberg and M. Kobel (Biochem. Z., 1931, **238**, 226—252).—I. In solutions containing $CCl_3·CO_2H$ sugars and closely related compounds cannot be determined by methods involving reduction of Cu salts, since the acid oxidises Cu_2O to CuO (cf. this vol., 873).

II. The Zn compound used in the Hagedorn and Jensen method for deproteinisation also precipitates hexosediphosphate and the hexosemonophosphates of Neuberg and Robison (but not sucrose- or trehalose-phosphoric acids). It follows that the method cannot be applied to solutions which contain hexose-mono- or -di-phosphate.

III. Since $CH_2I·CO_2H$ reacts with NH_2Ph, arginine carbonate, the Na salt of alanine, tryptophan, dihydroxyphenylalanine, and with substances which may occur in yeast extracts, an explanation of the inhibitory effect of the halogen acid on fermentation and of the occasionally observed disappearance of this effect is provided (cf. this vol. 263).

IV. Yeast preps. which had been kept for periods of up to 20 years are able to produce methylglyoxal from hexosediphosphate, although the amount of the older samples required is greater than that of the newer. Experiment also shows that glycolase is more stable than apozymase. Of the preps. only those not more than 3 years old were able to cause accumulation of pyruvic acid.

V. An invertase solution kept for 19 years in a brown glass-stoppered bottle at room temp. has lost none of its activity (cf. A., 1925, i, 336). W. McCartney.

Specificity of α-glucosidases. A. I. Virtanen (Biochem. Z., 1931, **235**, 490—491).—New results obtained by the author and also unpublished work of Myrback confirm Karstrom's finding that *B. coli* I hydrolyses maltose but not sucrose, and consequently contradict the results of Weidenhagen (this vol., 873), whose micro-organisms may have been in impure culture. W. McCartney.

Lipolytic systems. M. J. Galvialo and L. J. Simina (Biochem. Z., 1931, **238**, 24—43; cf. Falk and Nelson, A., 1912, i, 593).—Glycine, alanine, and aspartic acid apparently exert no lipolytic action. Leucine and glutamic acid exert a weak, and peptone in high concentration a perceptible, lipolytic action. The lipolytic action of peptone obtained from fibrin by digestion with gastric juice is strong. W. McCartney.

Relationship between chemical constitution and physiological action. III. Inhibitory action of certain synthetic urethanes on the activity of liver-esterase. E. Stedman and (Mrs.) E. Stedman (Biochem. J., 1931, **25**, 1147—1167).—Urethanes of the type which possesses physiological properties of the same kind as physostigmine possess the common property of inhibiting the activity of liver-esterase. This inhibitory action is exerted in high dilution. The following are the relative activities of the isomeric urethanes with Me butyrate as substrate. Hydrochlorides: Ph series, $m>p>o$; benzyl series, $m>p>o$; miotine series $m=p>o$. Methiodides: Ph series, $m\geq p>o$; benzyl series, $p>o>m$; miotine series, With tributyrin as substrate the following order of activity was obtained. Hydrochlorides: Ph series, $m>p>o$; benzyl series, $o>m>p$; miotine series, $m>o>p$. Methiodides: Ph series, $o>p-m$; benzyl series, $p>o>m$; miotine series, $o>p=m$. The inhibitory activity is greater in slightly alkaline medium than at p_H 6·8. In general, the methiodides exert a considerably smaller inhibitory effect than do the hydrochlorides. The relative inhibitory activities of the various urethanes do not correspond with their relative miotic activities. S. S. Zilva.

Proteolytic enzymes. VIII. Stability of the enzymes of malt. M. Sato (Compt. rend. Lab.

Carlsberg, 1931, **19**, No. 2).—The stability of the two peptidases of green malt (I and II) varies according to the extraction medium. Both I and II are stable in 44% glycerol, whilst the activity of I falls in 88% glycerol. Using the appropriate extraction medium enzyme solutions can be obtained with a ratio of activity of I : II between 7·3 : 1 and 0·08 : 1.

P. G. MARSHALL.

Nature of proteases. IX. Determination of the optimum p_H in the digestion of ovalbumin by frog-pepsin at 38°. N. P. PIATNITZKI (Z. physiol. Chem., 1931, **199**, 231—242; cf. this vol., 393).—The optimum for the digestion of coagulated ovalbumin at 38° by the gastric juice of the frog is 1·64—1·78, for extract of stomach substance 1·88—1·99, and for human gastric juice 1·44—1·72. The curves for p_H optimum for the pepsin of the frog and of man are similar.

J. H. BIRKINSHAW.

Complex nature of trypsin. E. ABDERHALDEN and E. SCHWAB (Fermentforsch., 1931, **12**, 559—571).—By successive adsorptions of a crude trypsin solution with Lloyd's reagent there were obtained (I) an enzyme solution not hydrolysing polypeptides in which tyrosine carried the CO_2H group, (II) a solution lacking acylase but attacking polypeptides in which leucine carried the CO_2H group, (III) a protease (exclusively). In the eluate from (I) tyrosine polypeptidase was present. For its elution tyrosine, gallic acid, and 3 : 4-dihydroxyphenylalanine were the most suitable.

J. H. BIRKINSHAW.

Adsorption affinity of the fractions with limited action in the enzyme-complex trypsin at varying p_H towards various ferric hydroxide gels. E. ABDERHALDEN and J. HEUMANN (Fermentforsch., 1931, **12**, 572—600).—A complete separation of carboxypolypeptidase from protease was not attained by the method of Waldschmidt-Leitz (adsorption on $Al(OH)_3$ gel). The separation of the enzyme fractions hydrolysing caseinogen, *dl*-leucylglycyl-*dl*-leucine, chloroacetyl-*dl*-leucine, and *dl*-leucyl-*l*-tyrosine, respectively, was compared after adsorption with different $Fe(OH)_3$ gels. With gel A at p_H 3·6, a separation of the protease from the other constituents was attained; gel B at p_H 3·6 showed a partial adsorption of the component hydrolysing chloroacetyl-*dl*-leucine, but the separation was incomplete. Gel C had a strong selective action; one adsorption at p_H 4 gave a 90% removal of the chloroacetyl-*dl*-leucine component and only 5% of that hydrolysing caseinogen. Gel D showed no special power of differentiation. Gels A and B were prepared by hydrolysis of $Fe(OEt)_3$ by H_2O and H_2O vapour, respectively, gel C by hydrolysis of $Fe(OEt)_3+FeCl_3$ in EtOH, and gel D according to Willstatter (A., 1924, ii, 767).

J. H. BIRKINSHAW.

Behaviour of dipeptides containing *l*-(—)histidine towards erepsin and trypsin-kinase. E. ABDERHALDEN and W. GEIDEL (Fermentforsch., 1931, **12**, 518—531).—The following dipeptides were prepared by ammation of the halogenoacylhistidine ester: *glycyl*-l-*histidine* (I), decomp. 130°, $[\alpha]_D$ + 12·78° (*glycollyl*-l-*histidine* as by-product); dl-*alanyl*-l-*histidine* (II), $[\alpha]_D^{19}$ +2·51°; dl-*valyl*-l-*histidine* (III), m. p. 115° (decomp.), $[\alpha]_D^{19}$ +1·83°; *dl*-leucyl-*l*-histidine (IV), $[\alpha]_D^{19}$ —3·28° (dl-α-*bromo*iso*hexoyl*-l-*histidine*, m. p. 117°, and its *Me* ester, m. p. 171°); *l*-histidine anhydride ($+H_2O$) (V), $[\alpha]^{20}$ —63·9°; l-*histidyl*-l-*histidine* (VI), $[\alpha]_D^{19}$ —3·56°; β-alanyl-*l*-histidine (VII) (*phenylcarbimido*-derivative, m. p. 226°). Trypsin-kinase hydrolysed none of the dipeptides, erepsin VI and very slightly I, II, III, IV, and VII. Carnosine (VII) was unattacked by an extract of pancreas powder.

J. H. BIRKINSHAW.

p_H optimum for the action of intestinal erepsin from various animals. M. I. RAVITSCH-SCHTSCHERBO (Fermentforsch., 1931, **12**, 546—558).—Aq. glycerol extracts of the material were employed, with peptone as substrate. The p_H optima for the intestinal peptase of the dog, ape, man, and pig were 7·77, 7·78, 7·85, and 7·88, respectively.

J. H. BIRKINSHAW.

Properties of the enzyme complexes on which the Abderhalden reaction is based. E. ABDERHALDEN and S. BUADZE (Fermentforsch., 1931, **12**, 465—508).—The action of the "defence" enzymes is accelerated by addition of serum, which in varying degree inhibits trypsin-kinase and cathepsin. H_2S favours A.R. enzyme but not trypsin action. Heavy metals inhibit the A.R. enzymes. Inactivated A.R. enzymes are not in general reactivated by addition of serum. Peptones of high mol. wt. injected into rabbits produced a positive A.R. enzyme reaction in 24 hr. and in dogs even sooner.

J. H. BIRKINSHAW.

Crystalline urease. III. Toxicity of crystalline urease. H. TAUBER and I. S. KLEINER (J. Biol. Chem., 1931, **92**, 177—185).—The min. lethal dose of cryst. urease (subcutaneous) to mice is 0·09 unit per g. body-wt. It is also toxic to rabbits, injected intravenously. Within 15 min. after injection, the blood-urea is completely converted into NH_3, to which the toxic effect is due. Tolerance is acquired by mice receiving a non-lethal dose.

A. COHEN.

Absorption spectrum of the component *c* of cytochrome. M. DIXON, R. HILL, and D. KEILIN (Proc. Roy. Soc., 1931, **B**, **109**, 29—34).—Cytochrome *c* was prepared from yeast (A., 1930, 1215) dissolved in a min. amount of alkali, and diluted. The cytochrome concentration of the solution (p_H 7·2—7·6) was determined by reduction and comparison with standard pyridine mesohæmochromogen solutions and also by determination of the Fe content (cf. this vol., 125). Following reduction by cysteine the ultra-violet absorption spectrum was determined, reduction by hyposulphite being used for the visible region. For the spectra of oxidised cytochrome the solution was made alkaline, so that autoxidation occurred on shaking with air (A., 1930, 1215). Both reduced and oxidised forms exhibit an intense absorption band in the extreme violet characteristic of hæmatin (cf. A., 1929, 1475). The reduced form alone exhibits an α-band at 550 mμ and a composite β-band at 520 mμ. Indications of a band at 260 mμ are due to the presence of a protein impurity.

F. O. HOWITT.

Co-zymase and adenylic acid. H. VON EULER and K. MYRBACK (Z. physiol. Chem., 1931, **199**, 189—199).—Moderate amounts of muscle-adenylic acid do not activate apozymase, nor is the activation by co-

zymase augmented by the addition of muscle-adenylic acid. Adenosinetriphosphoric acid shows a definite activation in large amounts, but it has only one tenth the power of the purest co-zymase. The activation may be due to co-zymase present as impurity.

J. H. BIRKINSHAW.

Effect of manganese, copper, and zinc on the growth of yeast. J. S. McHARGUE and R. K. CALFEE (Plant Physiol., 1931, 6, 559—566).—Small quantities of the sulphates of Cu, Mn, and Zn increased the dry wt. of yeast produced in cultures. Larger amounts decreased the growth or caused the death of the cells. Cu stimulated cell division, but the cells produced were smaller than in control cultures. The production of CO_2 by yeast was increased by Cu, Mn, and Zn, Cu being the most effective. Larger amounts of CO_2 were produced under anaerobic than under aerobic conditions. A. G. POLLARD.

Influence of ultra-violet light on the invertases. II. Role of tryptophan and yeast-gum. G. GORBACH and K. LERCH (Biochem. Z., 1931, 235, 259—266; cf. A., 1930, 640).—During dialysis the activity of yeast autolysates changes in proportion to the variations in tryptophan content. In contrast to tryptophan, yeast-gum does not absorb ultra-violet light selectively. W. McCARTNEY.

Mitogenetic radiation and mitogenetic effect. A. GURWITSCH (Naturwiss., 1931, 19, 423—424).—New experimental observations together with theoretical considerations seem to furnish a picture of the way in which the mitogenetic effect results.

W. GOOD.

Mitogenetic radiation. II. Yeast as an indicator of radiation. M. NAKAIDZUMI and H. SCHREIBER (Biochem. Z., 1931, 237, 358—379).—In 40 further induction experiments with germinating yeast, the authors were again (cf. this vol., 125) unsuccessful, in spite of using various methods, in detecting any so-called mitogenetic radiation.

P. W. CLUTTERBUCK.

Production of yeast-growth stimulants by moulds. I. *Aspergillus niger, Trichoderma lignorum*, and *A. clavatus*. H. SCHOPMEYER and E. I. FULMER (J. Bact., 1931, 22, 23—28).—In glycerol or sucrose media the above moulds produce a stimulant for *S. cerevisiæ*. The bios content of *A. niger* is examined. A. G. POLLARD.

Decomposition of hemicelluloses by micro-organisms. I. Nature, occurrence, preparation, and decomposition of hemicelluloses. II. Decomposition of hemicelluloses by fungi and *Actinomyces*. III. Decomposition of various hemicelluloses by aerobic and anaerobic bacteria. S. A. WAKSMAN and R. A. DIEHM (Soil Sci., 1931, 32, 73—95, 97—117, 119—139).—I. The general chemistry of hemicelluloses is discussed and an extensive bibliography given. The prep. and analysis of mannan, galactan, and xylan are recorded.

II. All fungi examined were able to decompose hemicelluloses, *Phycomycetes* being as active in this respect as the cellulose-decomposing species. Galactan was more resistant than mannan or xylan. *Actinomyces* were more active than fungi. The principal decomp. product is CO_2 and, in the case of fungi, small proportions of org. acids.

III. Many aërobic and anaerobic bacteria decompose hemicelluloses with the production of org. acids and mixtures of CO_2, CH_4, H_2, CO, N_2, etc. The nature of the gases produced by aerobes differs from that by anaerobes. Chemical purification tends to increase the resistance of hemicelluloses to bacterial decomp. The organisms concerned require available N for the synthesis of cell substances. The ratio, of hemicellulose decomposed to N consumed averaged 20—40 : 1. A. G. POLLARD.

Improved ferrocyanide-citrate agar for direct enumeration of colon-aërogenes organisms. F. O. TONNEY and R. E. NOBLE (J. Amer. Water Works Assoc., 1931, 23, 1202—1208).—Details for the prep. and use of this medium are given (cf. B., 1928, 318). C. JEPSON.

Differential tests for the colon-aërogenes groups. C. F. POE (J. Amer. Water Works Assoc., 1931, 23, 1218—1224).—Eosin-methylene-blue agar was found to be an excellent medium for differentiation. The Na citrate test gave almost perfect correlation with the Voges-Proskauer and Me-red tests with the aërogenes group and 77% with the colon group. The uric acid test gave unsatisfactory correlation for the colon group, and certain organisms exist for which the Voges-Proskauer and Me-red tests did not correlate. C. JEPSON.

Effect of silica gel on the assimilation of phosphorus by free nitrogen-fixing organisms. J. ZIEMIECKA (Rocz. nauk. Roln. Lesn., 1929, 22; Proc. Internat. Soc. Soil Sci., 1931, 4, 66—67).—SiO_2 gel favours the development of *Azotobacter* in the absence of sufficient P, but has no effect where the P supply is adequate. Aluminosilicic acid from kaolin does not affect the absorption of insol. phosphates by the organism. A. G. POLLARD.

Müntz' method [for the biological fixation of nitrogen]. A. P. FORJAZ (Rev. Chim. pura appl., 1930, 5, 99—102).—The presence of spectroscopically detectable traces of Mo, Ni, and Co in the root nodules of *Cytisus proliferus* suggests that an inorg. catalyst may be concerned in the fixation of N by *B. radicicola*.

H. F. GILLBE.

Oxidising power of the individual cell of *Nitrosomonas europæa*, Winogradsky. H. ENGEL (Arch. Mikrobiol., 1930, 1, 445—463; Bied. Zentr., 1931, 60A, 267).—The average C content of the single cell of *Nitrosomonas* is 0.50×10^{-10} mg. and its oxidising power 2.35×10^{-10} mg. N_2O_3 per hr. The oxidising power of a culture reaches an early max. and subsequently declines with age. The ratio N oxidised : C consumed is const. only in young cultures.

A. G. POLLARD.

Oxidases of killed acetic acid bacteria. I. D. MÜLLER (Biochem. Z., 1931, 238, 253—267).—When a suspension of *B. Pasteurianum* is dropped into 1C times its vol. of $COMe_2$ with stirring, a prep. is obtained which absorbs O_2 and oxidises added alcohols. EtOH and Pr$^{\alpha}$OH are most readily oxidised, Pr$^{\beta}$OH less readily, MeOH and ethylene glycol still less, dextrose only slightly, and glycerol and Ca

gluconate not at all. The living organisms oxidise $Pr^{\beta}OH$ to $COMe_2$, the amount representing 75% of that calc. from the O_2 absorption. The $COMe_2$ prep. also oxidises $Pr^{\beta}OH$ to $COMe_2$, the amount representing 100% of that calc. from the O_2 absorption. The extent of oxidation by the $COMe_2$ prep. is only 3—6% of that by the living organisms. A suspension of $COMe_2$-treated bacteria heated at 95° for 0·5 hr. is not able to oxidise $Pr^{\beta}OH$.

P. W. CLUTTERBUCK.

Enzymic synthesis of sucrose. O. OPARIN and A. KURSSANOV (Biochem. Z., 1931, **239**, 1—17).—Hydrolysis of Ca sucrosephosphate by invertase gives dextrose and lævulose as phosphate, the lævulose thus being stabilised in the *am*- and being unable to pass over into the β-form. In this way, after 40% of the material is hydrolysed, an equilibrium is set up depending on the synthetic action of the invertase. By the action of invertase and phosphatase or a solution of invert sugar and phosphate a synthesis of sucrose occurs amounting to 20% of the invert sugar.

P. W. CLUTTERBUCK.

Production and transformation of methylglyoxal by enzymes of the tubercle and Timothy-grass bacilli. M. KUROYA (Biochem. Z., 1931, **235**, 438—443).—Extracts obtained from cultures of the tubercle and Timothy-grass bacilli by shaking for 18 and 10 days, respectively, with $COMe_2$ produced methylglyoxal in yields of 18 and 36% of the theoretical from hexosediphosphate. The extract from the Timothy bacillus also dismuted methylglyoxal slowly. Hence the glyoxalase is neither destroyed nor completely freed from co-enzyme by treatment with $COMe_2$. One of the products of dismutation is lactic acid (29% yield, of which 40% is the *l*-form). In presence of co-mutase from yeast the dismutation proceeds as before, but is completed in one fifth of the time required when none is added and the yield of lactic acid (again 40% *l*-form) is more than doubled (66%).

W. MCCARTNEY.

Appearance of specific enzymes in the urine of tuberculous patients and of dogs after parenteral injection of protein of tubercle bacilli. E. ABDERHALDEN and H. MINGAZZINI (Fermentforsch., 1931, **12**, 542—545).—The urine contained a protease with a sp. action on tubercular lung tissue or on the protein of tubercle bacilli.

J. H. BIRKINSHAW.

Anatoxigenic substances and special characters of anæsotuberculin. G. FINZI (Atti R. Accad. Lincei, 1931, [vi], **13**, 235—240).—The advantages of iodised anæsotuberculin over crude tuberculin for diagnosing bovine tuberculosis are detailed.

T. H. POPE.

Determination of carbohydrates in bacteriological culture media. I. Application of the ferrocyanide reduction method to determine dextrose in peptone water. C. F. SCHMIDT, jun. (J. Bact., 1931, **22**, 31—48).—The ferrocyanide method is modified and a correction factor for the reducing action of peptone introduced.

A. G. POLLARD.

Transformations of iron in nature. III. Effect of carbon dioxide on the equilibrium in iron solutions. H. O. HALVORSON (Soil Sci., 1931, **32**, 141—165; cf. A., 1927, 425).—Under anaerobic conditions in dextrose or peptone media, heterotrophic micro-organisms may dissolve metallic Fe, and also dissolve and reduce $Fe(OH)_3$. These changes result from a decrease in the O_2 pressure and the formation of acid and may take place at reactions approaching neutrality. When CO_2 is formed under anaerobic conditions precipitation of $FeCO_3$ may occur. Fe bacteria are active only under conditions favouring spontaneous oxidation by chemical agencies. They do not reduce the Fe content of natural waters below that obtainable by purely chemical action under similar conditions. The conditions affecting the dissolution and precipitation of Fe by organisms are examined and discussed.

A. G. POLLARD.

Specific potency of certain cations with reference to their effect on bacterial viability. C. E. A. WINSLOW and E. T. HAYWOOD (J. Bact., 1931, **22**, 49—69).—The action of various cations on bacterial activity shows a general similarity, but each cation exhibits a "sp. potency" which is of the same relative order in low (stimulating) as in higher (inhibiting) concentration. Recorded sp. potencies are Na, 1; K, 1; Li, 3; Ba, 5; Mg, 9; Ca, 12; Mn, 400; Zn, 700; Cd, 3000. The bearing of these results on salt antagonism and on disinfection is examined.

A. G. POLLARD.

Antitoxic properties of certain phenols and their mode of action. L. VELLUZ (Compt. rend., 1931, **193**, 372—374).—Partly oxidised solutions of adrenaline or (less readily) adrenalone can inhibit the action of tetanus toxin in the guinea-pig; more conc. solutions of ephedrine or ψ-ephedrine do not possess this property. Such solutions do not cause adrenaline intoxication in the animal. In non-oxidised solutions no neutralisation of the toxin occurs.

C. C. N. VASS.

Physiology of internal secretion. (SIR) E. SHARPEY-SCHAFER (Nature, 1931, **128**, 441—452).—A lecture.

L. S. THEOBALD.

Internal secretions and human well-being. M. F. GUYER (Science, 1931, **74**, 159—166).—A review of the functions of the endocrine system.

L. S. THEOBALD.

Formation of adrenaline in the suprarenal gland. J. E. ABELOUS and R. ARGAND (Compt. rend., 1931, **193**, 369—372).—The medullary pulp of the suprarenal gland of the horse, after contact with air for 6 hr. in an alkaline medium, contains no adrenaline, whereas the cortical pulp contains more adrenaline than it did initially.

C. C. N. VASS.

Effect of ultra-violet radiation on the pressor action of adrenaline. D. J. VERDA, L. KNEER, and W. E. BURGE (J. Pharm. Exp. Ther., 1931, **42**, 383—386).—A solution of adrenaline hydrochloride (1 : 15,000) produced, after 35 min. irradiation, no pressor action but a marked depressor action, owing to destruction of the active substance.

P. G. MARSHALL.

Blood-sugar and antagonism of thymus and adrenal medulla. M. MESSINI (Arch. exp. Path. Pharm., 1931, **161**, 247—265).—In rabbits subcutaneous administration of thymus extract produces hyper-

glycæmia in a few hr. accompanied by a decrease in inorg. phosphates and frequently preceded by a slight hypoglycæmia. The hyperglycæmia caused by the administration of adrenaline is inhibited by the administration slightly previously or simultaneously of thymus extract, but there is no significant inhibition if the adrenaline is administered when the hyperglycæmic effect of the thymus is at its max. The thymus gland is probably involved in the regulation of carbohydrate metabolism. W. O. KERMACK.

Calorigenic action of adrenaline in frogs before and after hepatectomy. C. F. CORI and K. W. BUCHWALD (J. Biol. Chem., 1931, **92**, 367—375).—The O_2 consumption of immobilised frogs is increased by 51% in the 1st hr., 33% in the 2nd hr., and returns to normal in the 3rd hr. following injection of adrenaline. The additional amount of O_2 consumed approximates to the quantity required assuming the conversion into glycogen of 25% of the extra lactic acid produced under anaerobic conditions. After hepatectomy, adrenaline causes a smaller increase in O_2 consumption. The calorigenic action of adrenaline is due to the conversion of increased lactic acid into glycogen. A. COHEN.

Action of adrenaline and insulin in frogs under anaerobic conditions. K. W. BUCHWALD and C. F. CORI (J. Biol. Chem., 1931, **92**, 355—366).—The sugar and lactic acid content of frogs (whole bodies) is increased by injection of adrenaline under anaerobic as well as aerobic conditions. The effect is therefore not due to vasoconstriction and diminished supply of O_2 in muscle, but to acceleration of muscle glycogenolysis. Insulin, given 18—42 hr. before adrenaline, prevents aerobic and anaerobic increase in sugar and lactic acid. This is attributed to inhibition of liver glycogenolysis. A. COHEN.

Crystalline insulin. D. A. SCOTT (J. Biol. Chem., 1931, **92**, 281—288).—Details are given for the isolation of cryst. insulin from amorphous active preps. by precipitation with NH_3 at the isoelectric point from solution in 0·1N-HCl buffered with phosphate. Insulin so obtained from ox, sheep, hog, and fish had the same physical characteristics as a repeatedly recryst. prep. The possible causes of the uniformly high physiological activity (four samples possessed a potency of 27·0—27·3 units per mg.) are discussed. A. COHEN.

Presence of insulin in urine. K. UBERRACK and F. ZELL (Biochem. Z., 1931, **239**, 42—47).—Collip's method may be used for the detection of insulin in urine provided that concentration takes place in vac. at 40° but not at 60°. Insulin cannot be detected in the urine of insulin-resistant, hyperinsulinised diabetics. P. W. CLUTTERBUCK.

Action of acid alcohol on insulin. A. F. CHARLES and D. A. SCOTT (J. Biol. Chem., 1931, **92** 289—302; cf. A., 1929, 1495).—Cryst. insulin dissolved in 0·1N-HCl in 96% MeOH loses 92% of its activity in 16 hr. at 20°. Reactivation by NaOH does not exceed 60% over a fairly wide range of alkali concentration. The recovered insulin is identical with the original. Treatment with acid MeOH for a short period yields an equally potent product containing MeOH, probably as an adsorption compound. It is not regarded as an ester (cf. *loc. cit.*). Analytical data suggest that inactivation is accompanied by N-methylation. A. COHEN.

Action of proteolytic enzymes on insulin. W. CORNELI (Z. physiol. Chem., 1931, **199**, 217—220).—Insulin is not attacked by dipeptidase, aminopolypeptidase, protaminase, or carboxypolypeptidase, but activated proteinase and activated papain completely destroy its activity. J. H. BIRKINSHAW.

Action of successive small doses of insulin on the blood-sugar of normal and suprarenalectomised rabbits. B. BASILIOU and F. ZELL (Biochem. Z., 1931, **231**, 427—437).—Injection intravenously or subcutaneously of insulin in successive small doses in fed or in starved rabbits led to no important increase of blood-sugar. After extirpation of one or both of the suprarenals the hypoglycæmic action of successive small doses of insulin is increased. P. W. CLUTTERBUCK.

Hypoglycæmia and the reticulo-endothelial system. R. MESSINA (Arch. Farm. sperim., 1931, **52**, 197—216; cf. this vol., 516).—Injection of trypan-blue lowers the tolerance of rabbits to insulin. In contrast to the behaviour of normal organisms, the administration of dextrose to the trypanised animal, after injection of insulin, raises the depressed blood-sugar level. Adrenaline after insulin is, however, no longer able to raise the blood-sugar level. It is supposed that adrenaline normally stimulates glycogenolysis and dextrose stimulates pancreatic secretion of insulin, but that trypanisation interferes with cellular carbohydrate metabolism.

R. K. CALLOW.

Mechanism of the action of insulin. II. Effect of insulin on the ammonia content and ammonia formation in the liver. H. SCHWARZ and M. TAUBENHAUS (Biochem. Z., 1931, **239**, 201—208).—The NH_3 contents of the livers of white mice are obtained by grinding part of the liver with borate ("actual" content) and by grinding the rest with Tyrode solution and keeping. In Tyrode solution a rapid formation of NH_3, but no change in urea, occurs. Under the action of insulin, a considerable decrease of the "actual" NH_3 content is obtained.

P. W. CLUTTERBUCK.

Action of hormones, especially thyroxine, on fat-hydrolysing enzymes. O. MUHLBOCK and C. KAUFMANN (Biochem. Z., 1931, **238**, 377—390).—Tables summarise the inhibitions, if any, of the lipases of tissues, pancreas, liver, placenta, and serum by a number of samples of the hormones of pituitary, thyroid, pancreas, suprarenal, and ovary. Of these, only thyroxine showed any marked effect, its action being due to an affinity of the hormone for the lipolytic enzyme. The enzymic synthesis of fat is not affected by addition of thyroxine.

P. W. CLUTTERBUCK.

Effect of hypophysectomy on gestation in the rat. R. I. PENCHARZ and J. A. LONG (Science, 1931, **74**, 206).—Complete removal of the pituitary in the rat is followed by death, without parturition, at the end of a long pregnancy. L. S. THEOBALD.

Use of the uterus of certain ruminants for the determination of the oxytocic activity of posterior pituitary extracts. H. Penau, M. Prudhomme, and H. Simonnet (J. Pharm. Chim., 1931, [viii], **14**, 163—168).—The uterus of the sheep in place of that of the guinea-pig is recommended. F. O. Howitt.

Female sexual hormone. VI. Second crystalline hormone from urine of pregnancy and its physiological and chemical relations to crystallised follicular hormone. A. Butenandt and F. Hildebrandt (Z. physiol. Chem., 1931, **199**, 243—266; cf. A., 1930, 1480).—Marrian's hormone hydrate, $C_{18}H_{24}O_3$, was obtained (*a*) by his method from a $CHCl_3$ extract of urine of pregnancy or from a technical product, (*b*) from the residual oil obtained in Butenandt's method for isolating the follicular hormone $C_{18}H_{22}O_2$. The hormone hydrate, m. p. 276° (as obtained by Marrian, m. p. 269°), $[\alpha]_D$ +34·4° [*Me* derivative (with diazomethane), m. p. 169°, $[\alpha]_D$ +34·7°], on distillation with $KHSO_4$ yields the hormone [*semicarbazone*, m. p. 245—246° (decomp.)], which was also obtainable from the residues of the extraction with 50% aq. EtOH in Marrian's method. The physiological activity of the hydrate is much lower than that of the hormone and decreases with purification, the product of m. p. 276° having only 2% of the activity of the hormone. The hormone prepared by distillation from the hydrate is fully active. The two forms hormone and hydrate are not interconvertible by any of the steps in the isolation; both must therefore be present in urine of pregnancy. J. H. Birkinshaw.

Colorimetric determination of ovarian hormone (menformon). S. Kober (Biochem. Z., 1931, **239**, 209—212).—A colour reaction for menformon is described and adapted for its colorimetric determination. P. W. Clutterbuck.

Practical test for potency of extract of corpora lutea. R. G. Harris and D. M. Newman (Science, 1931, **74**, 182).—Daily injections of 0·25 c.c. of corpus luteum extract for 9—14 days produce in the vaginal mucosa of mice histological changes characteristic of pregnancy which can be used as a test of potency. L. S. Theobald.

Vitamin-*A* content of liver oil. H. von Euler and P. Karrer (Naturwiss., 1931, **19**, 676).—From flounder (*Hippoglossus*) liver oil a vitamin-*A*-rich prep. is obtained, which in the crude state has the equiv. of 6000 units by the $SbCl_3$ reaction. By fractionation at low temp. and fractional adsorption a pure prep. with the val. of 10,000 units has been obtained. A. J. Mee.

Liver oils of fish and birds. B. von Euler and H. von Euler (Svensk Kem. Tidskr., 1931, **43**, 174—178).—Light petroleum extracts of the livers of a no. of fish and of the livers and subcutaneous fat of a no. of sea-birds contain vitamin-*A*. Carotene was detected in one extract. No vitamin-*A* is formed from carotene by shark liver. A. Renfrew.

Vitamin-*A* and the antimony chloride reaction. A. Emmerie, M. von Eekelen, and L. K. Wolff (Nature, 1931, **128**, 495—496).—Treatment of a vitamin-*A* prep. from cod-liver oil or cow's liver with furan, methylfuran, pyrrole, indole, or skatole before the addition of $SbCl_3$ gives a purple colour; the 610 mμ band disappears, but that at 572 mμ remains unchanged. L. S. Theobald.

Mittelmann process for treating fish-livers. J. A. Lovern, R. H. Creed, and R. A. Morton (Biochem. J., 1931, **25**, 1341—1345).—Mittelmann's observation that the chromogenic val. of fresh cod-liver oils sometimes increases on keeping for a short time is confirmed. No cod-liver oil failed, however, to respond qualitatively to the $SbCl_3$ test. With codling-, cod-, and monk-liver oils the chromogenic vals. may increase on oxidation. Steamed cod-liver oil indicated the same tendency towards an increase in the blue val. as the autoclaved oils. The ultra-violet band discloses no qual. differences between autoclaved liver oils and oils prepared by other processes. Liver oils probably contain two distinct chromogens. S. S. Zilva.

The antimony trichloride colour test and the ultra-violet absorption of liver oils and concentrates. A. E. Gillam and R. A. Morton (Biochem. J., 1931, **25**, 1346—1351).—Liver oils contain two chromogens which give with $SbCl_3$ coloured substances with absorption max. at 606 and 572 mμ, respectively. In concentrates these max. are displaced to 620 and 583 mμ. There is no parallelism between the intensity of the 606 mμ band and the intensity of the 328 mμ characteristic of vitamin-*A* and given by the oil alone. The 572 mμ chromogen and the substance responsible for the 328 mμ are probably identical. The blue colour given by rich oils and concentrates is often much deeper than would be expected on the basis of correlation between blue colour and ultra-violet absorption. S. S. Zilva.

Specificity in tests for vitamin-*A*. A new conception of the chromogenic constituents of fresh and aged oils. I. M. Heilbron, A. E. Gillam, and R. A. Morton (Biochem. J., 1931, **25**, 1352—1366).—Monk-liver, codling-liver, and cod-liver oils with abnormally high and inconst. 572 mμ/606 mμ intensity ratio showed a threefold increase in the 606 mμ but no significant increase in the 572 mμ chromogen on treatment with O_3, H_2O_2, and Bz_2O_2. A number of oils which have shown a preponderance of the 572 mμ over the 606 mμ chromogen showed an increase in the concentration of the 606 mμ chromogen after several months' storage; the ultra-violet absorption exhibited a very much smaller increase in intensity, whilst the 572 mμ band was little changed. In some of these oils the "ageing" process could be carried further by treatment with O_3 and H_2O_2: in others in which the max. "ageing" was reached this treatment led to gradual destruction of both chromogens as manifested by decreased absorption at 572 mμ and 606 mμ in the colour test and 328 mμ in the oil alone. In some fresh oils the 606 mμ not only predominates slightly over the 572 mμ, but is present at its full intensity, ozonisation effecting no increase. When a small quantity of the $SbCl_3$ reagent is added first and the remainder after a minute, the intensity of 565—575 mμ band remains the same as when the whole reagent is added at once, whilst the 600—620 mμ becomes very much reduced in intensity. S. S. Zilva.

Distribution of the vitamin-*B* complex. II. Root vegetables. M. H. Roscoe (Biochem. J., 1931, 25, 1205—1212).—The vitamin-B_1 content of carrot is about 1/5 that of yeast (dry wts.), equal to that of the less good leafy vegetables, and better than that of egg-yolk or milk. Turnip is not quite so rich in the vitamin and potato is poor, being only 1/15 as rich as yeast. Carrot is 1/5 as good a source of vitamin-B_2 as yeast and about equal to milk, meat, and the less good leafy vegetables. Turnip is less potent, having the same potency as egg-yolk and wheat germ. Potato has a low content of this vitamin, comparable with that of the cereals and pulses. Potato-starch contains small amounts of vitamin-B_1 and -B_2. New spring carrots contain no more vitamin-B_1 or -B_2 than do old ones which have been stored throughout the winter. Vitamin-B_1 and -B_2 in carrots are not rendered more available to the animal by steaming for 2—3 hr. Vitamin-B_1 requirements of the rat do not seem to be related to the total amount of food consumed. S. S. Zilva.

Determination of vitamin-*A* in cod-liver oils biologically, chemically, and physically. K. H. Coward, F. J. Dyer, R. A. Morton, and J. H. Gaddum (Biochem. J., 1931, 25, 1102—1120).—The discrepancy between spectrophotometric measurements of the blue solutions obtained with cod-liver oil and $SbCl_3$ as well as of the oil itself and the biological measurements, as obtained by resumption of growth in rats, are much larger than the known sampling error of the biological test. The best agreement of the biological results was obtained with the figures given by the measurement of the 328 mμ absorption band of the oil and with the Lovibond blue vals. given by the unsaponifiable fraction of the oil, especially when the oils examined were fresh. The measurements of the 572 mμ and 606 mμ bands of the blue solutions obtained with the oils and $SbCl_3$ gave less good agreement. The Lovibond blue vals. obtained with the oils themselves gave the least satisfactory agreement with the biological method. S. S. Zilva.

Pigmentation of the liver of the monk (or angler) fish. J. A. Lovern and R. A. Morton (Biochem. J., 1931, 25, 1336—1340).—The liver contains irregular deposits of a red fat-sol. pigment which is not of a carotenoid type and was not previously found in other fish livers. It acts as a chromogen towards $SbCl_3$. S. S. Zilva.

Fate of carotene after absorption in the animal organism. B. Ahmad (Biochem. J., 1931, 25, 1195—1204).—In the case of rats carotene is absorbed much better when fat is present in the diet than when it is absent. There is also imperfect absorption in the case of cats fed on a diet of lean meat and separated milk. Spectroscopic and colorimetric examinations show that while the extracted pigment from fæces of rats fed on carotene and a diet free from vitamin-*A* is entirely due to carotene, the oil extracted from the contents of the cæcum contains a substance resembling vitamin-*A* (band at about 325 mμ). Carotene is not converted into vitamin-*A* by the action of intestinal bacteria or by incubation with liver tissue *in vitro*. Carotene is not converted in the liver during periods up to 17¾ hr. into vitamin-*A* by perfusing the organ in cats in which reserves of the vitamin had been depleted. Oral administration of large doses of carotene to cats with depleted vitamin-*A* reserves did not result in the appearance of vitamin-*A* in the liver or blood up to 40 hr. The pigment that entered the tissues is converted into other substances. S. S. Zilva.

Action of vitamin-*B* and insulin on disturbances of carbohydrate metabolism in *B*-avitaminosis. J. A. Collazo and C. Pi-Suner Bayo (Biochem. Z., 1931, 238, 335—350).—In *B*-avitaminosis, the blood-sugar, blood-lactic acid, and muscle-phosphate are increased and the glycogen and glutathione contents of blood and organs are decreased. Vitamin-*B* (yeast autolysate) has a general curative influence and cannot be replaced by insulin. P. W. Clutterbuck.

Influence of the ration of the cow on the vitamin-B_1 and vitamin-B_2 content of milk. C. H. Hunt and W. E. Krauss (J. Biol. Chem., 1931, 92, 631—638).—The milk shows a progressive increase in vitamin-B_2 content when the cows are fed on (*a*) dry feed, (*b*) over-mature pasture, and (*c*) early pasture, indicating that vitamin-B_2 is synthesised during the rapid growth of grass and is dissipated as the plants mature. The vitamin-B_1 content shows a similar series but less markedly. F. O. Howitt.

Effect of carbohydrates on the development of polyneuritic avitaminosis in pigeons. B. Janovskaya (Biochem. Z., 1931, 238, 125—130).—Experiments on pigeons fed with vitamin-*B*-free diets almost identical with those of Randoin and Simonnet (Compt. rend., 1924, 179, 700) show that absence of carbohydrates does not prevent avitaminosis, although the abundance of fat by which they are replaced may prolong life. The diets given by these authors were probably not quite free from vitamin. W. McCartney.

Vitamin-*C* in the orange and the grape fruit. M. F. Bracewell and S. S. Zilva (Biochem. J., 1931, 25, 1081—1089).—The vitamin-*C* content of the juice is the same whether the orange or grape fruit is picked at the beginning or at the end of the season. There is no marked loss of vitamin-*C* when the fruit is stored under ordinary conditions at about 15° for about 2 months. The conditions of cultivation, origin of stock, age of tree, soil, etc. do not affect the vitamin-*C* content of the orange or grape fruit. The Duncan variety of grape fruit (on one test only) is slightly more active than the Marsh or Florida varieties. The vitamin-*C* content of the grape fruit is rather higher than that of the Jaffa orange. There is no correlation between the sol. solids, acid content, p_H of the juice, and its antiscorbutic potency. S. S. Zilva.

Vitamin-*C*. IV. T. Matsuoka (J. Agric. Chem. Soc. Japan, 1931, 7, 19—28).—Vitamin-*C* was produced in 3 days by germination of rice under a 1000-watt electric lamp at 28—30°. Chemical Abstracts.

Effects of alkali disintegration on the vitamin content of cereal straws. H. Iwata (J. Sci. Agric. Soc. Japan, 1931, No. 326, 37—45).—Vitamin-*A*

and -*B* in barley-, wheat-, and rice-straw are more stable towards 1% $Ca(OH)_2$ than 1% NaOH.
CHEMICAL ABSTRACTS.

Vitamin-*D* problem. II. Optical rotation of vitamin-*D*. E. H. REERINK and A. VAN WIJK (Biochem. J., 1931, **25**, 1001—1010).—The rotation of ergosterol shows a linear dependence on its degree of transformation on irradiation above 284 mμ. Long-wave irradiation therefore gives rise to one reaction product only (A., 1930, 256). Rotation of vitamin-*D* is calc. to be $[\alpha]_D$ +66·7°±2·7 (in Et_2O). Cryst. ergosterol-free preps. of vitamin-*D* have been obtained by treatment with digitonin and recrystallisation from Et_2O. The properties of these preps. vary.
S. S. ZILVA.

Vitamin-*D*. III. E. TAKAMIYA (J. Agric. Chem. Soc. Japan, 1930, **6**, 967—974).—A solution of ergosterol in olive oil was antirachitic for mice, although excessive ozonisation diminished the activity. Vitamin-*D* may be a mono-ozonide of ergosterol.
CHEMICAL ABSTRACTS.

Vitamin-*D*. I. Evaluation in animal experiments. F. HOLTZ, F. LAQUER, H. KREITMAIR, and T. MOLL (Biochem. Z., 1931, **237**, 247—275).—Biological methods are described for evaluation of ergosterol preps. which permit the determination of both the antirachitic principle and the calcinosis factor which causes the deposition of Ca in vessels and organs when a large overdose of ergosterol is given. An antirachitic unit is defined as the smallest daily dose which when injected into rats for 14 days under determined conditions completely protects 80% of the animals from rickets. The animals must increase in wt. in the experimental period by at least 5 g. The calcinosis factor is determined in mice and defined as the smallest daily dose per animal which after 10 injections causes a decrease in wt. of more than 2·5 g. or the death of the animal, the majority then showing deposition of Ca in the kidneys. The ratio of the two vals. gives the therapeutic index of the vitamin-*D* prep. P. W. CLUTTERBUCK.

Effect of irradiated ergosterol on composition of gastric and pancreatic juices. W. BAUER, A. MARBLE, S. J. MADDOCK, and J. C. WOOD (Amer. J. Med. Sci., 1931, **181**, 399—413).—Cl′ was decreased, CO_3' increased, the fixed base content was unaffected. Free HCl was reduced in 3 of 4 cases, and pancreatic enzyme activity in 1 case. CHEMICAL ABSTRACTS.

Comparative value of irradiated ergosterol and cod-liver oil as a prophylactic antirachitic agent when given in equivalent dosage according to rat units of vitamin-*D*. D. J. BARNES, M. J. BRADY, and E. M. JAMES (Amer. J. Dis. Children, 1930, **39**, 45—58).—Cod-liver oil is the more effective.
CHEMICAL ABSTRACTS.

Influence of solvents on the activation of ergosterol. C. E. BILLS, E. M. HONEYWELL, and W. M. COX, jun. (J. Biol. Chem., 1931, **92**, 601—604).—0·1% EtOH, Et_2O, and *cyclo*hexane solutions of purified ergosterol, $[\alpha]_D^{20}$ −132° in $CHCl_3$, were irradiated and the vitamin-*D* activity–irradiation period curve was plotted for each solvent. The time of attainment of max. activity and its val. for the three solvents were : EtOH, 22·5 min., 250,000 units; *cyclo*hexane, 27 min., 330,000 units; Et_2O, 4 hr. 12 min., 710,000 units. The decline in activity with continued irradiation is most marked in EtOH and least in Et_2O.
F. O. HOWITT.

Fundamental nature of vitamin-*D* action. J. P. MCGOWAN, I. J. CUNNINGHAM, and D. W. AUCHINACHIE (Biochem. J., 1931, **25**, 1295—1303).—The probable mode of action of vitamin-*D* in the cure and prevention of rickets is the setting-free of inorg. phosphate from the body-lipins.
S. S. ZILVA.

Effect of sweetening agents on biocatalysts (vitamins, enzymes, etc.) and on metabolic processes. I. B. BLEYER and F. FISCHLER (Biochem. Z., 1931, **238**, 212—215).—Saccharin has no deleterious effect on the functions of vitamins.
W. MCCARTNEY.

Influence of acetic, propionic, *n*-butyric, and sulphuric acids and of potassium acetate on the elongation of primary roots of seedlings of white lupin. M. COGGESHALL (Plant Physiol., 1931, **6**, 389—445).—The growth of white lupin roots in nutrient solutions was retarded by additions of H_2SO_4, propionic and *n*-butyric acids, and KOAc to extents which increased with rising concentration until further growth ceased. With increasing concentration of AcOH the retarding effect was interrupted by a slight stimulative effect at an intermediate range of concentration. During a recovery period in which treated roots were washed and replaced in a normal nutrient solution, a definite stimulation was apparent in roots treated with propionic acid, AcOH, and KOAc, the effect increasing in the order of substances named. The p_H, whilst definitely a contributory cause, cannot be regarded as the index of toxicity of the various solutions. A. G. POLLARD.

Seasonal changes in total, soluble, soluble protein, non-protein, and insoluble nitrogen in shoots of Bartlett pear. A. S. MULAY (Plant Physiol., 1931, **6**, 519—529; cf. this vol., 990).—Periodical analyses of bark and wood are recorded. With the commencement of new growth the bark has a high total N content, which falls as growth proceeds and subsequently rises to a max. in winter. The insol. fraction is mainly affected by seasonal changes. In the wood, changes in total N are similar, but the seasonal fluctuations depend principally on changes in the sol. N portion. Sol. protein, which forms only a small fraction of the total N both in bark and wood, reaches high proportions in late summer and autumn and min. vals. in winter and spring.
A. G. POLLARD.

Carbohydrates and carbohydrate metabolism of foliage. I. Increase in the sucrose content during withering. H. SCHROEDER and F. HERRMANN (Biochem. Z., 1931, **235**, 407—424).—When foliage (*Tropæolum majus*) withers its sucrose content increases, but the amount of the sugar produced does not correspond with that of the starch which disappears. It is consequently possible that the dextrose and lævulose undergo rearrangement in the cells of the leaves. W. MCCARTNEY.

Consumption of alcohol during respiration of peas. M. F. BUGAJEVSKY (Biochem. Z., 1931, **238**,

60—66).—The consumption during respiration of the EtOH previously stored in them by germinating peas is inhibited by HCN, and further accumulation of EtOH then occurs. At 40° the consumption is more intense than at 16—20°. The HCN apparently interferes with the action of the zymase after all the Fe present has been bound. Both PhMe and $CHCl_3$ inhibit respiration and the latter also inhibits fermentation. In a normal atm. non-germinating peas in which the respiratory enzyme is damaged continue to accumulate EtOH until the cells are poisoned and autolysis occurs. W. McCartney.

Frost precipitation of proteins of plant juice. R. Newton and W. R. Brown (Canad. J. Res., 1931, **5**, 87—110).—Precipitation of the proteins in juice extracted from the leaves of unhardened wheat is max. after 5 hr. exposure at $-7°$ and is reduced by sucrose or dextrose up to 8% concentration. Precipitation by dil. acids and bases, as determined microscopically, reaches a max. at p_H 5·1 and 7·3, respectively, and is reduced by sucrose, which also reduces "salting out." The removal of natural electrolytes by dialysis increases frost precipitation. A. Renfrew.

Comparative characteristics of the proteins of members of the *Malvaceæ*. A. N. Beloserski (Bull. Univ. Asie centr., 1929, **18**, 1—4).—*Hibiscus cannabinus*, *H. esculentus*, *Abutilon avicennæ*, and *Althæa nudiflora* contain some globulins sol. in 2% and others sol. in 8% NaOBz solution; the three first-named contain also H_2O-sol. proteins. Details are given of the N, S, histidine, arginine, tyrosine, and lysine contents. H. F. Gillbe.

Ensilage under the pressure of carbon dioxide produced by the plants. F. Weckbrodt (Landw. Versuchs-Stat., 1931, **112**, 161—189).—Silage produced from various crops in sealed vessels is examined. The rate and quantity of CO_2 production varied with the nature of the crop, its stage of development, and the season. A. G. Pollard.

Positive gas pressure in poplar. F. C. Gates (Science, 1931, **74**, 153; cf. this vol., 886).—Three trees of *Populus balsamifera*, L., showed a positive gas pressure on insertion of a borer; one of the trees was sound throughout. Many borings in *P. tremuloides*, Michx., and *P. grandidentata*, Michx., revealed no such pressure. L. S. Theobald.

Gases contained in certain brown algæ. S. Colla (Atti R. Accad. Lincei, 1931, [vi], **13**, 232—234).—The gases of *Cystoseira abrotamifolia*, Ag, and *Sargassum linifolium* (Ag), Turn, collected 1 m. below the surface of the sea, are similar to those of other brown algæ, but contain less O_2 (max. about 38%) than those of *Fucus* and *Valonia*, which live nearer the surface (cf. A., 1930, 1072). T. H. Pope.

Effect of light on pigment formation in apples. G. W. Pearce and L. R. Streeter (J. Biol. Chem., 1931, **92**, 743—749).—The region of 360—450 mμ of the solar spectrum with an optimum at 410 mμ is the most effective for the development of the anthocyanin pigments in the McIntosh apple. It is suggested that light energy transforms a flavanol into the red pigment. F. O. Howitt.

Chemical effect of a Mendelian factor for flower colour. M. W. Onslow (Nature, 1931, **128**, 373—374).—A discussion. L. S. Theobald.

Crude fibre. E. Remy (Biochem. Z., 1931, **236**, 1—18).—By the action of enzymes (pepsin, trypsin, diastase) on dried vegetables, black pepper, oat clippings, etc. a substance is isolated which is practically identical in composition with the crude fibre prepared by the action of H_2SO_4 and KOH or of glycerol–H_2SO_4, but the yield is greater by the enzymic method. The different crude fibres isolated enzymically are degraded to different extents by the micro-organisms normally present in fæces. They are not, however, attacked by pure cultures of the organisms concerned and the action above appears to depend on a symbiosis. P. W. Clutterbuck.

Hemicelluloses. IV. Proximate analysis of box-wood, and the nature of its furfuraldehyde-yielding constituents. I. A. Preece (Biochem. J., 1931, **25**, 1304—1318).—Free pentoses are absent from box-wood, but hot H_2O extracts some non-pentosan furfuraldehyde-yielding substance. Lignosaccharide and free and combined hemicelluloses have been isolated. Xylose and uronic acid arise on hydrolysis of each of these substances. Free hemicellulose is a urono-xylan of relatively simple constitution. Different parts of the mol. of this substance possess different degrees of resistance to hydrolysis by dil. H_2SO_4. The wood residue remaining after extraction of the above constituents consists chiefly of cellulose, para-xylan, and some unextracted lignin. A method of analysis of woody tissue in which various types of furfuraldehyde-yielding substance are determined separately is described. S. S. Zilva.

Determination of assimilable pentosans. R. D. Rege (Proc. XV Indian Sci. Cong., 1928, 51).—The material is treated with cold 5% aq. NaOH for 24 hr. with occasional shaking. After neutralisation the extract is distilled with HCl by Krober and Tollens' method. Chemical Abstracts.

Plant colloids. XXVIII. Properties of various kinds of starch. M. Samec and R. Klemen (Kolloidchem. Beih., 1931, **33**, 254—268).—Examination of the properties of many starches shows that these can be divided into two groups, typified by potato- and wheat-starch, respectively, according to the behaviour of the amylopectin portion, and that the *X*-ray spectra of the starches show a corresponding classification. E. S. Hedges.

Mannitol and other substances in olives. E. Parisi and G. De Vito (Annali Chim. Appl., 1931, **21**, 323—332).—The H_2O of olives obtained by pressing contains a reducing substance which is non-fermentable, lævorotatory, sol. in EtOH, and not completely precipitated by basic Pb acetate. It is not readily hydrolysed by H_2SO_4 at 100°, but is decomposed by boiling HCl. After hydrolysis the liquid becomes dextrorotatory; dextrose is present together with other unidentified substances. Appreciable amounts of oleanolic acid are isolated from the cake by Et_2O extraction. The EtOH (90%) extract is evaporated and dissolved in H_2O. After a few days mannitol separates from the solution. O. F. Lubatti.

Alcohol and sugar content of olives. A. MANGINI (Annali Chim. Appl., 1931, **21**, 332—337).—The average results from samples collected in the province of Bari for the seasons 1928—29, 1929—30, and 1930—31 are, respectively, EtOH 2·19, 0·98, 1·77%, sugar 6·03, 2·38, 3·30%. The presence of sugars which reduce Fehling's solution after inversion is confirmed. No rule defining the ratio reducing sugar/invert sugar could be established. Excessive rainfall during the quarter July–September appears to have an adverse influence on the sugar content.
O. F. LUBATTI.

Organic acids in barley, maize, oats, and rye plants. E. K. NELSON and H. H. MOTTERN (J. Amer. Chem. Soc., 1931, **53**, 3046—3048).—Barley, maize, oat, and rye plants contain aconitic, malic, citric, and oxalic acids (0·019, 0·029, 0·04, and 0·048%, respectively, on fresh plant). Malonic acid is present in barley and oats, and tricarballylic acid in barley and maize plants. The dry plants are extracted with boiling H_2O (cf. this vol., 661) and the acids in the aq. extract determined.
H. BURTON.

Sterols of barley and their malting products. K. TAUFEL and G. GAMPERL (Biochem. Z., 1931, **235**, 353—358).—A cryst. deposit produced during 2 years in preps. of the fat from barley malt and spent malt consisted chiefly of sitosteryl palmitate, m. p. 88·5°. The free sitosterol had m. p. 137·2—137·4° and its acetate m. p. 126·5°. Of the crude sitosterol about 4·4% consisted of a dihydrositosterol, m. p. 134°.
W. McCARTNEY.

Vegetable phosphatides and lecithins. I. Phosphatide from carrots. II. A dialysable substance containing phosphorus from carrots. B. BLEYER and W. DIEMAIR (Biochem. Z., 1931, **235**, 243—258; **238**, 197—211).—I. A monoaminophosphatide which is probably a compound of lecithin with palmitic acid and oleic acid has been obtained in partly purified form from dried carrots by extraction with EtOH and precipitation with $COMe_2$ and MeOAc. The phosphatide is sol. to some extent in these two solvents, however. The carbohydrate (dextrose) which accompanies the phosphatide is probably adsorbed and not chemically combined.

II. A substance, probably a monoaminophosphatide, containing P and N in the ratio 1 : 1 can be obtained from carrots by dialysis in H_2O and subsequent precipitation with $Pb(OAc)_2$ or concentration of the dialysate. Dialysis in EtOH with subsequent precipitation does not produce satisfactory material. The purity of the substances obtained and the methods used by certain workers are questioned.
W. McCARTNEY.

Lignoceric acid from the seeds of *Adenanthera pavonina*. I. P. R. AYYAR (Proc. XV. Indian Sci. Cong., 1928, 161).—The seeds yield 14% of an oil which contains lignoceric acid (1·5% of seeds).
CHEMICAL ABSTRACTS.

Oil from the seeds of *Putranjiva Roxburghii*, Wall. S. KRISHNA and S. V. PUNTUMBEKAR (J. Indian Chem. Soc., 1931, **8**, 301—306).—The oil from the ripe fruit of *P. Roxburghii* becomes deep orange on keeping, and deposits a curdy substance, whilst the acid and Ac vals. increase greatly, and the I val. decreases. It contains mostly glycerides, with some sitosterol and (probably) a hydrocarbon of high mol. wt. The liquid acids contain oleic (80%) and linoleic acids (20%), yielding di- and probably tetra-hydroxystearic acids on oxidation with $KMnO_4$, and tetrabromostearic acid on bromination. Stearic and lignoceric acids were isolated, but palmitic acid was absent. The pulp of the fruit contains much mannitol, and a small amount of a saponin glucoside and an alkaloid. The oil has no vitamin activity, and the reputed physiological action, if real, is due to the glucoside and alkaloid.
R. S. CAHN.

Karité butter. J. BOUGAULT and G. SCHUSTER (Compt. rend., 1931, **193**, 362—364).—The butter contains 7·3% of tributyrin, dibutyrostearin, and arachidopalmitin and 92·7% of dipalmito-olein, dibutyro-olein, and palmitodiolein. C. C. N. VASS.

Two new glycerides from cacao-butter, αα-palmitostearo-β-azelain and α-monopalmito-α-monostearin. J. BOUGAULT and G. SCHUSTER (J. Pharm. Chim., 1931, [viii], **14**, 145—154).—Cacao-butter is oxidised by the method of Hilditch (cf. B., 1929, 331), tristearin extracted by Et_2O, and the aq. solution strongly acidified and extracted again with Et_2O, yielding *αα-palmitostearo-β-azelain*, m. p. 58—59° (Maquenne block). The Na salt, sol. in boiling, insol. in cold, H_2O, affords a means of purification. An Et_2O solution of the azelain (1 mol.) is neutralised, hydrolysed with KOH (2 mols.) in EtOH, filtered from K azelate, and the filtrate washed with H_2O and evaporated, yielding *α-monopalmito-α-monostearin*, m. p. 34° (block). The yield of the azelain indicates the presence of at least 36% of α-palmito-β-oleo-α-stearin in cacao-butter. F. O. HOWITT.

Salipurposide, a glucoside from *Salix purpurea*, L. C. CHARAUX and J. RABATÉ (Compt. rend., 1931, **192**, 1478—1480).—EtOH extraction of the bark of *S. purpurea* yields *salipurposide*, m. p. 227° (Maquenne block), $[\alpha]_D$ −116·87° (*hydrate*, $[\alpha]_D$ −109·72°), a monoglucoside, $C_{21}H_{22}O_{10}$, hydrolysed by emulsin to dextrose and *salipurpol*, $C_{15}H_{12}O_5$, m. p. 256·5°.
G. DISCOMBE.

Constituents of the bark of *Xanthoxylum carolinianum*. H. DIETERLE and K. HAUBOLD [with R. MEYER] (Arch. Pharm., 1931, **269**, 384—397).—Extraction of the bark with C_6H_6 yields about 10% of a non-drying oil. Saponification yields glycerol and a mixture of fatty acids (32·28%) and resin acids (27·59%) and unsaponifiable matter (29·04%). The fatty acids, separated by extraction with light petroleum, were examined by separation of the Tl salts, fractional crystallisation of the solid acids, and analysis of the liquid acids by bromination and oxidation, and contained 11·97% of solid acids (pentadecoic and arachidic) and 2·21% of linolenic, 23·86% of α-linoleic, 11·49% of β-linoleic, and 50·43% of oleic acid. The unsaponifiable fraction contained resin (25·02%) and with EtOH yielded a cryst. mixture of sitosterol (1·24%) (A., 1918, i, 388) and xanthoxylin-*S* (3·66%) (A., 1907, i, 68). These were easily separated by converting the sitosterol into the palmitate, insol. in EtOH.

Xanthoxylin-*S*, $C_{21}H_{20}O_6$, m. p. 120°, $[\alpha]_D^{20}$ −115·7°, contains three CH_2O_2: groups, yields a *dibromide*,

m. p. 63—65° (decomp.), and is oxidised by fuming HNO_3 to give 4 : 5-dinitropyrocatechol methylene ether. $CH_2O_2{:}C_6H_3{\cdot}CH{:}C{<}C_{10}H_{10}(CH_2O_2)_2$ is suggested as its formula. R. K. CALLOW.

Carotenoids from *Cucurbita*. The pigment from *Cucurbita maxima*, Duchesne. H. SUGINOME and K. UENO (Proc. Imp. Acad. Tokyo, 1931, 7, 251—253).—*Cucurbitene*, $C_{40}H_{56}$, m. p. 179—180°, sol. in C_6H_6, less sol. in EtOH, with H_2SO_4 gives a deep indigo colour, and *cucurbitaxanthin*, $C_{46}H_{56}O_2$, m. p. 180°, $[\alpha]_c^{20}$ +105°, insol. in light petroleum, are isolated from the $COMe_2$ extract. The absorption spectrum of cucurbitene resembles that of carotene. C. C. N. VASS.

Chemical study of *Senecio aureus*. E. A. KELLY and E. V. LYNN (J. Amer. Pharm. Assoc., 1931, 20, 755—759).—Representative samples (av. 10·76% H_2O, 8·33—11·85% ash) of *S. aureus* gave 0·2% of essential oil (n^{25} 1·4511) containing furfuraldehyde, alkaloids, and 1·22% S. The drug itself contains several alkaloids, some of them so weakly basic that they can be extracted from acid solution. The EtOH extract of the drug contains dextrose. E. H. SHARPLES.

Physiologically active constituents of the yew, *Taxus baccata*. II. Ephedrine. J. M. GULLAND and C. J. VIRDEN (J.C.S., 1931, 2148—2151).—C_6H_6 mixed intimately with dried yew leaves and moist $Ca(OH)_2$ extracts *l*-ephedrine (0·0017 g. per 100 g. dried leaves). W. O. KERMACK.

Leaf-diagnosis and the interpretation of fertiliser requirements of plants. A. E. LURNEEK and E. J. GILDEHAUS (Science, 1931, 74, 39—41).—A decrease in the N or K of the nutrient medium for *Pyrus malus* results in a decrease in K or N, respectively, in the leaves, but the ratio N : K remains of the same order. L. S. THEOBALD.

Analysis of tomato plants. II. Effect of manurial treatment of the composition of tomato foliage. O. OWEN (J. Agric. Sci., 1931, 21, 442—451; cf. B., 1929, 732).—In tomato foliage there was a seasonal variation in N content irrespective of manurial treatment. A direct relationship exists between the K content of the foliage and the P supplied to the plant, and an inverse relationship between the P content of the foliage and the K supplied to the plant. In the fruit, the latter relation probably becomes a direct one. The use of the tomato plant in determining soil nutrient requirements is discussed. A. G. POLLARD.

Variation of the physiological ratios of the mineral constituents of a plant. H. ZAGATU and L. MAUME (Compt. rend., 1931, 193, 103—106).—The concentrations of N, K, Ca, and P in the dried leaves of the tips of the potato varied with the concentrations of these substances in the soil. C. C. N. VASS.

Physiological importance of mineral elements in plants. II. Potassium in the potato. W. O. JAMES (Ann. Bot., 1931, 45, 425—442).—A definite correlation exists between H_2O and K contents of the plant as a whole. In the active parts the K concentration is 1·0—0·5%, sufficient to exert an appreciable effect on the osmotic pressure of plant-cells (5—20 atm.). There is a close relationship between K content and growth in the early stages. Migration of K follows the cycle : old tubers and soil⟶stalks⟶leaves⟶stalks⟶new tubers, but it does not return to the soil. P. G. MARSHALL.

Influence of phosphorus deficiency on the metabolism of the tomato. S. H. ECKERSON (Contr. Boyce Thompson Inst., 1931, 3, 197—217).—Tomato plants supplied with adequate nitrate but deficient phosphate show symptoms of N-starvation. Reductase activity in the plants ceases as the P supply is exhausted. There results an accumulation of nitrate in the tissues, an increase of sugar and starch, and enhanced acidity. Later (5th week) complex P compounds, phosphatides, and proteins break down, starch decreases rapidly, and the cell structure becomes disorganised. The reverse series of changes occurs when P is supplied to deficient plants. A. G. POLLARD.

Absorption of ammonium and nitrate ions by certain plant tissues. H. RICHMOND and W. H. PEARSALL (Proc. Leeds Phil. Soc., 1931, 2, 235—239).—The rate of absorption of $NH_4^{\cdot}$ by discs of potato tuber increases, and that of NO_3', above p_H 5·5, decreases, as $[H^{\cdot}]$ decreases. During 3 days wheat and *Eriophorum angustifolium* show min. NO_3' absorption at p_H 4·1 and 7, and higher absorption from 5 to 6·1 and at 8. In 7 days both plants removed almost all the NO_3' at all $[H^{\cdot}]$ vals. *Eriophorum* absorbs less $NH_4^{\cdot}$ or NO_3' than wheat, but more $NH_4^{\cdot}$ than wheat or potato as $[H^{\cdot}]$ increases. N. M. BLIGH.

Action of increasing amounts of iodine in the form of iodide, iodate, periodate, and elementary iodine on germination and embryonic growth of various plants. K. SCHARRER and W. SCHROPP (Biochem. Z., 239, 1931, 74—93).—In continuation of previous experiments (this vol., 1099) the effect of increasing doses of I (KI and NaI, iodate, periodate, and of aq. solution of I) on the germination and embryonic development of wheat, rye, barley, and oats grown in the same type of soil is investigated. The degree of injury to germination and growth follows the series $KI>NaI>I>KIO_3>NaIO_3>KIO_4>NaIO_4$ and the sensitivity oat>summer barley>wheat>winter barley>rye. P. W. CLUTTERBUCK.

Lignin as a nutrient for *Agaricus campestris*. S. A. WAKSMAN and W. NISSEN (Science, 1931, 74, 271—272).—*A. campestris* feeds largely on the lignin and protein of manure and, to a smaller extent, on hemicelluloses and cellulose. L. S. THEOBALD.

Presence of aluminium in leaves and intracellular liquids of the mulberry. D. ONGARO (Atti R. Accad. Lincei, 1931, [vi], 13, 202—207).—All the juices of mulberry trees grown on soils of varied character contain Al. In g. per 100 c.c. of the liquid, the amounts are : leaves without large veining, 0·0048—0·0144; stems, 0·0256—0·0424; bark, 0·0184—0·0372; veins, 0·0196—0·0244. The presence of such quantities of Al in the circulating liquids seems to rule out the view that this element can be completely deposited without taking part in the metabolism. T. H. POPE.

Relation between soil reaction and chemical composition of oats (*Avena sativa*). S. HJORTH-HANSEN (Biochem. Z., 1931, **235**, 359—366).—The yield of dry material, % of ash and of N, and amount of material sol. in Et_2O obtained from oats are dependent on the [H$^{\cdot}$] of the soil in which the seed is sown and also vary with the stage of growth. The alkalinity of the ash and its composition are also influenced by these factors. W. MCCARTNEY.

Absorption of mineral elements by plants in relation to soil problems. D. R. HOAGLAND (Plant Physiol., 1931, **6**, 373—388).—A discussion of the mechanism of plant nutrition and of controlling soil conditions. A. G. POLLARD.

Essential nature of copper for higher green plants. C. B. LIPMAN and G. MACKINNEY (Plant Physiol., 1931, **6**, 593—599).—Barley plants grown in the absence of Cu failed to produce seed. It is suggested that Cu is necessary for all phases of plant growth and not merely for seed production.

A. G. POLLARD.

Determination of silica in vegetables. L. LEMOTTE, G. BOINOT, E. KAHANE, and M. KAHANE (Bull. Soc. Chim. biol., 1931, **13**, 668—677).—Oxidation is effected by nitro-perchloric acid and the SiO_2 weighed. C. C. N. VASS.

Detection of the exceptional presence of mercury in vegetable tissues. L. PETRI (Atti R. Accad. Lincei, 1931, [vi], **13**, 331—332).—A strip of Ag is placed for some hrs. in a hot HCl extract of the plant sap, and the Hg is then detected spectroscopically in the amalgamated strip.

O. J. WALKER.

Comparison of methods for determining moisture in maize tissues. J. D. SAYRE and V. H. MORRIS (Plant Physiol., 1931, **6**, 577—583).—The EtOH extraction method yielded less variable results than sap expression, PhMe distillation, or air-drying methods. The last-named method indicated significantly lower vals. than the others, but the differences were small. A. G. POLLARD.

Effects of salts on the extensibility of protoplasm. W. SEIFRIZ and J. PLOWE (J. Rheology, 1931, **2**, 263—269).—The extensibility of cells of the epidermis of *Allium cepa*, treated with various solutions and then plasmolysed in sucrose solution, has been measured by determining the elastic limit and breaking length. The elastic limit is lowered by solutions of KNO_3, $NaNO_3$, $LiNO_3$, and $Al(NO_3)_3$ and raised by bivalent salts. The uni- and bi-valent cations give the series Ca>Sr>Mg>K>Li>Na. The extensibility of protoplasm is influenced only slightly by viscosity and surface tension.

E. S. HEDGES.

Sap concentration and inorganic constituents of mature citrus leaves. A. R. C. HAAS and F. F. HALMA (Hilgardia, 1931, **5**, 407—424).—Changes in the mineral constituents of orange and lemon leaves are related to the seasonal changes in soil and air temp. The total ash and total Ca increase with the advancing season, those of lemon being the greater. The sol. ash and sol. Ca show similar but narrower variations, orange having the higher proportions. The total and sol. K decline with advancing season, and those of Mg decrease at first and rise later. The sap concentration of lemon leaves is consistently greater than that of orange. A. G. POLLARD.

p_H and phosphorus content of the expressed liquids from soils and plant tissues. M. M. MCCOOL and W. J. YOUDEN (Contr. Boyce Thompson Inst., 1931, **3**, 267—275).—Liquids removed from peat soils and plant tissues by pressure become more acid and contain less phosphate as the pressure used is increased. A second pressing of re-wetted peat yielded liquid having nearly as great p_H and P content as that obtained initially. A. G. POLLARD.

Press for sap extraction. W. LEACH (Ann. Bot., 1931, **45**, 537).—An efficient and convenient press for small quantities of vegetable tissue is described. P. G. MARSHALL.

Nutrition and composition of the Deglet Naor palm in relation to the "Decline disease." A. R. C. HAAS and L. J. KLOTZ (Hilgardia, 1931, **5**, 511—530).—Diseased pinnæ of the palm contained less carbohydrate, total N, K, and P, but higher Ca than healthy pinnæ. No appreciable differences in the proportions of Na, Mg, total S and Cl appeared. Heavy applications of fertiliser caused no improvement in diseased trees, but applications of $CuSO_4$ to the soil around a diseased tree improved growth and induced changes in chemical composition towards the normal. In culture solutions date seedlings were uninjured by 4000 p.p.m. of NaCl. Small amounts of Be were extremely toxic. The ash content of date pinnæ varied considerably (12—29% of dry matter) and contained approx. 80% SiO_2. Of the total Ca 74—80% and of the total K 87—99% was H_2O-sol. Analyses of date pulp and roots are given.

A. G. POLLARD.

Mosaic disease of tobacco. II. Activity of the virus precipitated by lead acetate. C. G. VINSON and A. W. PETRE (Contr. Boyce Thompson Inst., 1931, **3**, 131—145).—The virus of mosaic disease is precipitated from the juice of diseased tobacco with $Pb(OAc)_2$. The ppt. is treated with $M/3$ KH_2PO_4 solution and washed and the virus subsequently extracted with a mixed solution of KH_2PO_4 and K_2HPO_4. Crystals sol. in $COMe_2$ are obtained which retain much of their activity after recrystallisation. The ash content is higher than that of other virus preps. and the N content of the org. matter approximates to that of the simpler proteins.

A. G. POLLARD.

Effect of enzymes on the infectivity of the virus of tobacco mosaic. M. LOJKIN and C. G. VINSON (Contr. Boyce Thompson Inst., 1931, **3**, 147—162).—Incubation of the virus with trypsin markedly decreased its infectivity. The effect was not increased by the use of trypsin in combination with other enzymes. Papain was particularly effective in inactivating the virus in neutral phosphate solution. Erepsin reduced infectivity only after incubation for several days. Emulsin, pepsin, and yeast extract had no effect. None of the enzymes reduced virus infectivity in untreated juice from fresh or frozen plants.

A. G. POLLARD.

Differential resistance thermometer for biological use. D. R. MCCULLAGH and E. M. CASE

(Biochem. J., 1931, **25**, 1213—1219).—The application of heat to 2 (opposite) arms of a Wheatstone bridge unbalances its resistance. The bridge is re-balanced by means of a variable resistance which gives a measure of the heat produced. S. S. Zilva.

Quinhydrone–collodion electrode of special applicability in experimental pathology. J. C. Bugher (J. Biol. Chem., 1931, **92**, 513—524).—A quinhydrone–Au-wire electrode is covered with a layer of collodion and inserted into an electrode vessel which is joined by a saturated KCl bridge to a calomel cell and through which the fluid under consideration slowly passes. The membrane potential is negligible in presence of electrolyte concentrations greater than $0{\cdot}01M$. The cell is applicable to closed systems and gas-containing biological fluids. F. O. Howitt.

Extractor for biological products. C. L. Shrewsbury (Ind. Eng. Chem. [Anal.], 1931, **3**, 320).—The apparatus has a capacity of approx. 5 litres and is designed to prevent escape of vapour and contamination of solvent by sealing compounds.
E. S. Hedges.

Quantitative micro-injections. R. Wurmser and L. Rapkine (Compt. rend., 1931, **193**, 430—432). —Light from a W arc passes through a condenser and illuminates a micro-injection pipette, the point of which is inserted in a drop-prep. under observation on a microscope slide, the vol. of liquid injected being obtained by calibration from the change in length of the column of liquid as measured on an enlarged image of the pipette on an adjacent screen. The rate of decolorisation of $0{\cdot}0125$-M (to H_2) 2 : 6-dibromophenol-indophenol on injection into cells was followed. J. Grant.

Alkaline ashing method in glass vessels for micro-analysis. I. S. Lorant and F. Blobner (Z. physiol. Chem., 1931, **199**, 112—116; cf. A., 1930, 181).—The blood-filtrate, freed from protein, is evaporated in presence of Na_2HPO_4 and $NaClO_3$ and heated for a short time at 400°. It is then evaporated with HCl and $FeCl_2$ to remove Cl_2 and ClO_2.
J. H. Birkinshaw.

Improved lactic acid [determination] apparatus. E. S. West (J. Biol. Chem., 1931, **92**, 483—485).—An apparatus for use with the $KMnO_4$ or MnO_2 oxidation methods (A., 1927, 800; 1929, 677) is described. F. O. Howitt.

Fractionation of mixtures of bases with permutite. R. Kapeller-Adler and E. Stern (Biochem. Z., 1931, **235**, 390—393).—The percentages of the N of the base adsorbed by permutite from solutions of NMe_3, $NHEt_2$, and guanidine were (in the best cases) 25·51, 26·13, and 44·67, respectively. From an extract of horse muscle only 10% of the N of the bases could be adsorbed by the permutite, which consequently cannot be used alone for the quant. separation of bases of biochemical interest.
W. McCartney.

Method of Stadie and Ross for micro-determination of base. W. M. Kirjan (Biochem. Z., 1931, **237**, 72—86).—The method (A., 1926, 100) is considered unsatisfactory for the following reasons: (*a*) the phosphate precipitation at p_H 8·0 is not quant. for Ca and Mg, and (*b*) ignition of $CaSO_4$ and $MgSO_4$ results in partial formation of insol. oxide. Precipitation at p_H 5·0 and omission of the ignition improves the method, but other sources of error, *e.g.*, mechanical loss of material, standardisation of the benzidine solution, and conditions for evaporation and removal of $(NH_4)_2SO_4$, are still present.
F. O. Howitt.

Copper determination in organic matter. S. Ansbacher, R. E. Remington, and F. B. Culp (Ind. Eng. Chem. [Anal.], 1931, **3**, 314—317).—For the micro-determination of Cu in biological materials org. matter can be destroyed without loss of Cu in small samples by wet combustion, using H_2SO_4, $HClO_4$, and fuming HNO_3. Larger samples can be burned in SiO_2 dishes at a temp. not exceeding 400°, followed by treatment with fuming HNO_3. The use of NH_3 to remove Fe and other metals leads to high results. Precipitation of Cu by H_2S is quant. when certain precautions are taken. With the redissolved ppt. the xanthate reagent tends to give high results. The carbamate reagent is applicable to solutions containing about 0·050 mg. of Cu and the chromotropic reagent can be used to determine quantities as small as 0·002—0·003 mg. with an accuracy of 0·0005 mg. The Biazzo reagent is most trustworthy for 0·050—0·150 mg. of Cu, but tends to give slightly low results. The method of preparing and using the chromotropic reagent is described. E. S. Hedges.

Gunther–Greenberg method for determining inorganic phosphorus on the filtrate from calcium analysis. R. P. Bolton (J. Lab. Clin. Med., 1931, **16**, 503—504).—The inorg. P may be determined by Benedict and Theis' method.
Chemical Abstracts.

Determination of nucleoprotein-phosphorus. M. Javillier and H. Allaire (Bull. Soc. Chim. biol., 1931, **13**, 678—684).—After removal of lipins by EtOH followed by Et_2O, the tissue is extracted with 100 c.c. of 12·5% aq. NaCl containing 0·5 c.c. of triacetin. The extraction fluid is boiled gently for ½ hr. A known wt. of the extract is just acidified with N-HCl, the ppt. is collected, washed with EtOH, dried, and the P content determined.
C. C. N. Vass.

Determination of phosphoric acid in presence of inositolphosphoric acid and separation of the acids. B. Bleyer, F. Fischler, and G. Schenck (Biochem. Z., 1931, **238**, 216—225).—PO_4''' can be separated by the method of Adler (Biochem. Z., 1916, **75**, 319) from inositolphosphoric acid, proteins, sugars, and glycerophosphoric acid or mixtures of them and can then be determined with reasonable accuracy by the method of Lorenz (Z. Unters. Nahr. Genussm., 1909, **17**, 446). For the determination of the PO_4''' in plant juices precipitation from an acid medium according to Lorenz and purification by the method of Schmitz (A., 1906, ii, 705) followed by the procedure of Lorenz is suitable. No parallelism between vitamin-A content and liberation of PO_4''' under the influence of phytase can be traced in plants of widely differing species. W. McCartney.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

NOVEMBER, 1931.

General, Physical, and Inorganic Chemistry.

Relationships between the continuous and the many-lined spectra of hydrogen. Y. HUKUMOTO (Sci. Rep. Tohoku, 1931, **20**, 433—449).—The variations in the intensity of the H spectra in the negative glow, Faraday dark space, and positive column have been followed. A. R. POWELL.

Dependence on field strength of intensity and sharpness of lines in the Stark effect components of H_γ. R. GEBAUER and H. R. VON TRAUBENBERG (Z. Physik, 1931, **71**, 291—298).

Broadening of the resonance atomic line of helium. W. WEIZEL (Physical Rev., 1931, [ii], **38**, 642—645).—Asymmetric broadening due to pressure is explained by the shape of the potential energy curves of the two-centre system of two He atoms. N. M. BLIGH.

Perturbations in the helium band spectrum. G. H. DIEKE (Physical Rev., 1931, [ii], **38**, 646—657).

Continuous absorption in lithium and sodium vapours. B. TRUMPY (Z. Physik, 1931, **71**, 720—734).—The results of an investigation of the boundary continuum of the Li principal series are given. A. J. MEE.

Ultra-violet absorption spectrum of fluorine. H. VON WARTENBERG, G. SPRENGER, and J. TAYLOR (Z. physikal. Chem., Bodenstein Festband, 1931, 61—68).—The ultra-violet absorption curve of F exhibits a max. at 2900 A. Combination of this figure with the difference between the convergence and max. absorption wave-lengths obtained by extrapolation from the values for the other halogens yields for the convergence wave-length 4470 ± 50 Å., which corresponds with a heat of dissociation of $63\cdot3\pm0\cdot6$ kg.-cal. Although the conditions are comparatively favourable for the processes which would be involved, H_2 and F_2 do not unite as a result of exposure to radiation from a spark between Mg electrodes, except in as far as the reaction on the walls is favoured by the increased circulation of the gases. H. F. GILLBE.

Emission spectrum of sodium hydride. T. HORI (Z. Physik, 1931, **71**, 478—531).—The emission spectrum, extending from 3540 to 5050 Å., is more complicated than the absorption spectrum. The analysis can be carried out only with the aid of the absorption spectrum. The moment of inertia of the normal state is $5\cdot65\times10^{-40}$ g.-cm.^{2}, that of the excited state $14\cdot66\times10^{-40}$ g.-cm.^{2} A. J. MEE.

Spectra of metals obtained by explosive reactions. T. TUCHOLSKI (Bull. Acad. Polonaise, 1931, **A**, 76—105).—Spectra from the detonation of the picrates of Na, K, Ca, Ba, Cu, and Fe with collodion and gelatin have been obtained and the temp. of explosion has been calc. W. R. ANGUS.

Low-voltage excitation of sodium. W. C. MICHELS (Physical Rev., 1931, [ii], **38**, 712—717).—Using a new type of tube, the optical excitation function of the resonance lines in Na vapour excited by low-velocity electron impact was investigated for the range 1·8—4·2 volts. N. M. BLIGH.

***f*-Values (oscillator strengths) of the *D*-lines from line-absorption measurements.** W. ZEHDEN (Naturwiss., 1931, **19**, 826—827; cf. A., 1928, 805; 1929, 1119).

Examination with large dispersion of a typical case of multiplet resonance in the vapour of diatomic sulphur. P. SWINGS and A. LEGROS (Bull. Acad. roy. Belg., 1931, [v], **17**, 808—811).—Using the 2967·64 Hg line as exciting ray the resonance spectrum of S_2 vapour has been examined. W. R. ANGUS.

General formulation of the absorption bands of sulphur vapour. J. GENARD (Bull. Acad. roy. Belg., 1931, [v], **17**, 812—815).—The author's equation (*ibid.*, 387) and that of Christy and Naude (this vol., 779) agree well with experimental data. Predissociation begins with $n'=10$. W. R. ANGUS.

Rotation quantum numbers of the resonance doublets of sulphur. P. SWINGS (Bull. Acad. roy. Belg., 1931, [v], **17**, 972—974).—The rotation quantum numbers corresponding with the doublets in the spectrum of S excited by various Hg lines have been calc. as 9, 20, 46, and 47. The optimum rotation quantum no. is 25. J. W. SMITH.

Intensities of the components of the rotation doublets in the resonance spectrum of sulphur. P. SWINGS (Bull. Acad. roy. Belg., 1931, [v], **17**, 956—971).—Some regrouping of the rotation doublets observed in the S_2 spectrum excited by Hg arc is suggested. J. W. SMITH.

Zeeman effect of quadrupole radiation. E. SEGRÈ and C. J. BAKKER (Naturwiss., 1931, **19**, 738).—The Zeeman effect in K has been studied longitudinally and obliquely ($\alpha=45°$). W. R. ANGUS.

Nuclear spin of potassium. F. W. LOOMIS and R. W. WOOD (Physical Rev., 1931, [ii], **38**, 854—856).—Photographs of certain bands in the absorption spectrum of the K mol. show branches with alternating intensities. The phenomenon of alternating missing lines does not occur, showing that the nuclear spin of K^{39} is not zero. N. M. BLIGH.

Fluorescence radiation of manganese vapour. J. FRIDRICHSON (Bull. Acad. Polonaise, 1931, A, 69—75).—The fluorescence of Mn vapour which has been heated to 700—800° and excited by a Mn spark consists of two sets of triplets. Only the longer wave-length triplet is produced by excitation with various light sources. W. R. ANGUS.

Fine structure of the spectrum lines of the zinc arc in vacuum and the energy levels of zinc. W. MOHAMMAD and P. N. SHARMA (Phil. Mag., 1931, [vii], 12, 726—728).—A revision of an earlier investigation (cf. this vol., 7). F. J. WILKINS.

Comparison of sources for zinc resonance radiation. A. C. G. MITCHELL (J. Franklin Inst., 1931, 212, 305—316).—Three sources are described and compared. H. J. EMELEUS.

Structure of the spectrum Se III. J. S. BADAMI and K. R. RAO (Nature, 1931, 128, 496).—A system of energy levels characteristic of the spectrum of Se III has been identified. L. S. THEOBALD.

First spark spectrum of rubidium (Rb II). O. LAPORTE, G. R. MILLER, and R. A. SAWYER (Physical Rev., 1931, [ii], 38, 843—853).—Ultraviolet and visible spectra were photographed; wave-lengths, separations, classifications, and intensities are tabulated for 121 lines. The ionisation potential of Rb II is 27·3 volts. N. M. BLIGH.

First spark spectrum of indium, In II. R. J. LANG and R. A. SAWYER (Z. Physik, 1931, 71, 453—459).—The term analysis of In II singlet and triplet terms resembles that of Al II and Ga II. The ionisation potential derived from the lowest term is 18·79 volts. A. J. MEE.

Nuclear moment of the indium atom. J. C. McLENNAN, (MISS) E. J. ALLIN, and K. E. HALL (Proc. Roy. Soc., 1931, A, 133, 333—335).—Lines in the ultra-violet region of the arc spectrum of In have been studied, using a quartz Lummer plate. *I* is probably L. L. BIRCUMSHAW.

Fine structure in the arc spectra of indium and thallium. A. L. NARAYAN (Nature, 1931, 128, 675).—Measurements of fine structure of the lines 4511, 4101, 3259, and 3256 Å. support Jackson's complex structure for In (A., 1930, 1075); the probable val. of the nuclear moment is 5/2 or 7/2. The nuclear moment of ½ for Tl is confirmed (cf. A., 1929, 1354). L. S. THEOBALD.

Spark spectrum of tellurium. Te IV and Te VI. K. R. RAO (Proc. Roy. Soc., 1931, A, 133, 220—228).—The spectrum has been examined in the region 1500—500 Å., and photographs of discharges through Te vapour in capillary tubes have been taken in the region 4000—2200 Å. The ionisation potentials are Te IV 37·7 and Te VI 72·0 volts approx. L. L. BIRCUMSHAW.

Remarkable resonance series in the vapour of diatomic tellurium. A. LEGROS (Bull. Acad. roy. Belg., 1931, [v], 17, 816—822).—The resonance spectrum excited in Te vapour by the 4481 Å. line of a Mg spark consists of five anti-Stokes lines and some 30 positive terms. W. R. ANGUS.

New resonance series in diatomic tellurium vapour. J. PIERARD (Bull. Acad. roy. Belg., 1931, [v], 17, 974—979).—On illumination with a condensed spark between Pb electrodes, Te_2 vapour at about 750° shows intense fluorescence. Two series have been measured, excited by the spark lines 4058 and 4248 Å. respectively. J. W. SMITH.

Nuclear moment of cæsium. H. BARTH and W. SCHÜTZ (Naturwiss., 1931, 19, 774).—The nuclear moment of Cs, calc. from the intensity ratio of the hyperfine structure components of the Cs blue doublet, is 3/2. W. R. ANGUS.

Fluorescent excitation of mercury by the resonance frequency and by lower frequencies. Further studies. (LORD) RAYLEIGH (Proc. Roy. Soc., 1931, A, 132, 650—666; cf. A., 1929, 1207).—The fluorescence of Hg vapour is excited by light of the frequency of the core of the resonance line 2537 (core excitation), and light of less frequency absorbed in the band which begins at the resonance line (wing frequency). L. L. BIRCUMSHAW.

Triple-spectrum discharge tube. R. W. SHAW and G. B. SABINE (Science, 1931, 74, 179).—The construction of an inexpensive substitute for a Hg-vapour lamp is described. Three distinct types of discharge can be obtained. L. S. THEOBALD.

Band absorption of mercury vapour in the extreme ultra-violet. N. KREMENEVSKI (Z. Physik, 1931, 71, 792—797).—Continuous bands were observed at 1850, 1807, 1694, 1403 Å. In the region of the Steubing fluorescence bands a series of diffuse absorption bands converging to 1900 Å. was found. A. J. MEE.

Ultra-ionisation potentials in mercury vapour. A. G. SHENSTONE (Physical Rev., 1931, [ii], 38, 873—875). N. M. BLIGH.

Effect of temperature on the continuous band spectrum of mercury vapour. W. M. NIELSEN (Physical Rev., 1931, [ii], 38, 888—898).—The structure and intensities of the 4850 and 3300 Å. bands are described. N. M. BLIGH.

Hyperfine structure of thallium II. J. B. GREEN and J. WULFF (Nature, 1931, 128, 409).—Details of a magnetic analysis are recorded. L. S. THEOBALD.

Isotopic displacement in hyperfine structure. J. H. BARTLETT, jun. (Nature, 1931, 128, 408—409).—A discussion relating to Tl. L. S. THEOBALD.

Hyperfine structure of thallium II. H. SCHULER and J. E. KEYSTON (Nature, 1931, 128, 409—410).—McLennan and Crawford's failure to discover an isotope effect (this vol., 993) is due to the limited resolving power employed. L. S. THEOBALD.

Resonance series of bismuth vapour. J. PARYS (Z. Physik, 1931, 71, 807—813).—The fluorescence spectrum of saturated Bi vapour at 800° consists of three doublet series. A. J. MEE.

Sparking potential of air for high-frequency discharges. E. W. B. GILL and R. H. DONALDSON (Phil. Mag., 1931, [vii], 12, 719—726).—The sparking potential of air for high-frequency discharges has been studied at different pressures with the electric field

parallel to the axis of the discharge tube, or at right angles to it. The results are discussed.

F. J. WILKINS.

Stark effect in band spectra. B. SVENSSON (Z. Physik, 1931, **71**, 450—452).—The four CO bands at 4835, 4511, 4393, and 4123 Å. have been studied; they show no appreciable splitting or displacement.

A. J. MEE.

Theory of hyperfine structure. G. RACAH (Z. Physik, 1931, **71**, 431—441).—The causes of the deviations noted between experiment and theory in the case of hyperfine structure are investigated. The experimental deviations cannot be completely explained.

A. J. MEE.

Intensity changes of hyperfine structure. H. SCHÜLER and J. E. KEYSTON (Z. Physik, 1931, **71**, 413—415).—Using identical light sources, but different excitation conditions, considerable intensity changes in the hyperfine structure of Cd, Tl, and Hg have been found.

A. J. MEE.

Intensity summation rules and perturbation effects in complex spectra. G. R. HARRISON and M. H. JOHNSON, jun. (Physical Rev., 1931, [ii], **38**, 757—778).—Intensity rules and formulæ are summarised, and a new J-group sum rule is derived and discussed.

N. M. BLIGH.

High-power source of continuous ultra-violet spectrum. G. B. KISTIAKOWSKY (Rev. Sci. Instr., 1931, [ii], **2**, 549—550).—A modified form of the hydrogen discharge tube of Bay and Steiner (A., 1927, 1117) is described.

Evidence for the spin of the photon from light scattering. G. PLACZEK (Nature, 1931, **128**, 410).

L. S. THEOBALD.

Relation of line absorption and brightness of spectral lines. W. SCHÜTZ (Z. Physik, 1931, **71**, 301—305).—The curves show a min. which is explained by the Doppler effect.

A. B. D. CASSIE.

Energy relations in complex spectra. D. R. INGLIS (Physical Rev., 1931, [ii], **38**, 862—872).

N. M. BLIGH.

Electrodeless discharge: method of measuring induced current; variation of current with pressure for various gases. C. T. KNIPP and J. K. KNIPP (Physical Rev., 1931, [ii], **38**, 948—954).

N. M. BLIGH.

Output of fluorescence in the L-region. G. VON HEVESY and E. ALEXANDER (Naturwiss., 1931, **19**, 825—826).

C. A. SILBERRAD.

Simple theory of X-ray spectra according to wave mechanics. V. S. VRKLJAN (Z. Physik, 1931, **71**, 403—411).—An attempt to form a theory of X-ray spectra analogous to that of the optical spectra of He and ionised Li.

A. B. D. CASSIE.

Interference bands of large path differences. E. LAU (Ann. Physik, 1931, [v], **10**, 71—80).—These are produced with the aid of the multiplex-interference spectroscope.

W. GOOD.

Diffraction of cathode rays by thin films. E. T. JONES (Phil. Mag., 1931, [vii], **12**, 641—657).—Films of Au and celluloid were used.

F. J. WILKINS.

Diffuse scattering of X-rays from sylvine. G. G. HARVEY (Physical Rev., 1931, [ii], **38**, 593—603; cf. this vol., 896).—Regarding the sylvine crystal as consisting of one kind of A-like atoms, values of the scattered intensity at room temp. are obtained, and when plotted as a function of the scattering angle and wave-length give a curve similar to that for rock-salt. The curve is compared with that of Wollan for A (cf. this vol., 781).

N. M. BLIGH.

Effect of temperature on the intensity of X-rays diffusely scattered from rock-salt. W. D. CLAUS (Physical Rev., 1931, [ii], **38**, 604—617).—Scattered intensity ratios for the temp. range 120—750° abs. preclude the Debye formula for the decrease in intensity with fall of temp., agree with Waller's modified formula at low temp., and satisfy the formula of Jauncey and Harvey (this vol., 896) at the higher temp.

N. M. BLIGH.

Shape of the Ag-L, Mo-K, and Cu-K lines. R. C. SPENCER (Physical Rev., 1931, [ii], **38**, 630—641).—Using the double X-ray spectrometer, components, widths, separations, and intensities were investigated.

N. M. BLIGH.

Reflexion of X-rays in thin sheets. E. NAHRING (Physikal. Z., 1931, **32**, 730—733).—With small angles of reflexion the reflective power of thin sheets of Ag and Pt is greater than that of thick sheets.

W. R. ANGUS.

Intensity of total scattering of X-rays by gases. I, II. Y. H. WOO (Proc. Nat. Acad. Sci., 1931, **17**, 467—475).—The general theory of the intensity of total scattering of X-rays by a polyat. mol. is considered on the assumption that only the coherent scattered radiations from the different atoms will interfere with each other, whilst the incoherent radiation will be simply added up.

II. The theory is applied to Barrett's experiments on the scattering of X-rays by O_2 and N_2 for various wave-lengths.

A. J. MEE.

Scattering by diatomic gases. E. O. WOLLAN (Proc. Nat. Acad. Sci., 1931, **17**, 475—479).—The theoretical work of Woo (cf. preceding abstract) is applied to the scattering data of the author for A, Ne, O_2, H_2, and N_2.

A. J. MEE.

Reflexion of long X-rays. C. B. O. MOHR (Proc. Roy. Soc., 1931, **A**, **133**, 292—303).—The refractive indices of long wave-length X-rays have been investigated by the total reflexion method, using a vacuum spectrograph.

L. L. BIRCUMSHAW.

Reflexion and diffraction of X-rays. T. H. LABY and R. T. W. BINGHAM (Proc. Roy. Soc., 1931, **A**, **133**, 274—291).—Experiments are described which verify the existence of reflexion at angles greater than the calc. crit. angle. The intensity of reflexion of C radiation from a glass mirror has been determined.

L. L. BIRCUMSHAW.

Vacuum spectrometer for long wave-length X-rays. R. T. W. BINGHAM (Proc. Roy. Soc., 1931, **A**, **133**, 266—274).—The Seeman form of spectrometer is used, together with a method of measuring angles on a single circle. The instrument is used to measure the wave-length of the Al-$K\alpha_{12}$ line relative to

the 5th and 6th orders of the Cu-$K\alpha_{12}$ doublet, using a sugar crystal. L. L. BIRCUMSHAW.

Fine structure of the K-absorption edge of potassium. G. A. LINDSAY (Z. Physik, 1931, 71, 735—738).—Determinations of the K-absorption of potassium have been carried out by reflexion from crystals of KCl, KBr, and KI. A. J. MEE.

Satellites of the M-series X-ray lines. F. R. HIRSH, jun. (Physical Rev., 1931, [ii], 38, 914—924).—Four satellites of the diagram line in the at. no. range U (92)—Yb (70), and 3 of the line $M\beta$ in the range U (92)—Gd (64) were measured and revealed, respectively, two satellites each, not previously reported. N. M. BLIGH.

New effect produced by action of X-rays on matter. G. I. POKROWSKI (Physical Rev., 1931, [ii], 38, 925—930).—The weak radioactivity acquired by Sn, W, Hg, Pb, and Bi after irradiation by X-rays was investigated by measurement of ionisation produced by the sample, and by counting scintillations produced by emitted particles. The mean energy of each emitted particle is of the order 10^{-6} erg, indicating a nuclear origin. N. M. BLIGH.

New form of Geiger point counter. M. STEENBECK (Z. Physik, 1931, 71, 422—430).—A counter is described which will indicate single quants, and for a single charge deals with about 100 times the charge of the former instrument. A. J. MEE.

Counting device for use with the Geiger counter. J. C. JACOBSEN (Nature, 1931, 128, 674). L. S. THEOBALD.

Application of the point counter for determination of external photo-electric effect. H. BAUER (Z. Physik, 1931, 71, 532—550).—The use of the counter for determining the no. of electrons discharged from a surface (metal or insulator) by the action of light is described. The position of the long-wave limits for the vaporised metals Au, Ag, Cu, Zn, Pb, Cd, and Al in vac. and for a variety of insulators was determined. A. J. MEE.

Physico-chemical nature of metal surfaces in the selective photo-electric emission of alkali metals. R. SUHRMANN (Z. Elektrochem., 1931, 37, 678—682).—When K is exposed to the vapour of a substance which reacts feebly with it and a layer of K is subsequently condensed on the surface there is a selective max. in the photo-electric emission for certain wave-lengths. The position of the max. depends on the thickness of the intermediate layer of K compound and its intensity on the degree of subdivision of the surface layer of K. The ready reactivity and volatility of the alkali metals suggest that the observed selective max. in photo-electric emission can be traced to this cause. E. S. HEDGES.

Photo-electric properties of potassium surfaces under the influence of hydrogen atoms. S. RIJANOV (Z. Physik, 1931, 71, 325—338).—The photo-electric sensitivity of K increases to 20—40 times its original val. in an atm. of H_2, and then diminishes. The H atoms adsorbed increase to 3×10^{16} per sq. cm. and then remain const. A. B. D. CASSIE.

Selective photo-effect and light absorption. R. FLEISCHMANN (Naturwiss., 1931, 19, 826). C. A. SILBERRAD.

Ionisation of Kr and Xe by positive alkali ions and the ionisation potentials of Ne, A, Kr, and Xe. O. BEECK and J. C. MOUZON (Physical Rev., 1931, [ii], 38, 967—968; cf. this vol., 542).—The most efficient ionisers are Cs^+ for Xe, K^+ and Rb^+ for Kr; K^+ is more efficient than Rb^+ for Xe, and Rb^+ is slightly less efficient than K^+ for A. N. M. BLIGH.

Cathode sputtering in mercury vapour at very low pressures. K. MEYER and A. GUNTHER-SCHULZE (Z. Physik, 1931, 71, 279—290).—The quantity of metal sputtered from a cathode surface in Hg vapour is independent of pressure near 0·005 mm. It is proportional to lower voltages across the tube, and at 1000 volts each Hg ion liberated one atom from Al, Si, Mn, Fe, Ni, Zr, Mo, Ta, and W cathodes, but Be, Co, Cr, Cu, Pd, Pt, and Ag showed no such relation. A. B. D. CASSIE.

Electron terms of the hydrogen molecule. E. A. HYLLERAAS (Z. Physik, 1931, 71, 739—763).—Theoretical. A comparatively simple method is given for calculating the characteristic function of H ions and the electron terms of the excited H_2 mol. A. J. MEE.

Excitation probabilities for electrons in helium, neon, and argon. L. C. VAN ATTA (Physical Rev., 1931, [ii], 38, 876—887).—Energy losses for electrons scattered inelastically in He, Ne, and A were determined as $21·13\pm0·04$, $16·64\pm0·05$, and $11·53\pm0·05$ volts, respectively. N. M. BLIGH.

Numerical calculations of atomic scattering factors. R. W. JAMES and G. W. BRINDLEY (Phil. Mag., 1931, [vii], 12, 729).—Correction of errors of an earlier paper (cf. this vol., 889). F. J. WILKINS.

Structure of absorption constants of light elements measured by means of the electron counting tube. H. NEUFELDT (Z. Physik, 1931, 71, 412).—Errors in a previous paper (this vol., 781) are corrected. A. B. D. CASSIE.

Diffraction experiments with very fast electrons. E. RUPP (Ann. Physik, 1931, [v], 10, 927—946).—The "atom form" factor for Au with electrons of 220 kv., the appearance of a new type of diffraction rings which can be characterised by fractional nos., and the proof of the de Broglie relation from voltage measurements in the region 100—250 kv. are dealt with. W. R. ANGUS.

Augular distribution of electrons scattered by gas molecules. C. RAMSAUER and R. KOLLATH (Ann. Physik, 1931, [v], 10, 143—154).—An extension of previous investigations (cf. this vol., 782) to Ne, Kr, Xe, N_2, CO, CO_2, and CH_4. W. GOOD.

Energy loss and scattering of electrons by passage through gases. II. Neon and argon. M. RENNINGER (Ann. Physik, 1931, [v], 10, 111—128).—In essentials the results for Ne and A are similar to those for N_2 (cf. this vol., 782) and are not more favourable than the latter for comparison with Bethe's calculations. W. GOOD.

Polarisation of a beam of electrons by scattering. N. F. MOTT (Nature, 1931, **128**, 454).
L. S. THEOBALD.

Electronic charge. W. N. BOND (Phil. Mag., 1931, [vii], **12**, 632—640; cf. this vol., 143).—The previous method has been applied to more extensive data, with the following results: $e=(4\cdot779_4\pm0\cdot001_1)\times10^{-10}$ abs. e.s. units, $h=(6\cdot558_6\pm0\cdot003_1)\times10^{-27}$ erg sec., $e/m=(1\cdot769_0\pm0\cdot004_6)\times10^7$ abs. em. unit g.$^{-1}$; $M_P/m=1846\cdot5\pm0\cdot4_8$, which differs from Eddington's val. of $(136)^2/10$ by more than six times the probable error. The val. of $hc/2\pi e^2$ is $137\cdot01\pm(0\cdot05_9\pm0\cdot00_5)$, agreeing with Eddington's val. of 137.
F. J. WILKINS.

Diffraction of electrons by single crystals. G. P. THOMSON (Proc. Roy. Soc., 1931, **A**, **133**, 1—25).—A detailed investigation has been made of the diffraction of electrons of 30—50 kv. by single crystals of Cu and Ag. The usual wave theory is extended to account for the diffraction patterns observed by assuming the etched surface of the crystal to consist of a series of lumps, through which the electrons can pass, of the order of 10^{-6} cm. in linear dimensions. Close agreement exists between theory and experiment, even in the case of certain irregular "exceptional" patterns. There is a complete absence of forbidden reflexions and half orders. Experiments with Cu electrolytically deposited on the etched surface of single crystals of Cu showed that the spacing of part at least of the added substance is larger than that of normal Cu, although the structure is roughly similar; that the deposited surface usually follows the orientation of the original crystal; and that certain spots appear which would correspond with "forbidden" planes of Cu. Diffraction patterns are produced from a cleavage face of rock-salt, and also strong Kikuchi lines. The depth of penetration of the rays is of the order of 10^{-7} cm.
L. L. BIRCUMSHAW.

Focussing method for producing electron diffraction patterns. A. A. LEBEDEFF (Nature, 1931, **128**, 491).—Details are given and electron diffraction patterns for NaCl, Au leaf, paraffin, and a Au film produced by cathodic sputtering are reproduced.
L. S. THEOBALD.

Diffraction of electrons by thin films of nickel and copper oxide. J. A. DARBYSHIRE (Trans. Faraday Soc., 1931, **27**, 675—678).—The electron diffraction spectra of the oxide films formed on the surface of Ni and Cu by heating correspond with those of the usual cryst. forms of NiO and Cu_2O. There is no evidence of the presence of metal. R. CUTHILL.

Ageing of ions in air and nitrogen. J. ZELENY (Physical Rev., 1931, [ii], **38**, 969—976; cf. A., 1930, 1231).—The mobilities of ions at different short ages in air and N_2 were investigated. With increase of age the negative ions of short age and high mobility transform into slower ions. The slow decrease of mobility with age, and the large effect of slight changes of gas composition on the rate of this decrease, indicate a gradual change of size of the ions.
N. M. BLIGH.

Reflexion of mercury from alkali halide crystals. H. A. ZAHL and A. ELLETT (Physical Rev., 1931, [ii], **38**, 977—997).—The distribution of Hg atoms scattered from NaCl, KCl, KBr, and KI was investigated as a function of the angle of incidence and temp. of the scatterer and incident beam.
N. M. BLIGH.

Structure of films from molecular rays. K. COPER, L. FROMMER, and H. ZOCHER (Z. Elektrochem., 1931, **37**, 571—577).—A description is given of the appearance and structure of thin films of Ag Au, Cu, Pt, Cd, PbO, B_2O_3, NaCl, AgCl, CaF_2, and $CrCl_3$ prepared by the rapid condensation of the vapours of these substances in vac. In general, the films consist of inhomogeneous, non-spherical particles.
E. S. HEDGES.

Density of ions at a polarised electrode. K. TEIGE (Chem. Listy, 1931, **25**, 277—278).
R. TRUSZKOWSKI.

Properties of atomic layers. P. LUKIRSKI, A. SOSINA, S. VEKSCHINSKI, and T. ZAREVA (Z Physik, 1931, **71**, 306—324).—Two methods of determining surface potentials by means of electron emission are described. Qual. measurements indicate that unimol. layers of Ba and Th lower the work function of the surface, and that the work function for any greater thickness is the same as that for a bimol. layer. Evaporation to a unimol. layer is much more readily attained than evaporation of the unimol. layer itself.
A. B. D. CASSIE.

Relative abundances of isotopes. H. C. UREY and C. A. BRADLEY, jun. (Physical Rev., 1931, [ii], **38**, 718—724).—To distinguish two types of nuclear stability, thermodynamic calculations are made for certain isotopic transmutation reactions. Results indicate that at. nuclei on earth do not represent an equilibrium mixture at any temp. N. M. BLIGH.

Relative amounts of lithium isotopes, Li^7 and Li^6. H. SCHULER (Naturwiss., 1931, **19**, 772).—The ratio of Li^7 to Li^6 isotopes is calc. from the intensities of hyperfine structure of the components of the Li^+ line at 5485 Å. The val. 10·5 is in good agreement with Aston's val. of $10\cdot2\pm0\cdot5$.
W. R. ANGUS.

Isotope separation in the spectra of Li I. D. S. HUGHES (Physical Rev., 1931, [ii], **38**, 857—861; cf. A., 1930, 1328).—A faint isotope component was found on the long wave-length side of the lines 6708 and 3232 Å., the measured separation of this component and the doublet being in good agreement with the calc. separation of the Li^6 and Li^7 lines. The line 6104 Å. showed no components other than the regular doublet.
N. M. BLIGH.

Isotopes of lithium, sodium, and potassium. K. T. BAINBRIDGE (J. Franklin Inst., 1931, **212**, 317—339).—Magnetic analysis of the positive rays of Li from a heated spodumene source shows no change with temp. in the relative abundance of Li^7 and Li^6 The isotopes Na^{21}, Na^{22}, Na^{25}, K^{40}, K^{42}, and K^{43} were found to occur only in very small amounts, if at all.
H. J. EMELÉUS.

At. wt. of fluorine. H. S. PATTERSON, R. WHYTLAW-GRAY, and W. CAWOOD (Nature, 1931, **128**, 375).—The at. wt. of F obtained from density measurements on MeF by the method used for Xe (this vol., 890) is 19·013 (C 12·010). The presence of small

quantities of a higher isotope of F is suspected. The compressibility coeff. $1+\lambda$ of MeF at 21° is 1·00823. Moles and Batuecas' vals. for this coeff. and for density are too high. L. S. THEOBALD.

Isotopic constitution and at. wt. of selenium, bromine, boron, tungsten, antimony, osmium, ruthenium, tellurium, germanium, rhenium, and chlorine. F. W. ASTON (Proc. Roy. Soc., 1931, **A**, **132**, 487—498).—By means of photometry of the mass spectra of a no. of elements, the no. and relative abundance of their isotopes have been obtained. Twenty new isotopes were discovered and the magnitude of many new packing fractions has been determined, including that of Si. At. wts. obtained by correcting the mean mass no. for the packing fraction and change to the chemical scale are: Se 78·96±0·04, Br 79·916$_5$±0·002, B 10·806±0·01, W 183·96, Sb 121·79, Os 190·31±0·06, Ru 101·1, Te 128·03±0·1, Ge 72·65±0·05, Rh 186·22±0·07. Most of these are in good agreement with the accepted chemical vals. but in the case of Se, Te, and Os the discrepancies are serious. L. L. BIRCUMSHAW.

Fundamental at. wts. X. At. wt. of iodine. O. HONIGSCHMID and H. STRIEBEL (Z. physikal. Chem., Bodenstein Festband, 1931, 283—290).—Determination of the ratio AgI : AgCl yielded for the at. wt. of I 126·917 (O=16). The AgI was prepared by heating Ag in I vapour and decanting the liquid salt from the excess of metal; the conversion into AgCl was effected by Cl_2 at 80—100°.
H. F. GILLBE.

Apparatus for preparing Ra-*B*+*C* sources. L. F. CURTISS (Bur. Stand. J. Res., 1931, 7, 215—218).—In the "emanation pipette" Hg has to pass through the capillaries of glass stop-cocks and through rubber tubing. These defects are remedied in an all-glass apparatus which is described and has been used for prep. of Ra-*B* and Ra-*C* from radon.
W. R. ANGUS.

Purification of radon. J. BANNON (J. Cancer Res. Comm. Sydney, 1931, 3, 86—89).—A liquid-air radon purification apparatus is described in which H_2 and O_2 are first removed by sparking, and the H_2O is absorbed by P_2O_5. C. C. N. VASS.

Radioactivity of potassium. G. VON HEVESY, W. SEITH, and M. PAHL (Z. physikal. Chem., Bodenstein Festband, 1931, 309—318).—Comparison of the activities of normal and "heavy" KCl demonstrates that the radioactivity of K cannot be ascribed to an isotope of at. wt. 40. The degradation of K is discussed. H. F. GILLBE.

Structure of atomic nuclei. H. BECKER and W. BOTHE (Naturwiss., 1931, **19**, 753).—The calculation of the energy of Be γ-radiation (A., 1930, 1086) is made. E_γ, the energy of a γ quantum, is equal to $E_C-E_{Be}+3\cdot6$ (10^6 e-volts) in agreement with the Gamow scheme of mass defects and quantum-mechanical theory of at. nuclei. W. R. ANGUS.

Properties of the electron and the behaviour of radioactive substances. R. D. KLEEMAN (Z. anorg. Chem., 1931, **199**, 225—234).
H. F. GILLBE.

Theory of the effect of resonance levels on artificial disintegration. N. F. MOTT (Proc. Roy. Soc., 1931, **A**, **133**, 228—240).—Calculations are made of the effective area a (E) that an α-particle must hit to eject a proton, being itself captured, and the area that it must hit in order that it shall be scattered into a given solid angle. The circumstances in which a resonance level should occur are investigated, and its breadth is estimated. L. L. BIRCUMSHAW.

Ionisation produced by radon in spherical vessels. G. GLOCKLER and G. B. HEISIG (J. Physical Chem., 1931, **35**, 2478—2491; cf. A., 1927, 1003).—Theoretical. L. S. THEOBALD.

Protoactinium. O. HAHN and L. MEITNER (Naturwiss., 1931, **19**, 738).—Attention is directed to the early work of Hahn and Meitner and of Soddy and Cranston. W. O. KERMACK.

Position of uranium-*Z* in the uranium disintegration series. E. WALLING (Z. physikal. Chem., 1931, **B**, **14**, 290—296).—Hahn's conclusions (A., 1921, ii, 478; 1923, ii, 111) as to the parent substance and its dual disintegration are confirmed, and his view that the product is U II is supported.
N. H. HARTSHORNE.

Destruction of zinc sulphide phosphors by α-rays. P. M. WOLF and N. RIEHL (Ann. Physik, 1931, [v], **11**, 103—112).—The diminution of the luminescence of ZnS phosphors by the action of α-rays is examined for different phosphors. The rate of change of the phosphor is independent of the source or method of prep. It is rather a sp. property of the compound ZnS. Dry ZnS is unaffected by β- or γ-rays. The destruction of a Lenard centre is not a result of the process of scintillation. The centre can be excited many times by α-particles without destruction taking place. A. J. MEE.

Hard component of the β-radiation of potassium. D. BOCCIARELLI (Nature, 1931, **128**, 374—375).—Data obtained for KCl and KBr by Occhialini's method indicate the existence of a less intense, hard component of the β-radiation of K.
L. S. THEOBALD.

Contribution to the study of β-rays by the method of magnetic spectra. J. D'ESPINE [with (in part) D. K. YOVANOVITCH and (MLLE.) I. CURIE] (Ann. Physique, 1931, [x], **16**, 5—70).—The apparatus and technique for the investigation of the magnetic spectra of β-rays from different sources are described and discussed. Magnetic spectra of β-rays from Ra-*B*+*C*, Ra-*E*, mesothorium 2, and Th-*B* and -*C* have been obtained. Thin-walled glass ampoules of radon were used as source of Ra-*B*+*C* and the spectra of β-rays of different velocities are given. The results are considered in the light of different theories of at. structure and the mechanism of radioactive transformation is discussed. W. R. ANGUS.

Biological effects of cosmic and γ-radiation. J. H. ORTON and S. T. BURFIELD (Nature, 1931, **128**, 376).—Speculative. L. S. THEOBALD.

Origin of the γ-rays. (LORD) RUTHERFORD and C. D. ELLIS (Proc. Roy. Soc., 1931, **A**, **132**, 667—688).—Measurements of the energies of the long-range α-particles from Ra-*C* render it almost certain

that the γ-rays are associated with transitions of α-particles in the nucleus. It is assumed that the α-particles form a normal quantum-mechanical system capable of existing temporarily in a series of stationary states, the energy differences of which are shown by the γ-rays and groups in the β-ray spectrum. Using a nuclear model in which different nos. of α-particles are excited to the same quantum state, an equation is deduced for the energies set free in transitions. This receives support from experiment.
L. L. BIRCUMSHAW.

Quantum-mechanical models of a nucleus. R. H. FOWLER (Nature, 1931, **128**, 453—454).—A theoretical investigation of models of a nucleus consisting of some 50 α-particles. L. S. THEOBALD.

Effect of γ-rays on velocity of radioactive disintegration. O. REINKOBER (Z. Physik, 1931, **71**, 460—464).—No effect was found. A. J. MEE.

Nuclear absorption of hard γ-rays. C. Y. CHAO (Naturwiss., 1931, **19**, 752).—Investigations on the scattering of the γ-radiation of Th-C'' have demonstrated a new scattered radiation in heavy elements accompanied by a change in wave-length. This results from a nuclear process.
W. R. ANGUS.

Scattering law for short wave γ-radiation. (FRL.) L. MEITNER and H. H. HUPFELD (Naturwiss., 1931, **19**, 775—776).—A preliminary account of an extension of earlier work (A., 1930, 976).
W. R. ANGUS.

Absorption of penetrating γ-rays by lead screens of 12 to 30 cm. thickness. A. PICCARD, E. STAHEL, and F. DONY (Compt. rend., 1931, **193**, 526—527).—Comparison of the γ-radiation of Ra-C passed through Pb screens of thickness of 12—30 cm., before and after subsequent passage through a Pb filter 1·5 cm. thick, shows the same relative difference irrespective of the screen thickness. There is therefore no ultra-penetrating component in this radiation, and the explanation of cosmic radiation thereby is negatived. C. A. SILBERRAD.

Photo-electric effect for γ-rays. H. R. HULME (Proc. Roy. Soc., 1931, **A**, **133**, 381—406).—Mathematical.

Oxidisable "active nitrogen." E. J. B. WILLEY and S. G. FOORD (Nature, 1931, **128**, 493).—Experiments with N_2 and N_2–O_2 mixtures failed to reveal any oxidisable modification of N_2 or any nitrogen oxide which reacts only with O_3 and not with O_2. Increased yields of NO_2 do result, however, when the air is ozonised before or treated with O_3 after it is sparked (cf. J.C.S., 1912, **101**, 1152).
L. S. THEOBALD.

Absorption and diffusion of penetrating corpuscular radiation in lead and in iron. B. ROSSI (Atti R. Accad. Lincei, 1931, [vi], **13**, 600—606).

Value of the cosmical constant. (SIR) A. EDDINGTON (Proc. Roy. Soc., 1931, **A**, **133**, 605—615).

Corpuscular explanation of cosmic rays. F. SODDY (Nature, 1931, **128**, 408).—A criticism.
L. S. THEOBALD.

Measurements on the absorption of the penetrating corpuscular rays coming from inclined directions. B. ROSSI (Nature, 1931, **128**, 408).—The inclined appear to be softer than the vertical rays.
L. S. THEOBALD.

Atmosphere of the planet Venus. E. SCHOENBERG (Sitzungsber. preuss. Akad. Wiss., 1931, **21**, 1—36).—The distribution of luminosity in the atm. of Venus has been determined, and from the results a method of estimating the constitution of the planetary atm. is obtained. W. R. ANGUS.

Light of the night sky. J. KAPLAN (Physical Rev., 1931, [ii], **38**, 1048—1051).—The lines 4416 and 4168 Å. reported by Rayleigh are identified as O II lines. An explanation of the green auroral line in the night sky and aurora borealis, and of the above lines of the night sky, is proposed. N. M. BLIGH.

Schrödinger potential function. R. M. LANGER (Physical Rev., 1931, [ii], **38**, 779—796).—The theory that the fundamental potential between charges is an even operator is developed and applied.
N. M. BLIGH.

Quantised singularities in the electromagnetic field. P. A. M. DIRAC (Proc. Roy. Soc., 1931, **A**, **133**, 60—72). L. L. BIRCUMSHAW.

Quantum theory of dispersion in metallic conductors. II. R. DE L. KRONIG (Proc. Roy. Soc., 1931, **A**, **133**, 255—265; cf. A., 1929, 871).
L. L. BIRCUMSHAW.

Conversion of energy into matter. F. G. DONNAN (Z. physikal. Chem., Bodenstein Festband, 1931, 131—134).—Since at a temp. in the neighbourhood of $10^{12°}$ an equilibrium of the type proton + electron $\rightleftharpoons$ photon (radiation energy) is conceivable, it is suggested that the reaction from right to left could be observed if a sufficiently dense stream of protons of frequency of the order of 10^{23} emerged into a cold space. The relation between this hypothesis and photochemical reactions is discussed.
H. F. GILLBE.

Life of metastable mercury and evidence for a long-lived metastable vibrating nitrogen molecule. M. L. POOL (Physical Rev., 1931, [ii], **38**, 955—966).—Rate of decay curves are discussed. An expression is found for the no. of metastable atoms. Consts. obtained are: for the excited vibrating metastable mol., max. observed life $0{\cdot}52\times10^{-3}$ sec.; natural life, ∞; distance between centres at impact, $0{\cdot}85\times10^{-8}$ cm.; probability of dissipative impact, 80×10^{-6}; diffusion coeff., 2·4. Corresponding vals. for the metastable atom are: $2{\cdot}54\times10^{-3}$ sec.; ∞; $3{\cdot}2\times10^{-8}$ cm.; $3{\cdot}3\times10^{-6}$; 0·129, respectively.
N. M. BLIGH.

Primary and secondary absorption bands and their relation to optical activity. W. KUHN and H. L. LEHMANN (Z. Elektrochem., 1931, **37**, 549—552).—A comparison of absorption spectrum, optical rotation, dichroism, and anisotropy of some org. compounds. E. S. HEDGES.

Emission spectra and predissociation in OH and NH. J. R. BATES (Z. physikal. Chem., Bodenstein Festband, 1931, 329—332).—The heats of dissociation of OH and NH, calc. from the vibrational

levels deduced from the emission spectra, having regard to the predissociation, are 116·05 and 102·2 kg.-cal., respectively. H. F. Gillbe.

Dissociation of water in the glow discharge. E. G. Linder (Physical Rev., 1931, [ii], 38, 679—692).—Ionisation in the dark space increasing exponentially with distance from the cathode leads to results in satisfactory agreement with experimental data for the dissociation of H_2O vapour. N. M. Bligh.

Absorption of light by flames containing sodium. C. D. Child (Physical Rev., 1931, [ii], **38**, 699—708; cf. Locher, A., 1928, 449).—The relation between the light transmitted by a series of flames into which NaCl is being introduced, the no. of flames, and concentration of the NaCl is investigated. An expression connecting these quantities is deduced showing a square root variation in satisfactory agreement with experiment. N. M. Bligh.

Total radiation of some oxides. G. Liebmann (Z. Physik, 1931, **71**, 416—421).—The total radiation of Pt, some pure oxides, and a mixture of oxides was determined in its relationship to temp., composition, and nuclear size. A. J. Mee.

Ultra-violet emission of calcium oxide phosphors. O. Schellenberg (Ann. Physik, 1931, [v], **11**, 94—102).—The effect of temp. on the ultra-violet emission range differs from that on the visible emission. With the latter the greater intensity and duration of emission are obtained at comparatively high temp. (200—300°), whereas for the ultra-violet emission optimum conditions are obtained at room temp. A. J. Mee.

Band spectrum of yttrium oxide. With a note on the scandium and lanthanum oxide systems. L. W. Johnson and R. C. Johnson (Proc. Roy. Soc., 1931, **A**, **133**, 207—219).—About 100 band heads in the spectrum of YO have been measured and assigned to 2 systems, having a common ground state. A vibrational analysis is given and the mol. consts. are evaluated. The band systems of YO, ScO, and LaO are very similar, and closely resemble those of CaF, SaF, and BaF. L. L. Bircumshaw.

Ultra-violet bands of phosphorous oxide. P. N. Ghosh and G. N. Ball (Z. Physik, 1931, **71**, 362—370).—A band system of PO ascribed to $^2\Sigma \rightarrow {}^2\Pi$ transitions was investigated under high dispersion; the heat of dissociation of the ground state is 7·4 volts. A. B. D. Cassie.

Spectrum of the hydrogen-nitrous oxide flame. A. Fowler and J. S. Bodami (Proc. Roy. Soc., 1931, **A**, **133**, 325—332).—Observations of the bright cone near the base of the H_2–N_2O flame in a mixed jet show that the spectrum is identical with that of the flame of NH_3 burning in O_2, apart from differences in intensities of certain bands in the spectra. The Schuster bands are not observed. L. L. Bircumshaw.

Interpretation of the spectra of CaF and SrF. A. Harvey (Proc. Roy. Soc., 1931, **A**, **133**, 336—350).—A comparison of the spectra in emission and absorption under high dispersion confirm the designations $^2\Sigma \rightarrow {}^2\Sigma$ and $^2\Pi \rightarrow {}^2\Sigma$ for the more, and less, refrangible band systems of CaF and SrF. For CaF, $I_0''=86\times10^{-40}$ g.-cm.^{2}, and $r_0''=2·0\times10^{-8}$ cm. for the lower $^2\Sigma$ state. The isotope effect for Sr^{88}, Sr^{86} is found in the SrF bands. L. L. Bircumshaw.

Diffuse bands occurring in mixtures of ammonia and excited mercury vapour. A. C. G. Mitchell (J. Franklin Inst., 1931, **212**, 341—342).—The spectrum of the fluorescence on illuminating NH_3–Hg mixtures with a cooled Hg arc consists of a very diffuse band between λ 2700 and 5600 Å. (max. intensity at λ 3400 Å.). H. J. Emeléus.

Absorption of light in single crystals. R. Hilsch and R. W. Pohl (Physikal. Z., 1931, **32**, 734—735).—The absorption of a single crystal of KBr and of the photochemical reaction product are given and discussed. W. R. Angus.

Measurement of absorption spectra in the ultra-violet. H. Conrad-Billroth (Z. physikal. Chem., 1931, **B**, **14**, 122—134).—Apparatus is described by which the ultra-violet absorption spectrum of a solution is photographed simultaneously with that of the pure solvent, using as light source an under-water Al arc. The method gives results in good agreement with previous work, but has certain limitations. N. H. Hartshorne.

Energy levels of gadolinium IV in the crystal lattice as obtained from the ultra-violet absorption spectra of $GdCl_3,6H_2O$ and $GdBr_3,6H_2O$. S. Freed and F. H. Spedding (Physical Rev., 1931, [ii], **38**, 670—678; cf. A., 1929, 1362).—Wave-lengths, intervals, and magnetic decomps. are tabulated, and discussed in relation to lattice structure. N. M. Bligh.

Spectroscopic investigation of dissociation relations of metal halides in solution. H. Fromherz (Z. Elektrochem., 1931, **37**, 553—558).—A discussion of published work (cf. A., 1929, 626; 1930, 853, 1234). E. S. Hedges.

Spectrum and photochemical behaviour of chlorine dioxide. W. Finkelnburg and H. J. Schumacher (Z. physikal. Chem., Bodenstein Festband, 1931, 704—716).—The band spectrum of ClO_2 between 5225 and 2700 Å. has been examined. Fine structure is apparent in the longer wave-length bands, but at 3750 Å. predissociation commences; the extrapolated convergence frequency is 39,000±1000 cm.$^{-1}$ The predissociation is ascribed to dissociation into ClO and O (^3P), whilst the convergence corresponds with the production of ClO and O (^1O). The dissociation energy of ClO is 45±5 g.-cal. ClO_2 has probably a cyclic structure. The photochemical reactions of ClO_2 are discussed and possible mechanisms of the formation of ClO_3 are described. H. F. Gillbe.

Visible absorption spectrum and specific vibration of the permanganate ion. K. Schnetzler (Z. physikal. Chem., 1931, **B**, **14**, 241—248).—The absorption spectrum of $KMnO_4$ in solid solution in $KClO_4$ shows seven equidistant bands between 5600 and 4400 Å., each band having a short-wave satellite of about half its strength. The band max. occur at longer wave-lengths than those previously found for solutions of $KMnO_4$. Modifications occur in single bands when light vibrating in the α, β, or γ

directions is used. The no. of oscillators is of the same order as the no. of mols. present.

N. H. HARTSHORNE.

Absorption band spectra of silver bromide and silver iodide vapours. B. A. BRICE (Physical Rev., 1931, [ii], **38**, 658—669; cf. A., 1930, 838).—Band heads were measured in the region 3165—3501 for AgBr, and 3016—3556 Å. for AgI; absorption was continuous below 3350, with a max. at 3170 A. A vibrational analysis is given. Heats of dissociation for the normal state are: AgBr 2·77, AgI 3·02, and for the excited states, AgBr 0·21, AgI, 0·10 volt, respectively. The vibrational isotope effect for AgBr confirms two Ag and two Br isotopes; no evidence for an I isotope was found. N. M. BLIGH.

Absorption spectra of sulphur compounds. I. L. LORENZ and R. SAMUEL (Z. physikal. Chem., 1931, **B**, **14**, 219—231).—The ultra-violet absorption spectra of $SOCl_2$, SCl_2, Na_2SO_3, $NaHSO_3$, $Na_2S_2O_4$, Na_2SO_4, $NaHSO_4$, $NaMeSO_4$, Me_2SO_4, SO_2Cl_2, Na_2SO_3, $Na_2S_2O_6$, $K_2S_3O_6$, $K_2S_4O_6$, $K_2S_5O_6$, and Na_2SeO_3, mostly in solution, have been determined. The results are discussed in relation to the mol. constitution of the substances. N. H. HARTSHORNE.

Rotation vibration spectrum of gaseous, liquid, and dissolved ammonia. G. JUNG and H. GUDE (Z. Elektrochem., 1931, **37**, 545—548).—The changes brought about by liquefaction of NH_3 and by dissolution in H_2O and some alcohols are described. E. S. HEDGES.

Influence of dissolved substances on the infra-red absorption spectrum of water. R. SUHRMANN and F. BREYER (Naturwiss., 1931, **19**, 772—773).—LiCl, NaCl, and KCl have been studied. Dissolved substances cause an intensification of H_2O bands. The sharpening increases with concentration, but does not follow the sequence of hydration. It is suggested that the greater ion exerts a bigger influence on the polymerised H_2O complex than the smaller. Undissociated dissolved substances give a slight sharpening of the bands. W. R. ANGUS.

Polymerides and new infra-red absorption bands of water. J. W. ELLIS (Physical Rev., 1931, [ii], **38**, 693—698).—New absorption bands at 1·79 and 1·74 μ and the bands at 19·5 and 4·7 μ are interpreted. The closely analogous bands of selenite are compared. Definite polymerides are indicated. N. M. BLIGH.

Double band of solid hydrogen chloride. G. HETTNER (Naturwiss., 1931, **19**, 815).—At approx. 90° abs. the HCl spectrum consists of a double band with max. at 3·63 and 3·70 μ, *i.e.*, at rather longer wave-length than the corresponding band of gaseous HCl. No fine structure is obtained. Preliminary investigations of liquid HCl give one band with max. at 3·61 μ. W. R. ANGUS.

Doppler effect in light scattering. (SIR) C. V. RAMAN (Nature, 1931, **128**, 636). L. S. THEOBALD.

Lines of large frequency shift in the Raman spectra of crystals. R. TOMASCHEK (Nature, 1931, **128**, 495).—The lines showing a large shift in the Raman spectrum of fluorite and calcite (this vol., 668) can be explained as phosphorescence lines of Gd.

L. S. THEOBALD.

Fine structure of spectral lines of light scattered by liquids. S. RAFALOWSKI (Nature, 1931, **128**, 495).—The phenomenon previously described (A., 1930, 1498) could not be confirmed under different experimental conditions. L. S. THEOBALD.

Widening of diffuse lines without change of frequency in the Raman effect. (MLLE.) M. J. NEY (Bull. Acad. Polonaise, 1931, **A**, 106—111).—From studies with C_6H_6 and quartz (at 18° and 500°) evidence is adduced in favour of the hypothesis that the widening of diffuse lines without change of frequency is due to mol. rotation. W. R. ANGUS.

Effect of varying concentrations of certain electrolytes on the violet band of the Raman spectra of water. C. C. HATLEY and D. CALLIHAN (Physical Rev., 1931, [ii], **38**, 909—913).—The Raman scattering by pure H_2O excited by the 3650 Å. group of the Hg arc showed a violet band of 3 components at 4150 Å.; the effect on this band of various concentrations of aq. KCl, NaOH, and KOH solutions was examined, and in all cases showed an energy shift towards the long wave-length side. N. M. BLIGH.

Raman spectra and catalysis. I. H. VON EULER and H. HELLSTROM (Z. physikal. Chem., Bodenstein Festband, 1931, 731—736).—Raman spectra of a homogeneous reacting mixture of KOH, EtOAc, and H_2O, and of the interfacial layer between a conc. solution of KOH and a mixture of EtOH and EtOAc were photographed. The second type shows faintly the normal lines, but two strong lines of frequencies 1050 and 1110 cm.$^{-1}$ appear; these undergo displacements towards lower frequencies on passing from the upper to the lower layer. The effect may correspond with activation of the reactant mols.

H. F. GILLBE.

Influence of exciting frequency on the intensities of lines in Raman spectra. S. C. SIRKAR (Indian J. Physics, 1931, **6**, 133—146).—The ratios of the intensities of Raman lines due to C_6H_6 and CCl_4 to those of the exciting Hg lines in the visible and ultra-violet have been measured. The intensities of the Raman lines in the ultra-violet increase more rapidly than is indicated by the fourth power law and the deviation is the greater the greater is the shift of the Raman from the exciting line. These deviations are satisfactorily accounted for by Placzek's theory of the Raman effect. F. J. WILKINS.

Raman spectra of glycol and some organic chlorine compounds. V. N. THATTE and S. M. SHAHANE (Indian J. Physics, 1931, **6**, 155—163).—The Raman spectra of glycol, chloral, C_2HCl_5, $C_2H_2Cl_4$, and $C_2H_2Cl_2$ have been studied. Increase in the number of Cl atoms in Cl-substituted ethanes causes an increase in the val. of a given Raman displacement. F. J. WILKINS.

Raman spectrum and chemical constitution of some chloroethylenes. G. B. BONINO and L. BRULL (Atti R. Accad. Lincei, 1931, [vi], **13**, 275—281).—The Raman spectra of *cis*- and *trans*-αβ-dichloroethylene have been measured. The character-

istic oscillation and deformation frequencies of these mols. are compared with those of C_2H_4 and of C_2Cl_4 (cf. A., 1930, 1236). O. J. Walker.

Retarded luminescence in carbon dioxide. (Mlle.) M. Kaczynska (Bull. Acad. Polonaise, 1931, **A**, 16—19).—A retarded luminescence has been shown in the case of CO_2. This varies with the intensity of the exciting discharge and with the pressure of the gas. A. J. Mee.

Colour and intensity of the chemiluminescence of solid sodium. R. M. Bowie (J. Opt. Soc. Amer., 1931, **21**, 507—512).—An investigation of the light by means of a Cs photo-electric cell gave a max. about 5100 Å. J. Lewkowitsch.

Galvano-luminescence. R. R. Sullivan and R. T. Dufford (J. Opt. Soc. Amer., 1931, **21**, 513—523; cf. A., 1927, 918; 1929, 378, 1364).—Various metals in typical Grignard solutions were examined. A solution of $MgBr_2,2Et_2O$ has the highest efficiency so far found. J. Lewkowitsch.

Permanent changes in the fluorescence of hæmatoporphyrin. S. Rafalowski (Z. Physik, 1931, **71**, 798—806).—The fluorescence spectrum in aq. NH_3 and glycerol has been investigated. The irreversible changes which occur in the fluorescence spectrum as the effect of temp. changes, concentration differences, and irradiation of the solution are due to oxidation. A. J. Mee.

Spectral fluorescence efficiencies of certain substances with applications to heterochromatic photographic photometry. G. R. Harrison and P. A. Leighton (Physical Rev., 1931, [ii], **38**, 899—908).—The efficiency of fluorescence in the visible and ultra-violet regions was investigated for fluorescein, chlorophyll, quinine sulphate, light and heavy fluorescent oil, aesculin, and U glass, and results are applied to the development of a simplified method of heterochromatic photographic photometry in the range 3900—2000 Å., with possible extension to the Schumann region. N. M. Bligh.

Absorption of metastable and ionised nitrogen by magnesium. P. I. Lukirsky and S. W. Ptizyn (Z. Physik, 1931, **71**, 339—349).—Neutral N_2 is absorbed only by a rapid evaporation of Mg, but ionised N mols. and metastable mols. of 8 volts energy are absorbed by a Mg layer to form Mg_3N_2. A. B. D. Cassie.

"Sperrschicht" photo-effect. E. Duhme (Z. Elektrochem., 1931, **37**, 682—683).—An electric current is produced when dry-plate rectifiers of the detector type (*e.g.*, Cu/Cu_2O) are illuminated. E. S. Hedges.

New photo-electric researches. Q. Majorana (Atti R. Accad. Lincei, 1931, [vi], **13**, 318—323).—Phenomena produced by intermittent light on triode valves and photo-electric cells are described. O. J. Walker.

Photo-electric effect in thin metallic films. W. G. Penney (Proc. Roy. Soc., 1931, **A**, **133**, 407—417).—Mathematical.

Preparation of sensitive vacuum thermo-elements and vacuum thermo-relays by cathodic sputtering. Z. Klemensiewicz and (Miss) Z. Wasowicz (Z. Physik, 1931, **71**, 817—820).—The deposition of thin layers of conductors on insulating material by cathodic sputtering provides a method of making vac. thermo-elements and relays of high sensitivity and reproducible characteristics. A. J. Mee.

Laws of the Becquerel effect at bismuth oxide electrodes. A. Coehn and R. Mykolajevycz (Z. physikal. Chem., Bodenstein Festband, 1931, 641—655).—The photosensitive constituent of the Bi oxide electrode, viz., Bi_2O_4, behaves when deposited on an insol. electrode as an electrode of high O pressure. The electrode potential varies with the nature of the base, probably because of local action. Illumination causes at first a decrease of potential, but at lower potentials the effect reverses. The magnitude of the Becquerel effect, for const. absorption and quantum yield, falls rapidly with increase of the wave-length of the incident light from 4500 to 6700 Å. The effect can be fully explained on the assumption that light exerts a reducing influence on Bi_2O_4. H. F. Gillbe.

Becquerel effect. III. C. Winther (Z. physikal. Chem., Bodenstein Festband, 1931, 341—351).—An artificial Becquerel electrode has been prepared, and comparison of its behaviour with that of the Cu/CuO electrode shows that the conductivity of the CuO film of the latter increases proportionately with the intensity of the incident light. H. F. Gillbe.

Becquerel effect. IV. C. Winther (Z. physikal. Chem., 1931, **155**, 225—237; cf. preceding abstract).—In support of the theory that the Becquerel effect is a photo-electric conductivity phenomenon the prep. of CuO electrodes having the properties of the Becquerel cell is described. R. Cuthill.

Mobility in crystalline solid bodies. A. Smekal (Z. physikal. Chem., Bodenstein Festband, 1931, 443—452; cf. A., 1928, 1330).—Theoretical. An equation is developed for the general case to express the temp. variation of the fraction of the total ionic conductivity in a solid which is due to each type of mobile ion; one term of the equation is concerned with the fraction which is dependent on the structure of the substance. The true conductivity is influenced by structure, and by chemical, mechanical, and electric disturbances. The conductivity of the high-temp. modifications of AgI and Ag_2S is discussed. H. F. Gillbe.

Electrical conductivity and the structure of thin metal films. III. Specific resistance and structure as a function of temperature. L. Hamburger (Ann. Physik, 1931, [v], **10**, 905—926).—An extension of previous work (this vol., 1112). W. R. Angus.

Electrical properties of dilute metallic mixed crystals. J. O. Linde (Ann. Physik, 1931, [v], **10**, 52—70).—The at. resistance increases of Cu, Ni, Co, Fe, Mn, Cr, Ag, Pd, Pt, Rh, In, and Sn in Au at temp. between +20° and −190° have been determined. Results concerning the solubility relationships in alloys of Au with Rh, Ru, Ir, Os, and In are given. W. Good.

Conductivity of silver sulphide. C. TUBANDT and H. REINHOLD (Z. Elektrochem., 1931, **37**, 589—593).—The electrical conductivity of Ag_2S has been measured between 200° and 500° both in the pure state and in presence of excess of S. The conductivity of α-Ag_2S above 197° is electrolytic in character and has a negative temp. coeff. In presence of S vapour the conductivity falls, following the v. p. of the S and reaching a const. value for the saturated vapour. This effect is reversible and the saturated vapour has a positive temp. coeff. H_2S has a similar effect to that of S vapour. It appears that two kinds of conducting Ag ions are involved: (*a*) a large no. of ions of small mobility, consistent with the ordinary diffusion velocity, and (*b*) a small no. of ions of abnormally high mobility, which no longer exert their effect when excess of S is present.

E. S. HEDGES.

Density, inner friction, dielectric constant, dipole moment, dissolving power, and dissociating power of hydrocyanic acid. K. FREDENHAGEN (Trans. Amer. Electrochem. Soc., 1931, **60**, 223—232).—The results of the author's recent experimental work (A., 1929, 498; 1930, 1501) are summarised and discussed (cf. this vol., 430).

H. J. T. ELLINGHAM.

Determination of dielectric constants. E. COHN (Physikal. Z., 1931, **32**, 687—688).—The ellipsoid method does not give an abs. determination. A comparison method is suggested. A. J. MEE.

Dipole moments of inorganic compounds. H. ULICH and W. NESPITAL (Z. Elektrochem., 1931, **37**, 559—562).—In agreement with Hund's theory (A., 1925, ii, 479), the symmetrical halides CCl_4, SnI_4, BCl_3, $SnCl_4$, $AlBr_3$, $BeCl_2$, $BeBr_2$, $SiCl_4$, and $GeCl_4$ have no dipole moment. Exceptions occur in $SbCl_3$ and $AsCl_3$. In some cases the dipole moment is traced to the formation of a compound between the halide and the solvent. E. S. HEDGES.

Dielectric constant and dipole moment of hydrogen cyanide and cyanogen. H. BRAUNE and T. ASCHE (Z. physikal. Chem., 1931, **B**, **14**, 18—26; cf. A., 1929, 1217).—From measurements of the dielectric consts. of the gases at various temp. the dipole moments of HCN and $(CN)_2$ are calc. as $2{\cdot}88\times10^{-18}$ and $0{\cdot}3\times10^{-18}$, respectively. J. W. SMITH.

Dipole moment of hydrogen cyanide. H. LUTGERT (Z. physikal. Chem., 1931, **B**, **14**, 27—30; cf. A., 1929, 1217, and preceding abstract).—From measurement of the dielectric consts. of dil. solutions in C_6H_6 at various temp. the dipole moment of HCN is calc. to be $2{\cdot}53\times10^{-18}$ and from the dielectric consts. of solutions in xylene at one temp. combined with existing electron and at. polarisation data $2{\cdot}60\times10^{-18}$.

J. W. SMITH.

Dipole moment and molecular orientation at a liquid–gas interface. B. I. TAMAMUSHI (Bull. Chem. Soc. Japan, 1931, **6**, 207—209).—The dipole moments of a number of fatty acids, alcohols, and esters have been calc. The consistent difference between the calc. and observed vals. indicates that other factors besides the electric moments of single mols., such as form of mol., position of natural electric moment, dielectric polarisation, and mol. association are of importance. H. F. GILLBE.

Electric moment of symmetrically hexa-substituted benzenes. Spatial requirements of substituents. H. LUTGERT (Z. physikal. Chem., 1931, **B**, **14**, 31—36).—From measurements of the dielectric const. of dil. solutions in CCl_4 and C_6H_6 at two different temp. it has been shown that three symmetrical hexa-substituted C_6H_6 derivatives (tribromomesitylene, trinitromesitylene, and tribromotrinitrobenzene) each have zero dipole moment. This is discussed with reference to the spatial arrangement of the C_6H_6 ring. J. W. SMITH.

Dipole measurements with benzene derivatives. I. Regularities with halogen, nitro-, and methyl derivatives. L. TIGANIK (Z. physikal. Chem., 1931, **B**, **13**, 425—461).—From the dielectric consts. of dil. solutions in C_6H_6, combined with refractivity data, the dipole moments of 47 C_6H_6 derivatives have been calc. The data confirm the hypothesis that the total induced polarisation of simple C_6H_6 derivatives is equal to the mol. refraction for Na light $+0{\cdot}4$. Almost const. ratios exist between the dipole moments of *m*-di- and mono-, *p*-di- and mono-, and *s*-tri- and mono-derivatives. From the behaviour of hexa-substituted derivatives it is concluded that the moments of *s*-tri-derivatives are perpendicular to the C_6H_6 ring. J. W. SMITH.

Dipole measurements in benzene derivatives. II. Amino-derivatives. L. TIGANIK (Z. physikal. Chem., 1931, **B**, 14, 135—148; cf. preceding abstract). —The following vals. of $\mu_D\times10^{18}$ have been obtained by extrapolation to infinite dilution in C_6H_6 solution, mostly at 20°: NH_2Ph 1·52; $C_6H_4(NH_2)_2$, *o*- 1·44, *m*- 1·79, *p*- 1·56; $C_6H_4Me{\cdot}NH_2$, *o*- 1·58, *m*- 1·44, *p*- 1·31; $C_6H_4Cl{\cdot}NH_2$, *o*- 1·77 *m*- 2·66, *p*- 2·97; $C_6H_4Br{\cdot}NH_2$, *o*- 1·77, *m*- 2·65, *p*- 2·99; $C_6H_4(NO_2){\cdot}NH_2$, *o*- 4·25, *m*- 4·94, *p*- 6·4. These show that the NH_2 and Me group moments act in the same direction. An expression is deduced for the moment of a mol. containing two freely rotating dipole groups, one or both of which have moments inclined to the valencies binding them to the rest of the mol. The inclination of the moment of the NH_2 group to its valency with the C_6H_6 nucleus is estimated to be about 40°.

N. H. HARTSHORNE.

Dielectric constants of certain organic liquids at medium frequency. W. R. PYLE (Physical Rev., 1931, [ii], **38**, 1057—1070).—At 85·8 kilocycles frequency the respective vals. of the dielectric const. and temp. are: C_6H_6 2·279, 22·9°; cinnamaldehyde 16·918, 24·2°; Et_2O 4·197, 26·9°; methyl*cyclo*hexane 2·071, 24·8°; Me *o*-nitrobenzoate 27·756, 26·9°; PhNO 34·369, 26·1°; oxalyl chloride 3·470, 21·2°; Pr^{α}_2O 3·394, 25·7°; Pr^{β}_2O 4·449, 25·9°; propylene chloride 8·925, 26·1°. At the same frequency the temp. coeffs. of the dielectric consts. for *o*-, *m*-, and *p*-xylenes were determined over a temp. range of about 30°. N. M. BLIGH.

Electric moments of hydrobenzoin and *iso*hydrobenzoin. O. HASSEL and E. NÆSHAGEN (Z. physikal. Chem., 1931, **B**, **14**, 232—236; cf. A., 1930, 1347).—Redeterminations at 60° and 18°

confirm previous conclusions (this vol., 894) that there is a marked difference, the present results being: hydrobenzoin $2 \cdot 3 \times 10^{-18}$, *iso*hydrobenzoin $2 \cdot 7 \times 10^{-18}$. N. H. HARTSHORNE.

Molecular and atomic volume. XXXIII. Atomic volume and atomic models. W. BILTZ (Z. physikal. Chem., Bodenstein Festband, 1931, 198—210).—Theoretical. For approx. half the elements, $v_0=11 \cdot 3n/N$, where v_0 is the zero at. vol., n the quantum no. of the outermost electron orbit, and N the group no. of the element in the periodic table. H. F. GILLBE.

Refraction and dispersion of some gaseous compounds. H. LOWERY (Proc. Roy. Soc., 1931, **A**, **133**, 188—207; cf. A., 1928, 220).—Using a Jamin interferometer, the refractivities of a number of gaseous compounds have been measured for the green Hg line 5461 Å., and the dispersion has been determined over the range 4358—6708 Å. The following vals. of $(\mu-1)_d$ (referring to the same no. of mols. d as 1 c.c. of H_2 contains at n.t.p.) were obtained: $SiCl_4$ 0·001969, $SiBr_4$ 0·002725, BCl_3 0·001404, BBr_3 0·002012, $COCl_2$ 0·001149, $COMe_2$ 0·001096, Et_2O 0·001509, C_2H_2 0·0005936, C_2H_4 0·0007192, C_2H_6 0·0007648, MeCl 0·0007804, CH_2Cl_2 0·001112, CH_2Br_2 0·001435. L. L. BIRCUMSHAW.

Refractive power of organic halogen compounds. W. LEITHE (Z. Elektrochem., 1931, **37**, 623—625).—The mol. refractions of several series of org. halogen compounds have been measured and deviations from the law of additivity are discussed. The increase due to each halogen atom substituted for H rises with the no. of halogen atoms in the mol. In general, in a series increasing refraction due to a linking is associated with increasing chemical reactivity. E. S. HEDGES.

Refractive dispersion of organic compounds. I. Experimental methods. II. *cyclo*Hexane. III. Benzene. T. M. LOWRY and C. B. ALLSOPP (Proc. Roy. Soc., 1931, **A**, **133**, 26—36, 36—47, 48—59).—I. Details are given of an interferometric method for measuring the refractive indices of thin films of liquid to four decimal places over a wave-length range from 5000 Å. up to the limit of transparency of the film in the ultra-violet.

II. Vals. are given for n of *cyclo*hexane for 21 wave-lengths from 6708 to 4358 Å., as measured with a refractometer, and for 97 wave-lengths from 5410 to 2452 Å., as deduced from photographic observations with an etalon. The results at 20° can be expressed by $n^2=2 \cdot 00519+[0 \cdot 0098035/(\lambda^2-0 \cdot 011923)]$. Deviations of $\pm 0 \cdot 001$ are found between 2800 and 3950 Å., but outside this range the mean deviation is $\pm 0 \cdot 0002$.

III. Vals. are given for n of C_6H_6 at 20° for 22 wave-lengths from 6707 to 4358 Å. with a refractometer, and for 122 wave-lengths from 4900 to 2700 Å. deduced from photographic observations with an etalon. The vals. in the visible region of the spectrum are less accurate than those determined by Gifford (A, 1923, ii, 705). Gifford's data in the visible region, the authors' in the violet and ultra-violet, and Rubens' in the infra-red (Ann. Physik, 1892, **45**, 238) corr. to 20°, can be expressed by $n^2=1 \cdot 51304+0 \cdot 66992\lambda^2/(\lambda^2-0 \cdot 030170)+0 \cdot 06143(\lambda^2-0 \cdot 070171)\lambda^2[(\lambda^2-0 \cdot 070171)^2+0 \cdot 0003448\lambda^2]-0 \cdot 0027\lambda^2$.

L. L. BIRCUMSHAW.

Crystal form and optical constants of acetylsalicylic acid. R. NIINI (Z. Krist., 1931, **79**, 532—536). — Monoclinic holohedral, $a:b:c$=1·7322 : 1 : 1·7322, β 95° 42·5′; differences in faces which should be similar preclude rhombohedral symmetry in spite of the equality of a and c. For λ 5760, 5460, and 4360, respectively, n_α is 1·5042, 1·6424, 1·6554; n_β 1·5066, 1·6464, 1·6604; and n_γ 1·5216, 1·6720, 1·6914. C. A. SILBERRAD.

Dispersion of ammonium bromide. M. HAASE (Z. Krist., 1931, **80**, 132—133; cf. A., 1929, 754).—n_F^{25}, n_D^{25}, and n_C^{25} for NH_4Br are respectively 1·729, 1·712, and 1·705 (all $\pm 0 \cdot 001$), giving $\nu=(n_D-1)/(n_F-n_C)=29 \cdot 7$. C. A. SILBERRAD.

Theory of optical activity and anomalous rotation dispersion. W. KUHN and H. L. LEHMANN (Chem. Weekblad, 1931, **28**, 517—520)—A reply to Scheringa (this vol., 895). H. F. GILLBE.

Mutarotation and rotatory dispersion of galactonic acid and lactone. T. M. LOWRY and V. K. KRIEBLE (Z. physikal. Chem., Bodenstein Festband, 1931, 881—889).—γ-Galactonolactone has m. p. 112°, $[\alpha]_{5461}^{20}$ (1—2% solution) $-93 \cdot 1°$. The rotatory dispersion between 6708 and 4358 Å. has been determined, and corresponds with characteristic absorption at 2420 Å. Na galactonate is dextrorotatory, and exhibits complex and anomalous dispersion, min. at 5700—5780 Å. Galactonic acid has $[\alpha]_{5461}$ $-9 \cdot 78°$; rotatory dispersion is normal but complex. Equilibrium between the acid and γ-lactone occurs at 25·2% of the former. The mutarotation curves for the formation of the lactone in 0·109N-HCl and 0·0653N-NaCl are unimol. for all wave-lengths, the velocity coeff. being 0·0087 and the catalytic coeff. of the acid 0·080; in 0·2—0·4N-HCl the catalytic coeff. is 0·0132—0·0136.

H. F. GILLBE.

Influence of salts on the optical rotation of gelatin. II. D. C. CARPENTER and J. J. KUCERA (J. Physical Chem., 1931, **35**, 2619—2626; cf. A., 1928, 125).—The characteristic lowering of the optical activity of 0·7% K gelatinate (calfskin) between p_H 6 and 7 by K salts is in the order $KCNS > KI > KClO_3 > KNO_3 > KBr > KCl$, KOAc, $EtCO_2K$, and HCO_2K. The effect of the salts of the org. acids is very small. Uni-bivalent salts follow the order $K_2SO_4 > (CO_2K)_2 > K_2CrO_4$, and their effect passes through a max. at concentrations between 0·1 and 0·3M. The changes in rotation are attributed to the equilibrium between the gel and sol forms of gelatin. L. S. THEOBALD.

Magnetic rotation dispersion of sulphur in solution. T. HORI and A. OKAZAKI (Z. Physik, 1931, **71**, 350—361).—The magnetic rotatory power of CCl_4 and of S_2 in solution was determined by means of a Savart plate. A. B. D. CASSIE.

Electro-optical Kerr constants of liquid and dissolved substances and the nature and cause of the mutual influence and orientation of mole-

cules in the liquid state. I. G. BRIEGLEB (Z. physikal. Chem., 1931, **B**, **14**, 97—121).—The Kerr consts. of several liquid org. compounds and the Kerr consts., dielectric consts., refractivities, and densities of $COMe_2$, Et_2O, $CHCl_3$, CS_2, and C_6H_6 dissolved in heptane have been measured. The mol. Kerr const. decreases with concentration, which in the case of the polar substances is attributable to association, as is the concentration effect on the mol. refractivities and mol. polarisation. The Kerr consts. extrapolated to infinite dilution are all lower than those of the substances in the gaseous state.

N. H. HARTSHORNE.

Molecular theory of electro-optic phenomena. R. DE MALLEMANN (Compt. rend., 1931, **193**, 523—526).—Theoretical. Mol. polarisation in a mol. possessing at least two planes of symmetry reduces to a single vector passing through a fixed point, (centre of polarisation) irrespective of the direction of the field. In an asymmetric mol. it consists of two vectors, a resultant and a couple with axis along the resultant and not in general passing through a fixed point. C. A. SILBERRAD.

Affinity. VI. T. DE DONDER (Bull. Acad. roy. Belg., 1931, [v], **17**, 780—787, 874—887).—Mathematical.

Possible existence of the free hydroxyl radical. K. F. BONHOEFFER and T. G. PEARSON (Z. physikal. Chem., 1931, **B**, **14**, 1—8).—A discharge in H_2O vapour gave OH bands the intensity of which increased linearly with the discharge current; H_2O therefore dissociates into an excited OH radical and a non-excited H atom. The OH radicals recombine to form H_2O and O within 10^{-3} sec., and isolation of OH is impossible. A. B. D. CASSIE.

Free methyl and ethyl. F. PANETH and K. HERZFELD (Z. Elektrochem., 1931, **37**, 577—582).—The duration of existence of free Me and Et (A., 1929, 788) is increased by replacing H_2 as the carrying gas by He or N_2. The free radicals combine completely with a Pb mirror. The kinetics of the processes are treated mathematically. E. S. HEDGES.

Formation of para-hydrogen under pressure at low temperatures. A. FARKAS and K. F. BONHOEFFER (Z. physikal. Chem., Bodenstein Festband, 1931, 638—640).—The formation of para-H_2 in a brass vessel at the temp. of liquid air and pressures up to 110 atm. was homogeneous. H. F. GILLBE.

Decomposition of molecules through collisions of the second kind. H. BEUTLER and W. EISENSCHIMMEL (Z. Elektrochem., 1931, **37**, 582—584).—Theoretical. E. S. HEDGES.

Electronic structure of nitrogen dioxide. W. A. NOYES (Z. Elektrochem., 1931, **37**, 569—571).—The electronic structure O N:O: is used to explain numerous reactions of NO_2. E. S. HEDGES.

Determination of molecular structure from optical and electrical data. E. BERGMANN and L. ENGEL (Z. Elektrochem., 1931, **37**, 563—569).—A lecture. E. S. HEDGES.

Relation between heat of activation and molecular structure. H. DOHSE (Z. physikal. Chem., Bodenstein Festband, 1931, 533—540).—The activation heats of dehydration, Q, of EtOH, $Bu^{\beta}OH$, and *tert.*-amyl alcohol in contact with bauxite are 31, 26, and 17·5 kg.-cal., respectively. An α-Me group thus lowers Q by 5500 g.-cal., a β-Me group by 2500, and a γ-Me group by 500 g.-cal. The calc. distances between the groups in the mol. are in moderate agreement with those deduced from spatial considerations, but the agreement is closer if it is assumed that the mols. are readily deformed when adsorbed on the catalyst.

H. F. GILLBE.

Compounds of the transition elements with metalloids of small atomic dimensions. G. HAGG (Svensk Kem. Tidskr., 1931, **43**, 187—198; cf. A., 1930, 1351).—A discussion of the at. structure of the borides, carbides, nitrides, and hydrides of Bohr's transition elements. Compounds in which the ratio of the at. radius of the metalloid to that of the metal is less than 0·59 exhibit a simple type of "insertion" lattice, whilst for greater ratios complicated structures result. Most of the former compounds contain a simple lattice, either the face-centred cube or close-packed hexagonal lattice, composed of the metal atoms, the atoms of the metalloids occupying positions in the lattice such that they are co-ordinated with either 6 or 4 metal atoms. Less common are the centred cube and simple hexagonal lattices; in these cases the metalloid atom is co-ordinated with 4 and 6 metal atoms, respectively. Structures in which the co-ordination no. of the metal is 12 predominate largely, but the actual factors which determine the particular type of metal atom lattice present in a compound are still unknown.

H. F. HARWOOD.

Structure of hexammino- and hexaquo-salts. O. HASSEL (Z. Krist., 1931, **79**, 531—532).—The author's views (cf. A., 1927, 1014; 1928, 974; 1929, 1222) are elaborated as against those of Pauling (cf. this vol., 151). C. A. SILBERRAD.

Stereochemistry of crystal compounds. VI. Compounds AB_2. Geometrical deduction of probable structure type. P. NIGGLI and E. BRANDENBURGER (Z. Krist., 1931, **79**, 379—429; cf. this vol., 411, 670).—The geometrically probable structures of such compounds, based on their classification according to at. distances (d_A, d_B, d_{AB}) and co-ordination nos. of the constituent atoms, are deduced with examples. In most cases $d_A > d_B > d_{AB}$, but where A is an anion and B a cation, or with a complex bivalent anion, d_B may be $< d_{AB}$.

C. A. SILBERRAD.

Group rotation in solid ammonium and calcium nitrates. F. C. KRACEK, S. B. HENDRICKS, and E. POSNJAK (Nature, 1931, **128**, 410—411).—Mol. rotations in the solid state have been detected in NH_4NO_3. At 105° the tetragonal modification of NH_4NO_3 has a 5·77, c 5·00 Å. with 2 mols. of NH_4NO_3 per unit structure. The separations of the rotating NH_4^+ and NO_3^- groups in the plane of the NO_3^- groups are 3·80 Å. At 155°, the cubic modification has a 4·40 Å. with 1 mol. of NH_4NO_3 per unit. The separation of the rotating NH_4^+ and NO_3^- groups is

3·79 Å. In solid NH_4NO_3 above 125° probably all the rotational degrees of freedom of both $NH_4^{\cdot}$ and NO_3' are fully excited. Rotation of NO_3' is often to be found in cryst. nitrates and many of the previously published crystal structures are probably incorrect.
L. S. THEOBALD.

Constitution and isomerism of thiosulphuric acid. P. RÂY (J. Indian Chem. Soc., 1931, **8**, 307—310).—The yellow to orange solutions of thiosulphatopentacobaltic acid (I), $H_4[(CN)_5CoS_2O_3]$ (A., 1928, 35), yield H_2SO_3 and S when heated; the Ba and Ca salts decompose similarly. The orange-red cryst. acid, obtained by evaporating the solution in vac. over H_2SO_4, dissolves in H_2O with separation of a little S and H_2S to give a yellow to orange solution, which, when warmed, liberates H_2SO_4 and more H_2S, the colour changing to dark red; SO_2 is not evolved, even on boiling. The Mg, Ca, and NH_4 salts from the solid acid are reddish-brown, and evolve H_2S, but not SO_2, on treatment with mineral acid. Isomerism is thus proved for the complex acid, and it is assumed that thiosulphuric acid can exist in two forms, $S\!:\!SO(OH)_2$ (α) and $HS{\cdot}SO_2{\cdot}OH$ (β), the former being present in solutions of (I), the latter in the solid (cf. A., 1924, ii, 103).
R. S. CAHN.

Principle of free rotation in molecules with single carbon linkings. C. WAGNER (Z. physikal. Chem., 1931, **B**, **14**, 166—168).—From a consideration of the sp. heat of C_2H_6 it is concluded that a kind of twisting oscillation instead of free rotation takes place between the Me groups.
N. H. HARTSHORNE.

Low-temperature rotational heat capacities and the relative amounts of the nuclear singlet, triplet, and quintuplet symmetry modifications of methane. D. S. VILLARS and G. SCHULTZE (Physical Rev., 1931, [ii], **38**, 998—1010).—Mainly mathematical. There should be 3 non-combining varieties of CH_4. Heat capacities of each variety, of the true equilibrium mixture, and of the "frozen equilibrium" mixture are calc. N. M. BLIGH.

Magneto-electric saturation effect. O. E. FRIVOLD and S. KOCH (Nature, 1931, **128**, 675).—The effect, required by classical magnetic theory, of the addition of a strong electrolyte on the apparent magnetic moment of mols. which possess fixed magnetic as well as electric moments could not be detected in magnetic susceptibility measurements on a solution of $Cr(NH_3)_3(CNS)_3$ in $COMe_2$ with KCNS as the added electrolyte. L. S. THEOBALD.

Gyromagnetic effect for paramagnetic substances. II. Results on salts of the iron group. W. SUCKSMITH (Proc. Roy. Soc., 1931, **A**, **133**, 179—188).—The means used to increase the sensitivity of the apparatus previously used for Dy_2O_3 (A., 1930, 1100) are described, together with results obtained for the paramagnetic salts from $MnCO_3$, $MnSO_4$, $CrCl_3$, $CoSO_4$, $CoCl_2$, and $FeSO_4$. L. L. BIRCUMSHAW.

Transition of ferromagnetic manganese arsenide into the paramagnetic form. A. SMITS, H. GERDING, and F. VERMAST (Z. physikal. Chem., Bodenstein Festband, 1931, 357—368).—The course of the vol.-temp. curve of MnAs between 15° and 50° resembles those of the intensity of magnetisation–temp. and the sp. heat–temp. curves. The transition from the para- to the ferro-magnetic form involves a series of irreversible metastable conditions; the density change is from 6·26 to 6·2. No vol. change results from the application of a magnetic field.
H. F. GILLBE.

Displacement of the Curie point for nickel by pressure. D. P. RAY-CHAUDHURI (Z. Physik, 1931, **71**, 473—477).—In the Curie point of a Ni wire under tension agreement with the Heisenberg theory of ferromagnetism is found. There is agreement between the curves of temp. against temp. coeff. of resistance, and against extension, and there is also similarity with the curve obtained between temp. and sp. heat for a ferromagnetic body. A. J. MEE.

Molecular forces. III. Derivation of the van der Waals expression a/v^2. A. EUCKEN (Z. physikal. Chem., Bodenstein Festband, 1931, 432—436).—The van der Waals expression a/v^2 has been deduced without making the assumption that the sphere of action of the forces of attraction is large compared with the mean distance between the mols. The so-called swarming effect of mols. at low temp., which requires a variation with temp. of the attraction term, consists merely of the formation of double mols. as a result of collisions between 3 mols., and possibly of the formation of triple mols. after further collisions.
H. F. GILLBE.

Molecular sphere of action of the metals. C. BENEDICKS (Z. physikal. Chem., Bodenstein Festband, 1931, 379—384).—The radii r of the mol. spheres of action of 13 metals, calc. from the equation $r=nH/K$ on the assumption that $n=2$, are of the same order as the apparent at. radii ρ of Bragg. r is a periodic function of the at. no., but the fluctuations are much greater than those of ρ and resemble those of the square of the at. vol. To a first approximation $r=$ const. $\times \rho^6$. H. F. GILLBE.

Empirical evaluation of the potential due to van der Waals forces surrounding molecules. K. WOHL (Z. physikal. Chem., 1931, **B**, **14**, 36—65).—The variation with temp. of the second virial coeff. for gases is more accurately described when a repulsive force characteristic of each atom replaces the rigid sphere (cf. London, this vol., 149; Slater and Kirkwood, *ibid.*, 675). The coeff. of the repulsive term, and the power of the reciprocal of the distance from the centre of the atom or mol. required to fit the experimental curves, are given for He, H_2, Ne, Ar, N_2, O_2, and CO_2. A. B. D. CASSIE.

Energy of C–C and C–H linkings in saturated hydrocarbons. M. REBEK (Arh. Hemiju, 1931, **5**, 192—196).—A review of the results obtained by various authors for the above vals. indicates that they are of the same order. R. TRUSZKOWSKI.

Quadrupole forces in van der Waals attractions. H. MARGENAU (Physical Rev., 1931, [ii], **38**, 747—756).—For van der Waals forces between non-polar atoms at distances apart of the order of the kinetic theory radius the contribution of the interactions between higher poles must be taken into account. Calculations are made for the interactions: dipole–

dipole, dipole–quadrupole, and quadrupole–quadrupole for H and He atoms. N. M. BLIGH.

Avogadro's number and "mean free path." S. RAY (Proc. XV Indian Sci. Cong., 1928, 141).—If the usual expression, $\lambda = 1/(2\pi N\sigma^2)^{\frac{1}{2}}$ is correct, the mean free path is not intimately related to vol., pressure, temp., or entropy; since Avogadro's no. is approx. the same for different atoms, the expression $\lambda = (N/3)^{\frac{1}{3}} - \sigma$ is preferred. CHEMICAL ABSTRACTS.

Effect of the application of a field of attraction to a gas. R. D. KLEEMAN (Science, 1931, **74**, 290). L. S. THEOBALD.

Abstracting schemes for X-ray structure determinations. J. D. BERNAL, P. P. EWALD, and C. MAUGUIN (Z. Krist., 1931, **79**, 495—530).—A complete synoptical table of the nomenclatures of Schwonflies, Wyckoff, and Mauguin is appended. C. A. SILBERRAD.

Accurate determination of lattice constants of polycrystalline materials. F. REGLER (Physikal. Z., 1931, **32**, 680—687).—The usual correction applied in the accurate determination of lattice consts. is not sufficient. A. J. MEE.

Kinematographic representation of the recrystallisation of rock-salt. K. PRZIBRAM (Z. Elektrochem., 1931, **37**, 535—536).—When rock-salt is subjected to a pressure of 2000 kg. per sq. cm. and subjected to Ra radiations it darkens, but slowly becomes lighter when pressure and radiation are removed. A kinematographic record of the process supports the view that the darkening is due to distortion of the space-lattice and the brightening to recrystallisation. E. S. HEDGES.

Theory of the oriented superimposition of ionic crystals; formation of Grimm mixed crystals. I. N. STRANSKI (Z. physikal. Chem., Bodenstein Festband, 1931, 230—238).—The upper limit of supersaturation at which a given type of crystal will deposit on an isomorphous crystal of a different compound has been calc. for the case in which both the substances are binary compounds and differ only in the charges on the component ions. The deposition of NaBr on PbS is considered in detail. H. F. GILLBE.

Recrystallisation. G. TAMMANN (Z. Elektrochem., 1931, **37**, 429—436).—A summary of the author's views on the formation and growth of crystallisation nuclei, especially as influenced by cold work. E. S. HEDGES.

Atomic states in metal lattices on the basis of magnetic measurements. E. VOGT (Z. Elektrochem., 1931, **37**, 460—466).—A lecture. E. S. HEDGES.

Isomorphism considered in relation to X-ray investigations. A. FERRARI (Gazzetta, 1931, **61**, 358—369).—The conditions which determine the occurrence of isomorphism between compounds are discussed. Complete miscibility can always occur when two lattices are made up of unit cells which have the same shape, and only slightly different vols. O. J. WALKER.

Constitutional formulæ of crystalline substances. H. RHEINBOLDT (Z. anorg. Chem., 1931, **200**, 168—172).—The formulæ of the occupants of the lattice points are enclosed in [ ], and there are added numbers representing the no. of immediately adjacent and equidistant or approx. equidistant groups. The NaCl lattice, for instance, is represented by $[Na]^6[Cl]^6$. R. CUTHILL.

Lattice constants. M. C. NEUBURGER (Z. Krist., 1931, **80**, 103—131).

Accurate determination of dimensions of crystal lattices. N. H. KOLKMEIJER and A. L. T. MOESVELD (Z. Krist., 1931, **80**, 63—90).

Increase in surface area due to crystal faces developed by etching. L. TONKS (Physical Rev., 1931, [ii], **38**, 1030—1039).—The actual surface of an etched cryst. body, being made up of cryst. faces, is greater than the apparent surface; the ratio of increase in area to apparent area is the face excess. Criteria for determining those faces which give min. face excess, and two methods for calculating face excess, are deduced for various types of faces. N. M. BLIGH.

Why crystals exist. F. ZWICKY (Proc. Nat. Acad. Sci., 1931, **17**, 524—532).—It is suggested that the cohesive forces having radii of action of the order of at. dimensions are responsible for the condensed state of matter, but not for the cryst. state. C. W. GIBBY.

Method of investigating fibre structure and of showing strains in pieces of metal. F. REGLER (Z. Physik, 1931, **71**, 371—388).—An X-ray method of determining structure and strains is fully described. A. B. D. CASSIE.

X-Ray fibre diagram as a quantitative measure of the change in the structure of the cellulose fibre by chemical processes. I. Quantitative relation between the intensities of the equatorial interference lines for fibre preparations of natural and mercerised cellulose of known composition. W. SCHRAMEK (Z. physikal. Chem., 1931, B, **13**, 462—474).—The observation made by previous investigators that technical mercerisation produces only an incomplete mercerisation effect is confirmed by X-ray investigation. It is possible to obtain a quant. relationship between the X-ray diagram and the degree of mercerisation. J. W. SMITH.

X-Ray investigation of space-lattice distortion in light metals. J. HENGSTENBERG and H. MARK (Z. Elektrochem., 1931, **37**, 524—528).—Changes in the X-ray spectrum of duralumin and "electron metal" on cold-working are described. E. S. HEDGES.

Hexagonal nickel. G. BREDIG and E. S. VON BERGKAMPF (Z. physikal. Chem., Bodenstein Festband, 1931, 172—176).—By cathodic dispersion of Ni in N_2 or H_2 a metallic mirror of non-magnetic, hexagonal Ni, having *a* 2·60—2·66, *c* 4·15—4·22 Å., is obtained. The metal passes into the ordinary cubic form on heating in H_2 at 300°. H. F. GILLBE.

Density and crystal structure of niobium. M. C. NEUBURGER (Z. Krist., 1931, **78**, 164—167).—A re-examination of the purest of Meisel's three samples of Nb (cf. A., 1930, 983) gave *d* 8·55 (calc.

8·56). The unit cell has a 3·303±0·002 Å., and contains 2 mols.; space-group O_h^9; at. radius 1·430 Å.
C. A. SILBERRAD.

Crystal structure of some carbides and borides. M. VON STACKELBERG (Z. Elektrochem., 1931, 37, 542—544).—A summary of work on carbides (cf. A., 1930, 672, 1351) shows that derivatives of CH_4 have a single C atom in the space lattice, whilst derivatives of C_2H_2 contain the lattice group C_2. A preliminary X-ray examination of borides of the type CaB_6, SrB_6, BaB_6, etc. shows them to possess a cubic lattice of the CsCl type, composed of metal atoms and B_6 groups. The B atoms in the B_6 group are arranged at the angles of a regular octahedron, having an edge of 1·17 Å. in the case of CaB_6. The method of linking is discussed. E. S. HEDGES.

Crystal structure of N_2O_4. L. VEGARD (Z. Physik, 1931, 71, 299—300; this vol., 548, 1115).—Experimental evidence is insufficient to confirm an N_2O_4 crystal unit, and is not inconsistent with a linear NO_2 unit. A. B. D. CASSIE.

Formation of mixed crystals in molecular lattices through exchange of molecules. L. VEGARD (Z. Physik, 1931, 71, 465—472).—Substances like solid N_2O and CO_2 which possess typical mol. lattices can form mixed crystals through the interchange of mols. The change in length of the elementary cube obeys the additive law. A. J. MEE.

Crystal structure of ammonium chromate. D. J. BUJOR (Z. Krist., 1931, 78, 1—15).—$(NH_4)_2CrO_4$ crystals (cf. A., 1889, 1117) are twinned about (001) and the b axis, a fact confirmed by etch figures. The unit cell has a 6·15, b 5·27, c 7·66 Å., β 115° 13′, and contains 2 mols.; space-group C_i^1.
C. A. SILBERRAD.

Crystal structure or potassium chromate. M. Y. COLBY (Z. Krist., 1931, 78, 168).—K_2CrO_4 has a 5·92, b 10·39, c 7·68 Å., with 4 mols. in the unit cell; space-group V_h^{16}; d^{18} 2·732. C. A. SILBERRAD.

Structure of beryllium sulphate tetrahydrate. P. SCHONEFELD (Z. Krist., 1931, 78, 16—41).—Previous results (cf. A., 1928, 463) are confirmed save that a should be 8·02±0·02 Å. The connexion between the structure, properties, and polarisation of the constituents is discussed. C. A. SILBERRAD.

Crystal structure of sodium nitrite, $NaNO_2$. G. E. ZIEGLER (Physical Rev., 1931, [ii], 38, 1040—1047).—The lattice is body-centered, orthorhombic, space-group C_{2v}^{20}, unit cell containing 2 mols. a 3·55, b 5·56, c 5·37 Å. The positions of the atoms and distances between atoms are recorded. The angle between the N–O linkings is 132°. N. M. BLIGH.

Crystal structure of eulytite. G. MENZER (Z. Krist., 1931, 78, 136—163).—A detailed account of work already noted (this vol., 550).
C. A. SILBERRAD.

Crystal structures of parisite, synchysite, and kordylite. I. OFTEDAL (Z. Krist., 1931, 79, 437—464).—Parisite, $2RFCO_3,CaCO_3$, and synchysite, $RFCO_3,CaCO_3$, (R=La, Ce, etc.), although very closely related, are distinct species; some reputed parisite is really synchysite. Their structures, as also that of kordylite, $2RFCO_3,BaCO_3$, are very approx. represented by hexagonal pseudo-cells having a 4·094, 4·094, 4·35 and c 27·93, 18·20, 22·8 Å., respectively, each cell containing 2 mols. For accurate description an $a\sqrt{3}$ times as great, or approx. 7 Å., is required, the unit cell containing 6 mols. and the symmetry being lower. Probable structures are deduced closely resembling that of bastnasite (cf. this vol., 1116). Parisite is very weakly, if at all, piezo-electric, and it and synchysite show parallel growths. The recorded density of kordylite is probably too low.
C. A. SILBERRAD.

Roentgenography of liquids. I. Diffraction of X-rays by organic liquids. G. E. MUCHIN and I. I. TSCHALENKO (Ukrain. Chem. J., 1931, 6, [Sci.], 9—51).—A review of the literature.
R. TRUSZKOWSKI.

Diffraction of X-rays in liquids and ionic solutions. J. A. PRINS (Z. Physik, 1931, 71, 445—449).—The continuous spectrum is greatly interrupted in certain circumstances by the scattering of X-rays on passing through liquids. The results of earlier work on aliphatic compounds are corrected and extended. A. J. MEE.

Two-dimensional crystals. N. FUCHS (Z. physikal. Chem., 1931, B, 14, 285—289).—Crystals of $C_{31}H_{70}$ formed on the surface of its slightly supersaturated solution in non-volatile liquid paraffin may be only 1 mol. thick. N. H. HARTSHORNE.

Crystal structure of the hydrates of copper formate. I. Copper formate tetrahydrate. II. Copper formate dihydrate. K. J. KABRAJI (Indian J. Physics, 1931, 6, 81—114, 115—132).—The space-group of both dihydrate and tetrahydrate is C_{2h}^3: the former has 16 mols. per cell and the latter 8. In the tetrahydrate the H_2O mols. lie entirely between consecutive (010) planes through the centres of the atoms of $(HCO_2)_2Cu$. The length of the H_2O mol. in both hydrates is 4·22 Å. F. J. WILKINS.

X-Ray study of the magnetic character of liquid crystalline p-azoxyanisole and a comparison with the isotropic liquid. G. W. STEWART (Physical Rev., 1931, [ii], 38, 931—942).—The effect of a magnetic field on the orientation of the large groups of mols. in the liquid-cryst. state was measured, and the data are applied to an interpretation of the magnetic character, and to a comparison of the liquid-cryst. and transparent liquid states. In the former the X-ray diffraction intensity is 10% greater than in the latter state, in which the existence of cybotactic groups is thus supported.
N. M. BLIGH.

Transformations in the crystal lattice. E. HERTEL (Z. Elektrochem., 1931, 37, 536—538).—The mol. compound formed of 4-bromo-α-naphthylamine with 2:6-dinitrophenol exists in two forms, which differ in m. p., solubility, colour, cryst. habit, and cryst. space lattice. The stable yellow modification (m. p. 91°) contains a linking between the OH of the nitrophenol and the NH_2 of the naphthylamine, which is absent in the metastable form (m. p. 85°), where the residual affinities of the benzenoid components are involved. Yellow o-bromoaniline picrate changes to a red modification at 95°. Changes in the lattice are discussed. E. S. HEDGES.

X-Ray investigation of *cyclo*hexane derivatives. I. General survey. II. Quebrachitol. III. *l*-Inositol, *i*-inositol, and quercitol. IV. *i*-Inositol dihydrate. A. L. PATTERSON and T. N. WHITE (Z. Krist., 1931, **78**, 76—100, and **80**, 1—4).—I. Previous investigations are discussed, and a table of possible and known *cyclo*hexanols is given. As working hypotheses the puckered ring and dextrose relationship theories are adopted with Lespieau's nomenclature (cf. A., 1895, i, 489; 1927, 98; 1928, 465; this vol., 69). II.—IV. The following data (in this order) are given: crystal class, dimensions of unit cell (a, b, c in Å.), β, density, no. of mols. in unit cell, probable space-group: quebrachitol, monoclinic sphenoidal, 6·60, 7·15, 8·65, not 90°, 1·54, 2, C_2^2 (C_2p2); *l*-inositol, monoclinic sphenoidal, 6·17, 9·11, 6·83, 106·6°, 1·598, 2, C_2^2 (C_2p2), $[\alpha]_D$ −65·8°, no hydrate was obtainable; *i*-inositol, monoclinic prismatic, 6·64, 12·0, 19·7, 105·8°, 1·61 (not 1·752; cf. A., 1881, 1022), 8, C_{2h}^5 ($C_{2h}p\alpha2$); *i*-inositol dihydrate, monoclinic prismatic, 8·98, 16·59, 6·49, 109·8°, 1·58, 4, C_{2h}^5 ($C_{2h}p\alpha2$); quercitol, monoclinic sphenoidal, 6·83, 8·53, 6·45, 110° 57′, 1·5806, 2, C_2^2 (C_2p2). Distances between atoms, *e. g.*, of C, in different mols. are much greater, in the same mol. much less, than would be expected from inorg. data, pointing to such mols. being tightly bound structures, but forming comparatively open crystal structures. Quebrachitol from *Hevea brasiliensis* is identical with that from *Heterodendron oleæifolium*. C. A. SILBERRAD.

X-Ray investigation of *cyclo*hexane derivatives. V. α- and γ-*cyclo*Hexane-1 : 2-diol, β-*cyclo*hexane-1 : 4-diol, and β-*cyclo*hexanediol 1 : 4-diacetate. T. N. WHITE (Z. Krist., 1931, **80**, 5—17).—α-*cyclo*Hexane-1 : 2-diol (cf. A., 1899, i, 22), m. p. 97—98°, d^{25} 1·182, orthorhombic, unit cell, a 7·62, b 8·55, c 19·57 Å., with 8 mols.; space-group V_h^{15} ($D_{2h}p\gamma\alpha\beta$). -*cyclo*Hexane-1 : 2-diol prepared according to runel's method for the β-isomeride (cf. A., 1903, i, 338; 1905, i, 869) differed from his account thereof, and is hence designated γ; m. p. 104°, d^{24} 1·147, monoclinic prismatic, $a:b:c$=1·954 : 1 : 0·716, β 103·9°; unit cell a 19·13, b 9·92, c 7·23 Å., with 8 mols., space-group C_{2h}^6 ($C_{2h}b\alpha1$). β-*cyclo*Hexane-1 : 4-diol, or *trans*-quinitol (cf. A., 1894, i, 174), d^{20} 1·18, monoclinic prismatic, $a:b:c$=0·293 : 1 : 0·339, β 96°; unit cell a 6·32, b 21·2, c 7·27 Å., with 6 mols., space-group C_{2h}^5 ($C_{2h}p\alpha2$). β-*cyclo*Hexanediol 1 : 4-diacetate, d 1·18 (approx.), monoclinic prismatic, $a:b:c$ = 2·344 : 1 : 1·168, β 107·4°; unit cell a 13·56, b 5·83, c 6·72 Å., with 2 mols., space-group C_{2h}^5 ($C_{2h}p\alpha2$). C. A. SILBERRAD.

***cyclo*Hexane problem.** O. HASSEL (Z. Elektrochem., 1931, **37**, 540—542).—The structure of *cyclo*hexane and its derivatives is reviewed in the light of crystallographic data. E. S. HEDGES.

Structure of the molecular compound veramon [pyramidone+veronal]. E. HERTEL (Z. physikal. Chem., Bodenstein Festband, 1931, 267—272).—Comparison of the X-ray diagrams of the mol. compound of pyramidone and veronal with those of the components shows that the substance conforms to the definition previously suggested for a true mol. compound. The crystals are rhombic; 4 mols. of each of the components in the unit cell; space-group C_{2v}^5 or C_{2v}^4. The identity periods of the triclinic crystals of pyramidone are 7·4, 18·1, and 10·8 Å.; 4 mols. in the unit cell. H. F. GILLBE.

Crystal structure of hexabromobutylenes. W. EISSNER and R. BRILL (Z. Krist., 1931, **79**, 430—436).—The isomeride of m. p. 185° (cf. A., 1926, 1120), d 3·30, is monoclinic prismatic, $a:b:c$=1·57 : 1 : 2·75, β 68° 35′, n 1·75; variations indicate impurities in spite of recrystallisation. The unit cell has a 11·5₅, b 6·40, c 10·0₆, β 44° 27′, containing 2 symmetrical mols., space-group C_{2h}^5. This is consequently the symmetrical isomeride $[CHBr_2{\cdot}CBr{:}]_2$, that of m. p. 114° being $CHBr_2{\cdot}CBr_2{\cdot}CBr{:}CHBr$. The atoms in the mol. are almost coplanar. C. A. SILBERRAD.

Crystallographic study of some organic substances. A. FERRARI and A. SCHERILLO (Z. Krist., 1931, **80**, 45—53).—2 : 5′-Di*iso*oxazolyl ketone (this vol., 968), d 1·48, is monoclinic prismatic, $a:b:c$= 1·038 : 1 : 0·8646, β 91° 37′; unit cell a 15·31, b 14·75, c 12·77 Å., with 16 mols. The ketone $C_{12}H_8O_6N_4$ (*loc. cit.*), d 1·492, is rhombic, $a:b:c$=1·18 : 1 : 0·87; unit cell a 12·98, b 11·00, c 9·57 Å., with 4 mols. The compound $C_4H_2O_3N_4$ (this vol., 1170) is monoclinic prismatic, $a:b:c$=1·500 : 1 : 3·546, β 105° 34′; unit cell a 7·38, b 4·92, c 17·45 Å., with 4 mols. 2 : 2′-Naphthacarbazole (cf. A., 1929, 1172), d 1·312, is monoclinic prismatic, $a:b:c$=1·169 : 1 : 0·6989, β 114° 14′; unit cell a 14·05, b 12·02, c 8·40 Å., with 4 mols. C. A. SILBERRAD.

Space-groups of carbohydrates. J. YOUNG and F. W. SPIERS (Z. Krist., 1931, **78**, 101—110).—The following data are given: crystal system, dimensions of unit cell (a, b, c) in Å., (if monoclinic) β, density, no. of mols. in unit cell, space-group: γ-*d*-mannonolactone, orthorhombic, 14·0, 11·1, 4·73, 1·61, 4, V^4; 2 : 3 : 5 : 6-tetramethyl-γ-*d*-mannonolactone, monoclinic, 9·79, 13·8, 4·50, 93·3°, 1·26, 2, C_2^2; 2 : 3 : 5-trimethyl-γ-*l*-rhamnonolactone, orthorhombic, 12·2, 18·3, 4·65, 1·27, 4, V^4; 2 : 3 : 4-trimethyl-δ-*l*-arabonolactone, orthorhombic, 10·8, 12·2, 7·30, 1·30, 4, V^4; 2 : 3 : 4-trimethyl-α-*d*-xylopyranose, monoclinic, 8·68, 8·31, 6·65, 91·0°, 1·30, 2, C_2^2; 1 : 3 : 4 : 5-tetramethyl-β-*d*-fructopyranose, orthorhombic, 9·22, 8·97, 14·8, 1·30, 4, V^4; 1 : 3 : 4 : 5-tetra-acetyl-β-*d*-fructopyranose, monoclinic, 10·7, 7·98, 17·0, 144·5°, 1·36, 2, C_2^2. C. A. SILBERRAD.

X-Ray investigations of cellulose derivatives. X. Fibre period of cellulose derivatives. K. HESS and C. TROGUS (Z. physikal. Chem., Bodenstein Festband, 1931, 385—391).—The fibre periods of numerous cellulose derivatives are $n \times 5{\cdot}15$ Å., where n is 2, 3, 4, or 5. This dimension, which is the length of a glucose group, is thus more closely related to the constitution of cellulose than is the length of the cellobiose group (10·3 Å.). H. F. GILLBE.

Calculation of characteristic atomic frequencies. A. MAGNUS (Z. physikal. Chem., Bodenstein Festband, 1931, 273—282).—For cryst. substances the formula $\nu = \sqrt{6v_M/Mr_0^2x}/2\pi$, where ν is the characteristic frequency, v_M the arithmetic mean at. vol. and M the harmonic mean at. wt. of the com-

ponents, r_0 the normal inter-at. distance, and x the compressibility, has been derived. The calc. characteristic temp. of various binary ionic compounds agrees well with the experimental vals., but for the elements the calc. vals. are frequently much too high. Although the discrepancy may in many cases be attributed to the Schottky transition, this does not hold for the alkali metals and Ca.

H. F. GILLBE.

Electric glow emission of iron. G. SILJEHOLM (Ann. Physik, 1931, [v], **10**, 178—222).—The dependence of the positive emission of Fe on temp. and its behaviour at the transition point A3, the influence of lattice change at A3 on the emission, and the alteration of thermo-power and electrical resistance with temp. have been studied. W. GOOD.

Physics and metallography of magnesium. E. SCHMID (Z. Elektrochem., 1931, **37**, 447—459).—A lecture on the physical anisotropy of Mg crystals, elastic parameter, thermal expansion, electrical conductivity, plastic deformation, and the formation of mixed crystals in the systems Al–Mg, Zn–Mg, and Mn–Mg. E. S. HEDGES.

Electric and magnetic properties of metals. R. BECKER (Z. Elektrochem., 1931, **37**, 403—414).—A lecture. E. S. HEDGES.

Elasticity of single crystals of iron. E. GOENS and E. SCHMID (Z. Elektrochem., 1931, **37**, 539—540).—In elastic properties the Fe crystal is strongly anisotropic. E. S. HEDGES.

Magnetic properties of copper–nickel alloys. E. H. WILLIAMS (Physical Rev., 1931, [ii], **38**, 828—831).—The change of susceptibility with temp. and composition for alloys containing 0·1—70% Ni was investigated. N. M. BLIGH.

Magnetisation of single crystals of cobalt at high temperatures. K. HONDA and H. MASUMOTO (Sci. Rep. Tohoku, 1931, **20**, 323—341).—Magnetisation is easiest in the direction of the [0001] axis and in weak fields reaches a max. at 230°. Magnetisation is difficult in the direction of the [10$\bar{1}$0] and [11$\bar{2}$0] axes, increases with rise of temp. up to 300°, and then remains const. The saturation val. at 0° abs. is 1446 c.g.s. A. R. POWELL.

Relation between Barkhausen effect and intensity of magnetisation. S. PROCOPIU and T. FARCAS (Ann. Sci. Univ. Jassy, 1930, **16**, 344—351).—For cast steel the Barkhausen effect is proportional to the intensity of magnetisation. H. F. GILLBE.

Barkhausen effect. S. PROCOPIU (Ann. Sci. Univ. Jassy, 1930, **16**, 352—374).—The Barkhausen effect with Fe is due to the orientation of the particles and is proportional to the variation of the intensity of magnetisation. H. F. GILLBE.

Kerr constant of nitrobenzene. R. MOLLER (Physikal. Z., 1931, **32**, 697—718).—The non-linear potential decrease in $PhNO_2$ is confirmed. $PhNO_2$ ($\Omega=3\times10^{-11}$) shows a Kerr const. of $3{\cdot}74\times10^{-5}$.

W. R. ANGUS.

Physics of the nitrobenzene "Kerr" cell. I. Distribution of a strong electrostatic field in the nitrobenzene Kerr cell. F. HEHLGANS (Physikal. Z., 1931, **32**, 718—727).—The inhomogeneity of a strong electrostatic field in the $PhNO_2$ Kerr cell is produced by impurities. W. R. ANGUS.

Hall effect in liquid metals. J. KIKOIN and I. FAKIDOV (Z. Physik, 1931, **71**, 393—402).—Hg showed a negligible Hall effect and K–Na alloys an effect in agreement with theory. A. B. D. CASSIE.

Dilatometric investigation of the vitreous state. O. KOERNER and H. SALMANG (Z. anorg. Chem., 1931, **199**, 235—240).—The abrupt change of length of a cryst. material at the transition point is independent of the rate of heating, but with silicate glasses the reverse is true. The temp. at which softening commences falls as the rate of heating is diminished. Glass is thus merely a supercooled liquid, and there is no justification for the assumption that the vitreous condition represents a fourth state of matter. H. F. GILLBE.

Transitions of crystalline substances at high pressures. G. TAMMANN and R. KOHLHAAS (Z. anorg. Chem., 1931, **199**, 209—224).—When pressure is applied to a graduated piston operating in a cylinder containing a cryst. material the occurrence of a transition is apparent from the pressure–vol. curve. An approx. val. only of the transition pressure can be obtained, since the pressure is not uniform throughout the material. Data are given for PhOH, AgI, FeS, borneol, and Sn. H. F. GILLBE.

Elastic anisotropy of iron. D. A. G. BRUGGEMAN (Naturwiss., 1931, **19**, 814—815).

Sintering of powdered iron by heat and pressure treatment. L. SCHLECHT, W. SCHUBARDT, and F. DUFTSCHMID (Z. Elektrochem., 1931, **37**, 485—491).—The structure of pure Fe powder, formed by the thermal decomp. of Fe carbonyl, is described and the sintering brought about by heating at various temp., with or without increased pressure, is illustrated by means of photomicrographs.

E. S. HEDGES.

Vibration method for investigating strength of crystals. V. D. KUSNETZOV and E. V. LAVRENTJEVA (Z. Krist., 1931, **80**, 54—62).

Dependence of crystal plasticity on temperature. III. Aluminium. W. BOAS and E. SCHMID (Z. Physik, 1931, **71**, 703—714).—The investigation of the extension of Al crystals in the temp. range −185° to 600° shows a very marked alteration of properties at about 400°. Above the latter temp. the crystals have different properties according to their orientation. A. J. MEE.

Vaporisation of magnesium in a vacuum. W. KAUFMANN and P. SIEDLER (Z. Elektrochem., 1931, **37**, 492—497).—Mg can be distilled at 650°/2 mm. and can be sublimed at 500—650°/0·05—2·0 mm. Mg. of 99·99% purity can be obtained by a single distillation, and on repeated distillation a product is obtained in which impurities cannot be recognised chemically or spectroscopically.

E. S. HEDGES.

Velocity of evaporation of crystals. G. TAMMANN and K. L. DREYER (Z. physikal. Chem., Bodenstein Festband, 1931, 1—18).—The velocity of evaporation of volatile crystals increases with increase

of the difference between the v. p. of the substance and the external pressure, and, unlike that of liquids, rises to a limiting val. with rise of temp. The temp. at the surface of the solid has been calc. from the temp. coeffs. of the evaporation velocity and the v. p.; for camphor and $C_{10}H_8$ the difference between the surrounding temp. and the surface temp. is of the order of 4—20°. H. F. GILLBE.

Determination of the mol. wt. of vapours at very low pressures by the method of Heller and Neumann. M. VOLMER (Z. physikal. Chem., Bodenstein Festband, 1931, 863—873).—The (solid) substance is placed in a rectangular box containing two small holes so placed that when the box is suspended by a thread and placed in a high vac. the issuing vapour produces a couple which causes the box to take up a definite position relative to its initial position. By measurement of the displacement angle the mol. wt. of the vapour may be calc. Owing to some difficulties the error is about 3·4%. Typical measurements with $COPh_2$ and NPh:NPh are described. Metaldehyde has the formula $(MeCHO)_4$, whilst the vapour of quinhydrone at room temp. has mol. wt. 109. H. F. GILLBE.

Molecular size and phase partition. J. N. BRONSTED (Z. physikal. Chem., Bodenstein Festband, 1931, 257—266).—On the assumption that the relative potential energies of chemically similar compounds are proportional to the sizes of the mols., *i.e.*, to the mol. wt. in the case of ordinary systems, equations are derived for calculating the v. p. of one compound from that of a similar compound, and for the solubility equilibria in two-phase systems. The theory appears to be applicable also to colloidal substances such as proteins. H. F. GILLBE.

Dependence of the Kirchhoff constant on temperature. F. RECHEL (Ann. Physik, 1931, [v], **10**, 1—14).—The velocity of sound in air, CO_2, O_2, N_2, and NH_3 was investigated from 16° to 910°. The deviations from theory in the variation of the Kirchhoff const. with temp. are confirmed. W. GOOD.

Behaviour of pulverised metals under pressure. F. SKAUPY and O. KANTOROWICZ (Z. Elektrochem., 1931, **37**, 482—485).—The variation of electrical resistance, R, of powdered metals with the pressure, P, is represented by the equation $1/R=c\sqrt{P}+C$, where c and C are consts. depending on the material and its previous treatment. The resistivities of powdered soft metals (Zn, Sn, Pb, Ag, graphite) in the pressed state are lower than those of the compact metals, whilst the resistivities of compressed powders of hard metals (Fe, Wo, Ni) are higher than in the compact state. The results are discussed in relation to sintering. E. S. HEDGES.

Resistance of lead to high-frequency currents at superconducting temperatures. J. C. MCLENNAN, A. C. BURTON, A. PITT, and J. O. WILHELM (Phil. Mag., 1931, [vii], **12**, 707—719).—The superconductivity of Pb which appears with direct current abruptly at 7·2° abs. does not appear when high-frequency currents of frequency 11×10^6 per sec. are used. A decrease is not obtained until 4·2° abs. F. J. WILKINS.

Resistivity of single-crystal zinc. E. P. T. TYNDALL and A. G. HOYEM (Physical Rev., 1931, [ii], **38**, 820—827; cf. Ware, A., 1930, 844).—Measurements of sp. resistance ρ as a function of orientation support the Voigt–Thomson symmetry relation. Vals. obtained were $\rho_{\parallel}$ 6·2 and $\rho_{\perp}$ $5·86\times10^{-6}$ ohm per c.c. for Kahlbaum Zn, and vals. each about 0·6% lower for spectroscopically pure Zn. A few crystals of the latter gave anomalous results as found by Bridgman (cf. A., 1929, 1136). N. M. BLIGH.

Electrical conductivity of metals. C. D. NIVEN (Canad. J. Res., 1931, **5**, 79—86).—When electrical resistance vanishes at low temp. it does so suddenly. It is suggested that a metallic atom is one with an incomplete electron configuration, and that in ordinary conduction an electron jumps from one atom to another, where it remains until it is in a type of equilibrium with the electrons already on that atom. In the superconducting state the electronic orbits of different atoms become synchronised, and when an electron leaves an atom another automatically replaces it. J. W. SMITH.

Electrical conductivity and structure of thin metallic layers. IV. E. HAMBURGER (Ann. Physik, 1931, [v], **11**, 40—52).—The applications of the relation between electrical conductivity and structure of thin metallic layers previously found (cf. this vol., 1112) are discussed. A. J. MEE.

Triple points of nitrogen and of oxygen as standard temperatures. E. JUSTI (Ann. Physik, 1931, [v], **10**, 983—992).—A resistance thermometer capable of reproducing the m. p. of N_2 or O_2 to ±0·002° is described. Data are: O_2, m. p. 54·24±0·04° abs., v. p. 1·20±0·05 mm.; N_2, m. p. 63·09±0·01° abs., v. p. 93·91±0·05 mm. W. R. ANGUS.

Discontinuities at the m. p. of bismuth. W. L. WEBSTER (Proc. Roy. Soc., 1931, **A**, **133**, 162—172).—Measurements of the temp. of emission of latent heat, the loss of rigidity, and the anomalous diamagnetic discontinuity coincide within an experimental error of 0·3°. Heating curves show that the melting of Bi takes place over several degrees. L. L. BIRCUMSHAW.

Preliminary determination of the latent heat of fusion and density of helium between 15° and 20° abs. F. SIMON and F. STECKEL (Z. physikal. Chem., Bodenstein Festband, 1931, 737—744).—An evaporation calorimeter for use at low temp. is described. The latent heat of fusion of He at 17° abs. is of the order of 40 g.-cal. per g.-atom, *i.e.*, about double the val. at the b.p. At 14·9° and 20·4° abs. liquid He has d 0·31 and 0·35, respectively, and solid He $d_{calc.}$ 0·32 and 0·37, respectively. H. F. GILLBE.

Nature of latent heat of fusion. K. HONDA and H. MASUMOTO (Sci. Rep. Tohoku, 1931, **20**, 342—352).—Assuming that the atoms of a solid element are making a simple harmonic motion, the dynamic internal pressure p_i (ratio of the internal work to the expansion in vol. caused by a rise in temp. of 1°) of numerous elements has been calc., and it is shown that the latent heat of fusion is the product of p_i and the change in sp. vol. at the m. p. For elements

with a cubic lattice p_i at the m. p. is directly, and the vol. increase of 1 g.-atom due to rise in temp. of 1° at the m. p. inversely, proportional to the abs. m. p., and the at. heat of fusion is proportional to the product of the vol. change during melting and the square of the abs. m. p. A. R. Powell.

Fusion under pressure and value of interpolation formulæ. E. Jänecke (Z. physikal. Chem., 1931, **156**, 161—175).—Theoretical. The equations $(p+a)(b-t)=c^2$ and $(p+a)^r(b-t)=c$ give the pressure-temp. vals. for the fusion of certain substances under pressure; the second equation also agrees with the data for change of vol. difference with temp. and pressure. The equations can be used as interpolation formulæ and the second gives approx. the equation of state for solid–liquid at high pressures (cf. A., 1925, ii, 495; 1926, 570, 894; 1927, 1031). M. S. Burr.

Calculation of the lattice energies and heats of sublimation of the alkali halides. K. Fajans and E. Schwartz (Z. physikal. Chem., Bodenstein Festband, 1931, 717—730).—Calculation of the lattice energy of the alkali halides, employing 9 as the exponent of the repulsion potential in the Born equation, leads to discrepancies as great as 15 kg.-cal. Although the anomalies in the b. p. and sublimation heats are not entirely explicable in terms of the relative sizes of the ions, quant. agreement with the observed vals. is obtained if the deformation of the ions in the vapour phase is taken into consideration. H. F. Gillbe.

General theory of b.-p. rules. T. S. Wheeler (Phil. Mag., 1931, [vii], **12**, 685—689).—The general theory of b.-p. rules for temp. of equal v. p. and of rules involving v.-p. relations other than that of equality is discussed. F. J. Wilkins.

Heat of dissociation of iodine. W. G. Brown (Physical Rev., 1931, [ii], **38**, 709—711).—Measurements of the visible absorption bands of I in the neighbourhood of their convergence are tabulated, and lead to the val. 1·535±0·001 volts for the heat of dissociation. N. M. Bligh.

Heats of vaporisation of organic compounds. J. H. Mathews and P. R. Fehlandt (J. Amer. Chem. Soc., 1931, **53**, 3212—3217; cf. A., 1926, 462).—The method previously described has been modified so that only 30 c.c. of liquid are required for determining the heat of vaporisation, L. Vals. of L for 22 org. compounds are recorded. J. G. A. Griffiths.

Metastability of elements and compounds as a result of enantiotropy or monotropy. XV. Study of mercuric iodide with the aid of the differential gas dilatometer. E. Cohen and H. L. Bradée (Z. physikal. Chem., Bodenstein Festband, 1931, 481—493).—HgI_2 (red) has d (X-ray) 6·31, d_4^{18} (pyknometer) 6·38, coeff. of expansion (18° to 125·1°) 0·000140, transition temp. 127°, vol. change on transition (1 atm.) 0·00349±0·00005 c.c. per g. When physically "pure," the red form has d_4^{t} 6·32, and the higher val. ordinarily obtained is ascribed to the presence of a previously unknown monotropic form of red HgI_2. H. F. Gillbe.

Chemical constants of the vapours of hydrogen and of hydrogen chloride, and the entropy change accompanying the reaction $H_2 + Cl_2 \leftarrow 2HCl$. T. E. Stern (Proc. Roy. Soc., 1931, A, **133**, 303—310).—Theoretical. A mistake in the author's recent calculations of the chemical const. i' of H_2 vapour (this vol., 295) is rectified. The val. for HCl vapour is calc. to be −0·42. Using the values for the entropies at 0° abs. of g.-mols. of H_2, Cl_2, and HCl, the entropy change accompanying the reaction $H_2+Cl_2 \leftarrow 2HCl$ between the cryst. phases at 0° abs. is calc. to be 1·63 g.-cal. per 1°. This value follows from the supposition that H_2 mols. rotate, whilst Cl_2 mols. do not, in the cryst. phase at the lowest temp. L. L. Bircumshaw.

Theory of corresponding states and the new theory of van der Waals forces. K. Wohl (Z. physikal. Chem., Bodenstein Festband, 1931, 807—816).—A discussion, particularly of London's theory. The apparent anomaly of H_2 and He is due to the disturbing influence of the zero energy on the crit. data. The approximation formula of Slater and Kirkwood, in which only easily accessible data are involved, is more satisfactory than that of London. H. F. Gillbe.

Density of nitrous oxide. T. Batuecas (Z. physikal. Chem., Bodenstein Festband, 1931, 78—84).—The mean density of N_2O, prepared by different methods, is 1·9804±0·00005 g. per litre, a val. which is about 0·1% higher than those in the literature. H. F. Gillbe.

Generalised thermodynamic properties of higher hydrocarbon vapours. J. Q. Cope, W. K. Lewis, and H. C. Weber (Ind. Eng. Chem., 1931, **23**, 887—892).—If vals. of PV/RT for the saturated vapours of hydrocarbons having more than two C atoms are plotted against P_r/T_r all the points obtained for all hydrocarbons lie on the same curve; the max. deviation is 3%. Further, for hydrocarbons with more than three C atoms the deviations from the gas laws are approx. equal for equal values of P_r and T_r whether the vapours are saturated or not if RT/P_cV is not greater than 4. It is therefore possible to determine graphically the vol. and thermal properties of the vapour of any higher hydrocarbon up to and somewhat beyond its crit. point. F. J. Wilkins.

Polarity and vapour pressure. A. R. Martin (Nature, 1931, **128**, 456). L. S. Theobald.

Change of density of carbon disulphide with temperature. J. Mazur (Nature, 1931, **128**, 673).—The density of CS_2 increases from 1·2628 at −20° to 1·4363 at −90° when the increase in d with a fall in temp. becomes more rapid; near the f. p. (−112°) d is 1·4751. L. S. Theobald.

Comparison of viscosities of liquids by oscillating columns. G. Subrahmaniam (Proc. XV Indian Sci. Cong., 1928, 86).—The rate of decay of small, steady oscillations of a liquid in a U-tube is related to the coeff. of viscosity by the expression $\nu=b^2\lambda/2\tau$, where ν is the kinematic coeff., λ is the logarithmic decrement, τ the free period, and b a const. assumed to be the same for the same tube and different wetting liquids. The relation has been verified for H_2O, EtOH, Et_2O, C_6H_6, xylene, turpentine, and CS_2. Chemical Abstracts.

Viscosity, heat conductivity, and diffusion in gas mixtures. XIX. Temperature coefficient, numerical and calculated values of the gas viscosity from the chemical formula and the critical temperature. M. TRAUTZ (Ann. Physik, 1931, [v], **11**, 190—226).—Temp. coeffs. of many vapours have been evaluated and are discussed. Experimental and theoretical vals. of η are compared.

W. R. ANGUS.

Densities of aqueous solutions of per-rhenic acid. W. FEIT (Z. anorg. Chem., 1931, **199**, 271—272).—Vals. for solutions containing up to 65·12% $HReO_4$ are given. H. F. GILLBE.

Dielectric constants of mixtures of ethyl alcohol and water from −5° to 40°. J. WYMAN, jun. (J. Amer. Chem. Soc., 1931, **53**, 3292—3301).—The method previously described (A., 1930, 666) is applied for frequencies $2\cdot15$—$4\cdot1\times10^8$ to $EtOH-H_2O$ mixtures. The polarisation at 20° is almost a linear function of the mol. fraction of EtOH. The dielectric const. (24·35) of pure EtOH at 25° is independent of wave-lengths between 3·97 and 17 m.

J. G. A. GRIFFITHS.

Diamagnetism of liquid mixtures. H. BUCHNER (Nature, 1931, **128**, 301—302; cf. this vol., 900).—Mixtures of $COMe_2$ and $CHCl_3$ obey the mixture law to within 2%, and show no trace of paramagnetism. Trichlorotrimethylcarbinol is diamagnetic with χ—$-0\cdot65\times10^{-6}$ (in the hydrated form $\chi=-0\cdot67\times10^{-6}$); *d* 1·5, m. p. 96·5° or 97° (76° for the hydrate) (cf. this vol., 676). For $COMe_2$ χ is $-0\cdot58\times10^{-6}$ and for $CHCl_3$ $-0\cdot485\times10^{-6}$. L. S. THEOBALD.

Diamagnetism of liquid mixtures. E. VAN AUBEL (Nature, 1931, **128**, 455; cf. this vol., 900).—Attention is directed to other liquid mixtures which show no max. magnetic susceptibility (A., 1918, ii, 388). L. S. THEOBALD.

Supposed diphasic nature of glass. F. W. PRESTON (J. Soc. Glass Tech., 1930, **14**, 349—350T; cf. B., 1921, 116A; 1923, 774A).—Heating for a short time close to the annealing point is suggested as a means of testing hypotheses previously put forward.

M. PARKIN.

Theory of orderly structure of solid solutions. II. Diffusion. C. WAGNER (Z. physikal. Chem., Bodenstein Festband, 1931, 177—186).—Formulæ are derived for the diffusion of the components in solid solutions of orderly structure, the γ phase in the Fe–N system being taken as an example of the type in which the atoms of one component are so small that any excess occupies a position between the lattice atoms, whereas an excess of the other component causes the appearance of spaces in the lattice. The formulæ provide a means of determining the fractions of interstitial diffusion and of diffusion by movement through empty places in the lattice.

H. F. GILLBE.

Interdiffusion of two metals with compound formation. G. TAMMANN and H. J. ROCHA (Z. anorg. Chem., 1931, **199**, 289—305).—If the diffusion layer between two metals is composed of a single type of crystal its rate of growth follows a linear law, whereas if mixed crystals are formed the growth obeys a parabolic law. Measurements have been made of the rate of diffusion of Sn into Au, of Cd from the Cd–Cu eutectics into Cu, and of Zn into Fe, Cu, and β-Cu–Zn mixed crystals. In all cases the parabolic law is valid. The state of aggregation of the metals is of importance for the formation of new cryst. forms, since the number of crystallisation centres in a cooling melt may be much greater than in the contact surface between two types of crystals capable of interdiffusion.

H. F. GILLBE.

Aluminium–chromium alloys. M. GOTO and G. DOGANE (Nihon Kogyokwaishi, 1927, No. 512, 931—936).—The system Al–Cr up to 36·63% Cr has been studied. CHEMICAL ABSTRACTS.

X-Ray study of the alloys of silver with bismuth, antimony, and arsenic. I. S. J. BRODERICK and W. F. EHRET (J. Physical Chem., 1931, **35**, 2627—2636).—No compound is formed in the system Ag–Bi (cf. Pogg. Ann., 1860, **110**, 21). The max. solubility of Bi in Ag is approx. 5·5 wt.-%, and within this phase *a* increases from 4·076 Å. for pure Ag to 4·087 Å. for the saturated phase. The max. solubility of Sb in Ag is approx. 6 wt.-%, and *a* increases from 4·076 to 4·109 Å. A homogeneous, hexagonal close-packed phase exists between 11 and 16% Sb; at 89% Ag, a_1 is 2·920 Å., a_3 4·774 Å., and a_3/a_1 1·632. Another homogeneous phase, either rhombic or deformed cubic, is present between 72 and 78% Ag; at 74·2% Ag, a_1 is 3·000 Å., a_2 5·178 Å., and a_3 4·830 Å. The X-ray examination of the system Ag–Bi, but not that of Ag–Sb, supports the thermal diagrams of Petrenko (A., 1906, ii, 667).

L. S. THEOBALD.

Röntgen analysis of the systems gold–antimony and silver–tin. O. NIAL, A. ALMIN, and A. WESTGREN (Z. physikal. Chem., 1931, **B**, **14**, 81—90).—The results for the system Au–Sb agree with previous work (A., 1906, ii, 679; 1928, 1079). An improved val. of *a* for $AuSb_2$ is 6·647±0·005 Å. Results for the system Ag–Sn agree with the thermal diagram (B., 1926, 792). The phase fields at 400° in passing from pure Ag to pure Sn are: α solid solution, face-centred cubic, *a* 4·077—4·125 Å.; α+ε; ε solid solution, close-packed hexagonal, *a* 2·925 to 2·953, *c* 4·774—4·771 Å.; ε+ε′; ε′ solid solution, orthorhombic, *a* 2·985—2·994, *b* 5·144—5·154, *c* 4·771 Å.; ε′+Sn. N. H. HARTSHORNE.

Röntgen analysis of gold–tin alloys. S. STENBECK and A. WESTGREN (Z. physikal. Chem., 1931, **B**, **14**, 91—96).—The compounds found by Vogel (A., 1905, ii, 640) are confirmed. Solid solutions are formed in the range 12—16 at.-% Sn, and these are close-packed hexagonal with *a* 2·896—2·932 and *c* 4·776—4·761 Å. Previous measurements (A., 1927, 815) of the lattice dimensions of AuSn are confirmed within narrow limits. N. H. HARTSHORNE.

X-Ray analysis of copper–silicon alloys. S. ARRHENIUS and A. WESTGREN (Z. physikal. Chem., 1931, **B**, **14**, 66—79).—Cu–Si alloys show at least five intermediate phases: β, 14·5% Si, appears at higher temp. and shows hexagonal packing; γ, 17% Si, appears at lower temp., and is like β-Mn; δ, 18% Si, appears at higher temp.; ε, 21% Si, appears at lower temp., and has a face-centred cubic lattice,

a 9·694 Å.; η appears on solidification of the alloy, and contains 25% Si. A. B. D. CASSIE.

Copper–magnesium alloys. IV. Equilibrium diagram. W. R. D. JONES (Inst. Metals, Sept., 1931, Advance copy, 25 pp.).—The equilibria were determined by thermal and micrographic examination using electrolytic Cu and Mg purified by sublimation in vac. The system contains two compounds Cu_2Mg, m. p. 820°, and $CuMg_2$, m. p. 567·5°, which yield a eutectic mixture (65·4% Cu, 552°). The solubility of Cu in Mg rises from 0·02% at 20° to 0·03% at 485°, and that of Mg in Cu from 2—2·2% at 20° to about 2·6% at 700°. $MgCu_2$ forms a eutectic with the Cu-rich solid solution (90·3% Cu, 722°) and Mg_2Cu forms a eutectic with the Mg-rich solid solution (30·7% Cu, 485°). There are no fields of solid solutions in the neighbourhood of either compound. No evidence for the compound MgCu could be obtained.
A. R. POWELL.

Physico-chemical study of the gold–copper solid solutions. N. S. KURNAKOV and N. V. AGEEV (Inst. Metals, Sept., 1931, Advance copy, 17 pp.).—Resistivity measurements at temp. up to 600° show that $AuCu_3$ forms solid solutions with 22—40 at.-% Au and AuCu solid solutions with 42·5—70 at.-% Au. The formation of both compounds is retarded by rapid chilling, but under normal rates of cooling the transformations occur at 425—450° and are accompanied by a marked fall in vol. Work-hardening of the quenched alloys assists the preservation of the metastable supercooled solid solution during tempering at 150—350° (cf. following abstract).
A. R. POWELL.

Transformations in the gold–copper alloys. J. L. HAUGHTON and R. J. M. PAYNE. **X-Ray examination of gold–copper alloys.** G. D. PRESTON (Inst. Metals, Sept., 1931, Advance copy, 24 pp.).—Measurements have been made between 18 and 70 at.-% Au of the electrical resistance with changing temp., and of the sp. resistance of slowly cooled alloys, supplemented by micrographic examination and by X-ray analysis. The results confirm the existence of AuCu and $AuCu_3$ and the presence of another transformation in alloys approximating to the composition Au_2Cu_3 has been established. The transformation temp. of AuCu rises steeply from 20° at 29 at.-% Cu to 323° at 38·2% Cu, then more slowly to a flat max. at 422° with 50 at.-% Cu, falling again slowly to a min. at 58·8 at.-% Cu, at which point the transformation curve of Au_2Cu_3 commences. This curve reaches a max. of 360° with 60 at.-% Cu, then falls sharply to a min. at 297° with 63 at.-% Cu. The transformation curve for $AuCu_3$ rises slowly from this point to a flat max. at 395° with 75 at.-% Cu, then falls steeply to room temp. with 82 at.-% Cu. In the AuCu group of alloys marked hysteresis in the transformation temps. occurs. The resistivity of slowly cooled alloys indicates that the Cu-rich limit of the transformation at 20° occurs at 17·5 at.-% Au and the Au-rich limit at 71 at.-% Au. Alloys quenched from above the transformation points have a homogeneous solid solution structure, whilst those cooled through these points have a more or less martensitic structure. The alloy AuCu when annealed at 400° for 20 hr. and quenched has a face-centred cubic structure, a 3·94 Å., with random orientation of the Cu and Au atoms, but when slowly cooled from 700° it has a body-centred tetragonal lattice, a 2·79 Å., c/a 1·31, the Au and Cu atoms being arranged regularly at the points of the lattice. The alloy Au_2Cu_3 has a body-centred tetragonal lattice, a 2·73 Å., c/a 1·36. No two-phase field could be detected by X-rays.
A. R. POWELL.

Constitution of the alloys of silver and mercury. A. J. MURPHY. **X-Ray examination of the alloys.** G. D. PRESTON (Inst. Metals, Sept., 1931, Advance copy, 21 pp.).—Progressive additions of Hg produce a continual reduction of the initial f. p. down to −38·8° and no alloy has a f. p. below that of Hg. The solidus falls in a smooth curve from the m. p. of Ag to 55% Ag at 276° and to about 51% Ag at 0°. Two intermediate phases of restricted composition are formed; the β-phase contains 40% Ag and has a close-packed hexagonal lattice, a 2·98 Å., c/a 1·62, whilst the γ-phase contains 29—30% Ag and has a body-centred cubic lattice, a 10·0 Å. Above 276° β dissociates into α+liquid and above 127° γ dissociates into β+liquid. Increase of pressure has practically no effect on the equilibria in the system.
A. R. POWELL.

System copper–lead and related heterogeneous systems. W. CLAUS (Kolloid-Z., 1931, 57, 14—16).—Consideration of the separation of a melt of Cu and Pb into two phases on cooling in the light of Stokes' law provides an explanation of the different vals. obtained by various observers for the temp. at which the separation occurs. The explanation holds for other systems of a similar type, where discordant results have been obtained by different methods. E. S. HEDGES.

Macro-etching of aluminium–silicon alloys. W. HUME-ROTHERY (Inst. Metals, Sept., 1931, Advance copy, 4 pp.).—The specimen is immersed in 15—16% solution of $CuCl_2$ for 5—10 sec., washed, and wiped with a woollen cloth to remove Cu. The procedure is repeated 3—4 times and the specimen finally brightened by immersion in dil. H_2CrO_4 solution. Oblique illumination is recommended for photographing the macrostructure revealed in this manner. A. R. POWELL.

Electrical conductivity of gold–nickel alloys. G. GRUBE and F. VAUPEL (Z. physikal. Chem., Bodenstein Festband, 1931, 187—197).—The resistance–temp. curves for a series of Au–Ni alloys between 20° and 900° show that the reduction of the mutual solubility of the components as the temp. falls causes the separation of Au-rich and Ni-rich mixed crystals. The segregation–temp. curve is in fair agreement with that of Fraenkel and Stern. The temp. of the magnetic transition of Ni falls as the Au content is increased up to about 15%, and thereafter remains const. The resistance of Au is increased considerably by addition of small quantities of Ni, but at 400—800° the resistance of alloys containing from 60 to 95% Ni is practically const.
H. F. GILLBE.

Superconductivity of gold–bismuth alloys. W. J. DE HAAS and F. JURRIAANSE (Naturwiss., 1931,

19, 706).—When the eutectic mixture of Au–Bi alloys is dissolved in HNO_3, some crystals remain which are completely insol. These are tetragonal Au_2Bi and are responsible for the superconductivity of Au–Bi alloys at 1·84° abs. The form of the crystal lattice appears to play an important role in superconductivity phenomena. W. R. ANGUS.

Solutions of ethyl alcohol in benzene, water, and in benzene and water. E. R. WASHBURN, V. HNIZDA, and R. VOLD (J. Amer. Chem. Soc., 1931, **53**, 3237—3244).—Miscibility data for the system EtOH–H_2O–C_6H_6 at 25° and the depression of the f. p. of C_6H_6 by 1·1—96·9 wt.-% EtOH have been determined. It is suggested that the addition of H_2O to C_6H_6–EtOH mixtures leads to a predominance of simple EtOH mols. by shifting the polymerisation equilibrium. J. G. A. GRIFFITHS.

Effects of dissolved substances on the solution temperature of a phenol–water system. J. L. CULBERTSON and E. S. PALMER (J. Physical Chem., 1931, **35**, 3063—3069).—For K salts the lyotropic series is $SO_4 > Cl > Br > NO_3 > I > CNS$. The crit. solution temp. appears to depend on the surface tension of the aq. solution. L. S. THEOBALD.

Solubility of naphthols in water. G. E. MUCHIN and I. I. TSCHALENKO (Ukrain. Chem. J., 1931, **6**, [Sci.], 117—119).—The crit. solution temp. for α-naphthol is 210·5°, and β-naphthol 192·0°. R. TRUSZKOWSKI.

Solubilities and solubility products of metallic sulphides in water. I. M. KOLTHOFF (J. Physical Chem., 1931, **35**, 2711—2721).—A crit. survey of the literature. The solubilities in pure H_2O and in equilibrium H_2O have been calc., but the vals. are too small to be of practical significance. The relation between solubility and [H˙] and [H_2S] should be expressed by the reaction const. Weigel's solubility data are untrustworthy. L. S. THEOBALD.

Iodine pentoxide and its hydrate. E. MOLES and A. PEREZ-VITORIA (Z. physikal. Chem., Bodenstein Festband, 1931, 583—590).—The solubility of I_2O_5 in 20—65% HNO_3 at 25° has been determined. Isobars of the thermal decomp. of HIO_3 show that HI_3O_8 is formed at 70°, and I_2O_5 at 200°. When heated in air I_2O_5 commences to decompose at 275°. The coloration usually observed at lower temp. appears only if H_2SO_4 is used during the prep. of the material. H. F. GILLBE.

Solubility of oxalic acid in aqueous solutions of hydrochloric acid. E. M. CHAPIN and J. M. BELL (J. Amer. Chem. Soc., 1931, **53**, 3284—3287; cf. A., 1924, i, 368).—The data refer to 0—34·5% HCl at 0°, 50°, and 80°. The solubility of oxalic acid is minimal in 10% HCl at 80°, 18% HCl at 50°, and 20% HCl at 0°. A solid phase other than $H_2C_2O_4,2H_2O$ was not detected. J. G. A. GRIFFITHS.

Calcium sulphate in sea-water. Y. TANAKA, K. NAKAMURA, and R. HARA (J. Soc. Chem. Ind. Japan, 1931, **34**, 284—287B).—The solubility of $CaSO_4,2H_2O$ at 0—100° and of $CaSO_4$ up to 200° in aq. NaCl has been determined interferometrically. With very fine crystals abnormal vals. are obtained for both salts and discordant results with $CaSO_4$ can be avoided only by using natural anhydrite. The data indicate the gypsum transition point for any given NaCl solution. The greater part of the $CaSO_4$ may be removed from brine by heating the latter at 200°. C. IRWIN.

Solubility influences (couple pyramidone veronal). L. IRRERA (Gazzetta, 1931, **61**, 614—618).—The solubility of veronal in H_2O is increased by the presence of pyramidone between 14° and 27°. For small concentrations of the latter the solubility coeff. is independent of temp., but at higher concentrations it increases with the temp. From calculations of the heat of dissolution by means of the van 't Hoff isochore it is shown that veronal and pyramidone form complex compounds only in conc. solutions. O. J. WALKER.

Solubilities of alkali bromides and fluorides in anhydrous methyl, ethyl, and butyl alcohols. F. G. GERMUTH (J. Franklin Inst., 1931, **212**, 343—349).—Solubility data for NaBr, KBr, NaF, and KF in MeOH, EtOH, and Bu^{a}OH between 20° and 55° are given. The solubility of each decreases with increasing mol. wt. of the solvent. NaBr in EtOH and BuOH shows a max. on the solubility–temp. curve. NaBr, KBr, and KF in MeOH, and KF in EtOH have a negative temp. coeff. H. J. EMELÉUS.

Iodine. II. J. LANZA (Anal. Fís. Quím., 1931, **29**, 470—489).—The partition of iodine between CS_2 and H_2O and the influence of halides on the distribution have been examined. H. F. GILLBE.

Laws governing the separation of traces of substances entering into the composition of mixed crystals. R. MUMBRAUER (Z. physikal. Chem., 1931, **156**, 113—134).—The crystallisation of solutions of Ba salts containing Th-*B* or Th-*X* has been studied. On slow crystallisation of supersaturated solutions the active substance is distributed between the solid solution and the liquid phase in accordance with the law of simple distribution (cf. A., 1927, 431), and is homogeneously dispersed in the mixed crystal. On rapid crystallisation from supersaturated solution or crystallisation by evaporation of the saturated solution, the distribution follows, however, a logarithmic law (cf. A., 1925, ii, 381). The observations recorded by Chlopin (A., 1930, 27) seem to have been complicated by recrystallisation effects. R. CUTHILL.

Discontinuities in adsorption isotherms. A. F. BENTON and T. A. WHITE (J. Amer. Chem. Soc., 1931, **53**, 3301—3314; cf. A., 1930, 990; this vol., 902, 1005).—Details are given of results outlined previously. The adsorption of H_2 at −183° by sintered Cu, and by Ni, Cu, or Fe poisoned with CO is less than that by the unpoisoned metals, but the isotherms exhibit similar discontinuities. H_2 is adsorbed on the top of the CO as well as on the bare metal. Fe alone affords discontinuous adsorption at −78·5°; the other metals afford the "chemical" or "activated" type. Differential heats of adsorption between −195° and −183° are <1800 g.-cal. per mol. Stepwise adsorption has no relation to catalytically active patches. The results support the theory that adsorption occurs in successive rows, that neighbouring mols. evaporate

from the surface less readily than isolated mols. and that physically adsorbed mols. possess mobility in the plane of the surface. J. G. A. Griffiths.

Activated adsorption. W. E. Garner (Nature, 1931, **128**, 583—584).—Theory and experiment support the view that in certain transitional regions the heat of adsorption increases with a rise in temp. L. S. Theobald.

Activated adsorption of hydrogen by zinc and chromium oxides. H. S. Taylor (Nature, 1931, **128**, 636).—At 0° and above, H_2 is slowly and reversibly adsorbed on ZnO prepared by igniting ZnC_2O_4 at 400°. All the H_2 is recovered by evacuation at 450°. The activation energy is 14 kg.-cal. for the main surface covered, with smaller vals. for the more active areas. The heat of adsorption (calc. by D. V. Sickman) is 21 kg.-cal. per mol. Below 0°, another type of adsorption occurs which reaches equilibrium almost instantaneously with no activation energy. The heat of adsorption in this case is 1100 g.-cal. per mol. At 0°, this type of adsorption is negligible. L. S. Theobald.

Adsorption and specific reactions at surfaces. H. S. Taylor (Z. physikal. Chem., Bodenstein Festband, 1931, 475—480).—The activation energy of adsorption processes is discussed in relation to the problem of sp. reactions at surfaces. The adsorption of H_2 on Al_2O_3 is slow but measurable at 445°, and its velocity increases seven-fold on raising the temp. to 525°; the activation energy of the process is thus about 27·5 kg.-cal. per mol. The adsorption is reversible and no H_2O is formed. In the dehydration range (200—300°), therefore, dehydrogenation cannot occur, and the dehydration activity is probably due to a rapid activated adsorption of H_2O. The velocity of adsorption of O_2 on Ag between 0° and 184° has been determined; the activation energy, calc. from the results at 0° and 56°, is 15 kg.-cal. per mol. H. F. Gillbe.

Adsorption of hydrogen by a zinc oxide-chromium oxide catalyst. F. E. T. Kingman (Trans. Faraday Soc., 1931, **27**, 654—661).—The rate of adsorption of H_2 by a $ZnO-Cr_2O_3$ catalyst at −80°, 0°, and 100° first falls and then rises again as the reduction of the catalyst progresses. It seems that the adsorption process involves a van der Waals type of adsorption, a type with a high heat of activation, but not causing reduction, and adsorption on the O atoms of the surface, leading to reduction. The speed of the last type of adsorption is appreciable only at 100°, and the speed of the second type increases as the temp. rises. R. Cuthill.

Energy transfer at adsorbed molecules. K. F. Herzfeld and M. G. Meyer (Z. physikal. Chem., Bodenstein Festband, 1931, 669—678).—Theoretical. The transfer of energy when a mol. is adsorbed on a cryst. surface is discussed on the assumption that such interaction may be regarded as taking place between two multipoles. In general the adsorbed mol. will be excited only if more than 1 energy quantum is transferred from the crystal. H. F. Gillbe.

Adsorption from mixed solvents. I. Benzoic acid. G. E. Muchin, N. G. Gurski, and T. M. Polonski (Ukrain. Chem. J., 1931, **6**, [Sci.], 135—145).—The adsorption by C of BzOH from EtOH–C_6H_6 and EtOH–$CHCl_3$ mixtures is smaller than from solutions in the pure solvents. R. Truszkowski.

Adsorption of electrolytes by crystalline surfaces. III. L. de Brouckère (Bull. Acad. roy. Belg., 1931, [v], **16**, 1263—1274; cf. A., 1930, 850).—The adsorption of NaBr, KBr, NaI, KI, and CdI_2 by $BaSO_4$ is a reversible phenomenon unaffected by capillary effects and by adsorption of solvent. Anions and cations are adsorbed in equiv. quantities. C. W. Gibby.

Adsorption on layers of barium fluoride sublimed in vacuum, and the structure of these layers. J. H. de Boer (Z. physikal. Chem., 1931, B, **14**, 149—165).—The adsorption of I on BaF_2 sublimed in vac. is represented by the same isotherm as is its adsorption on CaF_2 (A., 1929, 875; this vol., 902), and in both cases the max. quantity of I adsorbed depends on the amount of salt sublimed, indicating that the latter has a lamellar structure. The results also show that the fall in polarity of the I with increasing distance from the salt surface is greater with BaF_2 than with CaF_2, and that the I is more strongly polarised by the former; this is confirmed by a comparison of the absorption spectra of the I on the two surfaces. It is suggested that the surfaces consist of F ions, and that the I atoms occupy more space on the BaF_2 than on CaF_2, in conformity with the greater distance between the F ions in the former. N. H. Hartshorne.

Influence of hydrogen-ion concentration on the adsorption of weak electrolytes by pure charcoal. II. H. J. Phelps (Proc. Roy. Soc., 1931, A, **133**, 155—161).—The quantity of base adsorbed by charcoal prepared from "ashless" filter-papers is for NH_2Pr^a and NH_2Bu^a proportional to the concentration of the non-ionised mols. at any given value of [H˙], and the adsorption is uninfluenced by acid treatment of the charcoal. Some impurity in the charcoal appears to prevent attainment of true equilibrium with solutions of $EtCO_2H$, but after acid treatment the adsorption is proportional to the concentration of non-ionised mols. It is concluded that a sufficiently purified charcoal presents a perfectly neutral surface to aq. solutions of weak acids and bases and adsorbs these only as non-ionised mols. L. L. Bircumshaw.

Activated charcoal. I. S. Roychoudhury (J. Indian Chem. Soc., 1931, **8**, 433—467).—Animal (*a*), sugar (*b*), and gelatin (*c*) charcoals were purified by Miller's method (A., 1926, 898) and then activated under differing conditions of temp., time of heating, and presence of air, N_2, or CO_2. The extent of activation, measured by the absorption of BzOH (*loc. cit.*), varies considerably; CO_2 generally causes greatest activity and (*a*) is the best absorbent. In many cases, particularly with samples of (*b*), the amount of acid adsorbed per g. of charcoal does not fall with decrease in the end concentration; foreign substances are probably present on the surface. Samples of (*b*) frequently show no adsorption when small amounts (0·125 g.) are used. Further purification of activated charcoals by repeated washing with conductivity

H_2O gives products having a + charge (in contact with H_2O), even when the original prep. has a − charge; this shows that adsorbed ions are responsible for the charge (cf. A., 1922, ii, 689). The order of adsorption of BzOH, AcOH, formic, propionic, butyric, and mono-, di-, and tri-chloroacetic acids varies with different charcoals; dissimilar curves are obtained with differing amounts of the same sample. The orders resemble the mixed series of Dubinin (A., 1930, 1364) but they also depend on the mass of the absorbent. The amount of BzOH adsorbed by various charcoals is decreased to varying extents by EtOH.

Negatively charged (*a*) adsorbs alkali but not acid; in contact with aq. KCl, acid is liberated. Samples of (*b*) adsorb acid but not alkali; alkali is liberated in contact with KCl. The charges on (*a*), (*b*), (*c*), and active C (Merck) in presence of electrolytes are studied. The equiv. adsorption of the ions of HCl and H_2SO_4 found by previous workers is confirmed, and the theories of Frumkin (A., 1926, 1091, *et seq.*) and Schilov (A., 1928, 581, *et seq.*) are criticised.

H. BURTON.

Changes in sorption capacity of zinc oxide through pulverisation. G. F. HUTTIG and M. KANTOR (Z. anal. Chem., 1931, **86**, 95—98).—Finely-powdered ZnO adsorbs more Congo-red, Bordeaux-red R, and eosin than the coarser material, but the ratio of the adsorbent capacities of the two forms of ZnO is not const. E. S. HEDGES.

Adsorption of water and ethyl acetate vapours by silica gels. A. L. ELDER and O. L. BRANDES (J. Physical Chem., 1931, **35**, 3022—3024).—At relatively low partial pressures Patrick's commercial SiO_2 gel is more efficient than Holmes' chalky gel for adsorbing either H_2O or AcOEt from an air stream at 30°; at higher pressures the chalky gel has the larger adsorption capacity. L. S. THEOBALD.

Alumina as an ionising adsorbent. W. D. BANCROFT and J. W. ACKERMAN (J. Physical Chem., 1931, **35**, 2568—2580).—Adsorption experiments confirm the view (A., 1930, 28) that the colour of Al_2O_3–alizarin lakes is due to adsorption of the alizarate ion. These lakes coagulate and become lighter in colour when treated with aq. H_2O_2 owing to the reaction between unadsorbed Na alizarate and the acids present in the H_2O_2. Hydrous SnO adsorbs undissociated alizarin or Na alizarate giving an orange or purple lake, respectively, but it does not adsorb the alizarate ion. Hydrous ZnO adsorbs undissociated Na alizarate to form a purple lake. In the presence of silk or SiO_2, rhodamine is ionised and adsorbed, producing strong fluorescence, but Al_2O_3, ZnO, SnO, wool, and cotton show practically no fluorescence, indicating a different type of adsorption. Hydrous Al_2O_3 forms a violet lake with violuric acid, but adsorption is slight; hydrous Sn oxide adsorbs the undissociated acid to a slight extent, but gives no colour, whilst hydrous ZnO adsorbs neither the acid nor its Na salt. L. S. THEOBALD.

Study of adsorption processes in dilute non-aqueous solutions by the aid of dielectric measurements. L. EBERT and E. WALDSCHMIDT (Z. physikal. Chem., Bodenstein Festband, 1931, 101—112).—A general account is given of the applications of the method and of the experimental procedure. Measurements of the adsorption equilibria in the system C_6H_6–C–H_2O are described. Equilibrium between moist C and dry C_6H_6 is attained within about 1 hr., whereas if dry C is immersed in moist C_6H_6 the C_6H_6 blocks the active surface of the adsorbent and equilibrium is established only very slowly. The adsorption of EtOH from C_6H_6 by C is given approx. by $S=7{\cdot}15m$, where S is the quantity adsorbed, expressed as a percentage of the initial concentration, and m is the weight of the adsorbent. For feebly adsorbed substances the const. diminishes and the exponent of S becomes <1. The behaviour of different C and SiO_2 gel adsorbents after heating at various temp. has been studied; with some specimens of C the activity increases with rise in the temp. of heating and with others it decreases; with SiO_2 gel the activity appears always to diminish. H. F. GILLBE.

Calculation of equilibrium concentrations in adsorption from liquids. W. ROGERS, jun., and M. D. SCLAR (J. Physical Chem., 1931, **35**, 2758—2762).—A method is described by which the Freundlich isothermal may be used to calculate the equilibrium concentration and the amount of solute adsorbed when the initial concentration, vol. of solution, and wt. of adsorbent are known. The validity of the method is established by comparison with data for which Freundlich's isothermal holds.

L. S. THEOBALD.

"Anomalous" Kroeker curves. P. MEHL (Kolloid-Z., 1931, **56**, 299—305).—The variation of the adsorption function x/m with m (where x is the amount adsorbed and m the mass of adsorbent) has been studied at const. initial concentration and const. vol. with AcOH and picric acid in EtOH and H_2O, using blood charcoal and "carboraffin" as adsorbents. The form of this function (the Kroeker curve) varies regularly as the concentration and x diminish, the convexity towards the m axis becoming flatter and developing a marked max. in the region of small values of m. The so-called "anomalies" of the Kroeker curve are thus shown to be a characteristic feature of adsorption at low concentrations and for small amounts of adsorbent. An anomaly observed in the adsorption of AcOH in EtOH by C, the amount varying with the time during which the adsorbent is agitated with the solution, is traced to the formation of AcOEt under the catalytic influence of the C.

E. S. HEDGES.

Combination of gases with potassium permanganate. F. DURAU (Z. physikal. Chem., 1931, **156**, 195—209).—O_2 and N_2 are simply adsorbed, but only to a very small extent, by powdered $KMnO_4$. With H_2, CO_2, CO, and SO_2 chemosorption takes place in addition to a small adsorption which is not sufficient to cover the surface with a unimol. layer. There is little or no absorption. The adsorption of O_2 and N_2 is not influenced by previous treatment with one of the other gases. A comparison of the adsorption isotherms of C_3H_8 by NaCl (cf. A., 1928, 1317) and $KMnO_4$ shows that whilst the former is convex to the pressure axis, the latter is concave. This strengthens the theory (*loc. cit.*) that adsorption by the van der Waals

attraction is due to lattice disturbances. A method is described for determining the sp. gr. of a powder without interference by adsorbed or chemosorbed gases. M. S. BURR.

Combination of gases with decomposed potassium permanganate. F. DURAU (Z. physikal. Chem., 1931, **156**, 210—224; cf. preceding abstract).—By heating $KMnO_4$ under reduced pressure O_2 is given off and a product analogous to adsorbent charcoal is obtained. Simple adsorption of A and N_2 takes place, but N_2 is not adsorbed below a pressure of 1 mm. There is strong chemosorption of O_2, CO_2, and CO, but chemosorption of CH_4, C_2H_6, and C_3H_8 is small compared with the adsorption. Adsorption of N_2 is only slightly affected by change in surface properties, but in the case of other gases the effects of previous treatment, *e.g.*, with another gas, are more marked. A unimol. layer is probably formed by adsorption. Chemosorption appears to be due to the formation of more or less stablo compounds which are slowly decomposed at high temp. and reduced pressure, hence the slow continuous evolution of gas from the glass or other walls of evacuated vessels. M. S. BURR.

Anomalous first heats of adsorption. G. M. SCHWAB and W. BRENNECKE (Z. physikal. Chem., Bodenstein Festband, 1931, 907—911).—Measurements with H_2 and He at low pressure demonstrate that systematic calorimetric errors may occur in the determination of heats of adsorption on activated metals owing to the poor conductivity of the adsorbent, and that fictitious max. may occur on the adsorption–adsorption heat curves. H. F. GILLBE.

Coherer method of determining heats of adsorption. S. LENHER and G. H. CAMERON (J. Physical Chem., 1931. **35**, 3082—3085).—Reproducible vals. for the cohering voltages of W filaments in H_2, O_2, N_2, or in a vac. could not be obtained, and hence the coherer method of determining heats of adsorption is regarded as untrustworthy (cf. A., 1926, 239). Palmer's assumed mechanism for the action of the coherer is criticised. L. S. THEOBALD.

Kinetics of adsorption of vapours in an air stream. J. K. SYRKIN and A. J. KONDRASCHOV (Kolloid-Z., 1931, **56**, 295—299).—The velocity of adsorption of the vapours of CS_2, pyridine, $Bu^{\beta}OH$, and $CMe_2Et{\cdot}OH$ from an air stream by C between 10° and 100° may be expressed by the formula $\log A/(A-c)=0{\cdot}434Kt$, where A is the equilibrium concentration, c the adsorbed amount, t the time, and K a const. The val. of K varies with the temp.; the temp. coeff. is 1·06—1·32. The rate of adsorption is much slower than is to be expected from purely kinetic considerations. Probably, only those mols. are adsorbed which have their polar groups favourably oriented with respect to the adsorbent at the moment of striking the surface; mols. not so oriented act as inhibitors. E. S. HEDGES.

Effect of mercuric iodide and ammonium chloride on glass. C. E. MILLER (J. Physical Chem., 1931, **35**, 2985—2992).—Adsorption measurements with PhMe vapour show that fused pyrex glass is attacked when heated (450°) in contact with HgI_2 or NH_4Cl; considerable adsorption on the surface then results. With NH_4Cl the etching becomes visible, and HgI_2 leaves streaks of a black compound. Soft glass reacts with HgI_2 on heating to give a sol. iodide. The corrosive action is attributed to the existence of $Na^{\cdot}$ in the glass, and renders it unsuitable for use when the adsorption of polar compounds is studied. L. S. THEOBALD.

Wetting and adsorption at the boundary of three phases. D. TALMUD (Z. physikal. Chem., 1931, **156**, 237—238).—If, at the boundary of three phases, a fourth immiscible substance is placed, the latter spreads along the boundary line. The limiting condition is a unimol. adsorption thread. This represents unidimensional adsorption due to linear tension in the region of separation of the three phases. Point tension at the boundary point of four phases is also conceivable. M. S. BURR.

Method of measuring surface tension. J. H. GADDUM (Proc. Roy. Soc., 1931, **B**, **109**, 114—125).—The drop-wt. method has been modified by measuring the vol. of drops by means of the micrometer syringe. The procedure enables the surface tension of a liquid to be measured in abs. units and is especially suitable for following the slow fall of "static" surface tension in the newly-formed surface of a hydrophilic colloidal solution. The apparent viscous-elasticity of the surface of saponin solutions is shown by changes occurring in the shape of the drops. The rapid changes are due to concentration changes in the surface, and it is suggested that the slow changes are due to diffusion of saponin. Slow changes occurring in the tension of certain plastic bodies (*e.g.*, rubber and muscle) following a strain may also be due to the diffusion of mols. into positions where they affect the tension. E. S. HEDGES.

Thermodynamic study of surface tension. VIII. Affinity and velocity of adsorption. R. DEFAY (Bull. Acad. roy. Belg., 1931, [v], **16**, 1249—1263; cf. A., 1930, 1247).—Mathematical. Surface tension is independent of curvature in the absence of adsorption, both for a drop of liquid in contact with a mixture of vapours, and for the meniscus between two pure immiscible liquids. C. W. GIBBY.

Interfacial tension and hydrogen-ion concentration. R. A. PETERS (Proc. Roy. Soc., 1931, **A**, **133**, 140—154).—The interfacial tension of C_6H_6 solutions of long-chain carboxylic acids against "buffered" aq. solutions begins to fall at p_H 5·5 and tends to vanish at p_H 9·3 approx. For a given p_H the results are the same for phosphate- and glycine-buffered solutions and also for all the acids investigated except decoic, which shows certain abnormalities with phosphate buffers. With hexadecylamine the interfacial tension rises over roughly the same p_H range. K_a and K_b for $\cdot CO_2H$ and $\cdot NH_2$ in the interface are calc. to be $3{\cdot}2\times10^{-8}$ and $1{\cdot}0\times10^{-7}$, respectively. Et palmitate shows a fall similar to that for the acids, but hexadecyl alcohol shows no change. Some biological aspects of the results are discussed. L. L. BIRCUMSHAW.

Effect of light on the surface tension of Boys' soap solution. L. D. MAHAJAN (Indian J. Physics, 1931, **6**, 147—154).—The surface tension of a soap solution decreases rapidly if it is exposed to sunlight

or is boiled. Solutions kept in the dark show little change in surface tension. The fall in surface tension is not therefore an adsorption phenomenon, but is due to chemical changes which take place in the solution under the influence of light or heat rays.

F. J. WILKINS.

Effect of light on the surface tension of Boys' soap solution. P. L. DU NOUY (Nature, 1931, **128**, 674).—A criticism (cf. preceding abstract).

L. S. THEOBALD.

Surface tension of molten glass at temperatures near the m. p. W. B. PIETENPOL and H. H. SCOTT (Physical Rev., 1930, [ii], **35**, 296).—The surface tension of different glasses is approx. 250—350 dynes per cm. and varies only slightly with temp. up to approx. 200° above the softening point.

L. S. THEOBALD.

Formation of films at liquid–liquid interfaces. J. A. SERRALLACH and G. JONES (Ind. Eng. Chem., 1931, **23**, 1016—1019).—Solid films form at the interface of oil and aq. solutions of emulsifying agents when the two unagitated surfaces are kept in contact for some weeks. The properties of the film are due more to the influence of the oil than of the emulsifier. Olive oil, castor oil, cod-liver oil, and refined heavy mineral oil were studied with eight different emulsifying agents. Cod-liver oil is remarkable for forming tough, thick, opaque films and mineral oil has the least tendency. The observations are useful as a means of determining suitable conditions for preparing stable emulsions. They suggest, also, that in true emulsions the film of emulsifying agent may be thicker than 1 mol. E. S. HEDGES.

Very thin films and their physical properties. H. E. DEVAUX (J. Phys. Radium, 1931, [vii], **2**, 237—272).—A summary. A. J. MEE.

Free electrical charges on droplets of insoluble liquids in water. R. DU BOIS and A. H. ROBERTS (J. Physical Chem., 1931, **35**, 3070—3081).—The charges per sq. cm. measured by the null-point method (A., 1930, 1366) on oleic acid–H_2O or stearic acid–H_2O interfaces are of the same order of magnitude as those found for cetylsulphonic acid (*loc. cit.*); the fraction of the surface covered by free charges is $1/10^5$. Drops of tetradecane or tetrahydronaphthalene in H_2O show practically the same charge as do the fatty acids. The addition of KCl to the H_2O increases the charges, and conductivity measurements reveal adsorption on the drops. Drops of H_2O in the hydrocarbons are unaffected by an electric field. Cataphoretic velocity measurements with a horizontal electric field give vals. for the charge densities which differ only slightly from those obtained by the null-point method. Charge densities increase rapidly with diminution in the radius of the drop.

L. S. THEOBALD.

Surface conductance at the cellulose–water interface. K. KANAMARU (J. Cellulose Inst. Tokyo, 1931, **7**, 15—20).—A method has been evolved for calculating the sp. conducting capacity of the cellulose–H_2O interface from the data obtained in the measurement of ζ-potential by the streaming potential method (cf. this vol., 1232). A mathematical analysis of the method is given. The surface conductance of a diaphragm against H_2O is determined by the sp. conducting capacity F_s of the diaphragm, *i.e.*, the capacity to conduct current along the solid–liquid interface, and by the sp. surface s of the diaphragm. Electrodialysis, acid treatment, mercerisation, oxidation, and other similar modifications of cellulose cause an increase in F_s. Hydrolysis and esterification have the reverse effect. T. T. POTTS.

Surface phenomena on gels of thorium and ferric oxides. O. HAHN and G. GRAUE (Z. physikal. Chem., Bodenstein Festband, 1931, 608—619).—The sp. surface of $Th(OH)_4$ gels, prepared either from the sol or by precipitation by aq. NH_3 from Th salt solutions, is about 30%, and is independent of the conditions of its formation. With $Fe(OH)_3$ gels, on the contrary, the surface varies considerably with change of the precipitation conditions. The dispersion is greater in gels prepared at 20° than in those prepared at 100°, and ageing is more rapid than with $Th(OH)_4$ sols and takes place more slowly in the more thoroughly purified gels; Cl′ thus catalyses the ageing. Dry $Fe(OH)_3$ gels, when heated at 280°, undergo considerable increase of particle size. Gels prepared from the sol are much coarser than those obtained by precipitation. If the sol is fresh, the gel ages but slowly, but the rate of ageing increases with the age of the original sol. The measurements were made by the emanation method, and no difference was discernible between gels on which the radio-Th was deposited after prep. and those on which it was precipitated simultaneously. H. F. GILLBE.

Electro-osmosis and interfacial electrokinetic potentials. H. MURAOKA and K. HIRUMA (Res. Electro-Tech. Lab. Tokyo, 1930, No. 279, 18 pp.).—Determinations were made of the amount of liquid transported through diaphragms of earthenware or glass particles, and vals. obtained for the interfacial potential of Helmholtz' double layer.

CHEMICAL ABSTRACTS.

Molecular size of halides and of their complex compounds in indifferent solvents. I. H. ULICH (Z. physikal. Chem., Bodenstein Festband, 1931, 423—431).—Cryoscopic and ebullioscopic measurements with solutions of a variety of Al halides and complex halides in C_6H_6 and CS_2 show that no dissociation occurs at high dilutions. At higher concentrations typical dipole association takes place; in the case of $AlBr_3$ the association is attributable to the tendency of Al to a co-ordination number of 4, and results only in the dipole-free Al_2Br_6.

H. F. GILLBE.

Temperature of maximum refractivity of some aqueous solutions. N. GREGG-WILSON and R. WRIGHT (J. Physical Chem., 1931, **35**, 3011—3014).—The temp. of max. refractivity of 0·5 and 0·25N aq. solutions of the halides and nitrates of H, Li, Na, K, and NH_4, H_2SO_4, HCO_2H, AcOH, $EtCO_2H$ and of the corresponding Na salts have been determined by a graphical method which depends on the fact that the temp. coeff. of n decreases with a fall in temp. to zero at the temp. of max. refractivity. For aq. solutions this temp. lies below the f. p., and for any given solute the lowering of the temp. of max. refractivity increases with an increase in concentration. L. S. THEOBALD.

Quantitative limiting law for the viscosity of strong binary electrolytes. H. FALKENHAGEN (Physikal. Z., 1931, **32**, 745—764; cf. A., 1929, 1389; 1930, 155; this vol., 905).—The author's theory is extended to include any binary electrolyte, and yields results in good agreement with experiment.

J. W. SMITH.

Apparatus for quantitative investigations of disperse systems with the photo-electric cell. N. N. ANDREEV (Kolloid-Z., 1931, **57**, 39—42).—The construction and use of the apparatus are described.

E. S. HEDGES.

Determination of the mean size of particle in disperse systems by means of the photo-electric cell. N. N. ANDRÉEV (Kolloid-Z., 1931, **57**, 42—47).—The term A^2 in Rayleigh's equation can be measured by the strength of the photo-electric current and leads to the determination of particle size. The limiting particle size at which scattering of light is replaced by reflexion can be determined by observing the scattered light during coagulation by electrolytes.

E. S. HEDGES.

Molecules in a strong centrifugal field. T. SVEDBERG (J. Phys. Radium, 1931, [vii], **2**, 227—236).—The influence of the field on the mol. wt., speed of settling, and mol. symmetry has been examined. Results are given for several proteins. N. M. BLIGH.

Depth and rigidity of sediment in flocculated clay suspensions. R. K. SCHOFIELD and G. W. S. BLAIR (Trans. Faraday Soc., 1931, **27**, 629—632; cf. B, 1929, 446).—If a suspension of clay which has been treated with acid to replace metal ions with $H^{\cdot}$ is alternately allowed to settle for 16 hr. and shaken up, the vol. of sediment formed continually diminishes. Partial replacement of the exchangeable $H^{\cdot}$ by $Ca^{\cdot\cdot}$ or $Ba^{\cdot\cdot}$ does not affect the vol. of sediment, even if the solution is made $1N$ in regard to $CaCl_2$ or $BaCl_2$. A clay containing exchangeable $Na^{\cdot}$ or $K^{\cdot}$, however, passes into a thixotropic gel of larger vol. when suspended in a solution of the corresponding chloride of concentration exceeding about $1N$. The rigidity of the sediment depends both on the exchangeable ions present and on the nature and concentration of the added salt. R. CUTHILL.

Osmometer for lyophilic colloids. R. O. HERZOG and H. M. SPURLIN (Z. physikal. Chem., Bodenstein Festband, 1931, 239—246).—The osmometer described is especially suitable for the study of cellulose esters; at 50° the max. osmotic pressure is attained within 6 hr. Measurements with 0·1—30% solutions of cellulose benzyl ether in Me glycol acetate at 18°, 35°, and 50° show that in dil. solutions (up to about 1%) the osmotic pressure is a linear function of the concentration, whereas at concentrations greater than about 5% it is proportional to the square of the concentration; extrapolation indicates a mol. wt. of 29,000. With rise of temp. the osmotic pressure at low concentrations increases, but the pressure at high concentrations, *i.e.*, in the swelling interval, falls. Freshly prepared solutions yield the same types of curves, but the abs. osmotic pressure is lower.

H. F. GILLBE.

Hydrocarbons as dispersion media: a review. B. S. SOYENKOFF (J. Physical Chem., 1931, **35**, 2993—3009).—A review of the prep. and the behaviour in an electric field of sols dispersed in hydrocarbons. It is shown that a p.d. <5 kv. per cm. has, in general, no effect on such sols, and that electric charge is not an important stability factor. L. S. THEOBALD.

Molecular structure and solvation. W. HALLER (Kolloid-Z., 1931, **56**, 257—267).—Theoretical. The different properties of lyophobic and lyophilic colloids are due to differences in solvation, which in turn depend on the mol. structure of the colloidal substance. Lyophilic colloids generally consist of long, thread-like mols., which must not be assumed to be straight, but rather curved or rolled. These structural units can bind H_2O or other solvents both by adsorption and by rendering the mols. of solvent inactive by steric influence. The parts played by these two processes in swelling and in viscosity are discussed.

E. S. HEDGES.

Colloidal air. A. KRAUSE and K. KAPITAŃCZYK (Kolloid-Z., 1931, **57**, 50—56).—When 1 vol. of distilled H_2O is added to 9 vols. of 16—17N-NaOH the air dissolved in the distilled water is "salted-out" in the form of microscopic bubbles, which condense on ultramicroscopic particles of Na_2CO_3. By ultrafiltration of the NaOH solution, all the Na_2CO_3 can be removed and a true colloidal dispersion of air can then be obtained; this remains stable for 1—2 hr. at room temp., but for longer intervals at lower temp. The stability of the sols is increased also by increasing the concentration of NaOH, and by the addition of glycerol, probably by reason of the higher viscosity; soap has a protective effect on the sol. By mixing glycerol with 18·35N-NaOH polymerisation takes place, giving a liquid of very high viscosity (1958 × H_2O) in which the air sol remains stable for 50 days. These sols show the Tyndall cone; the particles have a weak Brownian movement and appear to be negatively charged. E. S. HEDGES.

Radio-colloids. O. WERNER (Z. physikal. Chem., 1931, **156**, 89—112).—No mol. groups can be detected in Th-X solutions by Chamié's photographic method (A., 1929, 620), but groups have been observed in Th-B and Th-C solutions, these disappearing on addition of HCl, NaCl, or mannitol. The groups are so large and formed in such dil. solution that it is probable that they consist of foreign particles which have adsorbed the active material, and that it is on such adsorption rather than merely on the possibility of the formation of sparingly sol. substances, *e.g.*, by hydrolysis, that the formation of radio-colloids depends (cf. A., 1930, 130). This view is supported by the observation that group formation, as measured by the amount of solute which can be removed by centifuging, is considerably reduced if the H_2O used for preparing the solution is first treated so as to remove suspended impurities. By addition of electrolytes the electric state of the carrier substance may be varied, owing to preferential adsorption effects, and the adsorption of the active substance influenced correspondingly. The adsorption of Th-B is affected quite differently from that of Th-C, for whereas Th-B is present in solution as cations, Th-C is mainly in the form of anions. At high electrolyte concentrations the small solubility of the adsorbate may

commence to influence the colloid formation, whilst in weakly alkaline solutions of Th-*C* the presence of undissociated $Bi(OH)_3$ may have some effect.

R. CUTHILL.

Role of dielectric constants, polarisation, and dipole moment in colloid systems. VIII. Dielectric and related data in polymeric series of high-molecular substances. W. GALLAY (Kolloid-Z., 1931, 57, 1—7).—The mol. wt., *d*, *n*, and dielectric const. of some poly-indenes and -styrenes have been measured and the dielectric and refraction polarisation and dipole moment calc. In both series the dielectric polarisation has a max. and the refraction polarisation a min. in the region of high colloidal dispersion, whilst the dipole moment increases with increasing size of the mol. E. S. HEDGES.

Magnetism of colloidal gold. V. I. VAIDYANATHAN and B. SINGH (Nature, 1931, **128**, 302—303; cf. A., 1930, 673).—The sp. susceptibility of a Zsigmondy Au sol was $0{\cdot}0804\times10^{-6}$ as against $0{\cdot}15\times10^{-6}$ for massive Au. The decrease may be due to the presence of amorphous material or to the difference of the cryst. structure in a small amount of the sol.

L. S. THEOBALD.

Electrolyte coagulation of colloids. X. Potentiometric titration of the coagulation process of aluminium hydroxide sols. P. S. VASSILIEV and A. J. RABINOVITSCH (Kolloid-Z., 1931, **56**, 305—317). —The potentiometric titration of $Al(OH)_3$ sols with different electrolytes shows that coagulation is preceded by a displacement of Cl ions from the surface of the colloid particles into the intermicellar liquid. This displacement takes place through exchange adsorption, and there is a close relation between the valency of the added anions, the concentration required for coagulation, and the amount of liberated Cl'. After coagulation has set in the activity of the Cl' generally falls. As coagulation proceeds the ζ-potential of the particles of $Al(OH)_3$ decreases. The colloidal micelle is represented by the formula $[mAl(OH)_3,nAlCl_3,pAl]^{3p+}+3pCl^-$. E. S. HEDGES.

Interaction of salts with inorganic compounds, and especially with hydrophilic colloids. K. H. MEYER and M. DUNKEL (Z. physikal Chem., Bodenstein Festband, 1931, 553—573).—The alkali halides are classified as aquo-acids and aquo-bases, the former being characterised by a large, slightly hydrated anion and a small, strongly hydrated cation. The two classes may be recognised by their mode of interaction with hydrophilic org. compounds and by their solubility relationships in different types of org. solvents; thus LiI, a typical aquo-acid, is soluble in pyridine, whereas CsF, a typical aquo-base, is insol. in pyridine, but is very sol. in PhOH. Similar relationships are exhibited by the relative influences of the halides on the solubility of acid and basic org. compounds in H_2O; the apparently anomalous effects observed in certain cases are due to complex formation, a view which is supported, *e.g.*, by the partition of LiI between BuOH and H_2O. H. F. GILLBE.

Preparation of chromic hydroxide gels. F. HEIN and H. BAR (Kolloid-Z., 1931, 57, 47—49).—Compounds of the type $CrX_2{\cdot}OR,3NH_3$ (where X is a halogen and R an alkyl radical) are precipitated when NH_3 is added to a solution of CrX_2 in R_2O; they dissolve in H_2O with hydrolysis and at sufficient concentrations a gel of $Cr(OH)_3$ is formed. The gels are fairly stable and undergo syneresis.

E. S. HEDGES.

Water relationships in colloids. I. Vapour-pressure measurements on elastic gels. D. R. BRIGGS (J. Physical Chem., 1931, **35**, 2914—2929).—The isotenoscope method provides a rapid means for determining the relative v. p. or activity coeff. of H_2O in colloids. Within certain limits, it is accurate to 1% and is preferable to the f. p. or the H_2SO_4 equilibrium method. V.-p. data for isoelectric casein and Na and Ca caseinates support the view that the change in H_2O-binding capacity (and swelling capacity) of a protein is the sum of the H_2O-binding capacities of the isoelectric protein and of the ionised atoms bound to the protein when salts are formed. The Na and Ca caseinates are practically 100% and 20% ionised respectively. L. S. THEOBALD.

Course of cooling curves of gelating systems. E. L. LEDERER (Kolloid-Z., 1931, 57, 16—22).—Theoretical. The evolution of heat on gelation is of the order of magnitude of the heat of solvation for both hydrosols and alcosols of soap. The temp. at which gelation begins is independent of the solvent. The thermal conductivities of soap gels and sols have been calc. from published data; the gel has in each case a val. of 60—80% of that of the sol.

E. S. HEDGES.

Gelatin in water-alcohol mixtures. H. SIEBOURG (J. Physical Chem., 1931, **35**, 3015—3021).—The viscosity of standard gelatin solutions diluted with H_2O–EtOH mixtures has been measured, and the relative vol. of the disperse phase calc. by means of Einstein's formula. For isoelectric gelatin the vol. appears to be a linear function of the composition of the solvent and for strongly acid or basic gelatin it shows a max. in the highly alcoholic solutions. The results agree with Loeb's curves for swelling effects.

L. S. THEOBALD.

Gum arabic. I. Viscosity and adsorption measurements. G. L. RIDDELL and C. W. DAVIES (J. Physical Chem., 1931, **35**, 2722—2731).—The viscosity of dil. aq. solutions of commercial gum arabic is practically unaffected by ageing treatments or by heating on a water-bath for 4 hr., and is insensitive to small changes in p_H. Adsorption of gum arabic, determined by changes in viscosity, by Zn, Al, lithographic stone, and bone charcoal increases rapidly at first with an increase in concentration and then falls more gradually to a const. value. This anomalous type of adsorption appears to be due to a change in the mol. condition of gum arabic. L. S. THEOBALD.

Viscosity of fibroin sol. I. Viscosity of fibroin dispersed in Loewe's reagent. M. HIRASAWA and K. KITAZAWA (Bull. Sericult., Japan, 1931, 4, 12—13).—η increases with the amount of fibroin in the reagent, and decreases with time.

H. DAVSON.

Measurements of structure-viscosity of cellulose derivatives in organic solvents and the influence of additions on their viscosity. III. Y. NISIZAWA (Kolloid-Z., 1931, **56**, 317—324; cf.

this vol., 1124).—Addition of H_2O to solutions of cellulose acetate in $COMe_2$ or $CH_2Ph{\cdot}OH$ raises the viscosity, enlarges the region of structure-viscosity, and leads to coagulation. Light petroleum causes the systems to gelate, and the gel shows marked syneresis. The syneretic liquid also shows structure-viscosity and does not consist of the pure dispersion medium. AcOH produces a lowering of viscosity. Camphor and Ph_3PO_4 cause a lowering of relative viscosity, but enlarge the region of structure-viscosity. Cellulose acetate dissolves in a mixture of $CHCl_3$ and EtOH, although not in either of the single components; in this system, structure-viscosity varies greatly with the composition of the solvent.

E. S. HEDGES.

Swelling. I. Regularities in the taking up of acid dyes by cotton. A. LOTTERMOSER and A. CSALLNER (Kolloid-Z., 1931, **56**, 324—334).—The adsorption of naphthol-yellow and crystal-ponceau by cotton is negative and the desorption positive, but the discrepancy can be explained quantitatively by the swelling of the adsorbent. The adsorption of Congo-red is only partly reversible. In presence of electrolytes the amount of dye taken up increases, the effect produced by salts being in the order $NaCl > Na_2SO_4 >$ Na citrate. E. S. HEDGES.

Electrokinetic potential on cellulose. K. KANAMARU (J. Cellulose Inst. Tokyo, 1931, **7**, 3—13).—The ζ-potentials of pure and modified celluloses and cellulose esters have been measured against H_2O and against solutions of electrolytes, the streaming-potential method being employed. Acid hydrolysis causes an initial increase in ζ-potential followed by a fall, oxidation producing a regular decrease with increasing Cu no. The potential is increased on esterification. On mercerisation, the potential decreases with increasing concentration of mercerising solution, approaching a limit at 17 vol.-% NaOH. The ζ-potential of pulps decreases as hydration ability or degree of beating increases, is lower for acid-treated than for alkaline-treated pulps, and is higher for bleached than for unbleached pulps. The effect of lignin is problematical. T. T. POTTS.

Thixotropy as a means of structure research on colloids. E. HAUSER (Proc. Chem. Eng. Group, 1930, **12**, 137—141).

Thixotropy of bentonite suspensions. H. FREUNDLICH, O. SCHMIDT, and G. LINDAU (Z. physikal. Chem., Bodenstein Festband, 1931, 333—340).—Electrodialysed suspensions of bentonite are rendered markedly thixotropic by addition of KCl and, especially, of KOH. The effect is closely related to the base exchange which occurs between H of the suspensoid and the K of the electrolyte. With KOH the end-point of the exchange reaction coincides with the max. thixotropy, but with KCl an equilibrium is set up, and the considerable quantity of KCl which is always present explains the relatively small tendency to gel formation; the dependence of the latter process on time is due to the slow establishment of the equilibrium. The swelling of bentonite in KOH and KCl solutions attains a max. at the same concentrations as those at which the thixotropic effect is a max. A parallel effect with the sedimentation vol. indicates that the swelling of the particles, and not their charge, is the determining factor in the sedimentation process.

H. F. GILLBE.

Migration studies with ferric oxide sols. I. Positive sols. F. HAZEL and G. H. AYRES (J. Physical Chem., 1931, **35**, 2930—2942).—The effects of [H$^{\cdot}$] and of the addition of electrolytes on the migration velocity of positive Fe_2O_3 sols. (0·006 g. Fe per litre) have been investigated by an ultramicroscopic method (A., 1928, 1323). Migration velocity falls with a rise in p_H, the isoelectric point lying at p_H 8·6 approx. For K_2CO_3, $CaSO_4$, K_2CrO_4, $K_2Cr_2O_7$, and KH_2PO_4 the velocity–log. concentration curves are linear. The discharging action of $Fe(CN)_6''''$ is the most pronounced, whilst that of Cl$'$ is the least. Bi- and ter-valent ions occupy intermediate positions. For a sol of p_H 7·3, Cl$'$ has no effect on migration velocity. It is unnecessary to deprive the particles completely of their charge in order to produce flocculation (A., 1915, ii, 138). L. S. THEOBALD.

Cataphoresis of suspended particles. I. Equation of cataphoresis. D. C. HENRY. **II. New experimental method and a confirmation of Smoluchowski's equation.** C. G. SUMNER and D. C. HENRY (Proc. Roy. Soc., 1931, **A**, **133**, 106—129, 130—140).—I. Smoluchowski's equation $U=cDX\zeta/\eta$ (where U is the velocity, X the field strength, ζ the potential difference across the double layer, D the dielectric const., η the viscosity of the medium, and $c=1/4\pi$) has been criticised on the ground that c varies with the shape of the particle. This conclusion is unsupported by most of the experimental evidence, and the theoretical relations have been re-examined without assuming that the applied potential gradient is everywhere parallel to the x axis and is undisturbed by the presence of the particle (which is the case only when the conductivity of the particle is the same as that of the medium). The results indicate that, subject to Smoluchowski's theoretical restrictions, his equation holds for spheres and cylinders (in both the axial and transverse positions), also for the electro-osmotic velocity at a plane surface or in a cylindrical channel of any cross-section. When the size of the particles is not large compared with the thickness of the double layer, U tends to a value $DX\zeta/6\pi\eta$ for very small particles. The dimension range includes most colloidal solutions.

II. By a modification of the experimental method of Billiter (Ann. Physik, 1903, **11**, 902) Smoluchowski's equation has been confirmed for the cataphoresis of cylindrical fibres. L. L. BIRCUMSHAW.

Energy exchange in gas mixtures. G. KORNFELD and K. HILFERDING (Z. physikal. Chem., Bodenstein Festband, 1931, 792—800).—Measurements of the heat conductivities of a variety of binary gas mixtures have been made with the object of ascertaining whether the inhibition of energy exchange required by the theory of Rice and Ramsperger actually occurs. The results suggest that such inhibition takes place only when H_2 is one of the components. H. F. GILLBE.

Equilibrium between chlorine, nitric oxide, and nitrosyl chloride. J. K. DIXON (Z. physikal. Chem., Bodenstein Festband, 1931, 679—686).—The

reaction has been studied between 196° and 465°. The equilibrium const. (atm.) is given by $\log_{10} K_p = -3860/T + 3\cdot348 \log_{10} T - 0\cdot002457T - 1\cdot8275$. The heat effect (25°) is 18,600±100 g.-cal., the free energy change 8600±200 g.-cal., and the entropy change 33·6±1·0 g.-cal. per degree.

H. F. GILLBE.

Calculations on water-gas equilibrium. Choice of suitable molecular-heat equations. Heat of reaction and free energy as a function of temperature. W. M. D. BRYANT (Ind. Eng. Chem., 1931, 23, 1019—1024).—Available thermal and equilibrium data for the water-gas reaction are discussed. The heat of reaction for $CO_2+H_2=CO+H_2O$ (all gases) is calc. to be 9751 g.-cal. Combined with mol.-heat equations from various sources, the val. gives expressions for the variation of heat of reaction with temp. The sp.-heat equations of Lewis and Randall and of Eastman give similar results, but Partington and Shilling's equations do not agree with these results. Expressions are derived for the free-energy change, its temp. coeff., and for the corresponding reaction isochores. The mol.-heat equations of Lewis and Randall, of Eucken, and of Eastman, but not those of Partington and Shilling, reproduce satisfactorily the experimental equilibrium consts. in the water-gas reaction. For the free-energy change numerical results between 6828 and 6750 g.-cal. are obtained, depending on the sp. heats used.

E. S. HEDGES.

Thermodynamic calculation of the affinities of some technically important gas reactions. H. SCHEIBEL (Monatsh., 1931, 58, 183—208).—Theoretical. Short general methods are developed for calculating the equilibrium consts. of gas reactions according to (1) classical thermodynamics, and (2) the Nernst heat theorem, using (*a*) conventional and (*b*) "true" chemical consts. The formulæ derived are tested for the combustion of C to CO_2 and to CO, the water-gas reaction, Deacon's Cl_2 process, and the formation of NH_3 from N_2 and H_2. Method (1) gives the best agreement with experiment, probably because it uses empirical consts. Simplified formulæ for methods (2*a*) and (2*b*) give as good results as the full formulæ. Method (2*b*) will probably be most accurate when the variation of *c* with temp. is fully understood.

R. S. CAHN.

General theory of solutions of strong electrolytes. T. S. WHEELER (Physikal. Z., 1931, 32, 674—680).—The electrical dilution work of a dil. solution of a strong electrolyte, the ions of which are governed by a special law of force, a modification of the Coulomb law, can be expressed in the form of a series each member of which represents a static potential energy raised to a power given by the ratio of the potential energy to the kinetic. The Clausius virial equation can be derived from the expression. The general form of thermodynamic functions which can be derived from the equation is shown. Several of the special expressions relating to the theory of strong electrolytes can be derived.

A. J. MEE.

Apparent dissociation constants of carbon dioxide in sea-water of different salt contents. K. BUCH, H. WATTENBERG, and H. W. HARVEY (Nature, 1931, 128, 411—412, and Naturwiss., 1931, 19, 773).—The apparent dissociation const. of H_2CO_3 in sea-water has been measured. The variation of K_1 with neutral salt content can be represented by $-\log K_1 = 6\cdot518 - 0\cdot588C^{\frac{1}{3}}$ at 18°, where C is the normality of all the cations present.

L. S. THEOBALD.

Apparent dissociation constants of methionine and *iso*serine. O. H. EMERSON, P. L. KIRK, and C. L. A. SCHMIDT (J. Biol. Chem., 1931, 92, 449—452).—For methionine (cf. A., 1930, 1026), $K_a' = 6\cdot17 \times 10^{-10}$, $K_b' = 1\cdot91 \times 10^{-12}$; for *iso*serine $K_a' = 5\cdot37 \times 10^{-10}$, $K_b' = 6\cdot03 \times 10^{-12}$. Their isoelectric points are at p_H 5·74 and 6·02, respectively.

A. COHEN.

Apparent dissociation constants of hydroxyvaline. E. J. CZARNETZKY and C. L. A. SCHMIDT (J. Biol. Chem., 1931, 92, 453—454).—The consts. recorded are $K_a' = 1\cdot97 \times 10^{-10}$ and $K_b' = 4\cdot05 \times 10^{-12}$; the isoelectric point is at p_H 6·15.

A. COHEN.

Relative hydration of sulphuric acid and alkali sulphates and its relation to catalytic activity. J. B. SENDERENS (Bull. Soc. chim., 1931, [iv], 49, 1138—1147).—The absorption of H_2O from air, under comparable conditions, by H_2SO_4, $NaHSO_4$, $KHSO_4$, Na_2SO_4, and K_2SO_4 decreases in the order given. The catalytic activity of the three first named in dehydration reactions runs parallel with their avidity for H_2O, and is attributed to the formation of temporary hydrates.

C. W. DAVIES.

Physico-chemical studies of complex formation involving weak acids. I. Hydrolysis of complex cyanides. H. T. S. BRITTON and E. N. DODD (J.C.S., 1931, 2332—2336).—By measuring the free HCN present in dil. aq. solutions of $KAg(CN)_2$, $K_4Fe(CN)_6$, $K_2Ni(CN)_4$, $K_2Zn(CN)_4$, and $K_2Cd(CN)_4$ it is found that the first three are stable, but that the last two are partly decomposed. $K_3Fe(CN)_6$ and $K_3Co(CN)_6$, although stable in H_2O, are markedly hydrolysed in KCN solutions.

C. W. DAVIES.

Electro-neutral dissociation of onium salts in the solution phase. G. SCHWARZENBACH (Helv. Chim. Acta, 1931, 14, 1071—1080).—The decomp. of onium salts in certain solvents to give free acid and free base is usually due to hydrolysis in H_2O and to a change in the activity coeffs. of the ions in org. solvents. The latter change has been studied colorimetrically in solutions of the NH_4 salt of *m*-nitrophenol, phenol-red, and bromocresol-purple in EtOH on addition of known amounts of LiCl to regulate the activity coeffs. Brucine salts of *p*-nitrophenol, bromocresol-purple, and bromophenol-blue were similarly investigated in $CHCl_3$ solution with the addition of $NPhMe_3Cl$. The results are shown in tables and curves.

F. L. USHER.

Aluminium phosphates. I. Formation of complexes in acid solutions. N. BJERRUM and C. R. DAHM (Z. physikal. Chem., Bodenstein Festband, 1931, 627—637).—Conductivity measurements and electrometric $[H^{\cdot}]$ determinations have been made with solutions containing $AlCl_3$ and H_3PO_4 or NaH_2PO_4, and the approx. complex and acid dissociation consts. of the phosphato-alumino-complexes have been

calc. It is improbable that only one complex is present in any given solution. H. F. GILLBE.

Problems of organic chemistry. III. Equilibrium in the system acetic acid–acetic anhydride–water. W. MUHLHAUSSER and M. TRAUTZ (Z. physikal. Chem., Bodenstein Festband, 1931, 319—328).—The equilibrium $AcOH \rightleftharpoons Ac_2O + H_2O$ has been studied from both sides, at temp. between 400° and 640°, in presence of catalysts consisting of a mixture of $Ca_2P_2O_7$ and $Al_4(P_2O_7)_3$ or of the same mixture containing 10% of free H_3PO_4. The percentage decomp. of the acid at 360°, 680°, 720° is 1·64, 87, and 92, respectively. The calc. heat effect of the reaction, viz., about 42 kg.-cal., is practically const. at 400—520°, but at higher temp. smaller vals. are obtained owing to the occurrence of side reactions. H. F. GILLBE.

Determination of tautomeric equilibria in various solvents by absorption measurements. Two forms of s-2-triquinolylmethane. G. SCHEIBE and G. KILIAN (Z. physikal. Chem., Bodenstein Festband, 1931, 468—474).—For the determination by extinction coeff. measurements of the concentration in different solvents of one form of a tautomeric substance it is necessary to establish both the magnitude and the extent of displacement of the absorption band in each solvent. Measurements with C_6H_6 solutions of *s*-2-triquinolylmethane show that the velocity coeff. of the tautomeric change is $9·6 \times 10^{-3}$ at 18° and $3·8 \times 10^{-2}$ at 40·6°. The position of the absorption max. varies with the equilibrium const. in a regular manner for the alcohols, but there is no regularity in the case of unrelated solvents. In C_6H_6 solution the transformation into the red form is endothermic, but in alcoholic solution it is exothermic. H. F. GILLBE.

Dissociation of acid–base indicators in ethyl alcohol with a discussion of the medium effect on the indicator properties. I. M. KOLTHOFF (J. Physical Chem., 1931, 35, 2732—2748).—From the work of previous investigators it is calc. that H_2O is approx. 400 times as strong a base as is EtOH. The dissociation consts. of various indicators in pure EtOH have been determined using alcoholic buffer solutions. The effect of traces of H_2O on the colour of indicators in alcoholic solutions of various types of acid–base systems is discussed. The colour of pentamethoxytriphenylcarbinol changes towards the alkaline side when traces of H_2O are added, and this exceptional behaviour is attributed to the *ψ*-base character of the indicator. The effect of EtOH on the colour of an indicator in aq. solutions of various acid–base systems is discussed. The colour of an indicator acid in an aq. buffer solution of an uncharged acid and its salt is scarcely affected by EtOH, but the colour of an indicator base changes strongly to the alkaline side. The titration of weak, uncharged acids or bases in EtOH has no advantages over titration in aq. solution. Other titrations in EtOH are discussed. L. S. THEOBALD.

Acid–base reactions in pyridine solution. L. E. KROHN and V. K. LAMER (J. Amer. Chem. Soc., 1931, 53, 3563—3565).—The colorimetrically determined changes of apparent "p_H" of pyridine with variation of concentration of added $NHEt_2$ or $CCl_3·CO_2H$ between $10^{-5}M$ and $1·0M$ are independent of the indicators used. The rapid decrease of apparent "p_H" on addition of pyridine to aq. $0·1M$-$NHEt_2$ suggests that pyridine has some acidic properties. Acids and bases of different strengths are not so sharply differentiated in pyridine as in aq. solution. The change of apparent "p_H" of an acid or base as the solvent is progressively changed from H_2O to pyridine is irregular with mol. fractions of pyridine $<0·2$. J. G. A. GRIFFITHS.

Activity coefficient of hydrochloric acid in aluminium chloride solutions. H. S. HARNED and C. M. MASON (J. Amer. Chem. Soc., 1931, 53, 3377—3380).—The e.m.f. of the cell $H_2|HCl(m_1)$, $0·0$–$0·45M$-$AlCl_3|AgCl|Ag$ has been determined at 25°. The activity coeffs. of HCl in $AlCl_3$ and alkali chloride solutions vary similarly with the ionic strength. At const. ionic strength of 1μ, $\log\gamma = \bar{1}·8495 + 0·0605m_1$, where $m_1 = 0·05$—$1·0M$. J. G. A. GRIFFITHS.

Effect of neutral electrolytes on the activity of water towards calcium carbonate. J. E. ORLOV (Z. anorg. Chem., 1931, 200, 87—104; cf. A., 1930, 1130).—The expression previously given for the activity of H_2O in presence of $H^·$ and HCO_3' ions holds also when neutral electrolytes are present in the solution. The coeffs. change in conc. electrolyte solutions, but a simple expression can be derived which holds for any added electrolyte. A reply is made to criticisms of the former paper (cf. this vol., 707). O. J. WALKER.

Thermodynamic properties of fused salt solutions. IV. Potassium bromide in silver bromide. E. J. SALSTROM (J. Amer. Chem. Soc., 1931, 53, 3385—3389; cf. this vol., 309).—Density data are given. From the e.m.f. of $Ag(s)|0·35$—$1·0$ mol. fraction $AgBr(l)+KBr(l)|Br_2(g)$, graphite, between 465° and 620° the free energies of formation and of dilution, heats of formation, entropy changes, activities, and activity coeffs. of AgBr at 500°, 550°, and 600° have been computed. The activity exhibits a large negative deviation from Raoult's law. J. G. A. GRIFFITHS.

Proton and electron activity in any solvent. G. SCHWARZENBACH (Helv. Chim. Acta, 1931, 14, 1069—1071).—Further discussion of a point raised in an earlier paper (A., 1930, 1526). F. L. USHER.

Equilibria existing in gas–water systems forming electrolytes. O. M. MORGAN and O. MAASS (Canad. J. Res., 1931, 5, 162—199).—The v. p. and conductivities of aq. solutions of SO_2, CO_2, and NH_3 have been determined at 0—25° at concentrations up to those corresponding with a v. p. of 1 atm. NH_3 in aq. solution is almost entirely combined with H_2O. SO_2 is only partly combined, and the amount not combined increases rapidly as the temp. rises; approx. values of the true dissociation const. have been calc. CO_2 is combined only to a small extent, the amount uncombined increasing with rise in temp. R. CUTHILL.

Transition point of potassium ferrocyanide. E. FABRIS (Gazzetta, 1931, 61, 527—537).—Measurements of the rate of dehydration of $K_4Fe(CN)_6,3H_2O$

with and without a current of dry air, and of the heating and cooling curves of saturated $K_4Fe(CN)_6$ solutions in contact with the solid phase between 80° and 90°, show the existence of a transition point at 87·3°. O. J. WALKER.

Equilibrium of certain non-metallic systems. I. FeO–MnO. II. MnS–MnO, MnS–MnSiO$_3$, and MnS–Fe$_2$SiO$_4$. J. H. ANDREW, W. R. MADDOCKS, and (I) D. HOWAT, (II) E. A. FOWLER (Iron and Steel Inst., Sept., 1931, Advance copy, 1—13, 13—26).—I. Pure FeO is obtained by heating FeC_2O_4 at 700° in vac. and pure MnO by heating MnC_2O_4 at 850° in vac. The two oxides form a complete series of solid solutions, the m. p. rising almost linearly from the m. p. of FeO, 1410°, to the m. p. of MnO, 1585°; throughout the range the liquidus is within 20° of the solidus.

II. The systems MnS–MnO, MnS–$MnSiO_3$, and MnS–Fe_2SiO_4 are of the simple eutectiferous type with limited solid solubility at both ends. The MnS–MnO eutectic (1285°) contains 50% MnS; the MnS–$MnSiO_3$ eutectic (1250°) contains 10% MnS, and the MnS–Fe_2SiO_4 eutectic (1055°) also contains 10% MnS. Pure $MnSiO_3$ has m. p. 1305°, pure MnS 1615°, and pure Fe_2SiO_4 1130°. The solubility of MnS in MnO is 7·5%, in $MnSiO_3$ about 1·5%, and in Fe_2SiO_4 about 2%. The solubility in MnS of MnO is 16%, of $MnSiO_3$ about 1%, and of Fe_2SiO_4 about 2·5%. As MnS is soluble in FeO, Fe_2SiO_4, and $MnSiO_3$ the S prints obtained from Fe and steel would appear to indicate not only the distribution of S, but also the distribution of slag inclusions, the S merely serving as a means of bringing about the detection of slag.

A. R. POWELL.

System cobalt chloride–zinc chloride. H. BASSETT and W. L. BEDWELL (J.C.S., 1931, 2479—2492; cf. A., 1930, 1251).—The f. p. of $CoCl_2$ and $ZnCl_2$ are 735±7° and 313°, respectively; discordant vals. of earlier workers are explained. On cooling fused mixtures, solid solutions are formed up to 7% $CoCl_2$, thereafter $CoCl_2$ separates; the eutectic point (7% $CoCl_2$) is at 312±1°. All mixtures have the blue colour of anhyd. $CoCl_2$, corresponding with the absence of compound formation. C. W. DAVIES.

Oxide hydrates and active oxides. XLVI. System bismuth oxide–water. G. F. HUTTIG, T. TSUJI, and B. STEINER (Z. anorg. Chem., 1931, **200**, 74—81; cf. this vol., 799).—Hydrated Bi_2O_3 dried over 40% H_2SO_4 has the composition $Bi_2O_3,2·5H_2O$. Isobaric dehydration and *X*-ray examination of hydrates containing up to 3·24 mols. H_2O point to the existence of a compound $Bi_2O_3,3H_2O$. Throughout the whole dehydration range the products consist of a mixture of two phases, one of which has the lattice of the trihydrate, the other that of Bi_2O_3. During isobaric dehydration the first mol. of H_2O is given off continuously, the second sharply at 310°, and the third continuously at higher temp.

O. J. WALKER.

Polyhalides. II. Physical properties. H. W. CREMER and D. R. DUNCAN (J.C.S., 1931, 2243—2254).—All polyhalides dissociate to leave the metal combined with one atom of the most electronegative halogen present. The dissociation pressures of $KIBr_2$, KIBrCl, and $KICl_2$ have been measured using a glass spring manometer. The relative stabilities of many alkali polyhalides and alkylammonium dibromoiodides have also been determined by distribution experiments with CCl_4. For cations the order of increasing stability is Na, K, NH_4, Rb, Cs, irrespective of the anion. With the substituted NH_4 compounds there is alternation, those with an even number of alkyl groups being the most stable. In the anion stability is favoured by symmetry, and by the presence of one, but not more than one, I atom. The m. p. are discussed and the effects of prolonged drying described. Data are given for the solubilities of the dibromoiodides in H_2O, for that of I in CCl_4 and for the v. p. of Br at 25°. Evidence is adduced that the *compound* CsIBrF exists. $KIBr_2$ crystallises from H_2O as a *monohydrate*, m. p. 58°. C. W. DAVIES.

System lithium sulphate–aluminium sulphate–water. J. P. SANDERS and J. T. DOBBINS (J. Physical Chem., 1931, **35**, 3086—3089).—Between 0° and 50°, Li_2SO_4,H_2O and $Al_2(SO_4)_3,18H_2O$ are the only stable phases in contact with aq. solutions; no alum exists as a stable solid between these temp. The solubility of each salt is depressed by the other. Change of temp. has little effect on the solubility of Li_2SO_4 in the presence of $Al_2(SO_4)_3$, but a fall in temp. decreases that of $Al_2(SO_4)_3$ in the presence of Li_2SO_4.

L. S. THEOBALD.

System silver–copper–oxygen; quasi-binary section, silver–cuprous oxide. J. A. A. LEROUX and K. W. FRÖHLICH (Z. Metallk., 1931, **23**, 250—254).—The quasi-binary system Ag–Cu_2O has been investigated by thermal analysis and by micrographic examination. In the liquid state there is a miscibility gap above 1134° extending from about 5 to 82% Ag. The Cu_2O–Ag eutectic contains 2·1—2·3% Cu_2O and melts at 941°; the solid solubility of Cu_2O in Ag is about 0·3% and that of Ag in Cu_2O about 2—3% according to the temp. No evidence of the formation of CuO in any of the alloys could be found but in Cu_2O-rich alloys the presence of Cu as Ag–Cu eutectic was observed. This is attributed to the reaction $Cu_2O \rightleftharpoons Cu+CuO$ taking place from left to right at high temp. with absorption of the CuO by the refractories used in the melting. A. R. POWELL.

Action of sulphur on the molten equilibrium $Fe+NiSiO_3 \rightleftharpoons Ni+FeSiO_3$. H. ZUR STRASSEN (Z. anorg. Chem., 1931, **200**, 46—56; cf. A., 1930, 1375).—The above equilibrium is only slightly displaced by the addition of S, which simply dilutes the metallic phase, and it still follows the mass action law. In concentrations greater than 0·5 mol. S to 1·0 mol. metal the S has a strong reducing action on the metallic oxide of the silicate phase. The metal sulphide melt dissolves NiO appreciably, FeO less, and this brings about secondary reactions which cause apparent deviations from the mass action law. In the melt $NiSiO_3$ is appreciably dissociated into NiO and SiO_2. O. J. WALKER.

Equilibrium diagram of the system magnesium hydroxide–potassium chloride–water at 25°. A. P. PALKIN (Bull. Univ. Asie centr., 1929, no. 18, 73—75).—The solubilities of $Mg(OH)_2$ and KCl are independent. CHEMICAL ABSTRACTS.

Measurement of heat effects. H. RAMSTETTER and G. HANTKE (Z. physikal. Chem., Bodenstein Festband, 1931, 662—668).—A method of calculating the heat effect of a reaction between a liquid and a gas is illustrated by reference to the manufacture of KOCl, the dissolution of NH_3 and of SO_2, and the neutralisation of aq. NaOH with SO_2. H. F. GILLBE.

Differential heats of dilution and the electrothermal effect. G. JUNG (Z. physikal. Chem., Bodenstein Festband, 1931, 298—302).—Theoretical. Part of the differential heat of dilution must be regarded as an electrothermal effect. H. F. GILLBE.

Heats of dissociation of chlorine monoxide and chlorine dioxide. (MISS) J. I. WALLACE and C. F. GOODEVE (Trans. Faraday Soc., 1931, **27**, 648—654).—The heats of dissociation of Cl_2O and ClO_2 have been found by direct measurement of the heats of explosion to be 560 and 26,585+390 g.-cal. respectively. R. CUTHILL.

Heat of formation of water and heats of combustion of methane and carbon monoxide. A correction. F. D. ROSSINI (Bur. Stand. J. Res., 1931, 7, 329—330).—The data previously recorded (this vol., 170, 433) were reduced to a const. pressure of 1 atm. This is incorrect. The corrected values for H_2O are 285,850+50, for CH_4 889,720±230, and for CO 282,938+110 abs. joules. W. R. ANGUS.

Heat of formation of titanium dioxide. W. A. ROTH and G. BECKER (Z. physikal. Chem., Bodenstein Festband, 1931, 55—60).—Combustion of Ti in O_2 at 38—40 atm. yields anatase, d^{21} 3·862. The heat of formation is 218·1±0·3 kg.-cal. per mol. H. F. GILLBE.

Hydrates of pentaphenylchromium hydroxide. F. HEIN and W. RETTER (Z. physikal. Chem., 1931, **156**, 81—85; cf. A., 1922, i, 77).—It is calc. from the dehydration isotherms that the heat of formation of the tetrahydrate from the dihydrate and H_2O vapour is 13·4 kg.-cal. per mol. and that of the dihydrate from the anhyd. base 23·4 kg.-cal. at about 30°. R. CUTHILL.

Free energy, heat and entropy of formation of *l*-malic acid. H. BORSOOK and H. F. SCHOTT (J. Biol. Chem., 1931, **92**, 559—567).—Using a potentiometric method (cf. this vol., 1189) the equilibrium ionic ratio, *l*-malate″/fumarate″, at 25° is approx. 3·1. The free energy of formation of solid *l*-malic acid at 25° is −210,450 ±500 g.-cal. whilst the free energy of the *l*-malate ion at 1-molar activity is −201,940 ±150 and the heat content −258,100 g.-cal. The entropy of solid *l*-malic acid at 25° is 49 units. F. O. HOWITT.

Transport numbers and transport potentials in metallic solutions. H. SCHWARZ (Z. physikal. Chem., 1931, **156**, 227—231; cf. this vol., 685).—The transport nos. of Zn, Tl, Sn, and Bi in amalgams of different concentrations at 25° and 35° have been calc. from e.m.f. determinations. No measurable values of the e.m.f. were obtained in Au and Pb amalgams. M. S. BURR.

Electro-endosmosis and electrolytic water transport. II. H. C. HEPBURN (Proc. Physical Soc., 1931, **43**, 524—537; cf. A., 1927, 422).—Measurements of liquid transport with 0·0005—1N-$CuSO_4$ solutions and a paper parchment diaphragm indicate a const. electrolytic water transport per faraday, modified by a sp. action of the diaphragm. A. B. D. CASSIE.

Mobility of ions in solvents which can yield a similar ion. P. WALDEN (Z. physikal. Chem., Bodenstein Festband, 1931, 19—29).—Solubility measurements have been made with various salts in MeOH, EtOH, $MeNO_2$, NH_2Et, PhOH, and $CH_2Cl{\cdot}CO_2H$, in order to determine whether the abnormally high mobility of the OH and H ions in aq. solutions is a general phenomenon. The results show, however, that salts having an ion in common with the solvent possess normal conductivities over a considerable concentration range. The observed mobilities of the H, OH, OEt, and OMe ions correspond with those of other ions, and may be explained in terms of solvation; the H ion, *e.g.*, in MeOH and EtOH is associated with 0·5—1·2 mols. of the solvent and in $MeNO_2$ with 2 mols. H. F. GILLBE.

Ionic mobility in highly conducting solid electrolytes. C. TUBANDT and H. REINHOLD (Z. physikal. Chem., Bodenstein Festband, 1931, 874—880).—α-Ag_2S differs from other solid electrolytes in its extremely high conductivity, negative temp. coeff., the inapplicability of the Einstein law, and the reversible depression of the conductivity produced by treatment with S vapour. Electrolytic conduction in α-Ag_2S must involve a mechanism different from that of the diffusion process. H. F. GILLBE.

Internal structure of solid inorganic compounds at high temperatures. IV. Diffusion in and conductivity of certain halides. W. JANDER (Z. anorg. Chem., 1931, **199**, 306—320).—Measurement of the extent of inter-diffusion in the systems K_2SrCl_4–K_2BaBr_4 (450—520°), Na_2CdCl_4–Na_2ZnBr_4 (230—260°), K_2SnCl_4–K_2PbBr_4 (190—250°) show that the halogen ions are much more mobile than those of Sr, Ba, Cd, Sn, Zn, or Pb. This result, together with conductivity measurements, indicates that these double salts possess simple ionic lattices. In K_2PtCl_4 and K_2PdBr_4, on the other hand, both the halogen and the Pt and Pd ions are immobile at temp. up to 380°, and the salts therefore possess complex ionic lattices. H. F. GILLBE.

Physico-chemical properties of solutions in liquefied gases. Conductivity of alkali nitrates in liquid ammonia. A. M. MONOSSON and W. A. PLESKOV (Z. physikal. Chem., 1931, **156**, 176—194).—The conductivity of solutions of Li, Na, K, Rb, and Cs nitrates in liquid NH_3 at −40°, at dilutions varying from 10 to 100,000 litres, has been measured. By the Kohlrausch extrapolation method the values of at −40° are 290, 300, 338, 344, and 345, respectively. The same calculation applied to Franklin and Bray's results at −33·5° gives 299, 315, and 354 for the Li, Na, and K salts, respectively. For concentrations below 0·0003—0·0002M the results agree qualitatively with the theory of Debye and Onsager, but the experimental val. of α in the equation $\mu=\mu_\infty-a\sqrt{c}$ is 2·5 to 4 times the theoretical val. calc. from Onsager's formula. The mobilities of the five cations at

$-40°$ are 121, 131, 169, 174, and 175, respectively, and of the first three at $-33 \cdot 5°$, 122, 138, and 177, respectively. M. S. BURR.

Resistance of an electrolytic conductor at various frequencies. D. E. RICHARDSON (Physical Rev., 1930, [ii], **35**, 297).—The equation connecting the resistance of a conductor with the frequency of current has been verified for 30% H_2SO_4 for wavelengths up to 37 m. L. S. THEOBALD.

Zinc electrode. F. H. GETMAN (J. Physical Chem., 1931, **35**, 2749—2757).—The e.m.f. of the cell $Zn|ZnCl_2$ $(0 \cdot 002-1 \cdot 0M)|Hg_2Cl_2,Hg$ has been measured at 25° with single crystals or cryst. aggregates of Zn. The former resemble single crystals of Cu and Cd (this vol., 569) in showing a tendency to give larger differences of potential than do the cryst. aggregates. The normal electrode potential of Zn, computed from e.m.f. measurements by three different methods, has the average val. of 0·7613 volt. L. S. THEOBALD.

Potential of the calomel electrode. L. E. SABININA (Bull. inst. res. biol. Perm, 1931, **7**, 333—336).—When H_2 is passed through a calomel electrode a potential change at 25° of 0·8—1·9 mv. is observed. In presence of O_2 a rise of the potential is explained by a shift to the right in the equilibrium Hg_2Cl_2 $Hg+HgCl_2$; in presence of H_2 the equilibrium $H_2+Hg_2Cl_2 \rightarrow 2HCl+2Hg$ is shifted to the left. CHEMICAL ABSTRACTS.

Galvanic potential and concentration changes of the relevant ion. M. ANDAUER and E. LANGE (Z. physikal. Chem., Bodenstein Festband, 1931, 247—256).—The problem of determining the conditions under which it is legitimate to calculate the changes of ionic concentration in two-phase systems from the accompanying changes of the galvanic potential has been examined. If the variations of concentration occur in only one phase, these may be calc., but if in both phases the change in one phase must be known for calculation of that in the other. The case of the system $Ag|AgNO_3$, $NaNO_3$ is treated in detail. The equations derived are in general applicable to systems in which complexes are formed, such as $Ag|AgCN,KCN$, without regard to the chemical condition of the ions which determine the potential. H. F. GILLBE.

Property of the glass electrode. G. BUCHBOCK and (FRL.) M. REISE (Z. physikal. Chem., 1931, **156**, 232—236).—Zirkler's observation (this vol., 914) that an e.m.f. may be set up between the inside and outside of the bulb of a glass electrode, although the metal electrodes and the inner and outer solutions are identical, has been confirmed. The phenomenon is attributed to the different states of tension of the two glass surfaces. A method for measuring the e.m.f. of the glass electrode is described. M. S. BURR.

Electrode potentials and adsorbed ionic films. H. V. TARTAR and H. K. MCCLAIN (J. Amer. Chem. Soc., 1931, **53**, 3201—3212; cf. A., 1930, 998).—When the distance between two accurately parallel polished Pt electrodes in $0 \cdot 056M$-Na_2HPO_3, $0 \cdot 01M$-KH_2PO_3, -$CuSO_4$, -$Pb(NO_3)_2$, -$Al_2(SO_4)_3$, or -$NiCl_2$, or $0 \cdot 2M$-H_3BO_3 containing $0 \cdot 01M$-KCl is diminished in the presence of air or O_2, the potential varies for distances less than 0·5—0·05 mm., the limiting distance depending on the solution. Similar effects are observed if one Pt electrode is replaced by Au; the potential is also affected by the proximity of quartz or bakelite. These and other observations support the theory that the potential is due partly to an adsorbed ionic film extending from the electrode to a measurable distance in the solution. J. G. A. GRIFFITHS.

Indefinite metal-solution potentials and their utilisation for the electrochemical separation of radio-elements. O. ERBACHER (Z. physikal. Chem., 1931, **156**, 135—141).—The potentials of certain metals have been followed for a period of 2 hr. after immersion in $0 \cdot 1N$-HCl at 20° and at 79°. The data afford a means of investigating the possibility of utilising these metals for displacing radioactive elements from their solutions. R. CUTHILL.

Electrochemical method [of separating radio-elements from solution]. O. ERBACHER (Z. physikal. Chem., 1931, **156**, 142—149).—Ra-*E*, Po, and Th-*C* may be displaced from solution by means of Pt charged with H, and by subsequent treatment of the Pt with acid solutions of the active compound free from inactive salts are obtained. R. CUTHILL.

Titration of hydroxy-organic acids in presence of ferric and cupric salts. C. V. SMYTHE (J. Biol. Chem., 1931, **92**, 233—244).—Glass electrode titration curves of lactic, glycollic, oxalic, malic, tartaric, and citric acids mixed with $CuCl_2$ and $FeCl_3$ respectively show that the mixtures are more acidic than the acids alone. The additional amount of alkali is the same as that required for the precipitation of the hydroxides from the pure salt solutions. This is explained by the formation of complexes between the Cu or Fe and the hydroxylic H atoms leading to enhanced acidity of the latter. A. COHEN.

Existence of e.m.f. in closed metallic electric circuits at the same temperature. O. SCARPA (Z. physikal. Chem., 1931, **156**, 225—226).—A claim for priority (B., 1929, 823) against Schwarz (this vol., 685). M. S. BURR.

E.m.f. developed between silicon and other elements in aqueous hydrofluoric or sulphuric acids, or sodium hydroxide. C. BEDEL (Compt. rend., 1931, **193**, 527—528).—The e.m.f. of cells consisting of Si (containing 0·1% Fe) and other elements in 13·7% HF, N-H_2SO_4, and N-NaOH has been measured. Although actual figures for different samples of Si show large variations, and the order of magnitude in the different solutions varies, it is found that Pt, Ag, and C (graphite) are always electropositive, Pb, Sn, and Zn electronegative; Cu, Ni, and Fe are negative in H_2SO_4 and positive in NaOH, whereas Cu and Ni are positive and Fe is negative in HF. Variation of concentration of HF has little effect. C. A. SILBERRAD.

E.m.f. relationships of formic acid. E. MÜLLER and J. GÖRNE (Z. physikal. Chem., Bodenstein Festband, 1931, 44—54).—The reduction potential of HCO_2H varies with the roughness of the electrode

surface, and approaches the reversible H potential only when the surface is extremely rough. It is suggested that the H atoms of the acid, prior to the decomp., are adsorbed on the electrode, and that on account of the configuration of the mol. such adsorption takes place with difficulty on a plane surface, but readily on a roughened surface. This view explains the fact that only highly dispersed metals are capable of catalytically decomposing HCO_2H at room temp.

H. F. GILLBE.

Deposition potential of nickel. F. FOERSTER and K. GEORGI (Z. physikal. Chem., Bodenstein Festband, 1931, 453—467).—The current density–voltage curves obtained during the electrodeposition of Ni from solutions of $NiCl_2$, $NiSO_4$, and $Ni(ClO_4)_2$ show that Glasstone's conclusion, viz., that deposition commences at a definite potential which differs considerably from the equilibrium potential and proceeds thereafter without retardation, is incorrect. Glasstone's result is attributed to the shortness of the period of observation; thus whereas under specified conditions and with a current density of $0{\cdot}56\times10^{-4}$ amp. per sq. cm. no deposition is apparent during the first 30 min., by prolongation of the experiment for 24 hr. the amount of Ni deposited is sufficient to permit the calculation of the current yield.

H. F. GILLBE.

Polarographic studies with the dropping mercury cathode. XXI. Limiting currents for electrodeposition of metals and hydrogen. I. ŠLENDYK (Coll. Czech. Chem. Comm., 1931, **3**, 385—395).—The limiting currents due to the electrodeposition of metals at the dropping Hg cathode, *e.g.*, Cu, Cd, or Mn from solutions of the chloride, follow Eucken's theory, decreasing to half val. when an excess of indifferent salt (KCl or $BaCl_2$) is added. The limiting current associated with H_2 deposition decreases with addition of indifferent salts to a greater extent than that indicated by Eucken's formula. The current is smaller the higher is the valency of the added cation. The phenomenon is discussed with reference to Heyrovsky's theory of H overvoltage (A., 1925, ii, 675; 1927, 1145).

M. S. BURR.

Polarographic studies with the dropping mercury cathode. XXII. Hydrolysis of cobaltous chloride. R. BRDIČKA (Coll. Czech. Chem. Comm., 1931, **3**, 396—405; cf. A., 1930, 1254).—The current–voltage curves registered polarographically, when aq. solutions of $CoCl_2$ are electrolysed using the dropping Hg cathode, show an increase in current at approx. $-1{\cdot}05$ volt, about 0·2 volt below the increase due to the deposition potential of Co. This gives a "wave" in the curve which becomes more pronounced when the solution is warmed, or when a small amount of alkali hydroxide is added to the solution. The wave disappears entirely after acidification to p_H 4. The first increase in current is probably due to the deposition of Co from the ion $[Co(H_2O)_5OH]^{\cdot}$, the hydrated form of the ion $CoOH^{\cdot}$. At the second increase $[Co(H_2O)_6]^{\cdot\cdot}$ ions are deposited. This is possible if the equilibrium $[Co(H_2O)_6]^{\cdot\cdot}+H_2O \rightleftharpoons H^{\cdot}+[Co(H_2O)_5OH]^{\cdot}$ is only slowly established, so that each kind of ion has its own deposition potential at which the complex ion is torn into the simple ions by the action of the strong electric field at the surface of a polarised electrode.

M. S. BURR.

Polarographic studies with the dropping mercury cathode. XXIV. Disappearance of adsorption currents at the electrocapillary zero potential. J. HEYROVSKY and E. VASCAUTZANU (Coll. Czech. Chem. Comm., 1931, **3**, 418—429).—The characteristic reproducible max., which appear at cathodic reduction potentials on current–voltage curves in electrolysis with the dropping Hg cathode, disappear if the reduction potential coincides with the potential at which the interfacial tension of polarised Hg is a max. Cd deposits at this electrocapillary zero potential ($=0{\cdot}56$ volt when the calomel electrode is zero) and a simple diffusion "wave" only is indicated on the polarogram, but this can be changed into a max. if reagents are added which either change the deposition potential of Cd, *e.g.*, cyanide or aq. NH_3, or which change the position of the electrocapillary zero, *e.g.*, iodide or thiocyanate. Similarly positive max. can be changed to negative, disappearing at the zero point. Similar results are obtained with Pb and Cr, which deposit near $-0{\cdot}56$ volt, and in the electro-reduction of undissociated mols., *e.g.*, maleic acid, when the reduction potential coincides with the electrocapillary zero. Adsorption at an electrode therefore vanishes at the electrocapillary zero (cf. A., 1930, 1527).

M. S. BURR.

Hydrogen and oxygen overvoltages on nickel–iron alloys. M. DE K. THOMPSON and A. L. KAYE (Trans. Amer. Electrochem. Soc., 1931, **60**, 9—14).—H and O overvoltages for alloys ranging from pure Fe to pure Ni have been determined at various current densities in N-KOH (cf. this vol., 570). H overvoltages increase almost linearly from 0% to about 50% Fe, but with higher Fe content remain approx. const. or fall slightly. At high current densities curves for O overvoltage against % Fe show a max. followed by a min. but at low current densities only a min. For an alloy of given composition the H overvoltage is approx. given by $\eta=a-b\log d$, where d is the current density and a and b are consts., but for O overvoltage vals. of a and b change when the current density exceeds a certain val.

H. J. T. ELLINGHAM.

Nature of the passive film produced anodically on iron in solutions containing sulphate. W. J. MÜLLER and W. MACHU (Z. physikal. Chem., Bodenstein Festband, 1931, 687—703).—The natural oxide film of Fe renders the metal passive towards Na_2SO_4 solutions, but is removed by very dil. acids. In H_2SO_4 solutions of concentration greater than $0{\cdot}5N$ a film of $FeSO_4,7H_2O$ is formed after removal of the oxide film. Chemical passivity is produced at potentials greater than 2 volts, and is due to a second type of oxide film, which is extremely sensitive towards conc. solutions of electrolytes, but is very stable in dil. solutions. By prolonged activation in dil. sulphate solutions a porous film of a basic salt is formed.

H. F. GILLBE.

Current-yielding process in the Leclanche element. C. DRUCKER (Z. physikal. Chem., Bodenstein Festband, 1931, 912—918).—The assumption that the essential reaction in the Leclanche cell yields

Mn_2O_3 and $Zn(NH_3)_2Cl_2$ is incorrect, since calculation from thermochemical data in conjunction with an initial temp. coeff. of the e.m.f. of about 0·6 mv. per degree yields 1·46 for the e.m.f. of the cell. It is probable that not MnO_2, but the free O adsorbed on natural, and more especially on artificial, MnO_2 is primarily involved in the production of the current, since the oxidation of Zn by O would yield an e.m.f. of about 1·8 volts and that of a new cell is often more than 1·7 volts. The recovery of a cell after a period on closed circuit is due to replacement of the adsorbed O by atm. O_2. H. F. GILLBE.

Electrical [etc.] phenomena in crystallisation [of sodium acetate]. A. TSCHERMAK (Z. Krist., 1931, **79**, 465—494).—The rise in temp. on crystallisation of a supersaturated solution of NaOAc decreases parabolically from about 42° at 0°, to nil at 56°; the velocity of crystallisation increases with concentration and with nearness to (above or below) 15°. The existence of a di- (tables) and mono- (long prisms) hydrate, and of only one form of the anhyd. salt is inferred (cf. A., 1887, 323; 1913, i, 1300). If a supersaturated solution of $NaOAc,3H_2O$ is inoculated at a point A, and electrodes (of Au or Pt) placed at B and C, A, B, and C being approx. in a line, a current passes when the crystallisation front reaches B, and a reverse one when it reaches C, due to the crystallisation front carrying a positive charge. Other possible causes are shown to be inadequate, the current being due to energy evolved on crystallisation. Its strength varies with concentration, and is of the order of 10^{-7} amp. C. A. SILBERRAD.

Reaction velocity in relation to the concentration and activity of the reacting components. H. M. DAWSON (Proc. Leeds Phil. Soc., 1931, **2**, 230—234).—The view that the velocities of certain reactions are determined by the activities of the reactants, and not by their respective concentrations, is reversed by a consideration of data for the hydrolysis of $MeCO_2Et$ and the transformation of *N*-chloro- into *p*-chloroacetanilide. N. M. BLIGH.

Empirical rule in the chemical kinetics of bimolecular reactions. W. A. HOLZSCHMIDT (Z. anorg. Chem., 1931, **200**, 82—86).—A survey of the data available for bimol. reactions in solution shows that the energy of activation, A, and the factor, B, in the Arrhenius equation are related by the expression $B=Ke^{A/C}$, where C is a const. and K is a quantity which depends on the nature of the solvent. This expression can be deduced from the similar one which holds for unimol. reactions (cf. this vol., 1014). O. J. WALKER.

Effect of pressure on rate of polymerisation. G. TAMMANN and A. PAPE (Z. anorg. Chem., 1931, **200**, 113—132).—The polymerisation of liquid styrene, isoprene, vinyl acetate, dimethylbutadiene, and indene follows the unimol. law, suggesting that the mols. undergo some change before union, the rate of this reaction determining the speed of the process as a whole. The velocity increases with increase in pressure much more rapidly than in other reactions occurring in liquids, but the form of the relation between the velocity coeff. and the pressure varies from one reactant to another. Increase in pressure also results in a fall in the temp. at which polymerisation starts. The physical properties of the products of polymerisation have been examined. R. CUTHILL.

Kinetics of a thermal *cis-trans* isomerisation. G. B. KISTIAKOVSKY and M. NELLES (Z. physikal. Chem., Bodenstein Festband, 1931, 369—378).—The isomerisation of Et dimethylmaleate into Et dimethylfumarate in the neighbourhood of 300° is a purely homogeneous, quasi-unimol. reaction. The activation energy of the reaction is 26·5 kg.-cal., and its rate is slower than that of any other known unimol. reaction. The abnormally low rate of activation, which is only about 10^{-3} that calc. on the assumption that only two degrees of freedom are involved, is discussed in relation to the mechanism of the intermol. movement and to the possibility of the reaction taking place through the formation of an enolic compound. H. F. GILLBE.

Discontinuity in the velocity coefficient of a chemical reaction at the critical temperature. H. S. SUTHERLAND and O MAASS (Canad. J. Res., 1931, **5**, 48—63).—A technique for investigating reaction mixtures at high pressures and relatively high temp. is described. The velocity of the reaction between propylene and HCl increases with rise of temp. in the liquid state, but above the crit. temp. becomes almost zero. This supports the view that regional orientation occurs in a binary liquid mixture and that this furthers the reaction. Decrease in the regional orientation with rise in temp. is more than compensated by increased activity of the mols. until the crit. temp. is reached, when the regional orientation and the temp. coeff. both fall rapidly. J. W. SMITH.

Kinetics of the combination of hydrogen atoms in triple impact. W. STEINER and F. W. WICKE (Z. physikal. Chem., Bodenstein Festband, 1931, 817—830).—The combination of H atoms in the pressure interval 0·3—0·7 mm. and at at. concentrations of 15—80% has been investigated. The surface reaction is negligible. The velocity coeff. k at 0·7 mm., calc. on the assumption that atoms and mols. are equally active in a triple impact, is $7{\cdot}6\times10^{15}$, whilst if it is assumed that the H mols. alone are active the coeff. k' becomes $9{\cdot}6\times10^{15}$; k, but not k', increases with increase of the mol. concentration. The results indicate, in contradiction to previous work, that a mol. as third partner in a triple impact is more active than an atom. H. F. GILLBE.

Spectrographic identification of the intermediate oxide of nitrogen in the reaction between nitrogen pentoxide and ozone. G. SPRENGER (Z. Elektrochem., 1931, **37**, 674—678).—Examination of the absorption spectrum and kinetic considerations indicate the intermediate formation of NO_3. E. S. HEDGES.

Reaction of hydrogen sulphide with oxygen. L. FARKAS (Z. Elektrochem., 1931, **37**, 670—673).—The reaction between H_2S and O_2 is a chain reaction, starting at the wall of the vessel at 220—320°. The steady reaction becomes explosive when the production of heat is sufficient to raise the temp. above 340°. E. S. HEDGES.

Oxidation of hydrogen sulphide. H. A. TAYLOR and E. M. LIVINGSTON (J. Physical Chem., 1931, **35**, 2676—2683).—The rates of pressure change for given mixtures of H_2S and O_2, saturated at 21° with H_2O vapour, show that the slow reaction near 300° is mainly homogeneous and partly heterogeneous. The crit. explosion pressures for different mixtures agree with Semenoff's theory. Oxidation proceeds by a mechanism involving both straight and branched chains. H_2S, O_2, H_2O, SO_2, SO_3, and S are present after explosion. The dryness of the initial gases affects the rate of reaction. L. S. THEOBALD.

Combustion limits of mixtures of air with gas or vapour at low pressures. II. E. BERL and K. BARTH (Z. physikal. Chem., Bodenstein Festband, 1931, 211—229).—The influence of low pressure on the limits of combustion of mixtures of air with Et_2O, C_2N_2, CS_2, C_2H_2, and EtOH, and of CS_2 with NO_2 and NO has been studied with the aid of the gas interferometer. In all cases the limits approach with decrease of pressure, until the crit. ignition pressure is attained, below which the reaction does not proceed. These crit. pressures are for most substances in the same order as the ignition temp. During the combustion of C_2N_2–air mixtures, even in presence of an excess of O_2, CO_2 is produced in addition to CO only if H_2O is present. In the neighbourhood of the crit. ignition pressure pre-combustion takes place, and even in presence of H_2O CO alone is formed during this process; it is probable therefore that CO is always formed as an intermediate product of the combustion of C_2N_2. H. F. GILLBE.

Low-temperature explosion of mixtures of ozone and hydrogen bromide. B. LEWIS and W. FEITKNECHT (J. Amer. Chem. Soc., 1931, **53**, 3565—3566; cf. this vol., 1130).—HBr reacts with pure O_3 almost instantaneously at room temp., and above a definite limiting pressure explosion occurs. The limiting pressure (20—30 mm. for an equimol. mixture) is only a little greater at −104°. The difference between the induction periods in different vessels, the effect of coating the walls with the products (Br and ice, at −104°) and of packing the vessel indicate that the reaction proceeds by way of chains initiated at a surface. Glass is less active than a Br–ice surface. At −104°, the slow reaction is completed in 20—240 sec., in accordance with the equation $2HBr+O_3=H_2O+Br_2+O_2$. With excess of O_3, the slow reaction ceases when all the HBr has disappeared, but in an explosion the excess of O_3 is decomposed. J. G. A. GRIFFITHS.

Oxidation of ethane. H. A. TAYLOR and E. W. RIBLETT (J. Physical Chem., 1931, **35**, 2667—2675).—The rate of pressure change for mixtures of C_2H_6 and O_2 at 450—470° under different conditions has been determined. The induction period (up to 5 min.), the effects of pressure, temp., composition, surface, and diluents show that the oxidation is a homogeneous chain reaction. The crit. explosion pressures agree with Semenoff's theory, but are best explained as chain explosions preceded by thermal accelerations. L. S. THEOBALD.

Velocity coefficients for the thermal dissociation of ethane and propane. L. F. MAREK and W. B. MCCLUER (Ind. Eng. Chem., 1931, **23**, 878—881).—The decomp. of C_2H_6 and C_3H_8 has been studied by passing them through a Cu reaction vessel heated at the required temp. With rapid rates of flow below 700° C_2H_6 gives C_2H_4 and H_2 as the chief products of decomp. C_3H_8 suffers dehydrogenation and loss of CH_4, the two reactions taking place at about the same rates. The pyrolysis of both these hydrocarbons follows a unimol. law. The velocity coeffs. and their temp. coeffs. have been determined. F. J. WILKINS.

Thermal decomposition of propylamine. H. A. TAYLOR and H. E. ACHILLES (J. Physical Chem., 1931, **35**, 2658—2666).—The decomp. of NH_2Pr^{α} at 520—580° is a homogeneous reaction, and above 200 mm. pressure the primary reaction is apparently unimol. Below 200 mm., the times for a given fractional decomp. increase with a fall in pressure. At lower pressures the addition of H_2, N_2, or He has little or no effect for the first 75% of decomp. The energy of activation, 44,400 g.-cal., is similar to that previously found for NH_2Et (43,400 g.-cal.), and may indicate a similar primary rupture of the mol. in the two cases. L. S. THEOBALD.

Application of the method of stationary velocities to the reaction $MeOH+H_2O \longrightarrow 3H_2+CO_2$. J. A. CHRISTIANSEN (Z. physikal. Chem., Bodenstein Festband, 1931, 69—77).—An expression is developed for the reciprocal velocities of a stationary reaction sequence, and application to experimental results for the reaction $MeOH+H_2O \longrightarrow 3H_2+CO_2$ yields for the sequence involved: $H_2O+CHO \longrightarrow CO_2H+H_2$; $CO_2H \rightleftharpoons CO_2+H$; $H+MeOH \longrightarrow 2H_2+CHO$. In absence of H_2O the sequence becomes, by analogy: $CHO+MeOH \rightleftharpoons CO_2Me+H_2$; $CO_2Me \longrightarrow CO+CHO+H_2$; $CO_2Me+MeOH \longrightarrow HCO_2Me+CHO+H_2$. H. F. GILLBE.

"After-burning" during gaseous explosions: its ability to cause ignition. O. C. DE C. ELLIS and R. V. WHEELER (J.C.S., 1931, 2467—2472).—Two types of "after-burning" are described, a "central" type, which is primarily a continued and uninterrupted equilibrium change caused by rise in pressure, and a "prolonged combustion," originating at the wall of the explosion vessel, which is primarily a resumed equilibrium change caused by fall in temp. The central type of "after-burning" projected into mixtures of either CH_4 or CO with air can cause their ignition. E. S. HEDGES.

Ignition of gases. VI. Ignition by a heated surface. Mixtures of methane with oxygen and nitrogen, argon, or helium. C. A. NAYLOR and R. V. WHEELER (J.C.S., 1931, 2456—2467).—When mixtures of CH_4 and O_2 (mixed with an inert gas) are admitted to a reaction vessel of quartz, the reactions resulting in the production of flame are thermal reactions catalysed by the products of an initial slow and flameless combustion. The total amount of heat acquired by the reacting gases depends on the thermal properties of the inert gas, which absorbs part of the heat developed by the oxidation. When the N_2 in CH_4–air mixture is replaced by A, having both a lower sp. heat and a lower thermal conductivity, the "ignition temps." are lowered, whilst replacement by

He, of high thermal conductivity, raises them. CH_2O and CO are produced during the period of "lag" on ignition. Addition of small amounts (0·02%) of CH_2O or CO to any CH_4–air mixture lowers its ignition temp. and shortens the lag on ignition, CH_2O being the more effective. Traces of I, EtI, EtBr, CCl_4, or $PbEt_4$ raise the ignition temp. of CH_4–air mixtures and decrease the speed of reactions occurring below the ignition temp. The inhibiting action of these substances appears to take place on the surface of the reaction vessel. E. S. HEDGES.

Explosions in closed cylinders. V. Effect of restrictions. W. A. KIRKBY and R. V. WHEELER (J.C.S., 1931, 2303—2306).—Synchronised records of the movement of flame and the development of pressure have been obtained during explosions of CH_4 and air and of CO and air in a cylinder containing restricting rings equally spaced apart. The restrictions greatly increase the speed of an explosion. The sudden expansion caused by the almost simultaneous combustion of the gas in each of the compartments formed by the restrictions, as a tongue of flame shoots through them, produces a shock wave yielding vibrations of large amplitude. E. S. HEDGES.

Velocity of decomposition of hydrogen peroxide by ferric salts as an index of their degree of hydrolysis. I. S. TELETOV and V. M. SIMONOVA (Ukrain. Chem. J., 1931, **6**, [Sci.], 75—92).—The activity at equimol. concentration of Fe salts is in the order: $Fe(OH)_3$ sol$<Fe_2(SO_4)_3<FeCl_3<Fe(NO_3)_3$. The reaction is in all cases unimol. The velocity is a function of the degree of hydrolysis of the given salt, and at a given concentration of Fe salt this val. diminishes as the reaction proceeds, to attain a const. val. at the equilibrium point. The velocity coeff. increases with increasing Fe salt concentration, eventually to attain a limiting val. Decomp. of H_2O_2 is due solely to colloidal $Fe(OH)_3$ produced by hydrolysis; mol. or ionic Fe is inactive.
R. TRUSZKOWSKI.

Equilibria and reaction rates for the reaction sodium arsenite–sodium tellurate. P. T. STROUP and V. W. MELOCHE (J. Amer. Chem. Soc., 1931, **53**, 3331—3338).—The velocity of the reaction $Na_3AsO_3+Na_2TeO_4=Na_3AsO_4+Na_2TeO_3$ has been determined in both directions at temp. between 89·6° and 120°. The equilibrium const. $K_{89\cdot6}=[AsO_4][TeO_3]/[AsO_3][TeO_4]$ is 2400 from the concentrations at equilibrium and 2320 from the bimol. velocity coeff. The crit. increment calc. by means of the Arrhenius equation is 14,380. The relatively slow rate of reaction may be related to the transfer of an O atom as well as an electron. The reaction in acid solution is extremely slow, but is accelerated by the addition of NaOH and the previously negligible reaction between arsenite and tellurite becomes prominent; the latter affords a purple solution of polytelluride. J. G. A. GRIFFITHS.

Decomposition of sodium hypochlorite—an ion reaction. W. F. UNDERWOOD and E. MACK, jun. (J. Physical Chem., 1931, **35**, 2650—2657).—Data for the decomp. of aq. solutions of NaOCl at 45° in the presence of NaCl, $CaCl_2$, Na_2SO_4, and Na_2HPO_4 show that the rate of reaction increases with an increase in salt concentration, and that the slope of the curve obtained by plotting log k against (ionic strength)$^{0.5}$ is $+1$, as is predicted from Bronsted's theory on the assumption that the reaction is $2ClO' \longrightarrow 2Cl'+O_2$. The reaction is bimol. in conc. salt solutions. L. S. THEOBALD.

Effect of solvent on the rate of acetylation of ethyl alcohol by acetic anhydride. F. G. SOPER and E. WILLIAMS (J.C.S., 1931, 2297—2303).—The rate of acetylation of EtOH by Ac_2O in hexane, heptane, CCl_4, PhCl, C_6H_6, PhOMe, $CHCl_3$, and $PhNO_2$ shows that the accelerating influence of the solvent is in the inverse order of the usual one, where solvents of high polarity accelerate the reaction. The increased rate of reaction in solvents of low polarity cannot be explained by assuming the formation of reactive associated mols. of EtOH, masking the more usual influence of the solvent. A study of the catalysis of the acetylation by acids and bases in CCl_4, $COMe_2$, and EtOH indicates that the uncatalysed reaction appears to predominate over a considerable range of concentration of the acid or base. The results are discussed in relation to the effect of the solvent on the resolution of the intermediate crit. complex (A., 1929, 1244). E. S. HEDGES.

Studies of stereokinetics. I. Saponification of chloroacetanilides. G. SEMERANO (Gazzetta, 1931, **61**, 501—519).—The rates of saponification of acetanilide and of some of its chloro-derivatives in aq.-alcoholic NaOH have been measured. The velocity coeffs. are in the order 2 : 4 : 5>2 : 5>2 : 4> 3 : 5>2>3>4, the numbers denoting the positions of the Cl atoms in the derivatives. The various theories on the effect of substitution in aromatic compounds on activity are reviewed, and the results shown to be in accord with the theory of Lapworth and Robinson. O. J. WALKER.

Relation between molecular structure and reaction velocity in the combination of triethylamine and ethyl iodide in different solvents. H. G. GRIMM, H. RUF, and H. WOLFF (Z. physikal. Chem., 1931, **B**, **13**, 301—315).—The velocity in hexane, *cyclo*hexane, PhMe, and C_6H_6 is low, as would be expected from their high electrical symmetry, and increases in the order given. In PhF, PhCl, PhBr, and PhI it is greater and increases in the order given, *i.e.*, with increasing size and deformability of the solvent mols. In *o*-, *m*-, and *p*-$C_6H_4Cl_2$ it decreases in the order given, *i.e.*, with decreasing dipole moment (cf. A., 1929, 404). The velocity in $NHPh_2$ is much greater than in Ph_2O and CH_2Ph_2 (which have nearly equal effects), but its dipole moment is only a little greater than theirs. Electrical asymmetry at one place in the mol. (*e.g.* the :NH group) may therefore have more influence than that of the mol. as a whole. Experiments with PhCN, $PhNO_2$, *p*-$C_6H_4Me{\cdot}NO_2$, *p*-$C_6H_4(OMe){\cdot}NO_2$, and *o*-$C_6H_4Cl{\cdot}NO_2$ also show that a direct relation between dipole moment and velocity is to be sought only in a range of *o*-, *m*-, and *p*-isomerides. In most of the cases studied the energy of activation is 12·0±0·5 kg.-cal. Addition of *cyclo*hexane to the other solvents retards the reaction, but their effects remain in the same order.
N. H. HARTSHORNE.

Mechanism of, and constitutional factors controlling, the hydrolysis of carboxylic esters. IV. Hydrolytic stability maxima of some dihydroxypropyl esters of aliphatic acids. C. K. INGOLD, A. JACKSON, and (MRS.) M. I. KELLY (J.C.S., 1931, 2035—2042).—Further esters of the series $R\cdot CO_2R'$ (cf. A., 1930, 869) are studied, where R′ is now dihydroxypropyl and R is Me, Et, Pr^{α}, Pr^{β}, Bu^{α}, and Bu^{β}; the methods are substantially those of the earlier paper. The propionate has the highest k_H at three temp. studied; but p^* (the p_H for min. velocity of hydrolysis), and also the consts. A and B in the equation $\log k_H = A - B/T$ and hence the crit. energy increment, vary regularly in the homologous series. C. W. DAVIES.

Mechanism of, and constitutional factors controlling, the hydrolysis of carboxylic esters. V. Effect of alkyl groups on hydrolytic stability maxima. C. M. GROOCOCK, C. K. INGOLD, and (MRS.) M. I. KELLY (J.C.S., 1931, 2043—2046).—Regularities are shown on intercomparing the hydrolysis data already reported for the three series $C_2H_3(OH)_2\cdot CO_2R$, $R\cdot CO_2C_3H_5(OH)_2$, and $MeCO_2R$; these afford support for the conclusion that the displacement of p_H^* caused by a substituent group is a direct function of the polar effect of the group, and is determined by the product of two numerical factors separately dependent on its nature and its position. Similar regularities on comparing these p_H^* vals. with the speeds of aromatic chlorination for corresponding compounds of the series $RO\cdot C_6H_4\cdot CO_2H$ and $RO\cdot C_6H_4Cl$ adumbrate a wider generalisation and show that the same quant. measure of polarity may be derived from different reactions. C. W. DAVIES.

Mechanism of, and constitutional factors controlling, the hydrolysis of carboxylic esters. VI. Kinetics of the hydrolysis of some paraffin-αω-dicarboxylic esters in very dilute aqueous solution, and the derivation, with corrections for solvent electrostriction, of their molecular dimensions. Spatial form of polymethylene derivatives in dilute solution. C. K. INGOLD (J.C.S., 1931, 2170—2179).—New measurements are reported of k_1 and k_2 for Me and Et esters of the series succinic to azelaic acids. A calculation of k_1 is given which eliminates interference from second-stage hydrolysis. The new vals. of r (cf. this vol., 1126) support the mol. model advanced; since they do not in this case relate to the bivalent anion they confirm the conclusion that the rigidity is conferred by an intrinsic property of the CH_2 group and not by ionic repulsion. C. W. DAVIES.

Inversion of sucrose by tartaric acid. D. SINGH, K. LAL, and C. ANAND (Proc. XV Indian Sci. Cong., 1928, 174).—The inversion of sucrose at different concentrations by a const. quantity of acid is linear, but for a given concentration of sugar with different quantities of acid the rates of inversion do not show a simple relation. CHEMICAL ABSTRACTS.

Dependence of reaction velocity on surface and agitation. I. Theoretical. A. W. HIXSON and J. H. CROWELL (Ind. Eng. Chem., 1931, 23, 923—931).—The relation between the time t during which a crystal has been dissolving and the wt. w remaining undissolved is of the form $t - f \cdot w^{\frac{1}{3}}$. F. J. WILKINS.

Dependence of reaction velocity on surface and agitation. II. Experimental procedure in study of surface. A. W. HIXSON and J. H. CROWELL (Ind. Eng. Chem., 1931, 23, 1002—1009).—The cube root law for the dissolution of solids in liquids has been verified experimentally for the case of $C_{10}H_8$ in various solvents under different conditions of agitation, and also for a solid–gas system ($C_{10}H_8$–air). When a solid dissolves in a liquid, forming a ppt. through chemical reaction (*e.g.*, alum in aq. NH_3), the action is normal provided the agitation is sufficiently intense to remove the coating as fast as it is formed; otherwise, the ppt. has a protective effect. E. S. HEDGES.

Velocity of decomposition of marble in acids. I. W. JACEK (Bull. Acad. Polonaise, 1931, A, 117—142).—The velocities of decomp. of marble in dil. AcOH and dil. HCl have been studied. W. R. ANGUS.

Theory of dissolution of metals. III. M. STRAUMANIS (Z. physikal. Chem., 1931, 156, 150—158; cf. this vol., 436).—The differences in the rates of dissolution of the various faces of a metal crystal cannot be explained by differences in equilibrium potential, for no such differences are possible. The suggested explanation is that the rate of dissolution at any face is determined by the conditions of local action at that face, and that since the inclusions of impurities in the crystal have a definite orientation, these conditions will differ from one face to another. R. CUTHILL.

Displacement of arsenic from solutions of its salts by hydrogen under pressure. V. V. IPATIEV, jun., M. N. PLATONOVA, and V. S. MALINOVSKI (Ber., 1931, 64, [B], 1959—1964; cf. A., 1930, 306; this vol., 52).—With pressure up to 150 atm. and small alterations of concentration (up to 50%) the quantity of As precipitated from solutions of $AsCl_3$ in HCl is proportional to the pressure. Between 15 and 250 atm. and with solutions not exceeding N, the displacement of As by H is a reaction of the first order. Between 125° and 175°, $\log K$ is a linear function of $1/T$. Assuming the reaction to proceed uniformly as a change of the first order, within the limitations of the first sentence the approx. expression $K' = (1/tp) \cdot \log[a/(a-x)]$ is derived, from which the amount of As separated under given conditions can be calc. to within about 5—8%. The activating energy of the replacement of As by H is calc. to be $28{,}000 \pm 2000$ g.-cal. It is calc. that the displacement of 1% of As from N-$AsCl_3$ solution at room temp. and 100 atm. pressure of H_2 requires 1140 years. Increase in the concentration of HCl accelerates the change, which is inhibited by NaCl or HCl. H. WREN.

Displacement of antimony from solutions of its salts by hydrogen under pressure. V. V. IPATIEV, jun., and V. I. TICHOMIROV (Ber., 1931, 64, [B], 1951—1959).—Under low pressures (up to 150 atm.) and with small variations in concentration (up to 50%), the amount of Sb displaced from solutions of $SbCl_3$ by H_2 under pressure is proportional to the

pressure. Within the limits of pressure, 15—150 atm., and with concentrations not exceeding N the reaction is of the first order. Between 100° and 150°, log K is a linear function of $1/T$. If it is assumed that the change proceeds uniformly as a reaction of the first order, and account is taken of the first sentence (see above) the approx. expression, $K'=(1/tp)\log[a/(a-x)]$ is obtained which, for any val. of pressure, time, and temp., permits the calculation of the amount of precipitated Sb to within 5—8%. The activation energy for the displacement of Sb by H, calc. from the Arrhenius expression, amounts to 26,000±1000 g.-cal. It is calc. that at room temp. 160 years are necessary for the separation of 1% of Sb from N-$SbCl_3$ solution under 100 atm. of H_2. The reaction is retarded by increase in the acidity of the solution. H. WREN.

Displacement of bismuth from solutions of its salts by hydrogen under pressure. V. V. IPATIEV, jun., I. R. MOLKENTIN, and V. P. THEODOROVITSCH (Ber., 1931, 64, [B], 1964—1970).—Under pressure up to 150 atm. and within slight changes of concentration (up to 50%) the amount of Bi displaced from solutions of its salts by H_2 is proportional to the pressure. Between 15 and 250 atm. and with approx. N-solutions the displacement is a reaction of the first order. Between 100° and 150° log K is a rectilinear function of $1/T$. The activating energy of the replacement of Bi by H_2 is calc. to be 25,400±600 g.-cal. It is calc. that about 37 years are necessary for the displacement of 1% of Bi from N-$BiCl_3$ by H_2 under 100 atm. and at room temp. Increase in the concentration of HCl retards the reaction. Displacement of Bi from solution in AcOH occurs more rapidly and more completely than from solution in HCl.

H. WREN.

Behaviour of purest aluminium towards acids and bases. M. CENTNERSZWER (Z. Elektrochem., 1931, 37, 598—603).—99·95% Al is practically unattacked by HNO_3 or H_2SO_4. Reaction with HCl becomes observable at 25° and a concentration of $2N$, the rate of dissolution increasing at an extraordinary rate with increasing concentration and rising temp. The increase of rate of dissolution with concentration of acid is given by $dv/dt=K_nC^n$, where K_n and n are consts. The temp. coeff. between 25° and 35° is 7·0, although it lies between 1·73 and 2·39 for 99% Al. In alkali, 99·95% Al behaves in a similar manner to 99% Al, previously investigated. The pure Al also dissolves in NH_3 aq., the velocity of the process varying with the [OH′] according to the formula $dv/dt=KC^{\frac{1}{2}}$. E. S. HEDGES.

Velocity of dissolution of thallium in acids. M. CENTNERSZWER [with S. LEVI] (Z. Elektrochem., 1931, 37, 603—610).—Tl dissolves readily in HNO_3 solutions, after passing through an induction period, the velocity increasing with increasing concentration up to $0·25N$, where it attains a max., falling at higher concentrations. The temp. coeff. of the reaction increases with rise of temp., eventually reaching the val. 4·4. The rate of dissolution is increased by stirring. In H_2SO_4 and HCl the rate of dissolution of Tl is relatively very slow, the ratio for $2N$-acids being $HNO_3 : H_2SO_4 : HCl = 428 : 1·78 : 1$. The velocity is almost independent of the concentration of H_2SO_4 or HCl and is approx. equal to the rate of dissolution in H_2O. E. S. HEDGES.

Dissolution of aluminium in alkaline solutions. G. SCHIKORR (Z. Elektrochem., 1931, 37, 610—613).—In solutions containing up to $0·95N$-NaOH the rate of dissolution of Al rises to a max., falls to a min. (zero velocity in the case of dil. solutions), and then rises to another max., at which it remains practically const. The amount of H_2 evolved during the first reactive period corresponds with the equation $Al+NaOH+2H_2O=Al(OH)_2ONa+1·5H_2$; the subsequent, second period of reaction is produced by the NaOH being freed once more through the reaction $Al(OH)_2ONa+H_2O=Al(OH)_3+NaOH$. The reaction is similar in $0·1N$-KOH, $Ba(OH)_2$, or Na_2CO_3. The presence of H_2SiO_3 increases the interval between the two periods of reaction by hindering the formation of nuclei of cryst. $Al(OH)_3$. The rate of dissolution is influenced very little by impurities in the Al.

E. S. HEDGES.

Effect of temperature on corrosion of zinc. G. L. COX.—See B., 1931, 928.

Cathodic passivity phenomena. E. LIEBREICH (Z. physikal. Chem., 1931, 156, 51—76).—The current–polarisation voltage curve of Zn in $0·1N$-H_2SO_4 exhibits irregularities soon after the commencement of polarisation; with increase of polarisation the curve does not progress directly to the point at which H_2 evolution begins, but moves to a position parallel to the original position of the curve, and it is at this stage that visible evolution of H_2 begins. With decreasing polarisation the curve at first follows this second portion and then falls suddenly to the normal position. The effect is attributed to mechanical passivity. In contrast to those on other metals, the passive film on Zn becomes loosened with decreasing polarisation, and the activity of the metal is then maintained until the current falls to zero.

H. F. GILLBE.

Reactivity of powdered metals. HAID, GOETZE, SELLE, KOENEN, SCHMIDT, and BECKER (Jahresber. Chem.-tech. Reichsanst., 1930, 8, 136—141; Chem. Zentr., 1931, i, 2717).—The reactivity increases greatly with increase in fineness. The ignition temp. is const. only for a particular surface; for Al it varies between 250° and 1000°, and depends also on the oxide content, Al free from O igniting more readily. The velocity of interaction with H_2O also increases with fineness. A. A. ELDRIDGE.

Kinetics of decomposition of hydrogen peroxide by ferric hydroxide sol. I. S. TELETOV and E. A. ALEXEEVA (Ukrain. Chem. J., 1931, 6, [Sci.], 61—74).—The decomp. of H_2O_2 by $Fe(OH)_3$ sol is a unimol. reaction. The velocity coeff. is proportional to the active surface, and can thus serve for the determination of the degree of dispersion of the colloid. This diminishes during the reaction, with eventual consequent coagulation of the sol.

R. TRUSZKOWSKI.

Kinetic analysis of the formation of calcium cyanamide. H. H. FRANCK, F. HOCHWALD, and G. HOFFMANN (Z. physikal. Chem., Bodenstein Festband, 1931, 895—906).—The reaction between CaC_2 and N_2 at 1050—1150° commences after an induc-

tion period which is reduced by addition of $CaCN_2$ or $CaCl_2$; addition of CaF_2 tends to increase the period. The velocity attains its max. val. within 1—3 min. and the reaction is then approx. unimol.; this stage may be prolonged by increasing the active surface, but when the surface is largely converted into $CaCN_2$ the rate of diffusion through the surface determines the reaction velocity. The presence of CaF_2, especially at 1065°, favours the diffusion and leads to a greater final yield. $CaCl_2$ tends to lower the yield.
H. F. GILLBE.

Kinetics of the evolution of nitrogen from ammonium nitrite. E. ABEL, H. SCHMID, and J. SCHAFRANIK (Z. physikal. Chem., Bodenstein Festband, 1931, 510—522).—The velocity of decomp. of NH_4NO_2 at a given ionic concentration is proportional to the $NH_4^{\cdot}$, NO_2', and HNO_2 concentrations, and diminishes with increase of the ionic concentration, but is independent of the NO pressure. The reaction takes place in two stages, viz., the formation and decomp. of an intermediate compound, probably of the diazo-type, produced from HNO_2, $NH_4^{\cdot}$, and NO_2'; the HNO_2 necessary is formed by hydrolysis. H. F. GILLBE.

Action of cyanogen on zinc. H. BRAUNE [with W. SCHULZE] (Z. physikal. Chem., Bodenstein Festband, 1931, 415—422).—The velocity of the reaction between Zn and C_2N_2 at 115°, at const. vol., rises in the early stages and then becomes proportional to the gas pressure; after a time it falls and the reaction finally ceases before all the C_2N_2 has disappeared. If the initial pressure is re-established by addition of more C_2N_2 the same phenomena occur, but the steady velocity is much smaller and the final pressure is higher. The gradual divergence from the unimol. law is less marked at room temp., and is due not to the impermeability of the $Zn(CN)_2$ formed but, probably, to the formation of a paracyanogen film. The velocity coeff. rises from $2{\cdot}34\times10^{-8}$ at 0° to $1{\cdot}16\times10^{-5}$ at 115°, and the heat of activation is 13·4 kg.-cal. Readily adsorbed compounds such as CO_2 and C_6H_6 vapour do not influence the reaction, but O_2 greatly reduces its velocity, and at sufficiently high concentration inhibits it completely.
H. F. GILLBE.

Formation of water vapour in the dissociation of a salt hydrate. B. TOPLEY and M. L. SMITH (Nature, 1931, **128**, 302).—The reaction $MnC_2O_4.2H_2O \longrightarrow MnC_2O_4+H_2O$ (in a vac. at 76°) is sensitive to small concentrations of H_2O vapour. The curve obtained by plotting the ratio, rate vac./rate at p_{H_2O} against p_{H_2O} falls rapidly to a min., then rises more slowly to a max. of the same order as the rate in a vac., and finally falls gradually to 0 at the dissociation pressure. An explanation is outlined.
L. S. THEOBALD.

Reactions in the solid state at high temperatures. VIII. Determination of the velocity of reactions which involve the evolution of gas. W. JANDER and E. HOFFMANN (Z. anorg. Chem., 1931, **200**, 245—256).—A simple form of apparatus is described. Measurements of the velocity of the reaction between $BaCO_3$ and SiO_2 at 970—840° agree well with the calc. vals. Measurements with $BaCO_3$ and Nb_2O_5 at 624—748° show that the reaction velocity increases 22-fold over this temp. interval. The velocities of the reactions in the systems $BaCO_3$–SiO_2 and $CaCO_3$–MoO_3 are independent of the external pressure between 73 mm. and 754 mm., and are therefore not influenced by the diffusion of CO_2 through the powder. H. F. GILLBE.

Reactivity in the solid state and its dependence on disjunctive factors. J. A. HEDVALL (Z. angew. Chem., 1931, **44**, 781—788).—Principally an account of work published at intervals during the last 20 years, with a discussion of the various factors which may reduce the stability of a crystal lattice and thus permit reaction between solids. H. F. GILLBE.

Influence of the halogens on the union of hydrogen and oxygen. C. N. HINSHELWOOD and W. L. GARSTANG (Z. physikal. Chem., Bodenstein Festband, 1931, 656—661).—I catalyses the oxidation of MeOH at 452° and of C_6H_6 at 540—550°. Cl_2 and Br retard the homogeneous reaction between O_2 and H_2 at about 500°, but when present in greater proportion they accelerate the surface reaction. Br resembles I in that it inhibits the explosion at low pressures more readily than does Cl_2. Possible explanations of the results are discussed. Removal of the intermediate reducing substance by free halogen is probably of greater importance than the decomp. of the oxidising substances (OH, H_2O_2) by the halide.
H. F. GILLBE.

Decomposition of ozone, sensitised by bromine. B. LEWIS and W. FEITKNECHT (Z. physikal. Chem., Bodenstein Festband, 1931, 113—125).—The decomp. of O_3 in presence of Br is characterised by two temp. intervals. In the lower the reaction takes place on a solid intermediate oxide, of which the rate of decomp. determines the rate of reaction; no decomp. takes place in the gas phase. At higher temp. the sphere of reaction extends to the gas phase, in which the decomp. then chiefly takes place. The decomp. velocity is proportional to the Br concentration up to a certain limit, above which the velocity increases at an increased rate; it is independent of the O_3 concentration provided that this exceeds a definite limit, below which it increases with decrease of the O_3 pressure. It appears that Br accelerates the decomp. of the intermediate oxide. On the assumption that only the surface mols. of the latter take part in the reaction, the velocity of decomp. of this compound, calc. from the temp. coeff., is $1{\cdot}2\times10^{-3}$, in satisfactory agreement with the val. obtained by Lewis and Schumacher.
H. F. GILLBE.

Bromine-sensitised oxidation of unsaturated hydrocarbons. G. R. SCHULTZE (J. Amer. Chem. Soc., 1931, **53**, 3561—3562).—A contraction greater than that corresponding with the unsaturated hydrocarbon present occurs when C_2H_4, C_3H_6, or C_4H_8, in the presence of pure O_2, is absorbed by Br water. A Br-sensitised oxidation of the hydrocarbon to CO_2 and H_2O is indicated. J. G. A. GRIFFITHS.

Chemical kinetics and ionic reactions. III. Neutral salt action and catalysis in ionic reactions. A. KISS (Magyar Chem. Fol., 1931, **37**, 17—23; Chem. Zentr., 1931, i, 2718).

Reduction of peroxysulphate by vanadyl ion with silver ion as catalyst. D. M. Yost and W. H. Claussen (J. Amer. Chem. Soc., 1931, **53**, 3349—3354; cf. A., 1926, 251, 365).—$VO^{\cdot\cdot}$ does not react with S_2O_8'' at room temp., but in the presence of $Ag^{\cdot}$ the velocity of the net reaction $S_2O_8''+2VO^{\cdot\cdot}+4H_2O=2SO_4''+2HVO_3+6H^{\cdot}$ is directly proportional to $[S_2O_8'']$ and $[Ag^{\cdot}]$, but independent of $[VO^{\cdot\cdot}]$. The sp. reaction rate is the same as that when $Cr^{\cdot\cdot\cdot}$ is the reducing agent, thus showing the absence of sp. effects due to $Cr^{\cdot\cdot\cdot}$ or $VO^{\cdot\cdot}$. The facts indicate the mechanism $S_2O_8''+Ag^{\cdot}=2SO_4''+Ag^{\cdot\cdot\cdot}$ (slow) followed by $Ag^{\cdot\cdot\cdot}+2VO^{\cdot\cdot}+4H_2O=Ag^{\cdot}+2HVO_3+6H^{\cdot}$ (rapid). The sp. effects of other reducing agents may be ascribed to the different reactivity of a Ag ion–reducing agent complex. The variation of velocity with change of ionic strength is qualitatively in accord with Bronsted's theory.

J. G. A. Griffiths.

Influence of strong electrolytes on the catalytic inversion of sucrose by hydrochloric acid at 30°. W. W. Floyd (J. Physical Chem., 1931, **35**, 2968—2984).—The velocity coeff. of the inversion of sucrose by $0{\cdot}1M$-HCl in the presence of N- and $2N$-NaCl, $BaCl_2$, K_2SO_4, and $MgSO_4$ have been determined at 30°. The chlorides increase the velocity of inversion at a rate which increases rapidly with concentration, and produce positive primary salt effects which in dil. ranges are linear, and in the complete range are exponential, functions of salt concentration. Sulphates decrease the velocity, producing negative salt effects. It appears that the more highly hydrated are the ions of the added salt the larger are the positive primary salt effects in the $H^{\cdot}$ catalysis of the sucrose inversion. The equation, $k=k_0\times10^{rM}$, (A., 1927, 21), does not represent the negative salt effects of the sulphates, but for concentrations $>0{\cdot}5M$ it describes the positive effects of the chlorides. The vals. of k_{30}/k_{25} for HCl solutions containing NaCl or $BaCl_2$ are practically the same as that (2·057) for HCl alone. The val. for $MgSO_4$ is lower. Calc. vals. of the heats of activation for HCl or HCl+chloride approximate to the classical val. of 26,000 g.-cal. per mol.

L. S. Theobald.

Acids and their catalytic action in water-alcohol mixtures. Oxidation of ethyl alcohol by chromic acid in presence of acids. M. Bobtelsky and C. Radovensky-Cholatnikov (Z. anorg. Chem., 1931, **199**, 241—261).—The oxidation of EtOH by H_2CrO_4 in dil. aq. solution is bimol., but at room temp. the velocity is zero in absence of a catalyst. Strong acids act as catalysts, although the reaction is not very sensitive to the p_H of the solution. The influence of $HClO_4$ is the same as that of HNO_3, and the velocity is proportional to the square root of the acid concentration, but with H_2SO_4 the relation is linear. HCl is anomalous, since its influence is small and independent of concentration above about N; this effect may be due to the formation of a labile compound between HCl and H_2CrO_4. With increase of the EtOH concentration from 30 to 60% the reaction velocity falls, but at higher concentrations the velocity increases at a rapidly increasing rate. It is suggested that in presence of an excess of H_2O_2 the oxidation is concerned principally with the oxidation of H_2O–EtOH complexes or of EtOH mols. surrounded by an aq. envelope, and that if an excess of EtOH is present the reaction consists of the oxidation of anhyd. EtOH mols.

H. F. Gillbe.

Basic catalysis in the decomposition of diacetone alcohol. J. G. Miller and M. Kilpatrick, jun. (J. Amer. Chem. Soc., 1931, **53**, 3217—3224; cf. A., 1930, 42).—The effect of NH_3, NH_2Me, $NHMe_2$, and NH_2Et on the velocity of decomp. of diacetone alcohol at 25° has been determined in buffer solutions of the type NH_3–NH_4Cl diluted with NaCl solution. In each case, the mol. base catalyses the reaction and catalytic consts. have been evaluated. The dissociation consts. of the bases have been calc.: NH_3 0·175, NH_2Me 6·32, $NHMe_2$ 6·7, and NH_2Et $3{\cdot}4\times10^{-4}$. When allowance is made for catalysis by the mol. base, Åkerlof's data (A., 1928, 485) afford dissociation consts. in better agreement with recorded vals. (this vol., 308). J. G. A. Griffiths.

Inhibitory action of anthracene in the autoxidation of benzaldehyde. H. L. J. Backstrom and H. A. Beatty (J. Physical Chem., 1931, **35**, 2530—2567).—Experiments on the induced oxidation of anthracene show that its inhibitory action in the autoxidation of PhCHO is connected with an induced oxidation of the inhibitor. The primary oxidation product is anthranol which is autoxidisable and reacts with O_2 to form a peroxide. This slowly decomposes, forming anthraquinone. With increasing concentration of anthracene the relative amounts of the oxidation products formed approach 1 mol. of BzOH per mol. of anthraquinone. The induced oxidation of the anthracene is the result of a reaction with a peroxide of PhCHO, and the assumption of the existence of an unstable primary peroxide, possibly $Ph{\cdot}CH{<}_{O}^{}{>}O$, is a necessary link in the reaction chain. The results can be explained by a chain mechanism (this vol., 572). In the photochemical reaction, there occurs a side reaction (20%) in which anthraquinol is an intermediate product and reacts with O_2 to give equimol. amounts of anthraquinone and H_2O_2. A second side reaction, favoured by a rise in temp. and common to both photochemical and thermal reactions, yields complex, coloured products. In the thermal reaction, the relative ratios of autoxidation reaction and induced oxidation depend only on the composition and temp. of the solution. The photochemical reaction is complicated by a screening effect of the anthracene. The solubility of anthraquinone in PhCHO at 0° and 25° is 0·0081 and 0·0210 mol. per litre, respectively. L. S. Theobald.

Oxidation of linseed oil emulsions in the presence of hæmatin and potassium cyanide. G. P. Wright and M. Van Alstyne (J. Biol. Chem., 1931, **93**, 71—82).—The acceleration of the autoxidation of linseed oil emulsions by hæmin and the failure of KCN to inhibit the reaction are confirmed (cf. A., 1924, ii, 320). Hæmatin–KCN accelerates the oxidation as effectively as hæmatin–pyridine, wide variations in the KCN concentrations having little influence on the rate of reaction. The acceleration

of oxidation by animal charcoal is inhibited by KCN. Hæmatin–pyridine has no influence on the rate of oxidation of cystine, whilst addition of small quantities of KCN induces a rapid oxidation, an effect also produced by addition of hæmatin–KCN in the absence of pyridine. F. O. HOWITT.

Spontaneous oxidation of cysteine. II. Autoxidation of cysteine free from iron. E. G. GERWE (J. Biol. Chem., 1931, **92**, 399—411; cf. this vol., 718).—The acceleration by a trace of Fe of the slow spontaneous oxidation of pure cysteine is proportional to the amount of added Fe. The oxidation rate of Fe-free cysteine is too high to be due to the minute trace of Fe calc. on the sensitivity of the colour reaction used for Fe. Pure cysteine is therefore autoxidisable. A. COHEN.

Spontaneous oxidation of cysteine. III. Action of cyanides and cystine on cysteine oxidation. E. G. GERWE (J. Biol. Chem., 1931, **92**, 525—533).—Autoxidation of Fe-free cysteine is not inhibited by CN′. The acceleration due to presence of Fe, however, is inhibited, due to conversion of the $Fe^{\cdot\cdot}$ or $Fe^{\cdot\cdot\cdot}$ into the corresponding Fe–KCN compound. Addition of Fe as $K_4Fe(CN)_6$ or $K_3Fe(CN)_6$ does not accelerate the reaction. Cystine does not influence the oxidation of cysteine (cf. A., 1923, i, 416). F. O. HOWITT.

Effect of iron and cyanides on the spontaneous oxidation of dialuric acid. E. S. HILL (J. Biol. Chem., 1931, **92**, 471—481).—The spontaneous oxidation of dialuric acid is greatly accelerated by addition of Fe except at the normal optimum range of p_H 7·0—7·4 due, perhaps, to the inability of O_2 to enter the solution at a rate greater than normal. Autoxidation of the acid is not inhibited by KCN, whilst the acceleration due to presence of Fe is inhibited. Comparison is made with cysteine and glutathione in cell oxidation. F. O. HOWITT.

Active centres in hydrogenation catalysis. G. M. SCHWAB [with L. RUDOLPH] (Z. Elektrochem., 1931, **37**, 666—669).—Theoretical. E. S. HEDGES.

Action of active charcoal on lead sulphide. F. PÜSCHEL (Arch. exp. Path. Pharm., 1931, **161**, 455—466).—Freshly prepared suspensions of PbS are oxidised in presence of animal charcoal so that the Pb becomes sol. in HCl and NH_4OAc. The action of the charcoal is independent of the Fe content, but is closely correlated with its adsorptive power and apparently depends essentially on the absorption of O on its surface. PbO and not $PbSO_4$ is the chief primary product from PbS in presence of charcoal. W. O. KERMACK.

Catalytic oxidation of nitric oxide. II. L. SZEGO and L. GUACCI (Gazzetta, 1931, **61**, 333—358; cf. A., 1930, 713).—The catalysis of the reaction $2NO+O_2=2NO_2$ by SiO_2 and Al_2O_3 gels has been studied between 13° and 110°. From 30° to 80° the reaction obeys Arrhenius' law, but at higher temp. reaction in the gaseous phase begins to prevail. Below 30° the catalytic effect is slower owing to a decrease of the free surface caused by adsorption of NO_2. The decrease of the apparent heat of activation and the variation of the integration const. with different types of gels are explained by variations in the sp. gr. and porosity of the gels. Measurement of the adsorption isotherms for two samples of SiO_2 gel indicate the existence of catalytically active centres. The high val. calc. for the heat of adsorption of NO is accounted for by the solubility of this gas in the adsorbed NO_2. This furnishes a possible mechanism of the catalytic reaction. The velocity coeff. of this reaction is inversely proportional to the diameter of the catalyst granules, and this relationship should hold theoretically for diameters having mol. dimensions. O. J. WALKER.

Kinetics of the reaction $2SO_2+O_2$ $2SO_3$ on platinum. G. B. TAYLOR and S. LENHER (Z. physikal. Chem., Bodenstein Festband, 1931, 30—43).—Study of the reaction at 525—700° from both sides of the equilibrium point shows that the rate of formation of SO_3 varies directly with the distance from equilibrium and with $1/[SO_3]^{½}$; the rate of the reverse reaction varies directly only with the distance from equilibrium. No single expression could be obtained by consideration of the process in terms of simultaneous reactions. The apparent heat of activation of the formation of SO_3 is 16 kg.-cal., and that of the dissociation on a Pt surface 40 kg.-cal. The mechanism of the reaction probably involves the combination of SO_2 mols. on striking O_2 mols. adsorbed at an active point on the catalyst; the SO_3 mols. formed do not evaporate immediately, and therefore prevent access of other mols. to the active centres. H. F. GILLBE.

Influence of heat on the preparation of nickel catalyst on infusorial earth. H. I. WATERMAN and M. J. VAN TUSSENBROEK (J.S.C.I., 1931, **50**, 227—228T).—The catalyst obtained by reducing Ni oxide precipitated on kieselguhr as a support at different temp. was heated with dil. HCl, which reacts with Ni with the evolution of H_2. The Ni oxide on the support was reduced successively at 400°, 500°, and 600°. At 400°, after passing H_2 over it during several hr., only a small quantity of Ni yielding H_2 with HCl was formed. The H_2O formed during the reduction apparently originates for the greater part from the moisture which was driven out. At 500° the expulsion of O_2 from the Ni oxide is much stronger; but reduction to Ni is not complete, the H_2 evolved scarcely exceeding half the theoretical quantity. At 600° reduction increased greatly, the percentage of Ni calc. from the evolution of H_2 approaching the theoretical. Also the products from which O_2 had not been completely removed have a good catalytic effect on the hardening of soya-bean oil. This applies to the products prepared at 400° and at 500°; those reduced at 600° had only a very low activity, except in a single experiment.

Reduction of sodium cyanate. J. DRUCKER and F. A. HENGLEIN (Z. physikal. Chem., Bodenstein Festband, 1931, 437—442).—The rate of decomp. of NaCNO at 700° is fairly small (about 1% per hr.), but in presence of Fe the decomp. is greatly accelerated. Reduction to NaCN by CO is complete at 700°, but at higher temp. decomp. with evolution of N_2 takes place. The composition of the gas phase at 500—700° has been determined. The heat effect of

the reaction is $-8{\cdot}5$ kg.-cal., that calc. from the heats of formation being $-10{\cdot}5$ kg.-cal.

H. F. GILLBE.

Binary mixed catalysts containing molybdenum for the synthesis of ammonia. A. MITTASCH and K. KEUNECKE (Z. physikal. Chem., Bodenstein Festband, 1931, 574—582).—The activities of binary catalysts containing Mo and Co, Fe, Cu, Cr, W, and Mn have been compared. An increase of activity occurs only when compounds are formed between the components; thus the activity of a Mo–Cu catalyst is purely additive. If mixed crystals, but no compounds, are formed, as in the Mo–W and Mo–Cr systems, the activity diminishes. Compound formation alone, however, does not necessarily cause an increase of activity, and in certain cases poisoning occurs. Sp. chemical factors, which vary considerably from one element to another, are of importance. The activation heat of the NH_3 synthesis varies from about 24 to 38 kg.-cal., according to the constituents and percentage composition of the catalyst.

H. F. GILLBE.

Intermediate compound formation in the catalytic synthesis of ammonia. Formation of a nitride film on tungsten. G. MESSNER and W. FRANKENBURGER (Z. physikal. Chem., Bodenstein Festband, 1931, 593—607).—Whereas NH_3 and H_2 are adsorbed normally on W with formation of a unimol. layer, the absorption of N_2 increases with rise of temp., and is irreversible, and is shown from kinetic considerations to be due to compound formation. In the temp. interval 20—200° the quantity of H_2 adsorbed rapidly by the nitride film is less than that adsorbed by the pure metal, but slow adsorption of H_2 persists for several hr.; with rise of temp. further absorption takes place. Hydrogenation therefore occurs in the nitride film. H. F. GILLBE.

Catalytic decomposition of ammonia by iron. E. WINTER (Z. physikal. Chem., 1931, **B**, 13, 401—424).—By using a streaming method it has been shown that the decomp. of NH_3 on Fe at 492—670° follows the equation $-dp_{NH_3}/dt=Kp^{0.9}_{NH_3}/p^{1.5}_{H_2}$. The heat of activation is 54 kg.-cal. at 500° and 51 kg.-cal. at 700°. The relation between the amount of FeN produced and the NH_3 and H_2 concentrations has also been investigated. The catalysis is explained by supposing that a chemical equilibrium is set up in the adsorption film. J. W. SMITH.

Determination of the increased activity at the interface between zinc carbonate and zinc oxide. G. F. HUTTIG [with E. ROSENKRANZ] (Z. physikal. Chem., Bodenstein Festband, 1931, 591—592).—Whereas $AgNO_3$ is decomposed only very slowly by basic $ZnCO_3$ and by ZnO, the activity of mixtures prepared by heating basic $ZnCO_3$ is a max. when about 50% of the $ZnCO_3$ has decomposed, *i.e.*, when the interface between the $ZnCO_3$ and the ZnO is a max. H. F. GILLBE.

Surface reactions of atoms and radicals. G. I. LAVIN and W. F. JACKSON (J. Amer. Chem. Soc., 1931, **53**, 3189; cf. this vol., 321).—The oxidation of CO is used as a test for OH, and from the yield of CO_2 it is shown that whilst a dehydration catalyst is efficient, a dehydrogenation catalyst is inefficient in causing the H+OH combination. A method of separating H and OH is indicated.

J. G. A. GRIFFITHS.

Catalytic hydrogenation of carbon suboxide. K. A. KOBE and L. H. REYERSON (J. Physical Chem., 1931, **35**, 3025—3035).—C_3O_2, catalytically hydrogenated by passage with H_2 over Ni- or Pd-coated SiO_2 gels, yields CO_2 and propylene as the two chief products. The principal reactions which occur are $C_3O_2+5H_2\longrightarrow C_3H_6+2H_2O$; $C_3O_2+2H_2O\longrightarrow CH_2(CO_2H)_2$; $CH_2(CO_2H)_2\longrightarrow AcOH+CO_2$ and $CH_2(CO_2H)_2+nC_3O_2\longrightarrow$ polymeride. The Ni catalyst favours the formation of the polymeride, whilst the Pd catalyst gives practically no polymeride but more AcOH. Only small amounts of saturated hydrocarbons are formed. C_3O_2 is an active poison for the hydrogenation of C_2H_4. An improved apparatus (A., 1922, ii, 641) gives 60—73% yields of C_3O_2 from diacetyltartaric anhydride. L. S. THEOBALD.

Catalytic action of an aluminium oxide catalyst. W. D. BANCROFT and A. B. GEORGE (J. Physical Chem., 1931, **35**, 2943—2949).—Previous theories concerning the catalytic activity of Al_2O_3 have been investigated by studying the decomp. of AcOEt at 450° by Al_2O_3 catalysts prepared in different ways. The increase in the amount of C_2H_4 obtained by sintering the catalyst is less than the difference which exists in this respect between the dehydrating and decarboxylating catalysts. Washed pumice alone gives large amounts of C_2H_4 and little CO_2, whilst catalysts prepared by heating $Al(NO_3)_3,9H_2O$ favour the formation of C_2H_4 when compared with those obtained by precipitation with aq. NH_3. The increase in C_2H_4 resulting from sintering is small compared with the effect, positive or negative, of adsorbed substances. Taylor's theory of sp. catalytic activities of the adsorbed ions explains the results better than does Adkins' theory of mol. porosity.

L. S. THEOBALD.

Rectifying action and heterogeneous catalysis with copper–cuprous oxide systems. WO. OSTWALD and H. ERBRING (Kolloid-Z., 1931, **57**, 7—14).—The relation between rectifying action, photo-electric effect, and catalysis previously suggested (this vol., 35) is confirmed by quant. investigations in which the rectifying action of Cu–Cu_2O plates has been compared with their catalytic effect on the oxidation of *p*-phenylenediamine. Plates which form good "detectors" give the best yields of aniline-black and quinhydrone. Oxidation and reduction of the plates produces a parallel effect on both the rectifying action and the catalytic power. E. S. HEDGES.

Catalysts for synthesis of methyl alcohol. V. N. IPATIEV and B. N. DOLGOV.—See B., 1931, 962.

Activity of mixed catalysts. E. PIETSCH and F. SEUFERLING (Z. Elektrochem., 1931, **37**, 655—665).—The activity of catalysts has been determined by measuring the amount of heat received by the catalyst from the reaction. Examination of the systems Pb–Tl and Pb–KCl as catalysts for the recombination of at. H has been directed at the mol. relations of the components. The activity of mixtures of Pb and Tl is consistently below that in accordance with an additive law, there being a sharp min. at about 33%

Pb. In the Pb–KCl system a considerable increase of activity is caused by the addition of the first 10% of Pb and a considerable decrease by the first 10% of KCl. The relation is additive only between 45 and 70 at.-%. E. S. HEDGES.

Determination of the activity of mixed catalysts. E. PIETSCH and F. SEUFERLING (Z. physikal. Chem., Bodenstein Festband, 1931, 523—532).—By thermo-electric measurement of the heat developed in the catalyst the activity of the latter may be determined. Details are given of the method and of apparatus suitable for use with various types of catalyst. H. F. GILLBE.

Decomposition of ethyl and *iso*propyl alcohols at surfaces of manganous compounds. A. T. WILLIAMSON and H. S. TAYLOR (J. Amer. Chem. Soc., 1931, 53, 3270—3275).—The reactions of EtOH and $Pr^{\beta}OH$ at 1 atm. at the surfaces of MnO, $MnSO_4$, $Mn_3(PO_4)_2$, and $Mn_2P_2O_7$ between 330° and 425° are mainly dehydrations and dehydrogenations. Under similar conditions, the rate of decomp. of $Pr^{\beta}OH$ is much greater than that of EtOH. Dehydration decreases more than dehydrogenation with increasing age of the catalyst, and with EtOH and MnO, the percentage of dehydrogenation decreases with rise of temp. The apparent energy of activation is therefore higher for the dehydration process. In accordance with the theory that dehydrogenation occurs at the positive ions of the surface and dehydration at the negative ions, the dehydrogenation/dehydration ratio decreases with increasing valency of the anion. J. G. A. GRIFFITHS.

Thermal decomposition of gaseous propaldehyde on the surface of platinum. E. W. R. STEACIE and R. MORTON (Canad. J. Res., 1931, 4, 582—590).—The reaction at 820—935° follows the unimol. law and occurs catalytically on the Pt surface, the main products being, however, different from those of the homogeneous reaction. Since the heat of activation is 96,500 g.-cal., it seems that only adsorbed mols. react. R. CUTHILL.

Autoxidation of benzaldehyde. II. Action of catalysts. E. RAYMOND (J. Chim. phys., 1931, 28, 421—441).—Since salts of Mn, Co, Ni, Fe, Ag, and Cu activate the autoxidation of PhCHO in the dark at rates which decrease in the order named, but are dependent on the nature of the anion, the activities of solutions of the respective benzoates, prepared both by double decomp. and from the metal oxide, were compared by determinations of the vol. of O_2 absorbed. Benzoates of Mg, Zn, Al, Pb, and Bi were inactive, those of Ag and Cu slightly active, whilst Mn, Co, Ni, and Fe gave highly active salts. Cu and Ag gave different rate of oxidation–time curves, especially during the period of induction. Primary oxidation of the aldehyde to BzO_2H probably occurs, followed by oxidation of the catalyst to an unstable per-salt which itself oxidises the aldehyde more rapidly than the per-acid. Since the rate of oxidation is proportional to (mass of catalyst)$^{\frac{1}{2}}$, it is probable that the primary oxidation is due to the formation of ions in solution, a conclusion confirmed by conductometric measurements. Since the rate of oxidation in light with a catalyst is never the sum of the rates observed in the dark with, and in light without, a catalyst, there is evidence that the cations concerned may also exercise an antioxygenic effect. J. GRANT.

Thermal dissociation of benzoic acid vapour. W. MOSER (Helv. Chim. Acta, 1931, 14, 971—997).—BzOH, when heated in glass vessels at 400—500°, is decomposed almost completely into C_6H_6 and CO_2 at a rate which increases with rise of temp. and with the surface area of the glass. Small amounts of PhOH and CO are also formed. Excess of CO_2 slightly retards the action. The main reaction is accelerated by Al slightly, by Zn or Fe greatly, and all three catalysts promote side reactions giving rise to Ph_2 and H_2. Cu or Cd accelerates the main reaction and suppresses side reactions. Cd increases the speed 200 times. The reverse change is not analytically detectable. F. L. USHER.

Preparation of fluorine by electrolysis. L. M. DENNIS, J. M. VEEDER, and E. G. ROCHOW (J. Amer. Chem. Soc., 1931, 53, 3263—3269).—A V-shaped cell of heavy Cu tubing in which foaming is avoided and no diaphragm is required is described. Difficulties encountered by other workers are eliminated by using pure graphite electrodes and specially pure electrolyte (KF,HF) dried at 130°. F_2 is evolved immediately on passing the electrolysing current; the cell may be used intermittently and has an efficiency of about 76% at 9·3 amp. J. G. A. GRIFFITHS.

Preparation of hydrogen peroxide and ammonium persulphate with streaming electrolytes. E. H. RIESENFELD and A. SOLOVIAN (Z. physikal. Chem., Bodenstein Festband, 1931, 405—414).—Since during the electrolytic prep. of both H_2O_2 and $(NH_4)_2S_2O_8$ the products undergo partial decomp. at the electrodes, the use of a streaming electrolyte considerably increases the yield. Under suitable conditions a concentration of 0·58 millimol. H_2O_2 per litre and a yield of 18% have been obtained. With $(NH_4)_2S_2O_8$ the yield at first rises with increase of the streaming velocity, but later falls; the max. yield obtained is 71%. If the cathode is placed above the anode, so that the O_2 liberated at the latter comes into contact with the former, and if the electrolyte passes first over the cathode and then over the anode, H_2O_2 and $(NH_4)_2S_2O_8$ may be simultaneously prepared. H. F. GILLBE.

Boron hydrides. XV. Electrolysis of solutions of boron trihydride in ammonia. A. STOCK, E. WIBERG, H. MARTINI, and A. NICKLAS (Z. physikal. Chem., Bodenstein Festband, 1931, 93—100).—Two principal reactions occur during the electrolysis of a solution of B_2H_6 in anhyd. NH_3 at −75°. In the first the salt $B_2H_4,2NH_4$, which is formed in the solution and is responsible for the conductivity, decompose into $B_2H_4(NH_2)_2$ and H_2, and the conductivity simultaneously diminishes; this reaction proceeds to completion. In the second reaction the B_2H_4 and NH_4 resulting from the electrolysis of the intermediate compound yield H_2, and amino-substituted B_2H_6, *e.g.* $B_2H_5NH_2$. This compound is still feebly acidic, and its NH_4 salt undergoes further electrolysis and slow and incomplete ammination, with the partial re-formation of $B_2H_4(NH_2)_2$; alternatively, the B_2H_4

group reacts with NH_3 to yield B_2H_6 and N_2. Ammination of B_2H_6 to the extent of 2·3 NH_2 groups per mol. has been observed. H. F. GILLBE.

Beryllium. I. Electrolysis in non-aqueous solvents. II. Electrolysis of beryllium compounds in organic nitrogen derivatives. H. S. BOOTH and G. G. TORREY (J. Physical Chem., 1931, **35**, 2465—2477, 2492—2497).—I. Starting with the purified basic acetate, methods for the prep. of the oxide, hydroxide, anhyd. chloride and nitrate, and acetylacetonate are described. The double K chloride or sulphate could not be obtained. Solutions of Be salts in EtOH, C_5H_{11}·OH, EtBr, glacial AcOH, acetylacetone, Me_2O–BF_3, $COCl_2$, PCl_3, liquid SO_2, and $SeOCl_2$ are mainly poor conductors of electricity and none is a satisfactory source of Be.

II. Solutions of different Be salts in the org. derivatives of NH_3 are either non-conducting or are poor conductors which yield Be only in small amounts (especially piperidine and pyrrole). In general, the solutions form gelatinous colloidal substances which make the practical separation of Be problematical. L. S. THEOBALD.

Electrodeposition of silver from sulphate, nitrate, fluoborate, and fluoride solutions. E. B. SANIGAR.—See B., 1931, 930.

Silver plating solutions. B. EGEBERG and N. PROMISEL.—See B., 1931, 930.

Electro-deposition of copper in the presence of gelatin. R. TAFT and H. E. MESSMORE (J. Physical Chem., 1931, **35**, 2585—2618; cf. Trans. Kan. Acad. Sci., 1929, **32**, 42).—The variations in form of the cathodic deposit from cells of the type Cu|$CuSO_4$, gelatin|Cu with the concentration and type of gelatin are recorded. Cathodes of Au, Pt, Ag, and brass have only an initial effect. The increase in wt. of the Cu deposit, determined for different concentrations of gelatin and $CuSO_4$, different current densities, times, and temp., is best explained by the assumption that the deposited Cu adsorbs gelatin on its surface. Measurements of cathodic polarisation indicate that complex ions are formed between $Cu^{\cdot\cdot}$ and gelatin, but that the electrochemical process occurring at the cathode is primarily a discharge of $Cu^{\cdot\cdot}$. L. S. THEOBALD.

Characteristics of working of the lead accumulator. E. DENINA and A. FRATES.—See B., 1931, 981.

Electrolytic manufacture of aluminium, and aluminium plating. V. O. PLOTNIKOV, M. M. GRACJANSKI, and M. S. FORTUNATOV.—See B., 1931, 979.

Changes produced on electrodes by electric sparks. L. BELLADEN (Gazzetta, 1931, **61**, 537—543).—The changes which occur at the surface of electrodes by passing a spark obtained by means of an induction coil and condensers have been studied using electrodes of Cu, Zn, brass, Cd, Sb, Bi, Tl, Mg, Pb and Al, and with turpentine, liquid vaseline, paraffin, abs. EtOH, and air as dielectrics. With the liquid dielectrics the size and no. of the craters formed on the electrode surface do not vary with the nature of the electrode or of the dielectric. In air, however, the changes produced depend largely on the nature of the metallic surface and on the properties of the oxide film. O. J. WALKER.

Definition and determination of "free cyanide" in electroplating solutions. W. BLUM.—See B., 1931, 930.

Electrodeposition of chromium and influence of the cathode metal. J. W. CUTHBERTSON.—See B., 1931, 929.

Electrodeposition of tungsten from aqueous solutions. C. G. FINK and F. L. JONES.—See B., 1931, 930.

Preparation of pure electrolytic nickel. III. C. G. FINK and F. A. ROHRMAN.—See B., 1931, 930.

Gaseous combustion in electric discharges. VIII. The cathodic combustion of hydrogen–oxygen mixtures. G. I. FINCH and E. A. J. MAHLER (Proc. Roy. Soc., 1931, **A**, **133**, 173—178; cf. this vol., 44).—The study of the cathodic combustion of electrolytic gas has been extended to that occurring at electrodes of Au, Ag, Ta, and W, and to the effect of such diluents as O_2, H_2, and H_2O. Dilution with H_2, even up to 99·5% of H_2, results in a rapid increase of combustion at a non-sputtering cathode, the effect being much less pronounced at a freely sputtering cathode. The formation of H_2O_2 during the combustion is favoured by increase of pressure, absence of sputtered metal particles, and dilution with H_2 (for a non-sputtering cathode). The presence of steam results in an increase in the rate of combustion at a non-sputtering cathode, but has no effect at a freely sputtering cathode. Electrolytic gas burns much more rapidly at a W than at a Ta cathode. L. L. BIRCUMSHAW.

Condensation of hydrocarbons by electrical discharge. VIII. Condensation as a function of time and pressure. S. C. LIND and G. R. SCHULTZE (J. Amer. Chem. Soc., 1931, **53**, 3355—3366; cf. this vol., 60).—With const. duration of discharge (1 hr.), the fraction of CH_4 which reacts and the % of H_2 produced increase rapidly with decrease of initial pressure. Appreciable quantities of C_2H_4 are found only at about 200 mm. With const. initial pressure of CH_4, a steady state of synthesis and decomp. of hydrocarbons is established in 20 min., and further action of the discharge increases the yield of liquid and H_2. In the case of CH_4 and C_2H_4, the ratio of hydrocarbon disappearing to H_2 produced is independent of duration of reaction between 20 and 60 min., and the formulæ of the liquid products are unchanged. Unlike the product from C_2H_2, those from CH_4 and C_2H_4 are slowly decomposed by further action of the discharge. H_2 is produced during the polymerisation of C_2H_2 and some hydrogenation occurs. J. G. A. GRIFFITHS.

Formation and decomposition of ammonia in high-frequency glow discharge. R. RINKEL (Ann. Physik, 1931, [v], **10**, 129—142).—The velocity of decomp. of NH_3 in a high-frequency glow discharge has been determined. With an initial pressure of 3—4 mm. the equilibrium lies at about 98% N_2 and 2% H_2. The formation of NH_3 from mixtures of N_2 and H_2 of varying composition was studied. The most

favourable ratio is $N_2 : H_2 = 1 : 1$. The influence of different electrode materials and of electrically neutral metal sheets and gauzes introduced between the electrodes was also studied. No alteration in reaction velocity with wave-length in the range 400—1700 m. was found. W. GOOD.

Reaction of previously illuminated chlorine with hydrogen. W. JOST and H. SCHWEITZER (Z. physikal. Chem., 1931, **B**, **13**, 373—378).—Reaction still occurs 10^{-4} sec. after illumination has ceased, but this is approx. the limit. The concentration of Cl atoms decreases more rapidly than calculation predicts owing to turbulence in the apparatus increasing the number of collisions with the walls. N. H. HARTSHORNE.

Photosensitised decomposition of ozone by bromine. J. W. T. SPINKS (Nature, 1931, **128**, 548).—The $Br-O_3$ photo-reaction has a high quantum efficiency. In general, there is no after-effect, and no appreciable change in transmission of 365 or 546 mμ takes place on insolation, indicating the absence of absorption of an intermediate compound on surface walls. The quantum efficiencies at 546 and 365 mμ are practically equal and the same efficiency is obtained for mixtures of 0·3—3·3% Br and 0·5—4% O_3. The rate of reaction is directly proportional to the intensity. An oxide of Br is considered to be the " carrier " in both the thermal and photo-reactions. L. S. THEOBALD.

Photochemical conversion of carbonic acid. G. KOGEL (Z. wiss. Phot., 1931, **30**, 196—201).—Theoretical. The synthesis of CH_2O is represented as a keto-enol change, activated by chlorophyll as light absorbent (cf. B., 1919, 738A). J. LEWKOWITSCH.

Kinetics and photochemistry of carbonyl bromide. H. J. SCHUMACHER and P. BERGMANN (Z. physikal. Chem., 1931, **B**, **13**, 269—284; cf. A., 1928, 1200).—K_c for the reaction $COBr_2 \rightleftharpoons CO+Br_2$ is $1·77\times10^{-4}$ at 20°, $1·50\times10^{-4}$ at 50°, and $1·21\times10^{-4}$ at 100°, whence the heat of formation at const. vol. of $COBr_2$ is 1035±100 g.-cal. per mol. within this temp. range. In visible and long-wave ultra-violet light atoms and activated mols. of Br take no measurable part in the reaction between 10° and 73°, nor do they affect the formation of CO_2 when O_2 is present between 20° and 250°. The absorption of light by $COBr_2$ begins at 3200 Å., increases rapidly, and then remains const. to 2100 Å. In this range the photochemical decomp. of $COBr_2$ requires 1 quantum per mol. Gaseous impurities which do not absorb the light have no influence on the velocity of the decomp., the temp. coeff. of which is 1·0 per 10° between 10° and 40°. Alternative mechanisms suggested are (i) $COBr_2+E=COBr+Br'$, then $COBr=CO+Br$; (ii) $COBr_2+E=CO+Br+Br'$. N. H. HARTSHORNE.

Formation of hydrazine during electrical and photochemical decomposition of ammonia. A. KOENIG and T. BRINGS (Z. physikal. Chem., Bodenstein Festband, 1931, 541—552).—Since N_2H_4 is formed during the decomp. of NH_3 both photochemically and under the influence of the glow discharge, it is probable that NH_2 and/or NH are formed as intermediate products. At about −80° the formation of N_2H_4 preponderates over that of N_2, although the yield, referred to the electrical energy used, is less than with the streaming gas at room temp. H. F. GILLBE.

Photochemical reduction of ferric iron in tri-iodide solution. S. F. RAVITZ and R. G. DICKINSON (J. Amer. Chem. Soc., 1931, **53**, 3381—3384; cf. this vol., 308).—I and $Fe^{\cdot\cdot}$ in approx. equiv. proportions are at first formed more rapidly in light of $\lambda>5000$ Å. than in the dark in fresh solutions at 0° containing appropriate concentrations of I, I′, and $Fe^{\cdot\cdot\cdot}$. The light accelerates the reduction of $Fe^{\cdot\cdot\cdot}$ by I′. J. G. A. GRIFFITHS.

Desensitisation of photolysis of uranyl formate. C. OUELLET (Helv. Chim. Acta, 1931, **14**, 936—966).—Photolysis of HCO_2H in the presence of $UO_2^{\cdot\cdot}$ is markedly retarded by Cl′, I′, $Fe^{\cdot\cdot}$, $K_2Cr_2O_7$, $AgNO_3$, $NaNO_2$, KCN, $HgSO_4$, or quinol. The effect is relatively greatest at low concentrations of the desensitising substance or of the photolyte. The velocity (v) of the reaction in the presence of a desensitiser (D) is related to that (v_0) in its absence as expressed by the formula $v=v_0/(\alpha+\beta[D])$. Baur's formula (A., 1929, 892) for the relation between a stationary state and intensity of illumination is confirmed by a study of the reversible photolysis of KI in the presence of UO_2SO_4. F. L. USHER.

Highly disperse [photographic] emulsions. LUPPO-CRAMER (Z. wiss. Phot., 1931, **30**, 201—207; cf. Phot. Korr., 1931, **67**, 1).—The sensitising properties of Na_2SO_3, $NaHSO_3$, $NaNO_2$, erythrosin, and pinachrome on an unripened " grainless " AgBr emulsion are compared. The changes on ripening, with and without the addition of 3% AgI, are studied. J. LEWKOWITSCH.

Photodichroism and photoanisotropy. X. Photographic experiments with polarised light. II. F. WEIGERT and F. STIEBEL (Z. wiss. Phot., 1931, **30**, 177—195; cf. following abstract).—Primary Ag is proved experimentally to act as sensitiser for the production of photodichroism; the proportion of primary Ag so available is estimated. CrO_3 treatment reverses the sign of the photodichroism. $Fe_2(C_2O_4)_3$ only develops extra-micellar Ag; developer containing Na_2SO_3 (*e.g.*, *p*-phenylenediamine) lays bare and develops intramicellar Ag as well, allowing its properties to be differentiated. Polarised light can even induce weak dichroism within the micelle. J. LEWKOWITSCH.

Photodichroism and photoanisotropy. VIII. F. WEIGERT and F. STIEBEL (Z. physikal. Chem., 1931, **B**, **13**, 285—298).—The anomalous additive dichroism produced by the simultaneous action of two beams of polarised light of different colours has been more completely studied (cf. A., 1930, 1238). The anomalies are especially marked when red light is one of the components. Experiments in which the one beam is polarised and the other is not show that red and blue polarised light are mainly concerned with the anisotropic " form factor " and with the " activation factor " of the latent image respectively. N. H. HARTSHORNE.

Intensifying action of hydrogen peroxide and organic peroxides on the latent photographic

image. C. E. BARNES, W. R. WHITEHORNE, and W. A. LAWRANCE (J. Physical Chem., 1931, **35**, 2637—2649).—Time-gamma curves indicate that latent image intensification by H_2O_2 depends largely on the developer used. H_2O_2 produces an increase in speed with all developers except "glycine"; pyrogallol and metol show the highest degree of intensification, but the time-gamma curves reveal a wide difference in their action. *m*-Chlorobenzoyl peroxide is the only one of the org. peroxides investigated which shows true intensification. The effect of treatment with H_2O before development is discussed.

L. S. THEOBALD.

Instability of silver halides, and photographic processes in the silver halide plate; light-sensitivity and development. K. FREDENHAGEN and (FRAU) M. WELLMANN (Z. physikal. Chem., Bodenstein Festband, 1931, 135—144).—The partial pressure of Ag over solid AgCl, AgBr, and AgI at room temp., calc. from existing v.-p. measurements, is considerably greater than the saturation v. p. of Ag. The gas phase in contact with a photographic plate is therefore supersaturated with respect to Ag, and many aspects of the behaviour of a plate on exposure and development are explained as due to removal of this supersaturation. H. F. GILLBE.

Elimination of ammonia from amino-acids and other substances by the light of the quartz lamp. F. LIEBEN and F. URBAN (Biochem. Z., 1931, **239**, 250—256; cf. this vol., 607).—The elimination of NH_3 from the α-NH_2-group of NH_2-acids ($NH_2{\cdot}CH_2{\cdot}CO_2H$, alanine, aspartic acid, cystine, arginine, lysine, tyrosine, tryptophan, histidine, anthranilic acid) and from guanine, guanidine, and benzidine by light from the quartz–Hg lamp has been measured. The acids exhibit great differences in regard to the amount of NH_3 lost; histidine, then cystine, loses most. No relation exists between the amount of NH_3 eliminated and the accompanying total decomp. (measured colorimetrically) of histidine, tyrosine, and tryptophan. The action proceeds more rapidly in acid than in neutral or alkaline medium. No NH_3 is eliminated from guanidine, but the NH_2-groups in guanine, anthranilic acid, and benzidine are affected by the light to much the same extent as is that of a straight chain. The ε-NH_2-group in lysine is probably also attacked. W. McCARTNEY.

Photochemical decomposition of amines and the photochemical interaction of amines and ethylene. H. J. EMELÉUS and H. S. TAYLOR (J. Amer. Chem. Soc., 1931, **53**, 3370—3377; cf. this vol., 442).—NH_2Me and NH_2Et at 125—260° in the full radiation of the quartz–Hg vapour lamp slowly decompose into H_2, CH_4, C_2H_6, N_2, and a non-volatile liquid containing N. In the presence of O_2, a relatively rapid reaction occurs. The photo-decomp. of the amines induces the polymerisation of C_2H_4, especially at the higher temp. The velocity of reaction is independent of the pressure of C_2H_4 between 2 and 25 cm. and of the pressure of the amines when the absorption of light is complete. Preliminary experiments indicate that C_2H_6 probably inhibits the photo-decomp. of NH_3 and amines, but some polymerisation of C_2H_6 occurs. J. G. A. GRIFFITHS.

Photo-reaction between bromine and *cyclo*hexane. W. JOST (Z. physikal. Chem., Bodenstein Festband, 1931, 291—297).—Contrary to Rideal's report, no appreciable reaction takes place between Br and *cyclo*hexane in the dark. Both the band and continuous regions of the Br absorption spectrum are photocatalytically active, and produce the same type of reaction. The velocity coeff., $(d\log[Br_2])/dt$, is approx. proportional to the square root of the *cyclo*hexane concentration. In presence of H_2 the velocity is unchanged; O_2 produces a marked decrease, and the gradual increase of the coeff. during the reaction indicates that O_2 disappears as the reaction proceeds. The quantum yield at 73—100° is of the order of 12 to 40. The temp. coeff. of the reaction is about 2 per 30°, and the quantum yield at room temp. is thus about 2. The mechanism is discussed.

H. F. GILLBE.

Quantum yield of 0·5 in photochemical reactions. F. WEIGERT and F. PRUCKNER (Z. physikal. Chem., Bodenstein Festband, 1931, 775—784).—The yield of the photochemical conversion of *o*-nitrobenzaldehyde, at concentrations of 0·02—8% in $COMe_2$, into *o*-nitrosobenzoic acid is 0·5 and is independent of wave-length between 3130 and 4360 Å. even when, as at 3130 Å., the solvent absorbs the greater part of the radiation. In presence of more than one absorbing substance, therefore, a photochemical Beer's law cannot be said to exist. This apparent anomaly is explicable on the assumption that the $COMe_2$ acts as a sensitiser in the same manner as does Cl at high concentrations on the decomp. of O_3. At concentrations below 0·5% the yield at 3130 and 3660 Å. falls, the min. val. being about 0·35, owing to a breakdown of Beer's law. H. F. GILLBE.

Effect of sea-water irradiated with ultraviolet light on the velocity of alcoholic fermentation of dextrose solutions. L. SANZO and F. PIRRONE.—See this vol., 1333.

Photochemical synthesis of carbohydrates. G. EMSCHWILLER (Bull. Soc. chim., 1931, [iv], **49**, 1167—1187).—A lecture.

Action of light on catalytic oxidation by complex metallic salts. Y. SHIBATA and S. GODA (Bull. Chem. Soc. Japan, 1931, **6**. 217—220).—The rate of oxidation of *d*-catechin in presence of racemic $[Co\ en_2NH_3Cl]Br_2$ is smaller in green light than in red or white light. The absorption spectrum of the complex salt exhibits bands at 5000 and 3640 Å., but both these wave-lengths are transmitted by the green screen used. It thus appears that excited H_2O mols. are more effective than excited mols. of the complex salt; this view is confirmed by the low reaction velocity in light which has passed through an aq. $CuSO_4$ screen. It is suggested that ordinary H_2O mols. are activated, possibly by dissociation, by the complex salt. H. F. GILLBE.

Decomposition of benzophenone diazide under the influence of *X*-rays. G. CRONHEIM, S. GOTZKY, and P. GÜNTHER (Z. physikal. Chem., Bodenstein Festband, 1931, 785—791).—*X*-Rays of wave-length 0·60—1·54 Å. cause rapid decomp. of benzophenone diazide, and evolution of N_2; the compound at first

fluoresces and finally becomes red. In this wave-length region the quantity of energy transferred to the secondary electrons per mol. of N_2 evolved is 25 kg.-cal., and is independent of the wave-length. The results confirm Glockler's theory (A., 1928, 970) of the chemical activity of X-rays. H. F. GILLBE.

Temperature coefficient of the synthesis of hydrogen bromide by α-particles. S. C. LIND and E. F. OGG (Z. physikal. Chem., Bodenstein Festband, 1931, 801—806).—The combination of H_2 and Br under the influence of α-particles is not a chain reaction at temp. up to 300°. The reaction velocity appears to be a function of the square root of the radiation intensity, and propagation of the reaction is therefore probably due to Br atoms; since, however, the photochemical reaction does not proceed at room temp., the atoms produced by the action of α-particles are more reactive than are those produced photochemically. At 40° the thermal rate is negligible, and the rate under α-particle bombardment, *i.e.*, the ratio of the no. of mols. of HBr formed to the no. of ion-pairs produced, is 0·54. The thermal rate is appreciable at 100° and is about 1/6 of the total rate. The α-particle rate rises to a max. val. of 1·51 at 192° and approaches zero at 265°; at higher temp. negative vals. may be obtained. The rate of HBr (liquid) decomp. under bombardment at room temp. is about 2·8, and this effect preponderates at higher temp.; the inhibitive influence of HBr is then negligibly small. For the interval 40—192° the temp. coeff. of the total reaction is about 1·1 per 10°, and at higher temp. it approaches that of the thermal reaction, viz., 2—2·3.
H. F. GILLBE.

Photographic action of α-rays. J. EGGERT and F. LUFT (Z. physikal. Chem., Bodenstein Festband, 1931, 745—754).—The blackening of a photographic plate by α-rays is directly proportional to the concentration of the emulsion. The range of action within the emulsion is about 25—30μ. Each nucleus with which a particle collides becomes capable of development. The sensitivity of the plate towards α-rays does not vary appreciably with temp.
H. F. GILLBE.

Photographic action of cathode rays. A. BECKER and E. KIPPHAN (Ann. Physik, 1931, [v], **10**, 15—51).—The effect has been investigated on 3 different AgBr emulsions for electron velocities 15—100 kv. The validity of the reciprocal law is confirmed. Almost to the appearance of solarisation the relationship between the blackening, S, and the electron quantity, Q, can be represented by S—C log $(aQ+1)$ where a and C are consts. The initial photographic sensitivity of all the films used is proportional, between 15 and 100 kv., to the electron energy falling on them. Vals. of the photochemical yield are given. W. GOOD.

Action of radon on unsaturated hydrocarbons. G. B. HEISIG (J. Amer. Chem. Soc., 1931, **53**, 3245—3263).—Under the action of α-rays from radon, the number of mols. of hydrocarbon reacting per ion pair (M/N ratio) is for allene 10·0, allylene 8·3, CMe·CMe 5·8, β-butene 3·8, and isoprene 12·7, decreasing to 10 during the reaction. Liquid products together with H_2 and CH_4 are obtained, but in the case of the first two, the liquids are transformed into solids. The results indicate that the M/N ratios are additive and constitutive. The M/N ratio varies inversely as the ratio $\Delta(H_2+CH_4)/-\Delta$(hydrocarbon). J. G. A. GRIFFITHS.

Action of atomic on molecular hydrogen. K. H. GEIB and P. HARTECK (Z. physikal. Chem., Bodenstein Festband, 1931, 849—862).—The reaction between H atoms and para-H_2 has been studied, by means of a special apparatus, at 0·5 mm. and 10—100°. The reaction mechanism is the same as that found by Farkas (this vol., 174) for the thermal reaction, viz., para-H_2+H=H+ortho-H_2. The heat of activation is 7250±250 g.-cal. The extent of decomp. of para-H_2 may be employed to detect H atoms at low concentrations, such as are produced, *e.g.*, in NH_3, HBr, or H_2O by irradiation with the Zn arc. In addition, the mean life of the H atoms may be estimated. Thus in NH_3 the mean life is 7×10^{-4} sec., and recombination by triple impact is therefore improbable. H. F. GILLBE.

Atomic hydrogen occluded in iron nitride. S. SATOH (Nature, 1931, **128**, 457).—At. H has been observed in Fe nitride prepared by heating Fe in gaseous NH_3 (cf. this vol., 53). L. S. THEOBALD.

Reaction between sodium vapour and oxygen. III. Autoxidation. F. HABER and H. SACHSSE (Z. physikal. Chem., Bodenstein Festband, 1931, 831—848).—The reaction between dil. Na vapour and O_2 at relatively high partial pressure, in presence of an inert gas, takes place in the gas phase, and consists primarily in the addition of O_2 mols. to Na atoms; subsequently further Na atoms react with the NaO_2 formed. H. F. GILLBE.

Complex potassium, ammonium, and sodium silver thiosulphates. I. Ammonium silver thiosulphate. G. SPACU and I. G. MURGULESCU (Z. anorg. Chem., 1931, **199**, 273—282).—Potentiometric measurements with 0·01—6M solutions show that when $Ag_2S_2O_3$ and $(NH_4)_2S_2O_3$ react 4 complexes are obtained, viz., $(NH_4)_2[Ag_4(S_2O_3)_3],H_2O$, $(NH_4)[Ag(S_2O_3)]$, $(NH_4)_4[Ag_2(S_2O_3)_3],H_2O$, and $(NH_4)_5Ag(S_2O_3)_3$. Details are given of the prep. of these compounds. H. F. GILLBE.

Formation of copper peroxides in non-aqueous media. I. S. TELETOV and A. D. VELESCHINIETZ (Ukrain. Chem. J., 1931, **6**, [Sci.], 53—60).—A ppt. containing CuO_2 and CuO in various proportions is obtained by the addition of an Et_2O extract of H_2O_2 to a MeOH solution of $Cu(NO_3)_2$. The proportion of CuO_2 in the ppt. increases with the relative H_2O_2 concentration of the solution. H_2O_2 is decomposed by the ppt., which also decomposes on consequent diminution in H_2O_2 concentration, and Cu again passes into solution. The stability of the ppt. is not affected by the presence of H_2O. Cu compounds catalysing the decomp. of H_2O_2 form CuO_2 as an intermediate product. R. TRUSZKOWSKI.

Chemical reactions in crystals. II. Cupric sulphate. V. KOHLSCHUTTER and H. NITSCHMANN (Z. physikal. Chem., Bodenstein Festband, 1931, 494—509).—X-Ray, microscopic, and chemical study of

the decomp. of $CuSO_4,5H_2O$ shows the process to be extremely complex. The hydrates with 5, 4, and 3 H_2O, and the anhyd. salt, possess very different lattice structures. The monohydrate, when prepared in vac. at 20—40°, is completely amorphous, but it becomes crystalline on warming. The product of dehydration of the pentahydrate to approx. $2H_2O$ in vac. at 20° consists of amorphous monohydrate and pentahydrate, and only on heating at 100° is the trihydrate formed. At 50°, in air, the decomp. of $CuSO_4,5H_2O$ commences at minute white points and greenish-blue surface streaks; the former consist of monohydrate and the latter of trihydrate. The streaks are parallel with the *c* axes of the crystals, *i.e.*, with the direction of the smallest lattice const. Similarly, crystals of $[Cu(NH_3)_4][SO_4(H_2O)]$, after being heated at 90—93°, become divided into a series of plates by fissures perpendicular to the longest axis. The significance of these and other observations is discussed in detail. H. F. GILLBE.

Silver ferrites. II. Structure of yellow hydroxide obtained by hydrolysis of a hot ferric chloride solution. A. KRAUSE and W. BUCZKOVSKI (Z. anorg. Chem., 1931, **200**, 144—152; cf. this vol., 695).—The yellow hydroxide obtained by hydrolysis of aq. $FeCl_3$ at 120—160° is ferrous acid (γ-FeOOH), for the H which it contains is replaceable by Ag. Owing to the position of its isoelectric point, it may contain basic chloride. At 160° the hydrolysis also yields α-Fe_2O_3. R. CUTHILL.

Behaviour of gold and its alloys with silver and copper towards nitric and sulphuric acids. G. TAMMANN and E. BRAUNS (Z. anorg. Chem., 1931, **200**, 209—231).—Au is practically unattacked by H_2SO_4 at temp. up to 200°; at 300° the quantity of Au dissolved is appreciable unless the acid has previously been boiled. Whereas HNO_3 of *d* 1·3 is inert at 20—100°, HNO_3 of *d* 1·5 dissolves appreciable quantities of Au at 20°, but the acid rapidly loses its activity. Au–Ag alloys containing 0·75 and 0·55 mol. Au are scarcely attacked by boiled H_2SO_4 at 100°. H_2SO_4 at 150° and HNO_3 (*d* 1·3) at 100° do not attack Au–Ag alloys containing more than 0·50 mol. Au, but with a lower Au content, even 0·49 mol., the action is marked; the same obtains with HNO_3 at 90° for Au–Cu alloys. After removal of the surface Ag, further atoms move from the interior of the alloy to the surface and are then dissolved; the quantity of metal dissolved is proportional to the quantity of Ag in the alloy. H. F. GILLBE.

Preparation of phosphorescent substances. IV. CaS, SrS, and BaS. N. F. ZHIROV (J. Appl. Chem., Russia, 1930, 3, 1007—1021).—SrS is best for investigating secondary solvents, the theory of which is developed. If tungstates are used the ignition temp. is lowered to 900—1000°. $CaWO_4$ shifts the spectrum to the violet and $SrWO_4$ to the red. MgO is the only satisfactory secondary solvent. CdS gives highly coloured luminophores of poor quality. CHEMICAL ABSTRACTS.

Stability of barium sulphate at high temperatures. E. G. MAHIN and B. KILIAN (Proc. Indiana Acad. Sci., 1929, **36**, 155—156).—$BaSO_4$ is stable at temp. obtainable with ordinary laboratory burners; small losses occur at higher temp. CHEMICAL ABSTRACTS.

Aluminium oxide as basis of luminescent systems: Al_2O_3–Pt and Al_2O_3–Mn phosphors. E. TIEDE and R. PIWONKA (Ber., 1931, **64**, [*B*], 2252—2258).—Al_2O_3 prepared at 900° is hygroscopic and incapable of yielding luminescent preps., for which only the α-form is suitable. Pure NH_4 alum is heated at 900°, then pressed into rods, and heated in SiO_2 boats at 1200—1300° until the corundum lattice is well developed. Portions which have been in contact with the boats are rejected. Before ignition the alum is mixed with the sulphates, nitrates, chlorides, etc. of Fe, Pd, Os, Rh, Ru, Ir, Au, Co, Ni, Ag, Bi, Cu, Cd, Ti, Cr, Mn, W, Pt, U. Only those preps. activated with Pt or Mn are true phosphors in Lenard's sense. Al_2O_3 containing Ti, Rh, or Cr must be classified separately. The luminescent behaviour of the phosphors is described in detail. Rh can be present in much higher concentration than Pt. It appears that in the true phosphors, Al_2O_3–Pt and Al_2O_3–Mn, the active metal or metallic oxide is to be regarded as attached to the corundum lattice as a lattice-foreign component with consequent distortion of both components. It appears essential that the smallest at. distances of the active elements, *e.g.*, Pt (2·76 Å.) or Mn (2·58 Å.), must be smaller than the smallest at. distances of the metal in the basic material, *e.g.*, Al (2·86 Å.). H. WREN.

Reaction between thallic chloride and potassium thiocyanate. I. K. TAIMNI (J.C.S., 1931, 2433—2435).—The reaction of $TlCl_3$ with KCNS in aq. solution can be represented by the equation $3TlCl_3 + 4KCNS + 4H_2O = 3TlCNS + 4KCl + HCN + 5HCl + H_2SO_4$. Evidently, $Tl(CNS)_3$ is unstable, and H_2SO_4 is formed through the oxidising power of $Tl^{\cdots}$ ions. E. S. HEDGES.

Residual silica from the attack of leucite with acids. G. A. BLANC (Atti R. Accad. Lincei, 1931, [vi], **13**, 327—330).—If a warm aq. solution of a mineral acid is circulated through a granular layer of leucite crystals the liquid at first becomes turbid and then clear. The resulting layer of SiO_2 hydrogel is able to remove SiO_2 from certain colloidal suspensions passed through it. It loses this property after washing with distilled H_2O, but its activity can be restored by addition of electrolytes. The phenomenon is not purely one of flocculation of the dispersed SiO_2, since addition of electrolyte alone to the stable colloidal SiO_2 suspension does not bring about coagulation. The granules of the SiO_2 hydrogel are able to adsorb an amount of electrolyte sufficient to discharge the ultramicrons of the disperse phase which are brought in contact with the solid phase. O. J. WALKER.

Preparation of pure cerium. M. BILLY and F. TROMBE (Compt. rend., 1931, **193**, 421—423).—A 70% yield of Ce is obtained by electrolysis for $1\frac{1}{2}$ hr. at 850° of 25 g. of $CeCl_3$, 16 g. of KCl, and 25 g. of CaF_2 at 10 amp. and 12 volts in a small quartz crucible at the bottom of a larger C crucible (anode), with a revolving axial Mo cathode, the top of which is protected in a quartz tube. The only impurity

was 0·08% Si; Brinell hardness 42·5 (250 kg.), *d* (in CCl_4) 6·75, m. p. (at 0·005 mm. pressure) 815±5°.

J. GRANT.

Lead halogenocarbonates. D. TSCHAVDAROV (Z. anorg. Chem., 1931, **200**, 200—208; cf. A., 1930, 164).—The substance formed by interaction of aq. Na_2CO_3 with aq. $PbBr_2$ or aq. $PbCl_2$ is not a pure compound, but a mixture in varying proportions of $PbCO_3$, $Pb_2(OH)_2CO_3$, Pb(OH)Br or Pb(OH)Cl, and $Pb_2Br_2CO_3$ or $Pb_2Cl_2CO_3$. Pure $Pb_2Br_2CO_3$ has been prepared.

R. CUTHILL.

Action of oxidising agents on hydrazine sulphate. A. PURGOTTI (Ann. ist. super. agrar. Portici, 1929, [iii], **3**, 47—54).—In alkaline solution: $3N_2H_4+4KMnO_4=4MnO_2+4KOH+4H_2O+3N_2$; in acid solution NH_3 is also formed. With $Fe^{\cdots}$ salts: $5N_2H_4+4Fe_2O_3=8FeO+4NH_3+3N_2+4H_2O$; with PbO_2 in acid or alkaline solution: $2PbO_2+N_2H_4=2H_2O+N_2+2PbO$. With $AgNO_3$ in alkaline solution: $2Ag_2O+N_2H_4=4Ag+N_2+2H_2O$. $K_4Fe(CN)_6$ in alkaline solution affords N_2 and H_2O but not NH_3. Cr may be determined by oxidation with Na_2O_2 to chromate, which is decomposed by N_2H_4 in presence of H_2SO_4, the vol. of N_2 liberated being measured.

CHEMICAL ABSTRACTS.

Action of nitric acid on phosphorous acid. B. BLASER and I. MATEI (Ber., 1931, **64**, [*B*], 2286—2289).—HNO_3 free from oxides of N has no action on H_3PO_3. In 55% acid containing oxides of N, H_3PO_3 is completely oxidised in 15 min. at 100°; under similar conditions with 44%, 31%, and 17% HNO_3 4%, 93%, and 100% of the H_3PO_3 is unchanged. The existence of two forms of H_3PO_3 is suggested.

H. WREN.

Trithiazyl trichloride, $(NSCl)_3$. A. MEUWSEN (Ber., 1931, **64**, [*B*], 2311—2315).—Analyses and determination of mol. wt. in freezing C_6H_6 show that the product obtained by the action of Cl_2 on N_4S_4 in $CHCl_3$ or CCl_4 is *trithiazyl trichloride* for which the constitution $N{<}^{SCl:N}_{SCl\cdot N}{>}SCl$ is suggested; by analogy the compound $N_4S_4Br_4$ is considered to be $(NSBr)_3$. It is violently decomposed by alkali, more quietly by dil. acids. When dry it remains unchanged for a few days but is best preserved under CCl_4.

H. WREN.

[Tetrathioltetrazole,] $(HSN)_4$. A. MEUWSEN [in part with H. HOLCH] (Ber., 1931, **64**, [*B*,] 2301—2311; cf. A., 1929, 1252).—The compound $N{<}^{SH:N\cdot SH}_{SH\cdot N:SH}{>}N$ (*loc. cit.*) is reduced by Na and EtOH to Na_2S and $(NH_4)_2S$; NH_4SH is not isolable as an intermediate product. It is hydrolysed by alkali hydroxide to NH_3 and $Na_2S_2O_3$ with small amounts of Na_2SO_3 and Na_2S. With $AgNO_3$ in MeCN and $COMe_2$ it affords the *compound* $(HSN)_4,2AgNO_3$, decomposing in the course of a few hr., immediately on contact with moisture. With NH_2K in liquid NH_3 it affords the *substance* KSN,NH_2K, immediately decomposed by moist air; it is freely sol. in liq. NH_3 if an excess of $(HSN)_4$ is present but so much NH_2K is invariably present in equilibrium that addition of PbI_2 ppts. a mixture of $Pb(SN)_2,NH_3$ with PbNH and PbN,PbI,NH_3. Direct action of solutions of PbI_2 or $Pb(OAc)_2$ on $(HSN)_4$ in liquid NH_3 never yields the compound $Pb(SN)_2,NH_3$ of Ruff and Geisel (A., 1904, ii, 396) whilst under the conditions used by the authors the action of PbI_2 on N_4S_4 in liquid NH_3 leads to the *substance*, $PbN_2S,N_4S_4,3NH_3$. When treated with MgEtBr in $Et_2O-C_6H_6$, N_4S_4 yields the *compound* $SEt{<}^{N}_{N}{>}SH$, b. p. 39—41°/0·2 mm. Repetition of the work of Lengfeld and Stieglitz on the action of NH_2Et on S_2Cl_2 confirms the isolation of the substance $(EtNS)_4$; since it evolves N_2 quantitatively as NH_2Et when hydrolysed with alcoholic alkali the constitution $NEt{<}^{S\cdot NEt\cdot S}_{S\cdot NEt\cdot S}{>}NEt$ is assigned to it.

H. WREN.

Oxalatoarsenious acid and its salts. I. T. P. BARAT (Z. anorg. Chem., 1931, **200**, 232—234).—Study of the system $As_2O_3-H_2C_2O_4-H_2O$ at 30° and of solutions of the two acids in a variety of solvents failed to indicate the existence of a solid complex acid. In aq. solution, however, the solubility of each acid is depressed by the presence of the other.

H. F. GILLBE.

Effect of some ions on the transformation of orange antimony trisulphide to the black form. L. LEHRMAN (J. Physical Chem., 1931, **35**, 2763—2765).—Ions accelerate the change in the order $S''>H_2O>NO_3'>Cl'>SO_4''>AcO'$ and $H^{\cdot}>H_2O>Na^{\cdot}>NH_4^{\cdot}$. The change to the black form is gradual, a series of colours being displayed. A rise in temp. also accelerates the transformation.

L. S. THEOBALD.

Internally complex salts of bismuth and of ter- and quinque-valent antimony and arsenic. A. ROSENHEIM [with I. BARUTTSCHISKY, W. BULGRIN, W. PLATO, and G. EBERT] (Z. anorg. Chem., 1931, **200**, 173—199).—Salts of bismuth have been prepared as follows. *Tartrates*: $[Bi(C_4H_4O_6)]OH,H_2O$, $NH_4[Bi(C_4H_2O_6)]$, $C_9H_8N[Bi(C_4H_2O_6)]$, $C_5H_6N[Bi(C_4H_2O_6)],7H_2O$. *Saccharate*: $K[Bi_2(C_6H_{10}O_{16})]$. *Citrates*: $Na[BiOH(C_6H_5O_7)],3H_2O$, $K[BiOH(C_6H_5O_7)]$. *Glycollates*: $[Bi_2(C_2H_3O_3)_3(OH)_2]NO_3,2H_2O$, $[Bi(C_2H_3O_3)_2]OH,H_2O$, $[Bi(C_2H_3O_3)_2]_2SO_4$. 3-*Nitropyrocatecholoxides*: $NH_4[Bi(C_6H_3O_2NO_2)_2]$, $K[Bi(C_6H_3O_2NO_2)_2]$. The following salts of Sb^{III} have been obtained. *Glycollates*: $K[Sb(CH_2O\cdot CO_2)_2]$, $Na[Sb(CH_2O\cdot CO_2)_2]$, $NH_4[Sb(CH_2O\cdot CO_2)_2],H_2O$, $C_5H_6N[Sb(CH_2O\cdot CO_2)_2],0{\cdot}5H_2O$. *Pyrocatecholoxides*: $NH_4[Sb(C_6H_4O_2)_2]$, $K[Sb(C_6H_4O_2)_2],1{\cdot}5H_2O$, $C_5H_6N[Sb(C_6H_4O_2)_2]$, $C_5H_6N[Sb(C_6H_4O_2)_2],C_6H_4(OH)_2$. *Homocatecholoxide*: $NH_4[Sb(Me\cdot C_6H_3O_2)_2],0{\cdot}5H_2O$. *Dipyrocatecholphenylstibinic acid*, $H_2[SbOPh(C_6H_4O_2)_2],4H_2O$, and its pyridine *salt*, $(C_5H_6N)_2[SbOPh(C_6H_4O_2)_2]$, are described. The following salts of As^{III} have been prepared. *Pyrocatecholoxides*: $C_6H_4O_2{:}As\cdot OH$, $NH_4[As(C_6H_4O_2)_2]$, $K[As(C_6H_4O_2)_2]$, $K[As(C_6H_4O_2)_2],C_6H_4(OH)_2,4H_2O$, $Na[As(C_6H_4O_2)_2],C_6H_4(OH)_2,6H_2O$, $Ba[As(C_6H_4O_2)_2]_2,5H_2O$, and corresponding pyridinium, quinolinium, and anilinium *salts*, all without H_2O of crystallisation. *Homocatecholoxides*: $K[As(C_6H_3O_2Me)_2]$, $NH_4[As(C_6H_3O_2Me)_2]$. *Pyrogalloloxide*: $OH\cdot As(C_6H_3O_2\cdot OH)$.

R. CUTHILL.

Distribution [and isolation] of protoactinium in the industrial treatment of the mineral from the Belgian Congo. F. Reymond (J. Chim. phys., 1931, 28, 409—410).—Pitchblende containing 75% U_3O_8 was digested with H_2SO_4, and the residual SiO_2 heated 3 hr. with warm HF (1 : 3) containing a little Ta_2O_5. The dry extract was fused with $BaSO_4$, $KHSO_4$, and $HTaO_3$, the sol. sulphates were removed by hydrolysis, the $BaSO_4$ (and Ra) by dil. HF, and Po by calcination. Comparative activity measurements of the resulting Ta_2O_5 showed that 4—6% of the proto-Ac was present in the residues, 85% being removed with the U in the preliminary digestion with H_2SO_4. This was recovered by adsorption on a gel of $HTaO_3$. Failure to confirm the results of Hahn and Meitner (A., 1921, ii, 150) is attributed to differences in the initial treatment of the mineral. J. Grant.

Sulphurous acid and its salts. IX. Action of sulphurous acid on sulphides of iron, zinc, and manganese. F. Foerster and J. Janitzki (Z. anorg. Chem., 1931, 200, 23—45; cf. A., 1929, 159).—When SO_2 is passed into aq. suspensions of MnS, FeS, or ZnS the action of the H_2SO_3 on the sulphide varies with the solubility of the latter in H_2O, since this determines the concentration ratios of the ions SH′, SO_3H', and H˙. The most sol. sulphide, MnS, gives almost entirely thiosulphate and free S, whereas the most insol. sulphide, ZnS, gives mainly pentathionate and tetrathionate. With FeS at first thiosulphate, S, and trithionate are formed, but on further action the thiosulphate formation decreases and higher polythionates are formed. At first the primary intermediate product SO reacts as follows: $SO+2HSO_3' \longrightarrow H_2O+S_3O_6''$, but this gives place to $SO+2HS_2O_3' \longrightarrow H_2O+S_5O_6''$. The higher is [H˙] the smaller is the concentration of thiosulphate necessary for the commencement of pentathionate formation.

O. J. Walker.

Alleged selenium trioxide of Worsley and Baker. G. B. L. Smith and C. L. Mehltretter (J. Amer. Chem. Soc., 1931, 53, 3562—3563; cf. A., 1930, 48).—SeO_2 contaminated with chlorides and H_2O is precipitated by the action of O_3 on solutions of Se in $SeOCl_2$. J. G. A. Griffiths.

Molybdenum octacyanides. G. A. Barbieri (Atti R. Accad. Lincei, 1931, [vi], 13, 375—377).—The brick-red molybdenum cyanide obtained by the action of warm HNO_3 on $K_4Mo(CN)_8,2H_2O$ (cf. A., 1928, 160) is not $H[MoO_2(CN)_2,2H_2O]$, but contains the ion $[Mo(CN)_8]''''$ and consists of 3 mols. of molybdic acid and 1 mol. of $H_4Mo(CN)_8$. It can also be obtained by treating $K_4Mo(CN)_8,2H_2O$ with a molybdate in acid solution. O. J. Walker.

Volatilisation of polonium and of a deposit of thorium in a current of gas. M. Lecoin (J. Chim. phys., 1931, 28, 411—420).—An electrolytic deposit of Po on Ni was heated in a quartz tube (0·2 cm. diameter) at 750—1000° for 30 sec. in a current of gas, which was then scrubbed with *N*-HCl. The phosphorescence of the tube was photographed, and the Po in solution and dissolved from the walls of the tube (in HCl containing 0·01% HF) was determined from the ionisation activity of a drop of known wt. Volatile Po compounds are produced in A (especially if impure) and in $CO+CO_2$, but not in N_2 or in H_2. A high yield of Th-*C*″ is obtained in O_2 (but none in O_2-free N_2) from a mixture of Th-*B*, Th-*C*, and Th-*C*″; complete separation of this mixture, although difficult, appears to be possible. J. Grant.

Rhenium tetrachloride and the rhenichlorides. H. V. A. Briscoe, P. L. Robinson, and E. M. Stoddart (J.C.S., 1931, 2263—2268).—$ReCl_4$ is the primary product of heating Re in Cl_2. No evidence has been obtained of the existence of the reported $ReCl_6$ and $ReCl_7$. K_2ReCl_6 can be made by synthesis; it gives ppts. with solutions containing the ions Ag˙, Hg˙, Tl˙, but not with solutions containing the ions Pb˙˙, Cu˙˙, Ba˙˙, Co˙˙, Ni˙˙, Mn˙˙, Mg˙˙, Fe˙˙, Fe˙˙˙, Zn˙˙, Li˙, and Hg˙˙. E. S. Hedges.

Monothioper-rhenic acid. W. Feit (Z. anorg. Chem., 1931, 199, 262—270).—By passing H_2S into a conc. solution of a per-rhenate, the monothioper-rhenate is produced quantitatively; the end-point may be estimated approx. by titration with aq. $TlNO_3$. The solution is not very stable, but if polythioper-rhenates are removed by addition of $TlNO_3$ a greenish-yellow solution of the pure compound is obtained. With $AgNO_3$ Ag_2S is precipitated; Pb yields a red ppt. which rapidly turns black and Hg a ppt. which is at first yellow and finally white. The free acid decomposes slowly after liberation in dil. solution yielding Re_2S_7. The *K* salt is very sol. in H_2O and EtOH; the *Rb* and *Cs* salts are less sol., and the pure *Na* salt has been prepared only in solution. The NH_4 and Tl salts are described. The stability of $HReO_4$ is considerably reduced by introduction of 1 atom of S, and the solubility relationships of the salts, all of which are anhyd., are markedly altered.

H. F. Gillbe.

Crystalline ferric oxide tetrahydrate. P. A. Thiessen and R. Koppen (Z. anorg. Chem., 1931, 200, 18—22; cf. A., 1930, 559).—The conditions for obtaining well-defined cryst. hydrates of Fe_2O_3 are discussed. By slow hydrolysis of a boiling dil. solution of $Fe(OEt)_3$ in abs. EtOH cryst. $Fe_2O_3,4H_2O$ has been obtained. The lattice is probably cubic, *d* 3·0—3·1. O. J. Walker.

Metallic carbonyls. IX. Reactions of iron tetracarbonyl. W. Hieber and H. Vetter (Ber., 1931, 64, [*B*], 2340—2346; cf. A., 1930, 1008).—$Fe(CO)_4$ is converted by EtOH into $Fe(CO)_5$ and the *substance* $2Fe(CO)_3,EtOH$, which appears to be dissociated in freezing H_2O into $Fe(CO)_3$ (or its hydrate) and $Fe(CO)_3,EtOH$. Higher alcohols, glycol, etc. appear to yield similar products, but their isolation is complicated by their instability towards heat and the difficult volatility of the reactant. Steam condensed on $Fe(CO)_4$ causes volatilisation of $Fe(CO)_5$ and formation of a red solution probably containing small amounts of $Fe(CO)_3$ hydrate. MeCN and $Fe(CO)_4$ afford $Fe(CO)_5$ and $2Fe(CO)_3,MeCN$, but the change is not accompanied by marked evolution of CO. Decomp. of the tricarbonyl derivatives by acids occurs essentially according to the schemes, $2Fe(CO)_3+2H^+ + Fe^{++}+2CO+H_2+Fe(CO)_4$ (polymerised) and $4Fe(CO)_3+2H^+=Fe^{++}+[Fe(CO)_4]_3+H_2$, which are seldom ideally fulfilled. Reactions depend greatly on the nature, temp., and concentration of acid and are

complicated by disproportionations, $3Fe(CO)_3 = Fe(CO)_5 + 2Fe(CO)_2$ or $2Fe(CO)_3 + 2H^+ = Fe^{++} + Fe(CO)_5 + CO + H_2$. H. WREN.

Complex ruthenium compounds. R. CHARONNAT (Ann. Chim., 1931, [x], **16**, 5—121).—The solution obtained by the action of HCl on RuO_4 contains principally $RuCl_4$, but after boiling with EtOH the *compound* $RuCl_3,HCl,2H_2O$, which exists in two isomeric forms, one red and the other green, separates, both forms yielding $RuCl_3$ when heated. By interaction of the red compound with NH_2Me,HCl the *compound* $[Ru(H_2O)_2Cl_4](H{\cdot}NH_2Me)$ (red) may be obtained. *Pyridinium chlororuthenite*, $(C_5H_5NH)_3RuCl_3,H_2O$ (red), has been prepared in the same way as the NH_4 salt (cf. A., 1925, ii, 586). The only satisfactory method of preparing K_2RuCl_5 is to heat $K_2Ru(H_2O)Cl_5$ or K_2RuCl_6. This compound takes up Cl_2 with formation of K_2RuCl_6, whereas with Br progressive substitution of Cl and finally destruction of the mol. occur. The following complex *compounds* of Ru chlorides with ethylenediamine and pyridine have been prepared: $[Ru(H_2O)Cl_7]H_4,en_2$ (red), $[Ru(OH)Cl_7]H_4,en_2$ (brown), $[RuC_5H_5NCl_5]H_2,(C_5H_5N)_2$ (brown), $[Ru(C_5H_5N)_2Cl_4]$, and $[Ru(C_5H_5N)_2Cl_4]H(C_5H_5N)$ (yellow), and also the *compound* $[Ru(NO)Cl_5]H_2,en$ (red). R. CUTHILL.

Reaction between alkali phosphates and chloroplatinic acid in ammoniacal solution. B. E. DIXON (J.C.S., 1931, 2306—2313).—By reaction of Na_2HPO_4 with $(NH_4)_2PtCl_6$ in presence of excess of aq. NH_3, using very dil. reagents at room temp., the *compound* $H_2PO_4[Pt(NH_3)_4Cl(NH_2)]OH$ is obtained in a pure state. The action of H_3PO_4 gives the *compound* $[Pt(NH_3)_4Cl(NH_2)](H_2PO_4)_2$, evidence of the basicities of the two salts and of the nature of the phosphate radicals being obtained by titrations, using methyl-orange and phenolphthalein in presence of $CaCl_2$. The former compound furnishes a concrete example of the type of intermediate basic salt assumed in the formation and hydrolysis of the chloroamidotetrammine series. The behaviour of Pt dissolved from Pt apparatus during the course of silicate analyses is discussed with special reference to its co-precipitation with $MgNH_4PO_4$. In the accurate analysis of high Fe- and Cr-bearing silicate rocks and minerals it is advisable to separate the Pt at an early stage. E. S. HEDGES.

Sensitivity of chemical precipitation reactions. I. M. KOLTHOFF (Z. anal. Chem., 1931, **86**, 34—40).—A discussion of the relations between solubility, particle size, turbidity, and the sensitivity of nephelometric tests. E. S. HEDGES.

Nephelometric titrations. IV. Effect of shaking and cooling the analytical systems. C. R. JOHNSON (J. Physical Chem., 1931, **35**, 2581—2584; cf. this vol., 1141).—The effect of shaking and cooling on typical systems used in at. wt. determinations is to leave an excess of chloride in the supernatant liquid, yielding a low val. for the calc. at. wt. L. S. THEOBALD.

Determinations with the centrifuge and factors affecting them. H. S. GREENE (J. Amer. Chem. Soc., 1931, **53**, 3275—3284; cf. A., 1922, ii, 309).—Under const. conditions of rate and duration of centrifuging, temp. and rate of precipitation, concentration of solutions, time of keeping before centrifuging, and nature of precipitant, the relation between wt. and vol. of $BaSO_4$ is reproducible to within 1% for appropriate quantities. A similar degree of accuracy is approached in determining S in steel, CaC_2O_4, $Al(OH)_3$, Ni dimethylglyoxime, and nitron nitrate, provided the bore of the capillary is varied between 1·1 mm. for dense crystalline ppts. and 10 mm. for gelatinous ppts. J. G. A. GRIFFITHS.

Systematic analysis of the anions. A. B. DUSCHAK and M. C. SNEED (J. Chem. Educ., 1931, 8, 1177—1186). CHEMICAL ABSTRACTS.

Absorption and separation of hydrogen by means of silver permanganate solutions. F. HEIN and W. DANIEL (Chem. Fabr., 1931, 381—383).—The absorbent consists of 300 c.c. of saturated $KMnO_4$ solution to which are added 40·6 g. of $AgNO_3$ and 20 g. of silvered SiO_2 gel. Absorption of H_2 is complete within 6—10 min., but CH_4 and C_2H_6 are not appreciably absorbed in 90 min. Excellent results are obtained for the analysis of coal gas if CO and unsaturated hydrocarbons are removed before determination of the H_2. A special type of pipette and a mechanical shaking device are described. H. F. GILLBE.

Micro-acidimetric studies. III. Micro-titration of strong acids. J. MIKA (Z. anal. Chem., 1931, **86**, 54—61).—The errors involved are discussed and a procedure is recommended. E. S. HEDGES.

Oxidation-reduction indicators of the triarylmethane group. J. KNOP (Z. anal. Chem., 1931, **85**, 253—275).—The following 12 indicators of this group give satisfactory reversible colour changes in oxidation-reduction titrations and may be used for $KMnO_4$ titrations without making allowance for the quantity of indicator used: acronol brilliant-blue, cyanin B, cyanol fast-green 2G, erioglaucin A, erio-green B, patent-blue A, setocyanin O, setoglaucin O, setopalin conc., xylene-blue AS, xylene-blue VS and xylene-cyanol FF. For the titration of Fe with $KMnO_4$ after reduction with $SnCl_2$ in HCl setoglaucin is recommended; $MnSO_4$ should be added and Ni and Co do not interfere. The colour change with all the above indicators takes place within the oxidation-reduction potential range of $+0{\cdot}71$ to $0{\cdot}81$ volt, *i.e.*, very close to the equivalence point of the $Fe^{\cdot\cdot}$-$KMnO_4$ titration, the potential of which is 0·73 volt. A. R. POWELL.

Determination of water content by distillation with liquids less volatile than water. I. Tetrachloroethane. H. LUNDIN (Chem.-Ztg., 1931, **55**, 762—763).—An apparatus and procedure for the determination of small or large amounts of H_2O in various materials by distilling with $C_2H_2Cl_4$ are described. Experiments with yeast gave results which were independent of the distillation time, provided this exceeded 25 min. E. S. HEDGES.

Conductometric studies. I. Influence of small amounts of carbonic acid on the conductometric titration of acids and alkalis and its elimination. W. POETHKE (Z. anal. Chem., 1931,

86, 45—54).—In the conductometric titration of strong acids with a strong base a small amount of carbonate in the base may generally be neglected, but when a strong base is titrated with a strong acid in an open vessel the CO_2 taken up from the air produces a measurable error. The smallest amount of CO_2 affects the titration of a strong base with a weak acid or a weak base with a strong acid. A procedure for determining the true end-point by taking a large no. of readings in its neighbourhood and extrapolating is described; this is more convenient than attempting the complete exclusion of CO_2. E. S. HEDGES.

Volumetric determination of water. J. LINDNER (Z. anal. Chem., 1931, **86**, 141—153).—Improvements in apparatus and manipulation for the determination of H_2O by decomp. of $C_{10}H_7{\cdot}POCl_2$ (A., 1925, ii, 901) are described. The modified procedure, applied to the determination of H in an org. substance, gives a mean error of only 0 05% on a 1 mg. sample. E. S. HEDGES.

Halogen determinations by Gasparini's method. IV. K. HELLER [with E. FRANKE and G. PEUCKER] (Z. anal. Chem., 1931, **86**, 25—29; cf. A., 1929, 528, 1158).—Gasparini's method (A., 1907, ii, 650) is not recommended for org. halogen compounds which sublime or are decomposed with difficulty by electrolysis. After electrolytic oxidation of the org. substance in H_2SO_4–HNO_3 mixture, Cl can be determined gravimetrically. Illari's method (A., 1930, 101) is inaccurate. E. S. HEDGES.

Determination of chlorides with the highest accuracy. A. B. KEYS (J.C.S., 1931, 2440—2447).—The method recommended is essentially a small-vol. Volhard titration, using only 1—2% excess of $AgNO_3$, all operations being carried out in a single vessel. Only 1—2 c.c. of solution are required and the abs. sensitivity is of the order of 0·001 mg. Cl. A scheme for routine chloride determinations is given. E. S. HEDGES.

Determination of traces of chloride in bromides. I. E. ORLOV.—See B., 1931, 971.

Determination of traces of bromide in concentrated chloride solutions by a single titration. M. BOBTELSKY and R. ROSOVSKAJA-ROSSIENSKAJA (Z. anorg. Chem., 1931, **199**, 283—288).—The method is based on oxidation of the mixture by H_2CrO_4–H_2SO_4 at room temp. and under specified conditions, whereby Br alone is evolved. $MgCl_2$ behaves anomalously and if it is present the total halogen evolved is determined and the amount of Cl, which is proportional to the $MgCl_2$ concentration, is subtracted; Mn should be absent. HCl and $FeCl_3$ are not decomposed at concentrations below $4N$. In presence of Ca an excess of K_2SO_4 must be added. H. F. GILLBE.

Determination of small amounts of bromide in chloride. B. S. EVANS.—See B., 1931, 1009.

Separation and detection of halogen ions involving the use of chloramine-*T*. E. M. GERSTENZANG (J. Chem. Educ., 1931, **8**, 1187—1189). CHEMICAL ABSTRACTS.

Determination of fluorine as calcium fluoride by the method of Berzelius. M. KARASIŃSKI (Bull. Acad. Polonaise, 1931, **A**, 143—147).—Berzelius' method has been modified by discontinuing the use of AcOH in the analysis since CaF_2 is fairly soluble in AcOH. CaF_2 is precipitated alone with $CaCO_3$ and residues in the filtrate are worked up. The gelatinous ppt. of CaF_2 is changed by roasting into a cryst. form which facilitates filtration. The cryst. CaF_2 is less sol. in H_2O. The modified method is more accurate than the old method. W. R. ANGUS.

Determination of oxygen by the polarographic method. J. HEYROVSKY (Arh. Hemiju, 1931, **5**, 162—173).—The content of electro-reducible substances in solutions can be determined from the current–voltage curves obtained in electrolysis with a dropping Hg cathode and a large Hg anode. When solutions exposed to air are examined, the curves exhibit two summits, corresponding with reduction of O_2 first to H_2O_2 and then to H_2O. The method is applicable to the determination of peroxides and atm. O_2, in the absence of ions of noble metals, which should previously be removed by alkali hydroxides. R. TRUSZKOWSKI.

Determination of oxidising agents by the aid of the residual current. G. TAMMANN and H. THIELE (Pflüger's Archiv, 1931, **226**, 694—696; Chem. Zentr., 1931, i, 2785).—O_2 can be detected, and H_2O_2 determined approx., by measurement of the residual current, using a Pt wire anode and platinised Pt foil cathode, and stirring in a closed glass vessel. Blood shaken with O_2 gives a max. residual current of 0·002 milliamp.; in venous blood it is less than 0·0001 milliamp. A. A. ELDRIDGE.

Determination of thiocyanate using the step-photometer. C. URBACH (Biochem. Z., 1931, **237**, 189—198).—$FeCl_3$–HNO_3 reagent is added to the suitably-diluted fluid, and the extinction coeff. is determined and compared with standard extinction coeff.–concentration curves. F. O. HOWITT.

Determination of nitrogen. W. SHIMIDZU (J. Imp. Fisheries Inst. Japan, 1931, **26**, 35—39).—NH_3 is distilled over with steam and the residual liquid removed by passing steam in the reverse direction. CHEMICAL ABSTRACTS.

Determination of nitrates by the brucine method. A. BYCICHYN (Chem. Listy, 1931, **25**, 302—303).—1 c.c. of 2% brucine in $CHCl_3$ and 21 c.c. of conc. H_2SO_4 are added to 10 c.c. of the H_2O, and HNO_3 is determined by comparison of the coloration produced with a standard. R. TRUSZKOWSKI.

Determination of nitrates by Grandval and Lajoux' method. B. A. SKOPINTZEV (Z. anal. Chem., 1931, **85**, 244—252; cf. A., 1885, 1093).—The colorimetric determination of NO_3' with phenol-disulphonic acid gives good results only when the solution contains less than the equiv. of 0·5 c.c. of $0{\cdot}1N$-free alkali or alkali carbonate. NH_4 salts should be destroyed by adding the equiv. NaOH prior to evaporation. Contamination with SO_2 from the burner gases leads to loss of NO_3' during evaporation. The amount of K_2SO_4 in each test should not exceed 80 mg. A. R. POWELL.

Determination of nitrate by electrolytic reduction. L. SZEBELLÉDY and B. M. SCHALL (Z.

anal. Chem., 1931, **86**, 127—134).—NO_3' can be determined by electrolytic reduction at a Cu or Ni cathode in presence of H_3BO_3, followed by direct titration of the NH_3. Some improvements in manipulation are described. The fact that Ni cathodes in addition to Cu cause quant. reduction to NH_3 indicates that the process is not a catalytic effect of the $Cu^{\cdot}$ ion.
E. S. HEDGES.

Reduction of phosphomolybdic acid by methyl-*p*-aminophenol and its use in the determination of phosphorus. S. L. LIEBOFF (J. Lab. Clin. Med., 1931, **16**, 495—499).—The reducing agent is satisfactory, and is stable in presence of Na_2SO_3.
CHEMICAL ABSTRACTS.

Determination of phosphoric acid by the filtration method. H. T. BUCHERER and F. W. MEIER (Z. anal. Chem., 1931, **85**, 331—344).—Precipitation of H_3PO_4 as $Pb_3(PO_4)_2$ or as $(NH_4)_3PO_4,12MoO_3$ is untrustworthy for its gravimetric determination. A hydroxyquinoline molybdate method which is capable of very high accuracy is described. This method is also applicable to the determination of citric acid or citrate-sol. P_2O_5 in fertilisers.
J. W. SMITH.

Determination of small quantities of phosphate. S. G. CLARKE.—See B., 1931, 928.

Micro-analytical determination of phosphoric acid by the molybdate method. H. THURNWALD and A. A. BENEDETTI-PICHLER (Z. anal. Chem., 1931, **86**, 41—45).—The phosphomolybdate ppt. is dissolved in aq. NH_3, $MgCl_2$ is added to the boiling solution, and the ppt. is weighed as $MgNH_4PO_4,6H_2O$. The greatest deviation from the theoretical val. was 0·07%.
E. S. HEDGES.

Use of iodide catalyst in the titration of arsenious acid and permanganate. R. LANG (Z. anal. Chem., 1931, **85**, 176—180).—For a smooth functioning of the KI catalyst in titrations of As_2O_3 with $KMnO_4$ the solution should be at least 0·5*N* with respect to $H^{\cdot}$ and at least 0·1*N* with respect to Cl'. Increase of either concentration separately has no effect, but increase of both simultaneously above the equiv. of 1·3*N*-HCl retards the reaction. HCN and $HgCl_2$ act as catalyst poisons and the presence of F', PO_3', and WO_3'' which form complexes with $Mn^{\cdot\cdot\cdot}$ interferes with the reaction by retarding the rate of reduction of $Mn^{\cdot\cdot\cdot}$.
A. R. POWELL.

Determination of silicon in ferrosilicon. W. HARTMANN.—See B., 1931, 976.

Decomposition flask for the determination of carbon by the wet method. H. ENGEL (Z. anal. Chem., 1931, **85**, 242—243).—The flask has a wide neck through which is passed a H_2O-cooled condenser extending just below the bottom of the neck; the condenser carries a removable glass apparatus through which air is passed into the flask through a tube passing down the centre of the condenser and reaching to the bottom of the flask. The air is freed from CO_2 by passage through 50% KOH solution contained in the inner tube of the apparatus above the condenser. All joints are ground glass.
A. R. POWELL.

Determination of carbon monoxide. H. A. J. PIETERS (Z. anal. Chem., 1931, **85**, 50—60).—In admixture with air CO may be determined by measuring the decrease in vol. when the gases are bubbled through a 10% suspension of I_2O_5 in oleum (25% SO_3). If CH_4 or H_2 is present the oleum should contain only 10% SO_3 and 15—20 min. are necessary for removal of CO. Traces of CO in air may be determined colorimetrically by a method based on the green colour produced in the above reaction using oleum with 25% SO_3. In gases free from O_2 CO may be determined by adding an excess of H_2 and passing the mixture at 250° over asbestos impregnated with reduced Ni, whereby CO is reduced to CH_4 with a reduction in vol. equal to 3 times the vol. of the CO; the method is applicable to the determination of CO in water-gas and in coal gas after the CO_2, O_2, and unsaturated hydrocarbons have been removed in the usual way. A modification of Nicloux' blood method is also described.
A. R. POWELL.

Determination of carbon monoxide in admixture with air. H. A. J. PIETERS (Z. anal. Chem., 1931, **85**, 113—117).—CO is completely oxidised to CO_2 at room temp. by Ag_2O saturated with CO_2 and by MnO_2 prepared by reducing a solution of NH_4MnO_4 with MeOH and drying the ppt. at 120°. The MnO_2 can also be prepared by reducing $HMnO_4$ with $H_2C_2O_4$ or $MnSO_4$. CO is also quantitatively oxidised to CO_2 at 150° by CuO deposited on quartz.
A. R. POWELL.

Helium. X. Determination of traces of radium. F. PANETH and W. KOECK (Z. physikal. Chem., Bodenstein Festband, 1931, 145—161).—The method described permits the determination of quantities of Ra-Em of the order of 10^{-13} Curie with an error of about 20%; it is applicable to a few g. of mineral or ferrous meteorite, and in combination with the method described previously for the determination of the He content of the latter may be employed to calculate the age of the meteorite. The basis of the determination is the differential measurement of the charge in two ionisation chambers, one of which contains the emanation.
H. F. GILLBE.

Determination of potassium together with sodium and magnesium. V. K. FEDORENKO (Ukrain. Chem. J., 1931, **6**, [Sci.], 105—116).—The material is ignited to remove NH_4 salts, if present; the residue is dissolved in 25% H_2SO_4 at 100° (5 c.c. per g. of substance), and digested 1·5—2 hr., in order to expel HCl, when excess of 4% $Ba(OH)_2$ is added (100 c.c. per 5 c.c. of acid+5 c.c. per 0·1 g. of substance). The solution is boiled for 15 min., CO_2 is passed for 5—10 min., and the filtrate and washings are evaporated to a small vol. The solution is titrated on the water-bath with 0·1*N*-H_2SO_4 with Me-red indicator, acid being added as the red coloration fades, until a dry, red residue remains. This is extracted with H_2O, and the solution is filtered, the residue being washed free from SO_4''. The filtrate, containing K, Na, and Mg sulphates, is evaporated to dryness, and the residue is dried to const. wt. and dissolved in 300 c.c. of H_2O. SO_4'' is determined in one 100-c.c. portion and Mg as pyrophosphate in another. The wt. of residue less the calc. val. gives the sum of K and Na sulphates, from the SO_3 content of which the proportion of K to Na is calc. An accuracy of 3% is obtained.
R. TRUSZKOWSKI.

Determination of potassium and nitrite in very dilute solution. R. A. HERZNER (Biochem. Z., 1931, **237**, 129—132).—The coloration produced by sulphanilic acid and α-naphthylamine in AcOH solution in presence of nitrite is applied to the determination of nitrite directly and to that of K following precipitation as K Na cobaltinitrite.

F. O. HOWITT.

Colorimetric micro-determination of potassium. J. FISCHER (Biochem. Z., 1931, **238**, 148—161).—The K in 1 c.c. of neutral or slightly acid solution is precipitated with 1 c.c. of freshly prepared 10% solution of purified stable $Na_3Co(NO_2)_6$. After keeping for 5 hr. in the cold the ppt. is washed free from nitrite with 96% EtOH and dissolved in hot H_2O. The nitrite content (and hence also the K content) of the solution is then determined colorimetrically with the help of Riegler's reagent (A., 1897, ii, 464). From 0·001 to 1·0 mg. of K can thus be determined (error ±3%). Salts of NH_4, Rb, Cs, Ba, Ag, Pb, and Hg^I and also large amounts of H_3PO_4 interfere with the precipitation. If NH_4 salts are present the solution is boiled with dil. NaOH and then neutralised with dil. H_2SO_4.

W. MCCARTNEY.

Volumetric method of determining sodium. J. T. DOBBINS and R. M. BYRD (J. Amer. Chem. Soc., 1931, **53**, 3288—3291).—20—25 mg. of Na in 2—3 c.c. of H_2O are precipitated as Na Zn uranyl acetate by adding 20—30 c.c. of reagent (85 g. of uranyl acetate in 50 c.c. of AcOH+400 c.c. H_2O mixed with 200 g. of $Zn(OAc)_2$ in 25 c.c. of AcOH+250 c.c. of H_2O). The liquid is kept in ice for 1 hr. and the ppt. is then dissolved in 100 c.c. of H_2O and titrated with NaOH, the end-point being determined at the b. p. by means of phenolphthalein. The results agree with the equation $NaZn(UO_2)_3(OAc)_9+10NaOH=9NaOAc+Na_2U_2O_7+ZnUO_4+5H_2O$.

J. G. A. GRIFFITHS.

Determination of cæsium and rubidium, especially in mineral waters. L. FRESENIUS (Z. anal. Chem., 1931, **86**, 182—190).—Details are given of a spectral method and a gravimetric method for determining small quantities of Cs and Rb in presence of complex mixtures of other salts. E. S. HEDGES.

Accurate titration. II. W. PONNDORF (Z. anal. Chem., 1931, **85**, 1—44; cf. this vol., 1022).—Details are given of methods for the standardisation, with an error of 0·01—0·02%, of $AgNO_3$ solutions with NaCl, of KI solutions with $AgNO_3$, and of $Na_2S_2O_3$ solutions with KI, I, or $K_2Cr_2O_7$; possible sources of error and methods for avoiding these are also discussed. 0·1*N* solutions of $Na_2S_2O_3$ which has been twice recryst. from H_2O containing a small quantity of NaOH undergo a slow decrease in titre which is linearly proportional to their age when stored in amber bottles in the dark. A. R. POWELL.

Determination of silver in colloids and organic compounds. V. R. CHERTOK (Farm. Zhur., 1929, 507—509).—Korndörfer's method (Apoth.-Ztg., 1914, **29**, 901) is one of the simplest giving accurate results.

CHEMICAL ABSTRACTS.

Modifications of the micro-determination of calcium and potassium. M. MOUSSERON (Bull. Soc. Chim. biol., 1931, **13**, 831—834; cf. A., 1930, 1011).—A colorimetric method based on the production of a green colour when $CaK_2Ni(NO_2)_6$ is treated with an aq. solution of antipyrine is described.

C. C. N. VASS.

Determination of calcium as oxalate. L. VELLUZ and R. DESCHASEAUX (Bull. Soc. Chim. biol., 1931, **13**, 797—808).—The precipitated oxalate is washed first with an $EtOH-Et_2O$ mixture, finally with Et_2O, dried, suspended in 5% H_2SO_4, and treated with cold 0·066*N*-$KMnO_4$, the excess being determined iodometrically after 5 min. This procedure allows the determination of 0·1—0·5 mg. of Ca with an error less than 3% or, in the presence of Mg, less than 5%.

C. C. N. VASS.

Determination of calcium with picrolonic acid. R. DVORZAK and W. REICH-ROHRWIG (Z. anal. Chem., 1931, **86**, 98—113).—Ca may be determined very accurately as picrolonate, the ppt. $Ca(C_{10}H_7O_5N_4)_2,8H_2O$ containing only 5·64% Ca and crystallising readily. The procedure is suitable for micro-determinations, giving an error of only 0·01 mg. with 2 mg. of Ca. A quant. separation from Mg can be effected, provided that the ratio Ca : Mg does not exceed 1 : 10. The method is particularly suitable for determining the hardness of potable and industrial waters.

E. S. HEDGES.

Nephelometric determination of calcium. A. I. POLINKOVSKI (Trans. State Inst. Test. Building Mat., 1929, No. 27, 11—26).—CaC_2O_4 is unsuitable for nephelometry; NH_3, NH_4 salts, excess of precipitant, and manner of introduction and mixing greatly affect the character of the ppt. CHEMICAL ABSTRACTS.

Determination of strontium in minerals and rocks. W. NOLL (Z. anorg. Chem., 1931, **199**, 193—208).—Various methods of determination of Sr, and especially of the separation from Ca, are reviewed. The usual method, of precipitation with Ca as oxalate and separation by EtOH and Et_2O, yields low results in presence of much Ca; *e.g.*, with a Sr : Ca ratio of 1 : 100 only about 60% of the Sr is recovered. The results are considerably improved if completely anhyd. EtOH and Et_2O are used, but the HNO_3 separation of Rawson is preferable. Sr may be precipitated quantitatively with $PbCrO_4$ from neutral solution, but separation of Sr and Ca cannot be effected by this method since the ppt. is insufficiently stable in slightly acid solution. H. F. GILLBE.

"Oxinate" precipitations. I. Magnesium Precipitation; titration of residue. F. L. HAHN (Z. anal. Chem., 1931, **86**, 153—157; cf. A., 1927, 637).—In presence of NH_4Cl, aq. NH_3, and $COMe_2$, Mg is precipitated by 8-hydroxyquinoline. The excess of 8-hydroxyquinoline is determined by adding standard $KBrO_3$–KBr mixture and titrating back with KI and $Na_2S_2O_3$. Mg combines with 2 mols. of 8-hydroxyquinoline. E. S. HEDGES.

Determination of magnesium as pyrophosphate. V. NJEGOVAN and V. MARJANOVIĆ (Arh. Hemiju, 1931, **5**, 243—252).—The solution containing 0·2—0·3 mg. MgO is evaporated to dryness, 5 c.c. of conc. H_2SO_4 are added, and the vessel is heated at 100° to eliminate HCl and $H_2C_2O_4$, if present. On cooling, 15—20 c.c. of saturated aq. Na_2HPO_4 are

added, and a few drops of phenolphthalein. A mixture of equal vols. of 25% NH_4NO_3 and conc. NH_3 solutions is added to alkalinity, when 150—200 c.c. of H_2O are added, and the solution is maintained for 1 hr. at 100°. On cooling, the ppt. is washed with 2·5% aq. NH_3 and ignited to const. wt. The mean error is 3—4%. R. TRUSZKOWSKI.

Potentiometric titration of zinc chloride solutions. M. PRYTZ (Z. anorg. Chem., 1931, **200**, 133—143).—From the potentiometric titration of aq. $ZnCl_2$ with NaOH by means of a Pt electrode at 25° the val. $1·53\times10^{-10}$ has been obtained for the equilibrium const. of the reaction $Zn^{\cdot\cdot}+H_2O=ZnOH^{\cdot}+H^{\cdot}$ in terms of activities, the value in terms of concentrations being $1·08\times10^{-9}$. The solubility product of $Zn(OH)_2$ is calc. to be $6·28\times10^{-18}$ in terms of activities, and $1·29\times10^{-17}$ in terms of concentrations. The point of inflexion on the titration curve occurs before 2 equivs. of NaOH have been added. R. CUTHILL.

Determination of zinc as oxide, silicate, ferrite, sulphate, and sulphide. II. V. TAFEL and G. SILLE (Z. angew. Chem., 1931, **44**, 792—793).—Nissenson's method for the determination of Zn yields good results with pure Zn ferrite, but will not effect a quant. separation of ZnO,Fe_2O_3 and ZnS, as part of the latter dissolves also. The NaOH method previously described (A., 1930, 1545) is not entirely satisfactory for Zn residues, especially if org. materials are present, and has therefore been modified. The residue is mixed with NaOH and covered with EtOH in a crucible. By careful heating frothing can be avoided, and after being heated at 300° the melt may be analysed for Zn and Fe in the usual way. H. F. GILLBE.

Micro-determination of zinc. M. MOUSSERON and (MME.) M. MOUSSERON (Bull. Soc. Chim. biol., 1931, **13**, 821—830).—Zn is precipitated at 50° in presence of KNO_3 with an excess of $K_4Fe(CN)_6$ as $K_2ZnFe(CN)_6,Zn_2Fe(CN)_6$ which when boiled with aq. NH_3 yields NH_4CN which is titrated with $AgNO_3$ solution. Details are given which enable this technique to be employed in presence of Si, Co, Cu, Fe, Mn, and Al. C. C. N. VASS.

Potentiometric titration of zinc with potassium ferrocyanide. E. BRENNECKE (Z. anal. Chem., 1931, **86**, 175—182).—Potentiometric titration of Zn with $K_3Fe(CN)_6$ at 70° gives results which are uniformly low by 0·98%. The error is reduced to $-0·73\%$ by adding most of the reagent in the cold and finishing the titration at 65—75°. Titration of $K_4Fe(CN)_6$ with Zn salts gives an error of only $-0·46\%$. E. S. HEDGES.

Solid electrodes in electrometric analysis with precipitation reactions. J. A. ATANASIU and A. J. VELCULESCO (Z. anal. Chem., 1931, **85**, 120—138).—The value of two solid electrodes instead of the usual Pt–*N*-$HgCl_2$ system for electrometric analysis has been studied in cases involving titrations with $K_4Fe(CN)_6$ and with $AgNO_3$. The combinations Pt–Ni and Pt–SiC give very sharp potential changes at the end-point of all titrations with $K_4Fe(CN)_6$, whether in neutral or feebly acid solutions. Pt–platinised Pt, Pt–graphite, and Pt–Ta are suitable for titrations of Zn, Cd, Pb, Cu, Ce, Th, La, Ni, and Co, but not of Ag, with $K_4Fe(CN)_6$. For titrations of halogen or SCN ions with $AgNO_3$ only the systems Pt–Ni, Pt–SiC, and Pt–graphite give accurate results. A. R. POWELL.

Quantitative separation of lead and iron. H. FUNK and O. VON ZUR-MUHLEN (Z. anal. Chem., 1931, **85**, 435—438).—The Pb is precipitated as $PbCrO_4$ from the hot solution in presence of AcOH, and the Fe determined in the filtrate. R. CUTHILL.

Analysis of lead ores containing barium. L. GUZELJ.—See B., 1931, 978.

Qualitative analysis of small amounts of cations. A. SCHEINKMANN (Z. anal. Chem., 1931, **85**, 344—346).—The washed group I ppt. is treated with NH_4OAc to remove Pb, and after dissolving the AgCl in aq. NH_3, NH_4OAc is again poured through the filter-paper to dissolve the $HgClNH_2$. NH_4OAc can also be used to dissolve the $HgClNH_2$ and $Pb(OH)_2$ in group IIa. For the detection of Sb and Sn in group IIb, after dissolving the sulphides of these metals in HCl, a little $KMnO_4$ is added. Decolorisation shows the presence of $SbCl_3$ or $SnCl_2$. These are oxidised completely and then starch and aq. KI added. $SbCl_5$ is then reduced with liberation of I, but not $SnCl_4$. Sn in presence of Sb can be confirmed by adding a little Fe powder, warming, filtering, and adding a drop of $Hg_2(NO_3)_2$ and excess of NH_4OAc, when the grey ppt. is formed without the white ppt. normally obtained with Sb present. J. W. SMITH.

Separation and determination of copper and zinc. H. BRINTZINGER (Z. anal. Chem., 1931, **86**, 157—159).—Cu is determined by the KI and $Na_2S_2O_3$ method. The filtrate from the CuI is treated with NH_3 and AcOH and Zn is precipitated as $ZnNH_4PO_4$. The procedure is suitable for the analysis of Cu–Zn alloys. These are preferably dissolved in AcOH or H_2SO_4 with the addition of H_2O_2, which can be removed by boiling before adding KI. Dissolution in HNO_3 is not recommended. E. S. HEDGES.

Determination of metals in solution by means of their spark spectra. F. TWYMAN and C. S. HITCHEN (Proc. Roy. Soc., 1931, **A**, **133**, 72—92).—Details of the sparking vessel, the spectrographs, and the photometric apparatus are given. Experiments were carried out with chlorides of Cu, Zn, Bi, Pb, Ni, and Co in HCl solution, over a concentration range of 0·01—1·00%. The results are given in the form of curves connecting lengths of spectral lines with percentages of metals. It is claimed that the method offers as many advantages for the analysis of solutions of metals for minor constituents as those realised in the spectrographic analysis of alloys, and that the accuracy as regards amounts up to 0·50% equals that obtained by ordinary chemical methods. For percentages lower than 0·5, the spectrographic methods could usually be substituted with advantage for the chemical. L. L. BIRCUMSHAW.

Mercury ammonium derivatives in quantitative analysis. B. ŠOLAJA and V. MATOVINOVIC (Arh. Hemiju, 1931, **5**, 232—235).—$Fe^{\cdot\cdot\cdot}$ and $Co^{\cdot\cdot}$ can be quantitatively separated by double precipitation with $HgNH_2Cl$ in presence of NH_4Cl, or by single precipitation with $C_5H_5N,HgCl_2$ in presence of NH_4Cl. R. TRUSZKOWSKI.

Determinations and separations of the cations of the hydrogen sulphide group. P. WENGER and C. CIMERMAN (Helv. Chim. Acta, 1931, 14, 718—743).—A crit. study. N. H. HARTSHORNE.

Determination of the basicity relationships of samarium and gadolinium by quantitative X-ray analysis. P. GÜNTHER, A. KOTOVSKI, and H. LEHL (Z. anorg. Chem., 1931, 200, 287—304).—Quant. X-ray analysis of rare-earth mixtures by comparison of the true intensities of the $L\alpha_1$ lines is possible in certain cases if the intensity is regarded as proportional to the at. concentration. Accurate analyses are possible with Pr and Nd mixtures, but with mixtures containing Ce the results are less satisfactory. X-Ray analysis of mixtures of Sm and Gd fractionated by aq. NH_3 shows that the basicities of these elements differ very little, that of Sm being the greater. H. F. GILLBE.

Determination of aluminium sulphate and sodium acetate. V. P. ZEMLIANITSIN (J. Chem. Ind. Russ., 1931, 8, 629).—The aq. solution of $Al_2(SO_4)_3$ is filtered from insol. impurities, lime water is added, and excess of the latter is determined by titration with $0{\cdot}1N$-HCl. The no. of c.c. of lime water used multiplied by 0·000747 gives the Al_2O_3 content in g. NaOAc (2 g.) is ignited in a Pt crucible, and the Na_2CO_3 so formed is dissolved in H_2O and titrated with N-HCl. R. TRUSZKOWSKI.

Determination of gallium. A. BRUKL (Z. anal. Chem., 1931. 86, 92—94).—A discussion of methods of procedure. E. S. HEDGES.

Modification of the silver salt–persulphate method for the determination of large quantities of manganese. R. LANG and F. KURTZ (Z. anal. Chem., 1931, 85, 181—185).—The Mn is oxidised to $KMnO_4$ in boiling N-H_2SO_4 by the addition of 10 g. of HPO_3, 3—5 c.c. of $0{\cdot}1N$-$AgNO_3$, and 2 g. of $K_2S_2O_8$. Boiling is continued for 25 min. to destroy excess of $K_2S_2O_8$ and the cooled solution is titrated with $FeSO_4$ to a pale rose colour ($Mn^{\cdots}$ salt), 3 drops of a 1% solution of diphenylamine in H_3PO_4 are added, and titration is continued until the colour changes from violet to yellowish-green. The method is applicable to the determination of Mn in steels. A. R. POWELL.

Manchot's theory of formation of iron peroxide. F. VETTER (Z. anal. Chem., 1931, 86, 134—140).—Experiments are described which show that the production of Cl_2 in the titration of $Fe^{\cdot\cdot}$ by $KMnO_4$ in presence of HCl is not due to the intermediate formation of a peroxide of Fe. E. S. HEDGES.

Application of hexamethylenetetramine as analytical reagent for the determination of metals of the ammonium [hydroxide] group in presence of manganese, nickel, cobalt, and magnesium. P. RAY [with A. K. CHATTOPADHYA and D. BHADURI] (Z. anal. Chem., 1931, 86, 13—24).—Hexamethylenetetramine precipitates quantitatively hydroxides from solutions of $Fe^{\cdots}$, Al, $Cr^{\cdots}$, Ti, U, Zr, and Th salts, but in presence of NH_4 salts Zn, Mn, Ni, Co, and Mg remain in solution. The procedure permits the quant. separation of Fe from all the metals in the latter group; Al is readily separated from all except Ni, although the separation from large quantities of Zn is incomplete, the separation of Ti is quant. except when large amounts of Zn are present, and the separation of U presents no difficulties. E. S. HEDGES.

Detection of iron. F. FEIGL and H. HAMBURG (Z. anal. Chem., 1931, 86, 7—13).—2 : 2′-Dipyridyl in slightly acid solution gives a red coloration with $Fe^{\cdot\cdot}$ salts, the limiting concentration being 10^{-8}. Applied as a spot test, $Fe^{\cdot\cdot}$ may be recognised at a limiting concentration of $1{\cdot}66\times10^{-7}$. $Fe^{\cdots}$ salts give a yellow coloration which interferes with the test only if the ratio $Fe^{\cdots}/Fe^{\cdot\cdot}$ is very high; in such a case KF is added, converting $Fe^{\cdots}$ to $[FeF_6]'''$. Special directions are given for the detection of traces of Fe in fluorides, Hg salts, Al_2O_3, pyrolusite, and Ni. E. S. HEDGES.

Micro-titration of iron with permanganate. I. J. KNOP and O. KUBELKOVÁ (Z. anal. Chem., 1931, 85, 401—428; cf. A., 1929, 670).—By micro-titration with $0{\cdot}001N$-$KMnO_4$, using various $CHPh_3$ dyes as indicators, as little as 0·1 mg. Fe may be determined with a precision of 0·3—0·4%. The titration can be carried out in presence of either H_2SO_4 or HCl, but a considerable excess of $MnSO_4$ should be present. R. CUTHILL.

Determination of iron in presence of manganese by hydrazine hydrate. A. JÍLEK and V. VICOVSKÝ (Coll. Czech. Chem. Comm., 1931, 3, 379—384).—About 2 g. of NH_4Cl are added to a dil. solution of $Fe^{\cdots}$ and $Mn^{\cdot\cdot}$ salts and then dil. aq. NH_3 until the solution turns Me-red to yellow (p_H=4·4—6·2). The boiling solution is precipitated by a slight excess of aq. N_2H_4,H_2O (1 : 25) added in one portion. A granular ppt. is obtained which, after further boiling, must be filtered and washed with hot aq. NH_4Cl (1 g per 100 c.c. and 1 c.c. N_2H_4,H_2O) and then with hot H_2O until the Cl′ is removed, and finally calcined and weighed as Fe_2O_3. The method compares satisfactorily with the determination by hydroxyquinoline or pyridine. The Mn may be determined in the filtrate by the phosphate, hydroxyquinoline, or sulphide method. M. S. BURR.

Polarographic studies with the dropping mercury cathode. XXIII. Simultaneous determination in the groups iron, chromium, aluminium and nickel, cobalt, zinc, manganese. J. PRAJZLER (Coll. Czech. Chem. Comm., 1931, 3, 406—417).—The height of the "wave" in the current-voltage curve, obtained in the electrolysis, with a dropping Hg cathode, of solutions containing elements of the $(NH_4)_2S$ analytical group in the presence of indifferent salts may be taken as a measure of the concentration of the element and a method for the detection and determination of mixtures is based on it. In the sub-group Fe, Cr, and Al the three metals may be simultaneously determined in solution. The solution must be diluted to 10^{-4}—$10^{-3}M$ and be only slightly acidic. In the sub-group Zn, Ni, Co, and Mn, under similar conditions, Co and Mn may be determined directly, but Zn and Ni deposit together. After the addition of $(NH_4)_2C_2O_4$, however, Ni, Co, and Mn form more stable complexes than Zn. The Zn, in these circumstances, gives an easily measurable

wave on the polarographic curve, and can thus be determined directly, Ni being found subsequently by difference. The degree of accuracy depends on the constancy of the height of a wave and the precision of measurement. It is within 5%, the precision remaining the same down to a concentration of 10

M. S. BURR.

Detection of cobalt in presence of elements of group III. T. BERSIN (Z. anal. Chem., 1931, **85**, 428—433).—The following brown *compounds* have been obtained by interaction in solution of thioglycollanilide with Co^{III}, Ni, and Fe^{II} salts, respectively ($X=S\cdot CH_2\cdot CO\cdot NHPh$): $CoX_3,4H_2O$, $[Co(S\cdot CH_2\cdot C(O)\colon NPh)_3]Co$, NiX_2, and FeX_2. By means of the precipitation of the first compound as little as 0.5×10^{-6} g. Co may be detected in 5 c.c. of solution, and, as this compound, but not the others, is insol. in dil. acids, Co may be detected in presence of Fe^{II}, Ni, Al, Zn, Cr, and Mn, the sensitivity of the test being, however, diminished by these metals.

R. CUTHILL.

Iodometric determination of chromium and separation from iron and nickel. E. SCHULEK and A. DÓZSA (Z. anal. Chem., 1931, **86**, 81—92).—$Cr^{\cdots}$ is oxidised to Cr_2O_7'' by means of NaOBr, excess of NaOBr is removed by PhOH, KI is added, and the liberated I titrated with $0.1N$-$Na_2S_2O_3$. If Fe and Ni are present, a single oxidation does not suffice to separate Cr and the process must be repeated according to the amounts present. $Cr(OH)_3$ is readily occluded by $Fe(OH)_3$.

E. S. HEDGES.

Determination of uranous ion in presence of formic acid. C. OUELLET (Helv. Chim. Acta, 1931, **14**, 967—971).—The addition of KCl as an anti-oxidant enables the precipitation and subsequent manipulation of uranous compounds to be carried out in the presence of air without danger of oxidation within 1—2 hr. Uranous salts in presence of HCO_2H may also be titrated with $KMnO_4$ in cold acid solution if only relative vals. are required. The actual results are too high.

F. L. USHER.

Determination of antimony in the presence of tin. D. BARKOVIC (Arh. Hemiju, 1931, **5**, 236—238).—The mixed Sb and Sn sulphides are dissolved in boiling 20% HCl, and aq. H_2S is added gradually until a slight ppt. forms. The solution is boiled further until the ppt. redissolves and is cooled slowly, when a red ppt. appears in the presence of Sb (min. 0·01 mg. $Sb^{\cdots}$). This method allows 1 part of Sb to be detected in the presence of 100 of Sn.

R. TRUSZKOWSKI.

Detection of bismuth. G. LOCHMANN (Z. anal. Chem., 1931, **85**, 241—242).—A large drop of 5% KI solution is placed on a piece of thin filter-paper; the hydroxide ppt. to be tested for Bi is dissolved in 10% HNO_3 and 1 drop of the solution is placed in the middle of the KI drop. If Bi is present a black spot surrounded by a yellow circle appears; on washing this spot with hot H_2O the dark centre suddenly turns bright red due to the formation of BiOI.

A. R. POWELL.

Adiabatic calorimetry at high temperatures. W. KANGRO and R. GRAU (Z. physikal. Chem., Bodenstein Festband, 1931, 85—92).—Details are given of the construction and operation of a high-temp. adiabatic calorimeter based on the principle previously described (A., 1928, 729). Measurement of the heat of conversion of opianoximic anhydride into hemipinimide yields 52·5±0·1 kg.-cal. per mol., in close agreement with the val. derived from the heat of combustion of the two compounds, viz. 52·5±0·8 kg.-cal. per mol.

H. F. GILLBE.

Combustion of substances containing chlorine in Berthelot's bomb. L. SMITH [and, in part, E. SCHJANBERG] (Svensk Kem. Tidskr., 1931, **43**, 213—226).—Errors in the determination of heats of combustion of substances containing Cl by the Berthelot–Matignon method due to the presence of unreduced Cl_2 in the gaseous products are not satisfactorily eliminated by use of As_2O_3. The gaseous phase contains NOCl, Cl_2, and HCl and methods for their determination and the corresponding heat corrections are described. The proportion of Cl_2 decreases as the concentration of the As_2O_3 solution is increased from 0·07 to 0·38N, and if 99·7 instead of 96% O_2 is used. Addition of increasing amounts of paraffin to the substance causes first an increase and subsequently a decrease in the amount of Cl_2 in the gaseous phase. Correction for liquid products involves the determination of H_3AsO_3 (by $KMnO_4$ titration), total $HCl+HNO_3+As_2O_5$ (by titration with alkali and Me-orange to p_H 4·3), and of Cl′ by Volhard's method. Dissolved Au is determined by precipitation with H_2O_2 in alkaline solution, and Pt by precipitation with H_2S, the amount of these metals (from the bomb) dissolved increasing with increasing Cl content of the substance. An approx. determination of heat tone by this method is described. The use of quartz-wool slightly lowers the water equiv. The action of quartz-wool is not merely acceleration of the reduction of Cl by As_2O_3 since, under the same conditions more of the latter is oxidised when quartz-wool is absent (Cl remains in gas phase) than when it is present (no Cl remaining), but is also due to the sp. action of the moist wool, probably in displacing the equilibrium $2H_2O+2Cl_2 \rightleftharpoons 4HCl+O_2$. Using the above corrections the vals. of the heats of combustion of α- and β-chlorohydrin, αα′- and αβ-dichlorohydrin, and epichlorohydrin are 3641±1·3, 3647·4±2·1, 3152·8±2·2, 3187·9±1·7, and 4532·3±2·2, g.-cal. per g., respectively.

J. W. BAKER.

Use of a hot-cathode helium lamp as a source of monochromatic light for the polariscope. A. ROTHEN (Science, 1931, **74**, 204—205).—With the He lamp described, polariscopic measurements can be made to ±0·003° and ±0·002°, respectively, with the yellow and red He lines.

L. S. THEOBALD.

Standardisation of turbidity values in nephelometric determinations. II. Simplified preparation of a turbidity standard. J. A. DE LOUREIRO (Biochem. Z., 1931, **239**, 310—313; A., 1930, 1391).—By adapting the instrument used and plotting the curves on exponential paper (since the changes conform to the exponential law) the procedure previously described is improved and simplified.

W. MCCARTNEY.

Comparative spectrophotometric measurements. M. BARNARD and P. MCMICHAEL (J. Opt.

Soc. Amer., 1931, **21**, 588—614).—The American Photoelectric Corporation spectrophotometer is described. Data obtained with it are compared with the findings of the Bureau of Standards. A discussion is appended. J. LEWKOWITSCH.

Spectrophotometry. K. S. GIBSON (J. Opt. Soc. Amer., 1931, **21**, 564—587).—The methods and apparatus in use at the U.S. Bureau of Standards are described in detail. The degree of agreement of visual, photo- and thermo-electric methods is illustrated. J. LEWKOWITSCH.

Applicability of photo-electric cells to colorimetry. H. E. IVES and E. F. KINGSBURY (J. Opt. Soc. Amer., 1931, **21**, 541—563).—The accuracy and reproducibility of various types of photo-electric cell have been examined. Precision is obtainable only when a substitution method is used, as in visual photometry. J. LEWKOWITSCH.

Neutral ultra-violet lighting in investigation of structure. H. LANGENBRUCH (Chem.-Ztg., 1931, **55**, 761—762)—A vertical illuminator has been constructed for ultra-violet photography. The "neutral" effect of this method of lighting is especially useful in forensic investigations such as the examination of paint films on metals, the effect obtained being independent of the direction of spreading the paint. E. S. HEDGES.

Observation of striæ in chemical processes. III. Observation with the unaided eye ("visual method"). H. ALBER and M. VON RENZENBERG (Z. anal. Chem., 1931, **86**, 114—127; cf. A., 1929, 24).—A simple method described for the observation of striæ in liquids is sensitive to a change of 0·0001—0·0002 in the value of n and has the advantage over the microscopical method that it is applicable up to changes of 0·025. E. S. HEDGES.

Iron resistance lamps. C. KROGER (Chem. Fabr., 1931, **4**, 365—367).—The construction of Fe wire resistances for the automatic control of electric furnaces is described (cf. Ostwald and Luther, "Physikochemische Messungen," Leipzig, 1925, 452). N. H. HARTSHORNE.

Bridge for the measurement of the conductance of electrolytes. P. H. DIKE (Rev. Sci. Instr., 1931, [ii], **2**, 379—395).—An improved bridge for d.c. and a.c. measurements is described. N. M. BLIGH.

Direct electric heating of the micro-furnace in Pregl's method of organic micro-analysis. F. ENGELHARD (Z. anal. Chem., 1931, **85**, 61—64).—The furnace for heating the PbO_2 tube comprises a cylindrical Cu block covered with asbestos paper around which is wound the heating wire. The whole is covered with an insulating paste and several layers of asbestos and inserted in an unglazed porcelain tube. The temp. is regulated by an external resistance comprising lamps with Fe wire filaments in H_2. A. R. POWELL.

Sodium coulometer. O. J. STEWART (J. Amer. Chem. Soc., 1931, **53**, 3366—3369; cf. A., 1925, ii, 921; 1927, 1049).—Each electrode is an evacuated glass tube 1·3 cm. in diameter and 9 cm. long through the wall of which is sealed a Pt wire brazed to a stout Ni wire extending to the bottom of the tube, and contains 15 g. of Cd; the anode also contains 0·5 g. of Na. Electrolysis in $NaNO_3$ baths at 340° leads to a slight etching of the cathodes, probably due to small electrolytic loss of silicate ions. The results of the anodic Na coulometer agree with those of the Ag coulometer and are accurate to 1 part in 10^4. J. G. A. GRIFFITHS.

Measurement of the electrical resistivity of mineral waters at their source. A. GUILLERD (Ann. Falsif., 1931, **24**, 411—422).—A portable "auditometer" is described; the electrical resistivity of H_2O can be measured with 200 c.c., using the principle of Kohlrausch's modification of the Wheatstone bridge. The H_2O is placed in an oblong vessel of ebonite, fitted with two parallel plates of Ag or Ag-plated Cu. A table is given so that all results may be calc. to 18°. The determination of the resistivity of H_2O is an accurate method of detecting pollution, whether this be from H_2O of a higher stratum or the surface. T. MCLACHLAN.

Processes in electro-filtration. G. MIERDEL and R. SEELIGER (Naturwiss., 1931, **19**, 753—754).—The influence of the electric blast, the structure of macroscopic streams, and the radial transportation of particles to the precipitation electrodes are discussed. W. R. ANGUS.

Stirrer-condensers. J. FRIEDRICHS (Chem. Fabr., 1931, 367—368).—Improved forms of combined reflux condenser and stirrer, in which wear at glass bearing surfaces is eliminated, are described. N. H. HARTSHORNE.

Effect of storage of distilled water in glass ampoules on the alkalinity and total solids content. A. O. MATTHEWS (J. Amer. Pharm. Assoc., 1931, **20**, 767—770).—The corrosion of Jena glass ampoules by freshly distilled sterile H_2O (p_H 6·2, total solids 1·5 mg. per litre) when kept at 22—27° for 18 months was relatively slow. The inorg. solids rose from 1·5 to 3·7 mg. per litre and the average p_H was 6·7. No glass splinters or platelets were liberated. E. H. SHARPLES.

Fractionating heads. J. ERDOS (Z. anal. Chem., 1931, **85**, 118—119).—Modifications of the Hempel fractionating head are illustrated; they permit intermediate fractions of the distillate to be collected from below the glass bead column. A. R. POWELL.

Isolation of readily volatile substances in very dilute solution. A. A. BENEDETTI-PICHLER and F. SCHNEIDER (Z. anal. Chem., 1931, **86**, 69—80).—The distillation flask described permits a highly conc. solution of the more volatile component to be obtained in a single distillation of 0·01% solutions of EtOH, $COMe_2$, $CHCl_3$, and Et_2O and 0·1% MeOH. E. S. HEDGES.

Ionisation manometer. E. K. JAYCOX and H. W. WEINHART (Rev. Sci. Instr., 1931, [ii], **2**, 401—411).—A gauge for pressure measurements of the order 10^{-9} mm. Hg, and free from Barkhausen oscillation difficulties, is described. N. M. BLIGH.

Manometer for measuring low pressures of readily condensable gases. T. G. PEARSON (Z. physikal. Chem., 1931, **156**, 86—88).—The apparatus

consists essentially of a U-tube to the bend of which is sealed a vertical capillary. The Hg meniscus in one arm, which is closed, is always adjusted to a fixed point, and the displacement in the other arm when connected to the source of pressure is reproduced in magnified form by the meniscus in the capillary. A precision of 0·005 mm. is attainable. R. CUTHILL.

Improved McLeod gauge. S. D. BRYDEN, jun. (Rev. Sci. Instr., 1931, [ii], **2**, 514—518).—The connexion to the vac. system is made through the top of the compression chamber, instead of by means of the usual T-joint below it. C. W. GIBBY.

Glass electrode determination of sodium in sodium chloride–potassium chloride mixtures. F. URBAN and A. STEINER (J. Physical Chem., 1931, **35**, 3058—3062).—The determination of Na in mixtures of NaCl and KCl by means of the glass electrode is outlined. An equation for the mixed electrode potential is given. L. S. THEOBALD.

Glass electrode. D. A. MACINNES and D. BELCHER (J. Amer. Chem. Soc., 1931, **53**, 3315—3331; cf. A., 1930, 423; 1929, 673).—With an improved apparatus, it is shown that between p_H 2 and 8 the H_2 and glass electrodes agree to within $\pm$0·0001 volt if corrections are made for the "asymmetry potential." Deviations depending on the nature of the positive ion are observed at $p_H>8$, and at $p_H<2$ deviations of an opposite kind, dependent on the negative ion, occur. Most of the apparent resistance of glass electrodes determined by d.c. measurements is due to polarisation. This resistance is increased greatly by drying even at room temp. Theories of the glass electrode are discussed. J. G. A. GRIFFITHS.

Apparatus for effecting exact micro-dilution. L. DEVILLERS (Bull. Biol. Pharm., 1931, **3**, 309—310).—Exact dilutions of min. quantities of liquids can be effected by use of a modified Pasteur's pipette and a burette. C. C. N. VASS.

Sampling burette. E. SCHILLER (Chem.-Ztg., 1931, **55**, 732).—A sampling tube, into the lower part of which is sealed an internal tube with graduated scale, has a stopcock near its upper end and can be closed by a stopper at the lower end. Into the ground upper end is fitted a detachable burette with top and bottom stopcocks, this being protected by a glass cap attached to the sampling tube. In operation, samples from various sources are collected in any desired, measured quantities in the sampling tube and mixed by inverting the tube. They are then drawn into the burette. Contamination by exposure to air is thus avoided. W. J. WRIGHT.

Syringe-pipette for precise analytical usage. A. KROGH and A. B. KEYS (J.C.S., 1931, 2436—2440).—The apparatus delivers rapidly a desired vol. of liquid (1—2 c.c.) with an accuracy of 0·1 cu. mm. By counteracting expansion with another expanding system the temp. error is eliminated. E. S. HEDGES.

Capillary viscosimeter with a device at the orifice to prevent the disturbing effect of surface tension on the determination. A. PARLOW (Chem.-Ztg., 1931, **55**, 683).—The apparatus comprises a cylindrical glass reservoir terminating in a capillary tube the lower end of which opens out into a small glass bell from the bottom of which a thin glass rod protrudes upwards into the mouth of the capillary so that the drops of liquid run down the rod into the glass bell, from which they emerge through a small hole at the side. The whole is mounted in the usual water-jacket with stirrer and thermometer for maintaining a constant temp. A. R. POWELL.

Filtration of colloidal solutions. W. D. JANKOVSKI (Biochem. Z., 1931, **238**, 101—103).—A simple method of filtering colloidal solutions is described. W. McCARTNEY.

Simple muffle furnace with low gas consumption. R. HOEVERS (Chem. Weekblad, 1931, **28**, 550—551).—A simple construction, in which special attention has been paid to heat insulation, is illustrated. S. I. LEVY.

Method of obtaining air currents of different humidities. J. B. SETH (Nature, 1931, **128**, 638—639).—Any desired humidity can be produced by regulating the strengths of a current of dry air and of air saturated with H_2O. L. S. THEOBALD.

Conversion of the Mohr–Westphal balance for other normal temperatures and density units. W. BLOCK (Chem. Fabr., 1931, 374—376, 383).—The balance may be employed for determination of vals. of d_4, and of d^{15} and d^{20} of liquids, by modifying either the wt. of the rider of the volume of the float; the necessary calculations are given, together with a table of corrections for use when the balance is employed in its normal form. H. F. GILLBE.

Use of chromium steel vessels in analysis. A. KRUGER (Chem.-Ztg., 1931, **55**, 682—683).—Evaporating dishes of Cr steel are suitable for analytical operations involving strongly alkaline solutions, *e.g.*, the separation of Al from Fe with NaOH. The vessels also resist the action of aq. NH_3 and feebly alkaline Na_2S solution. A. R. POWELL.

Tables and charts of specific gravity and hardness for use in determination of minerals. J. L. ROSENHOLTZ and D. T. SMITH (Rensselaer Poly. Inst., Eng. and Sci. Series, no. 34, 83 pp.).—Alphabetical lists and charts for facilitating identification are given. C. W. GIBBY.

Applications of the Schlieren method of photography. D. B. GAWTHROP (Rev. Sci. Instr., 1931, [ii], **2**, 522—531).—Photographs are given illustrating the uses of the method, which depends on the disturbances in density produced in air by heat, by the motion of projectiles, by the emergence of other gases from jets, etc. C. W. GIBBY.

Geochemistry.

Changes in the ozone concentration of the atmosphere. R. RUEDY (Physical Rev., 1930, [ii], **35**, 295).—Increased O_3 has not been detected for the few days before or after strong magnetic storms.
L. S. THEOBALD.

Significance of the ozone content of the atmosphere. R. MECKE (Z. physikal. Chem., Bodenstein Festband, 392—404).—By consideration of existing spectroscopic data it is shown that the photochemical equilibrium between O_3 and O_2 is determined by two processes: the first is the formation of O atoms and O_3 from O_2 and O_2 excited by radiation of wave-length below 2025 Å., and the second the decomp. of the O_3 into excited O atoms and mols. under the influence of radiation of wave-lengths up to 2655 Å. At low O_3 concentrations and sufficiently low pressures the mass action relationship $k=[O_3]^2/[O_2]^3$ is valid. Calculation from the pressure and the intensity of de-ozonising radiation which exists at a height of 50 km. yields for the max. O_3 content of the atm. at that level 2×10^{-4}, compared with an observed content at ground level of about 10^{-8}. At higher or lower pressures the calc. O_3 content falls very rapidly.
H. F. GILLBE.

Phenomena of the upper atmosphere. S. CHAPMAN (Proc. Roy. Soc., 1931, **A**, **132**, 353—374).—Data relating to the upper atm. are summarised and correlated. Subjects dealt with are: solar ultra-violet radiation; absorption of solar radiation; separate absorbing layers in the earth's atm.; dissociative effects of solar radiation; O_3 layer; ionisation by ultra-violet radiation; absorption coeffs.; max. electron densities and corresponding gas densities; level of the layer ionised by ultra-violet radiation; ionising agent in the lower layer; nature of, and daily variation of, ionisation in the two layers; green light of the night sky.
L. L. BIRCUMSHAW.

Sea-water at Puget Sound Biological Station from Sept. 1928 to Sept. 1929. T. G. THOMPSON and M. W. JOHNSON (Pub. Puget Sound Biol. Sta., 1930, 7, 345—368).
CHEMICAL ABSTRACTS.

Occurrence of fluorides in some waters of the United States. H. V. CHURCHILL (Ind. Eng. Chem., 1931, **23**, 996—998).—Traces of CaF_2 have been found in certain natural waters. The localities are those in which the dental defect known as "mottled enamel" is prevalent. The relative severity of the defect in the different areas appears to be correlated with the concentration of CaF_2, but a causal connexion is not definitely established.
E. S. HEDGES.

Specific gravities and vapour pressures of concentrated sea-water at 0—175°. K. HIGASHI, K. NAKAMURA, and R. HARA (J. Soc. Chem. Ind., Japan, 1931, **34**, 72B).—The sp. gr. and v. p. were determined for ordinary up to nearly saturated concentrations of NaCl in the temp. range 0—175°. The stable modification of $CaSO_4$ in equilibrium with the brines and the effect of its saturation on the sp. gr. of the brines were taken into consideration.
F. SALT.

Samelia meteorite. L. L. FERMOR (Rec. Geol. Survey, India, 1931, **65**, 161—162).—A section of this meteorite, polished and etched, confirms it as a coarse octahedrite. The lamellæ are 1—2·5 mm. wide and consist of broader bands of kamacite bordered by narrower bands of tænite. These cross one another, the interspaces being filled with plessite, which appears to be a eutectic mixture of kamacite and tænite.
C. A. SILBERRAD.

Unusual iron meteorite from Mexico. H. H. NININGER (Amer. J. Sci., 1931, [v], **22**, 360—363).—The meteorite (wt. about 70·8 kg.) has an unusually high content of Ni (16·23%) and of Pt metals (0·014%), and is low in S (0·07%); Mg is present in traces.
C. W. GIBBY.

Differentiation in the Shonkin Sag laccolith, Montana. F. F. OSBORNE and E. J. ROBERTS (Amer. J. Sci., 1931, [v], **22**, 331—353).—A detailed petrological description is given. Differentiation into chemically dissimilar rocks is due principally to crystal settling. Its great extent is probably due to the alkalic nature of the magma.
C. W. GIBBY.

Twinned plagioclase felspars in rocks from Sirohi State, Rajputana. A. L. COULSON (Rec. Geol. Surv. India, 1931, **65**, 163—172).

Diamonds with quartz intergrowths. C. W. CORRENS (Z. Krist., 1931, **80**, 37—44).—Diamonds with quartz intergrowths occur in the Campo do Sampaio mine (Diamantina, Minas Geraes, Brazil), in a conglomerate of coarse sandstone cemented by sericitised material. It has probably been deposited in fissures in the diamond, first formed by rock movements, and then enlarged by hot alkaline solutions or superheated steam, either of which would also cause the sericitisation.
C. A. SILBERRAD.

Density and structure of millerite. N. H. KOLKMEIJER and A. L. T. MOESVELD (Z. Krist., 1931, **80**, 91—102).—Millerite, prepared according to Thiel and Gessner's method (cf. A., 1914, ii, 277), d^{18} 5·348, has a rhombohedral unit cell, r 5·636 Å., α 116° 35′, with 3 mols. The at. radius of S is 1·6, of Ni 0·7 Å. (cf. A., 1928, 390).
C. A. SILBERRAD.

Acid volcanic rock of Kara-Dagh, Crimea. D. V. SOKOLOV and A. F. FIOLETOVA (Trans. State Inst. Test. Building Mat., Moscow, 1930, no. 34, 33—45).—Liparite (K_2O+Na_2O 8·75, Fe 0·44, Ti 0·10%) should be suitable for glass manufacture. The presence of 0·050% V_2O_5 in andesite is recorded.
CHEMICAL ABSTRACTS.

Fergusite from Talasser Alatau, Turkestan. V. NIKOLAIEV (Zentr. Min. Geol., 1931, **A**, 33—42; Chem. Zentr., 1931, i, 2599).—The fergusite contains orthoclase 45, 37; nepheline 8·8, 16·9; granaphyre 9·7, 7·0; pyroxene 23·5, 12·0; biotite 6·0, 12·8; melanite 4·1, 10·8; apatite 0·5, 0·8; magnetite 2·1, 1·7; calcite 0·5, 0·6%.
A. A. ELDRIDGE.

Aegirite-augite glaucophane quartz schist from the province of Teshio, Hokkaido, Japan. J. SUZUKI (Proc. Imp. Acad. Tokyo, 1931, 7, 283—286).—The schist obtained from the bed of the river Chirashibe shows microscopically successive layers of different mineralogical composition, thin layers of quartz and felspar grains, and others rich in glauco-

phane and aegirite-augite arranged in layers sub-parallel to the plane of schistosity.

C. C. N. VASS.

Danburite from Obira, Japan. Z. HARADA (Z. Krist., 1931, 79, 349—366; cf. this vol, 415).—Danburite occurs in good crystals exhibiting 72 forms; *d* 2·994±0·002; analysis: SiO_2 48·04, B_2O_3 27·80, CaO 21·97, MgO 0·76, $Fe_2O_3+Al_2O_3$ 1·00, loss on ignition 0·60%. n_α, n_β, n_γ were determined for numerous wave-lengths from λ 7082·0 (1·6267, 1·6296, 1·6324) to λ 2967·3 (1·6752, 1·6777, 1·6815).

C. A. SILBERRAD.

Constitution of mica. IX. Biotites. J. JAKOB (Z. Krist., 1931, 79, 367—378).—Analyses of single crystals of phlogopite from (1) Val Cannobino, Italy, (2) Burgess, Ontario, and of biotites (3) and (4) from Montido Daro, Bellinzona, (5) and (6) Claro, Ticino, and (7) St. Gotthard give, in this order: SiO_2 40·21, 40·82, 37·88, 37·71, 35·35, 35·30, 37·43; TiO_2 2·80, 1·15, 2·06, 1·64, 3·16, 2·71, 1·95; Al_2O_3 12·60, 12·79, 19·23, 19·29, 18·46, 18·86, 16·50; Fe_2O_3 0, 0, 4·09, 2·24, 4·03, 4·08, 5·03; FeO 2·52, 1·90, 10·47, 9·72, 16·26, 16·85, 15·84; MnO 0·02, 0·04, 0·30, 0·31, 0·61, 0·44, 0·22; MgO 25·45, 26·45. 13·19, 14·22, 8·46, 8·06, 11·17; Na_2O 1·78, 1·50, 1·40, 1·33, 1·34, 1·64, 1·69; K_2O 9·26, 10·80, 9·85, 9·33, 6·69, 8·97, 8·90; $H_2O(+110°)$ 4·58, 3·93, 1·56, 4·29, 5·72, 3·13, 2·22%; (1) contains also Cr_2O_3 0·76, and NiO 0·18; and (2) F 1·00. From (1) the Fe was readily removed by HCl, the colour changing from brown to the green of Cr_2O_3. On the basis of these analyses and a method of determining the amount of original FeO oxidised to Fe_2O_3, the composition of the biotites, like that of the muscovites (cf. A., 1930, 1016), can be expressed by varying nos., always totalling 25, of units containing the radicals $Al(SiO_4)_3$, $Mg(SiO_4)_3$, and $Mg(SiO_5)_3$, Si being partly replaced by Ti, Al by Fe^{III}, Cr^{III}, Mn^{III}, and Mg by Fe^{II}, Ca, etc. The number of possible varieties is 510.

C. A. SILBERRAD.

Physico-chemical properties of Japanese acid clay. VI. X-Ray studies. I. K. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1931, 34, 244—247B).—Japanese acid clays of various origin give the same 7 characteristic *X*-ray diffraction lines as English fuller's earth or German activated clay, attributed to a cryst. kaolinite common to them all. This is stable at 600—900° and is unaffected by the extraction of 40% of the total SiO_2 by 20% NaOH.

C. HOLLINS.

Silberkiese as a solid solution. V. NIKITIN (Arh. Hemiju, 1931, 5, 184—192).—Crystallographic and analytical data indicate that silberkiese is a solid solution in FeS_2Ag of FeS or of $(FeS_2)_2Fe$.

R. TRUSZKOWSKI.

Vanadium in Chibiny. M. B. ZAPADINSKI (Ukrain. Chem. J., 1931, 6, [Tech.], 23—31).—Chibiny egerite and titanomagnetite contain about 0·5%, apatite 0·04%, and nepheline traces, of V_2O_5.

R. TRUSZKOWSKI.

Occurrence of the platinum metals in the earth's crust. I. NODDACK and W. NODDACK (Z. physikal. Chem., Bodenstein Festband, 1931, 890—894).—Various analyses are summarised. The ratio of the fractions of the Pt metals in meteorites to those in the earth's crust is for Ru 500, Pd 583, Pt 140, Os 122, Rh 86, and Ir 43. The crust thus appears to be impoverished with regard to these metals, but a probable cause is the preponderance of eruptive rocks in the crust. Below 16 km. considerable quantities of Ru, Os, and Pd may exist.

H. F. GILLBE.

Forest types in the south-west as determined by climate and soil. G. A. PEARSON (U.S. Dept. Agric. Tech. Bull., 1931, no. 247, 143 pp.).—The distribution of forest trees is largely controlled by the mean temp. and H_2O content of the soil. All species have approx. the same wilting point in the same soil. Soil conditions other than depth, texture, and org. matter content rarely become limiting factors in the distribution of species.

A. G. POLLARD.

Chemical composition of some chernozem-like soils of N. Dakota. T. H. HOPPER, L. L. NESBITT, and A. J. PINCKNEY (N. Dakota Agric. Exp. Sta. Tech. Bull., 1931, no. 246, 72 pp.).—Numerous analyses of various depth samples are recorded and their characteristics discussed.

A. G. POLLARD.

Phosphoric acid and lime contents of some arctic and Norwegian soils. E. G. DOERELL (Superphosphate, 1931, 4, 105—109).—The P content of the soils examined is the result of cultural operations and fertiliser treatments and is not dependent on the P content of the primitive rock.

A. G. POLLARD.

Organic Chemistry.

Possibility of detection of rotation isomerism. K. L. WOLF and W. BODENHEIMER (Z. physikal. Chem., Bodenstein Festband, 1931, 620—626).—A discussion.

H. F. GILLBE.

Biosynthesis. VI, VII, VIII. H. EMDE (Helv. Chim. Acta, 1931, 14, 881—911).—VI. The (empirical) formation of fats from sugars is discussed. γ-Fructose probably plays an important rôle in the synthesis of fatty acids from sugars. Glycerol and fatty acids are (reductive) products formed from sugars by oxidation–reduction processes.

VII. The possibility of various natural products (*e.g.*, carotene, cholesterol) being derived from straight-chain compounds (*e.g.*, lævulic acid, hexoses) instead of from isoprene is discussed.

VII. [With T. HORNEMANN.] A detailed study of the reaction between NH_4Cl and CH_2O solution (containing some MeOH and a trace of HCO_2H) shows that the following compounds are produced: CO_2, HCO_2H, HCO_2Me, MeOH, $CH_2(OMe)_2$, and mono-, di-, and tri-methylamine hydrochlorides; MeCl is not formed (cf. A., 1930, 453). $CH_2(OMe)_2$ and HCO_2Me are not obtained when MeOH-free CH_2O solution is used, or from hexamethylenetetramine (I) and conc. HCl. $CH_2(OMe)_2$ is prepared in

almost quant. yield from (I). MeOH. and conc. HCl (cf. B.P. 338,624; B., 1931, 237); a little HCO_2Me is also produced. H. BURTON.

Condensation of hydrocarbons by electrical discharge. VIII. S. C. LIND and G. R. SCHULTZE. —See this vol., 1249.

Configurative relationship of hydrocarbons. III. Optical rotations of the hydrocarbons of the series methyl*iso*butylmethane. P. A. LEVENE and R. E. MARKER (J. Biol. Chem., 1931, **92**, 455—460; cf. this vol., 931).—Et β-methylhexoate (free *acid*, $[M]_D^{24}$ +1·08°) by a Grignard reaction gave βδ-*dimethylheptan*-β-*ol*, b. p. 134—136°, which was distilled with $(CO_2H)_2$ to obtain the unsaturated *hydrocarbon*, b. p. 134—136°, $[M]_D^{24}$ −7·69°, hydrogenated to 1-βδ-*dimethylheptane*, b. p. 131—131·5°, $[M]_D$ −4·49°. Similarly there were prepared: βδ-*dimethyloctan*-β-*ol* (from β-methylheptoic acid, $[M]_D$ +1·83, by way of the Et ester), *dimethyloctene*, b. p. 62°/30 mm. $[M]_D^{24}$ −5·04°, 1-βδ-*dimethyloctane*, b. p. 70°/40 mm., $[M]_D$ −3·57°, βδ-*dimethylnonan*-β-*ol* (from β-methyloctoic acid, $[M]_D^{24}$ +2·47), *dimethylnonene*, b. p. 79°/30 mm., $[M]_D^{24}$ −4·76°, 1-βδ-*dimethylnonane*, b. p. 75°/25 mm., $[M]_D$ −2·84°. The saturated hydrocarbons all rotate in the same direction and the val. falls with increasing mol. wt. in accordance with the authors' theory.

J. H. BIRKINSHAW.

Plant colouring matters. XXXVII. High-molecular hydrocarbons containing numerous methyl groups. P. KARRER, M. STOLL, and P. STEVENS (Helv. Chim. Acta, 1931, **14**, 1194—1204).—Electrolysis of the Na salt of perhydrobixin in MeOH gives, in addition to various by-products, about 50% of an *ester* (I), $C_{44}H_{88}(CO_2Me)_2$, b. p. 265—270°/0·02 mm. Reduction of (I) with Na and EtOH to the corresponding glycol, conversion of this into the dibromide by aq. 33% HBr at 150°, and subsequent reduction with Cu–Zn and 60% AcOH gives *dibixane*, $C_{46}H_{94}$ (probably 4 : 8 : 12 : 16 : 23 : 27 : 31 : 35-*octamethyloctatriacontane*), b. p. 270—275°/0·2 mm. The mixture of about 70% of Me H ester and 30% of free acid, obtained by partial hydrolysis of (I) with MeOH–NaOH in MeOH–Et_2O, is electrolysed (as Na salt in MeOH), whereby some of the *ester*, $C_{88}H_{176}(CO_2Me)_2$, is produced. Treatment of this with MgMeI and subsequent reduction with red P and HI (*d* 1·7) at 200° gives a *hydrocarbon*, $C_{91}H_{180}$ (probably 2 : 5 : 9 : 13 : 17 : 24 : 28 : 32 : 36 : 41 : 45 : 49 : 53 : 60 : 64 : 68 : 72 : 75-*octadecamethylhexaheptacontane*), which does not resemble hydrocaoutchouc. H. BURTON.

Action of radon on unsaturated hydrocarbons. G. B. HEISIG.—See this vol., 1252.

Hydration of olefines to alcohols. A. V. FROST (J. Appl. Chem., Russia, 1930, **3**, 1069—1076).—Free energies of formation of alcohols up to C_6H_{13}·OH are calc. High pressures, and temp. of 227—427°, favour the reactions. CHEMICAL ABSTRACTS.

Influence of substituents on the additive reactivity of ethylene derivatives. I. Addition of bromine in solution. C. K. INGOLD and E. H. INGOLD (J.C.S., 1931, 2354—2368).—The comparative effects of substituents on additive reactivity in ethenoid compounds, on substitution reactivity in the aromatic nucleus, and on tautomeric mobility are discussed on theoretical grounds. Measurements of the relative rates of addition of Br in competition experiments to C_2H_4 and some simple substituted ethylenes are recorded and these are shown to be consistent with theory. When several substituents are present, these may contribute in different ways and there is the possibility of inverted mutual action, a case of which is experimentally demonstrated.

F. R. SHAW.

Thermal chlorination reactions in the gaseous phase, with short heating periods. J. MASON and T. S. WHEELER (J.C.S., 1931, 2282—2293).—A high space velocity method, with high reaction-tube temp., has been developed for controlled chlorination in the gaseous phase. Tubes of a special refractory were used, either empty or (preferably) packed with pieces of the same material. Conditions must be adjusted to avoid pyrolysis, which occurs if the tube temp. is too high, even at high rates of flow. At temp. not exceeding 900° and with excess of CH_4 and suitable space velocities, the method is efficient for producing MeCl, with small amounts of CH_2Cl_2. The yield of MeCl is about 80% of the Cl_2 input. Using C_3H_8, Pr$^\alpha$Cl was formed in greater amount than Pr$^\beta$Cl. Yields of CH_2Cl_2 slightly greater than 90% were obtained in the chlorination of MeCl.

E. S. HEDGES.

Determination of alcohol in dilute solution by means of acid dichromate, compared with the sp. gr. method. S. G. LIVERSEDGE (Analyst, 1931, **56**, 595—596).—EtOH present in small amounts such as 0·1% of Et esters in org. acids, or EtOH in Et esters, after hydrolysis and/or separation from other org. matter, may be determined by oxidation with acid $K_2Cr_2O_7$ (90 c.c. of N-$K_2Cr_2O_7$ and 600 c.c. of H_2SO_4 per litre). The results are comparable with those given by the sp. gr. method.

T. MCLACHLAN.

Reaction of bromine with *iso*propyl alcohol. J. F. J. DIPPY, H. B. WATSON, and E. D. YATES (J.C.S., 1931, 2508).—The main products of the action of Br on Pr$^\beta$OH are Pr$^\beta$Br and *as*-tetrabromoacetone, along with monobromo-, *as*-dibromo-, and ααα-tribromo-acetone. F. R. SHAW.

Alkyl peroxides. VII. Hydroxyalkyl hydrogen peroxides. A. RIECHE [with R. MEISTER] (Ber., 1931, **64**, [*B*], 2328—2335).—The action of aldehydes with aq. H_2O_2 leads generally to dihydroxyalkyl peroxides. When MeCHO and H_2O_2 react at 0° in the presence of anhyd. Et_2O and Na_2SO_4 and the solvent is subsequently removed as rapidly as possible at room temp., α-*hydroxyethyl hydrogen peroxide*, CHMe(OH)·O·OH, *d* 1·160, remains as an almost odourless liquid which decomposes vigorously when heated. With aq. KI it liberates about 75% of the expected I, acid being simultaneously produced. With aq. $FeSO_4$ about half of the expected AcOH is formed: MeCHO is simultaneously produced and a part of the active O is consumed in oxidising the Fe^{II} salt. With aq. NaOH only about half of the expected acid is produced. H_2O appears to facilitate the conversion of α-hydroxyethyl hydrogen peroxide into

di-α-hydroxyethyl peroxide, which furnishes ½ mol. of AcOH with $FeSO_4$, and AcOH and MeCHO with aq. NaOH. The yield of AcOH increases to 75% when the H peroxide in Et_2O is shaken with aq. $FeSO_4$ and to 86% if the solutions are allowed to rest in contact with one another. The C_7—C_{12} aldehydes are more readily isolated by reason of their cryst. nature. *α-Hydroxyheptyl*, m. p. 40° after softening, *α-hydroxyoctyl*, m. p. 46° after softening at 40°, *α-hydroxynonyl*, m. p. (indef.) 50—54°, *α-hydroxydecyl*, m. p. 61°, *α-hydroxyundecyl*, m. p. 62° after softening at 58°, and *α-hydroxydodecyl*, m. p. 65—67° after softening at 58°, *H peroxides* have been isolated. They are not explosive, and merely decompose vigorously when superheated. With HI they liberate 75—80% of the calc. amount of I and the corresponding quantity of O_2 when boiled with $TiCl_3$; with the latter reagent the higher dihydroxyalkyl peroxides yield the calc. amount of O_2. The H peroxides when treated with CH_2O or butaldehyde yield mixtures of the *s*-dihydroxyalkyl peroxides instead of the expected *as*-products. They tend to pass into acids by elimination of H_2O. H. WREN.

Alkyl peroxides. VIII. Ethylidene peroxide. A. RIECHE and R. MEISTER (Ber., 1931, **64**, [*B*], 2335—2340).—The formation of ethylidene peroxide is observed (1) by treatment of α-hydroxyethyl H peroxide in Et_2O with P_2O_5 and evacuation of the residue at 40°, (2) by action of P_2O_5 on dihydroxyethyl peroxide in Et_2O and subsequent warming of the product at 90°/vac., (3) by prolonged preservation or by warming (vac.) butylene ozonide, whereby MeCHO is evolved, and (4) by autoxidation of Et_2O. Immediately after prep. it is a very viscous oil, *d* 1·160—1·165, which explodes violently when heated, but is not markedly sensitive to friction. After some days in a closed vessel or some hr. if exposed to air it explodes with extraordinary violence when rubbed; only the portions actually touched are thereby affected. With warm, acidified KI it evolves 90% of the calc. amount of active O_2. It is hydrolysed by warm dil. H_2SO_4 to MeCHO and H_2O_2 and by alkali to AcOH in almost quant. yield. Mol. wt. determinations in freezing C_6H_6 give results varying from $[Me{\cdot}CHO_2]_4$ to $[Me{\cdot}CHO_2]_8$. H. WREN.

Esters of pyrophosphorous, hypophosphorous, and pyrophosphoric acids. II. Mechanism of action of bromine on sodium diethyl phosphite. A. E. ARBUSOV and B. A. ARBUSOV (J. pr. Chem., 1931, [ii], **131**, 337—341; cf. this vol., 820). —The interaction of equiv. amounts of Br and $PO(OEt)_2{\cdot}O{\cdot}P(OEt)_2$ in light petroleum gives the *compound* $PO(OEt)_2{\cdot}O{\cdot}PBr_2(OEt)_2$, which can be preserved unchanged in a closed vessel for 24 hr., but evolves HBr in contact with atm. moisture. On addition of 1 mol. of $NaPO(OEt)_2$ a ppt. forms, but only a very small amount of substance volatile at 200°/11 mm. $[P(OEt)_3]$ is formed; addition of a further mol. of $NaPO(OEt)_2$ results in a marked reaction, with further precipitation, and $[P(OEt)_2]_2O$ can now be isolated in quantity. H. A. PIGGOTT.

Colour reaction for soluble organic sulphur compounds. I. W. GROTE (J. Biol. Chem., 1931, **93**, 25—30).—Treatment of Na nitroprusside in $NaHCO_3$ solution with NH_2OH,HCl followed by Br yields a dark-coloured solution. The compound to be tested is dissolved in H_2O and excess of solid $NaHCO_3$ added, followed by the reagent. The following colour changes may occur. Purplish-red within 10 min. indicates C·SH, whilst an intense blue or green indicates E:S (where E is any single non-metallic element including S). Aq. KCN is added if no colour appears, when C·S·S·C compounds give a pink- to purplish-red within ½ hr. Thioacetic acid destroys the reagent, but a transient blue indicates the formula Me·CS·OH rather than Me·CO·SH. Ring compounds do not generally react. The use of the reagent for colorimetric determination of thiosulphate, thiocyanate, thiocarbamide, etc. is recommended. F. O. HOWITT.

Stability of the carbon–sulphur linking in aliphatic sulphonic acids. F. C. WAGNER and E. E. REID (J. Amer. Chem. Soc., 1931, **53**, 3407—3413).—When alkane-α- and -β-sulphonic acids are heated with aq. NaOH at 310—375° the main decomp. is $CH_2R{\cdot}SO_3Na+NaOH=CH_2R{\cdot}OH+Na_2SO_3$; this is probably followed by the change $CH_2R{\cdot}OH+NaOH=R{\cdot}CO_2Na+2H_2$. The (second order) velocity coeff. and heats of activation of the reactions studied are calc. The figures quoted after the following sulphonic acids are the % decomp. occurring when a *M*-solution of the Na salt is heated with an equal vol. of 3·7*N*-NaOH at 345° for 3 hr.: methane-, 1·5; ethane-, 62·7; propane-α-, 20·2, and -β-, 88·6; butane-α-, 17·3, and -β-, 75·2; pentane-α-, 13·3, and -β-, 64·2; hexane-α-, 11·7, and -β-, 54·9; $PhSO_3H$, 5; $CH_2Ph{\cdot}SO_3H$, 5. The stability of both α- and β-acids increases from C_2 to C_6; $MeSO_3H$ is very stable. The β-acids are less stable than the α-, but all are more stable than the corresponding mercaptans (this vol., 63). The acids are prepared either from alkyl iodides and $(NH_4)_2SO_3$ or by HNO_3-oxidation of mercaptans and purified through their *Ba* salts. H. BURTON.

Isomeric isoprenesulphones. III. E. EIGENBERGER (J. pr. Chem., 1931, [ii], **131**, 289—292).—*cis*-Isoprenesulphone is readily, and the *trans*-compound with greater difficulty, reduced by H_2 and colloidal Pt to the same *dihydro*-compound, m. p. 0·2°, b. p. 125—130°/12 mm. (some decomp.), thus confirming the view (this vol., 600) that the two forms are geometrical isomerides. The dibromo-compound reacts exothermally with Zn dust yielding isoprene, whilst Zn dust and EtOH affords only *cis*-isoprenesulphone. J. W. BAKER.

Catalytic hydrogenation of the carboxyl group in organic compounds, particularly in those of high mol. wt. O. SCHMIDT (Ber., 1931, **64**, [*B*], 2051—2053).—Contrary to Schrauth and others (this vol., 932), the use of high temp. and pressure is not essential for the hydrogenation of the CO_2H group if a sufficiently active contact is employed. The reduction of Et oleate to octadecyl alcohol is effected at 270—280°/atm. in the presence of a $CuCrO_4$ catalyst, whilst castor oil at 220°/200 atm. in presence of a Co catalyst yields octadecyl alcohol and octadecanediol. H. WREN.

Catalytic reduction of the carboxyl group. W. Normann (Z. angew. Chem., 1931, **44**, 714—717).—Aliphatic carboxylic acids can be reduced to the corresponding alcohols by H_2O under high pressure and in presence of a catalyst (Cu, Ni, etc.). The reaction may be carried out with the free acid or with an ester. Aldehydes and ketones are similarly reduced. J. W. Smith.

Acetylation in aqueous alkaline solutions. F. D. Chattaway (J.C.S., 1931, 2495—2496).—Many compounds containing OH or NH_2 groups can be easily acetylated by adding Ac_2O to their dil., ice-cold solution in alkali hydroxide. F. R. Shaw.

Monoglycerides of lower fatty acids. P. G. Gilchrist and H. A. Schuette (J. Amer. Chem. Soc., 1931, **53**, 3480—3484).—Direct esterification of glycerol in presence of H_3PO_4 and CCl_4 is impracticable with acids higher than butyric; *glyceryl monoisobutyrate*, b. p. 128—130°/2 mm., is prepared by this method. *Glyceryl* n-*valerate*, b. p. 129—131°/2 mm., iso*valerate*, b. p. 145—147°/3·5 mm., and n-*hexoate*, b. p. 132—134°/2 mm., are prepared from α-chlorohydrin and the Na salts of the fatty acids. The coeffs. of viscosity and surface tensions of the above esters and glyceryl acetate, propionate, and *n*-butyrate are determined. Other physical data are recorded. H. Burton.

Relation between ultra-violet absorption and structure of derivatives of acetic and malonic acids. R. Dolique (Ann. Chim., 1931, [x], **15**, 425—521).—The mutual influence on the absorption spectra of two neighbouring chromophores diminishes with separation, and ceases when they are separated by more than 3 C atoms. In the prep. of disubstituted malonic esters the yield is improved if that substituent which contains a Ph nucleus is introduced first. Excess of Et malonate improves the yield in the prep. of monoalkyl derivatives of Et malonate. Improvements in the prep. of several of the following compounds are recorded. The Na derivative of Et *n*-butylmalonate (b. p. 127°/12 mm.) with γ-phenylpropyl bromide gives *Et γ-phenylpropyl*-n-*butylmalonate*, b. p. 212—213°/15 mm. (35% yield), also obtained by reversing the order of introduction of the substituents (yield 33%), and purified by re-esterification of the *acid*, m. p. 137·5—138° (yield of acid 91%). The heated acid gives *α-(γ-phenylpropyl)hexoic acid*, m. p. 38°, b. p. 215°/19 mm. Similar reactions give Et ethyl-*n*-butylmalonate, b. p. 128°/13 mm., α-ethylhexoic acid, b. p. 222°/755 mm., 131°/18 mm. (*benzyl* ester, b. p. 150°/13 mm.) (cf. A., 1923, i, 81), Et *n*-butylbenzylmalonate, b. p. 187°/15 mm. (yield 35% from Et *n*-butylmalonate, or 52% from Et benzylmalonate) (A., 1922, i, 681) (*acid*, m. p. 104·5°), *α-benzylhexoic acid*, b. p. 185°/14 mm., 179°/10 mm. (yield 95%) [*Et* ester, b. p. 274°/756 mm., 156°/16 mm. (yield 82%); *benzyl* ester, b. p. 234—236°/28 mm., 222—223°/16 mm. (yield 80%)], Et di-*n*-butylmalonate, b. p. 151—152°/18 mm. (yield 55%; yield of acid 96%), α-*n*-butylhexoic acid, b. p. 149°/15 mm. [Et ester, b. p. 218°/752 mm., 110°/18 mm. (yield 84%), *benzyl* ester, b. p. 177°/15 mm., *amide*, m. p. 134·5° (sublimes 100—110°)] (cf. A., 1918, i, 250), *Et β-phenylethyl*-n-*butylmalonate*, b. p. 203°/15 mm., 205°/17 mm. (yield 34%, or 40%) [*acid*, m. p. 139° (yield 86%)], *α-(β-phenylethyl)hexoic acid*, b. p. 201—202°/17 mm., 238—239°/28 mm., Et dibenzylmalonate, b. p. 238°/22 mm. (yield 75%) [*acid*, m. p. 174° (yield 90%)], β-phenyl-α-benzylpropionic acid, m. p. 91° [Et ester, b. p. 202°/18 mm. (yield 75%); *benzyl* ester, m. p. 81° (yield 87%); amide, m. p. 129·5°]. Et phenylmalonate gives *Et phenyl*-n-*butylmalonate* (yield 58%), hydrolysed to the *acid*, m. p. 153°, and *α-phenylhexoic acid*, b. p. 182—183°/20 mm. (also obtained by heating phenyl-*n*-butylmalonic acid, and by hydrolysis of *α-phenylhexonitrile*, b. p. 151·1—152·5°/20 mm., obtained from $CH_2Ph\cdot CN$ by means of $NaNH_2$ and BuBr). Et α-ethylhexoate reduced by Bouveault's method gives β-ethylhexanol, b. p. 180°/758 mm., 96—97°/27 mm., 89—90°/18 mm. (yield 58%). Similarly are obtained β-butylhexanol (yield 63%; also obtained by similar reduction of α-butylhexoamide, yield 8%) (*phenylurethane*, m. p. 39°), *β-benzylhexanol*, b. p. 170—171°/27 mm. (yield 60%, also from the amide in small yield) (*phenylurethane*, m. p. 55·5°). β-Phenyl-α-benzylacetamide by similar treatment gives *γ-phenyl-β-benzylpropanol*, m. p. 27—28°, b. p. 197°/10 mm. (*phenylurethane*, m. p. 94°) (in better yield than from the ester), and a little γ-phenyl-β-benzylpropylamine (*Bz* derivative, m. p. 104°). α-Methyl-α-ethylpentanol, b. p. 79—80°/27 mm., α-methyl-α-benzylpentanol, b. p. 155°/27 mm., 144°/18 mm., *β-phenyl-α-benzyl-α-methylethanol* (from AcOEt and $CH_2Ph\cdot MgCl$), b. p. 182°/15 mm., and α-benzyl-α-methylpentanol (from $Me\cdot CO\cdot CH_2Ph$ and MgBuBr), b. p. 155°/27 mm., 144°/18 mm., could not be obtained optically pure. A. A. Levi.

Differing behaviour of α- and β-chloropropionic acids and of α- and β-chloroethylbenzenes during catalytic hydrogenation. C. Paal and C. Muller-Lobeck (Ber., 1931, **64**, [*B*], 2142—2150; cf. A., 1929, 1270).—The free chloropropionic acids are little attacked by activated H_2. Ca α-chloropropionate is quantitatively reduced to $CaCl_2$ and propionic acid, whereas the salt of the β-acid suffers only slight similar change. The action of the α-chloropropionate is considerably accelerated by the addition of MgO, which combines with the liberated HCl, but the oxide has little effect on the β-chloropropionate. Et α-chloropropionate is readily transformed into Et propionate in presence of MgO, whereas Et β-chloropropionate absorbs little H_2 before reaction ceases. The anticatalytic action of the liberated HCl is much more marked in the case of saturated than of unsaturated acids, probably owing to the negativing action of the ethylenic linking in the latter and the consequent loosening of the C–Cl linking.

In presence of the requisite quantity of MgO, α-chloroethylbenzene is quantitatively converted into PhEt, whereas under similar conditions β-chloroethylbenzene suffers only slight reduction. With larger amounts of Pd and prolonged period of action, the β-derivative yields PhEt. Reduction of α-chloroethylbenzene proceeds more rapidly than that of Ca α-chloropropionate or α-chlorobutyrate. The *semihydrated Ca* and the *Ag* salts of α- and β-chloropropionic acid are incidentally described.

H. Wren.

Highly-polymerised compounds. LV. Polyacrylic acid. H. STAUDINGER and H. W. KOHLSCHUTTER (Ber., 1931, 64, [B], 2091—2098).—Polymerisation of acrylic acid by irradiation occurs more rapidly in CO_2 than in O_2, and is particularly rapid when the operation is commenced in O_2 or air and continued in CO_2. The influence of O_2 is marked with 30% and 5% aq. solutions. Below 100°, individual specimens of acrylic acid show individual behaviour towards polymerisation, but at 110° or above polymerisation occurs rapidly in all cases, yielding non-homogeneous products varying from glassy, transparent masses to hard, porcelain-like materials. All are amorphous. Polymerisation is considered to follow the scheme: $\cdots CH(CO_2H){\cdot}CH_2 \cdots + xCO_2H{\cdot}CH{:}CH_2 \longrightarrow CH(CO_2H){\cdot}CH_2{\cdot}[CH(CO_2H){\cdot}CH_2{\cdot}]_{x-1}{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}$. Solid polyacrylic acids swell strongly in H_2O without dissolving completely at low temp.; at 100—120° homogeneous sols. are more or less rapidly obtained. They are polybasic acids of unknown mol. wt. They are weaker than the monomeric acid and the Na salts are feebly alkaline. Titration of the acids with NaOH in presence of phenolphthalein shows about 96% of the CO_2H group, but exact results are obtained potentiometrically. The conductivity of the poly-acids and their salts is lower than that of the monomeric substances. The viscosity of polyacrylic acid sols depends on p_H in the same manner as that of the proteins. Viscosity is at a max. at the neutral point and decreases with increase of NaOH. With heteropolar compounds such as the polyacrylic acids, high $\eta_{sp}c$ vals. do not necessarily imply a high mol. wt., since viscosity varies with p_H and there is no evidence of the identity of the dissolved particles and the mols. The changes of viscosity are due to causes other than those operative with homopolar mol. colloids. Since the behaviour of the admittedly highly-polymerised acrylic acids resembles that of the proteins, it is probable that the latter also are highly polymerised and not specially structured. Depolymerisation of polyacrylic acids can be effected by contact with H_2O at different temp. or with aq. NaOH. H. WREN.

Configurative relationships of the α-bromo-acids obtainable from the optical isomerides of *iso*leucine and of *allo*leucine to the amino-acids obtainable from these by amination. Walden inversion. E. ABDERHALDEN and W. ZEISSET (Z. physiol. Chem., 1931, 200. 179—190).—By known reactions (bromination with NOBr, chlorination with $SOCl_2$, amination with aq. NH_3, etc.), the following were obtained: chloroacetyl-*l*(+)-*iso*leucine, m. p. 71—73°, $[\alpha]_D$ +26·0° in EtOH, *glycyl*-l(+)-iso*leucine*, m. p. 242—243° (decomp.), $[\alpha]^{20}$ −14·1° in H_2O; chloroacetyl-*d*(−)-*iso*leucine, m. p. 72—74°, $[\alpha]_D^{20}$ −26·1° in EtOH, glycyl-*d*(−)-*iso*leucine, m. p. 240—242° (decomp.), $[\alpha]_D^{20}$ +13·6° in H_2O; *chloroacetyl*-l(+)-allo*leucine*, m. p. 80—86°, $[\alpha]_D^{20}$ +19·1° in EtOH, *glycyl*-l(+)-allo*leucine*, m. p. 245—247° (decomp.), $[\alpha]_D^{19}$ −9·4° in H_2O; *chloroacetyl*-d(−)-alloiso*leucine*, *glycyl*-d(−)-alloiso*leucine*, m. p. 244—246° (decomp.), $[\alpha]_D^{18}$ +9·2° in H_2O; [d]-(+)-allo-*α-bromo-β-methylvaleric acid*, b. p. 107—108°/2—3 mm., $[\alpha]_D^{18}$ +12·80° from *d*(−)-alloiso*leucine*; [d](+)-allo-*α-bromo-β-methylvaleryl chloride*, b. p. 76—78°/12—13 mm.; [l](−)-*allo-α-bromo-β-methylvaleric acid*, b. p. 124—126°/7 mm., $[\alpha]_D$ −12·90°, from *l*(+)-*allo*iso*leucine* [*phenylcarbimido*-derivative, m. p. 151°, $[\alpha]_D^{20}$ +31·6°], [l](−)-allo-*α-bromo-β-methylvaleryl chloride*, b. p. 51°/3 mm.; [d](+)-*α-bromo-β-methylvaleric acid*, m. p. 40—41°, $[\alpha]_D^{19}$ +24·2° in C_6H_6, giving *d*(−)-*iso*leucine (*phenylcarbimido*-derivative, m. p. 125—130°, $[\alpha]^{20}$ −32·1° in EtOH), [d](+)-*α-bromo-β-methylvaleryl chloride*, b. p. 57—59°/3 mm.; [l](−)-*α-bromo-β-methylvaleric acid*, m. p. 38—40°, $[\alpha]_D^{17}$ −22·3° in C_6H_6 [*chloride*, b. p. 69—71°/10 mm.], giving *l*(+)-*iso*leucine (*phenylcarbimido*-derivative, m. p. 123—127°, $[\alpha]_D^{20}$ +32·4° in EtOH); [l](−)-allo-*α-bromo-β-methylvalerylglycine*, m. p. 77—79°, $[\alpha]^{20}$ −48·1° in EtOH, giving d(−)-iso*leucylglycine*, m. p. 212—214° (decomp.), $[\alpha]_D^{21}$ −18·8° in H_2O; [d](+)-allo-*α-bromo-β-methylvalerylglycine*, m. p. 81—82°, $[\alpha]^{20}$ +49·4° in EtOH (*α-bromo-fatty acid*, $[\alpha]_D^{18}$ +12·80°), giving l(+)-iso*leucylglycine*, m. p. 220° (decomp.), $[\alpha]_D^{19}$ +16·6° in H_2O; [*d*](+)-α-bromo-β-methylvalerylglycine, m. p. 107—108°, $[\alpha]_D^{20}$ +62·7° in EtOH (*α-bromo-fatty acid*, $[\alpha]_D^{19}$ +24·2°), giving *l*(+)-*alloiso*leucylglycine, m. p. 260—261° (decomp.), $[\alpha]_D^{20}$ +57·0° in H_2O (*phenylcarbimido*-derivative, m. p. 151°, $[\alpha]_D^{20}$ +30·4° in EtOH); [l](−)-*α-bromo-β-methylvalerylglycine*, m. p. 105—106°, $[\alpha]^{20}$ −60·9° in EtOH (*α-bromo-fatty acid*, $[\alpha]_D^{17}$ −22·3°), giving d(−)-alloiso*leucylglycine*, m. p. 252—255° (decomp.), $[\alpha]_D^{21}$ −62·7° in H_2O. J. H. BIRKINSHAW.

Behaviour of octoic, hexoic, valeric, *iso*valeric, and benzoic acids on extraction from aqueous solution with light petroleum. J. GROSSFELD and A. MIERMEISTER (Z. anal. Chem., 1931, 85, 321—330).—The partition coeffs. of the above acids between H_2O and light petroleum have been determined, and all follow the law $k=c/\sqrt{c_2}$. The % extracted when solutions of different concentration are agitated with equal vols. of light petroleum are tabulated. J. W. SMITH.

Hydrogenation of unsaturated lactones to deoxy-acids. II. W. A. JACOBS and A. B. SCOTT (J. Biol. Chem., 1931, 93, 139—152).—Catalytic reduction (Adams) of ααβ-trimethyl-Δ^{β}-angelicalactone in EtOH at 20—25° gives *ααβ-trimethylvaleric acid* (about 50%), b. p. 137—138°/43 mm., and *ααβ-trimethyl-γ-valerolactone*, b. p. 121—123°/33 mm. Similarly, β-methyl-Δ^{β}-angelicalactone affords β-methylvaleric acid (about 50%), b. p. 197—198° (corr.)/758 mm. (*Ag* salt), and β-methyl-γ-valerolactone; ααβ-trimethyl-Δ^{β}-butenolide yields ααβ-trimethylbutyric acid (21%) and (mainly) ααβ-trimethylbutyrolactone; β-phenyl-αα-dimethyl-Δ^{β}-butenolide furnishes β-*phenyl-αα-dimethylbutyric acid* (about 25%), m. p. 61—62°, and β-*phenyl-αα-dimethylbutyrolactone*, m. p. 91—92°, whilst complete hydrogenation gives the same proportions of β-cyclo*hexyl-αα-dimethylbutyric acid*, m. p. 39—40°, and β-cyclo*hexyl-αα-dimethylbutyrolactone*, m. p. 51—52°. The yield of deoxy-acid formed during reduction of βγ-unsaturated γ-lactones (cf. A., 1930, 1162) is diminished by β-substitution. α-Anisylidene-Δ^{β}-angelicalactone undergoes a preliminary 1 : 4-addition of H_2 and finally gives (mainly) *α-anisyl-γ-valerolactone*, m. p. 60—61°, and 17% of *α-anisylvaleric acid*, m. p.

50—52°. Δ^{α}-Butenolide (prepared by thermal decomp. of γ-chlorocrotonic acid) affords butyrolactone (90%) and butyric acid (10%); the acid is probably formed from Δ^{β}-butenolide which may arise during the reduction or is present in the original material. Reduction of δ-keto-β-phenylhexoic acid with Na–Hg in EtOH gives *β-phenyl-δ-hexolactone*, b. p. 197—200°/19 mm., reduced catalytically to a *mixture*, b. p. 194—198°/20 mm., of stereoisomeric β-*cyclo*hexyl-δ-hexolactones. H. BURTON.

Synthesis of straight-chain unsaturated acids. R. BHATTACHARYA and J. L. SIMONSEN (Proc. XV Indian Sci. Cong., 1928, 153).—λ-Iodododecoic acid, prep. from castor oil by way of undecenoic, λ-bromoundecoic, cyanoundecoic, decamethylenedicarboxylic, and λ-hydroxylauric acids, was condensed with decin to yield behenolic acid.

CHEMICAL ABSTRACTS.

Alcoholysis. I. M. GOSWAMI and S. RAMANUJAM (J. Indian Chem. Soc., 1931, 8, 413—416).—The conversion of fat (coconut oil) into the Me esters of its fatty acids by boiling with MeOH in presence of various catalysts is studied. $POCl_3$ is as effective as, and more readily manipulated than, dry HCl (cf. A., 1907, i, 9; 1919, i, 308). Benzene- (I) and naphthalene-stearosulphonic acids (II), pyridine, piperidine, and piperidine hydrochloride have little or no effect. When (I) and (II) contain traces of mineral acid catalytic activity is observed. H. BURTON.

Unsaturated fatty acids and their derivatives. III. Four stereoisomerides of dihydroxy- and dibromo-stearic acids. IV. Mechanism of forming stearolic acid from dichlorostearic acid. Y. INOUE and B. SUZUKI (Proc. Imp. Acad. Tokyo, 1931, 7, 261—264, 265—268).—III. The hydroxy-acids are prepared by the action of 1% aq. $KMnO_4$ on a 1% solution of oleic or elaidic acid in 1% aq. KOH, at 1—3°; *elaido-* and *oleo-dihydroxystearic acid* have m. p. 100° and 130°, respectively. The acids were resolved through the strychnine salts; the active *elaidodihydroxystearic acids* have $[\alpha]_D^{22}$ −27·45° and +27·6° in MeOH, whilst the corresponding oleic acids have $[\alpha]_D$ −23·6° and +23·0° in MeOH. All the stereoisomerides were readily racemised. The dibromides were readily prepared by the action of Br in the cold and were separated by the strychnine salts. l-*Oleodibromostearic acid* had $[\alpha]_D$ −18·5°. Inactive dihydroxy-acids were obtained on treatment of the dibromo-compounds with Ag_2O.

IV. Treatment of oleodichlorostearic acid with 20% KOH in EtOH for 12 hr. at 100° and oxidation of the Me esters by Armstrong and Hilditch's method showed that in addition to stearolic acid, $\Delta^{\zeta\theta}$-octadecadienoic acid, $C_{18}H_{32}O_2$ (*Me* ester, b. p. 192—193°/4 mm.; *Zn* salt, m. p. 85°), was obtained. Treatment of the second acid with 20% KOH in EtOH at 150° converted it almost quantitatively into stearolic acid. Sorbic acid with 10% KOH in EtOH gave Δ^{β}-*pentinenecarboxylic acid*, m. p. 128°. C. C. N. VASS.

Oxidation of oleic acid by means of hydrogen peroxide with and without the addition of copper sulphate: a possible analogy with its oxidation *in vivo*. I. S. MACLEAN and M. S. B. PEARCE (Biochem. J., 1931, 25, 1252—1266).—When oleic acid was oxidised by H_2O_2 at 95° (A., 1908, i, 119) a fraction agreeing in composition with that of diketostearic acid was formed. An α-keto-derivative of nonoic or decoic acid and some dihydroxystearic acid were also present. The yields of H_2CO_3, AcOH, and HCO_2H corresponded with the complete oxidation of 5—10% of the total oleic acid. Increasing the proportion of H_2O_2 increased the proportion of dihydroxystearic acid present. Small amounts of Cu^{II} salts greatly increased the extent of oxidation. At 95° with a large excess of H_2O_2 more than 70% of the original oleic acid was completely broken down to H_2CO_3, HCO_2H, and AcOH. Succinic and δ-keto-η-hydroxyoctoic acids were also formed at the same time. Oxidation in the presence of Cu^{II} salt at 60° produced amounts of H_2CO_3, HCO_2H, and AcOH corresponding with complete oxidation of about 20% of the total oleic acid. The product obtained in greatest amount was δ-keto-η-hydroxyoctoic acid. Succinic acid and a mixture of various oxygenated derivatives of stearic acid were also present. Among the products of oxidation of octoic acid succinic and δ-keto-η-hydroxyoctoic acid were found.

S. S. ZILVA.

Action of concentrated sulphuric acid on oleic acid and oleyl alcohol. C. RIESS (Collegium, 1931, 557—588).—A max. amount of H_2SO_4 is combined at the point of unsaturation during the first hr. of its action at room temp. on oleic acid. The amount of organically combined SO_3 is reduced by more prolonged action and hydroxystearic acid is formed, the amount being greater as the amount of reacting H_2SO_4 is increased or the temp. raised. Most of the hydroxystearic acid is esterified. The combination of the H_2SO_4 is much slower at 0°, and it is practically the only reaction which occurs, since very little hydroxystearic acid is formed even after 24 hr. The sulphonation proceeds furthest at low temp., whilst the hydrolysis of the H_2SO_4 esters proceeds only very slowly. Oleyl alcohol is sulphonated at the point of unsaturation and at the OH group, but the reaction is slower than with oleic acid. Within the limits 0—40°, the reaction of the H_2SO_4 with the unsaturated atoms is almost independent of the temp. The reaction of the H_2SO_4 with the OH group proceeds very slowly at low temp. and is accelerated appreciably as the temp. is raised. The H_2SO_4 is eliminated again at still higher temp., especially if 40% of H_2SO_4 is used. D. WOODROFFE.

Preparation and purification of linoleic acid. H. I. WATERMAN and J. A. VAN DIJK (Verfkroniek, 1931, 4, No. 2, 15—19; Chem. Zentr., 1931, i, 2740).—Linoleic acid, prepared from sesame oil fatty acids by bromination and debromination, distilled in a cathode-light vac., freed from oleic and saturated acids by cooling in $COMe_2$, and finally cryst. from $COMe_2$ by cooling, had I val. 179·9, CNS′ val. 91·2, d_4^{20} 0·9031, n_C 1·46643, n_D 1·46944, n_F 1·47642, n_G 1·48228; $[M]_C$ 86·02, $[M]_D$ 86·49, $[M]_F$ 87·60, $[M]_G$ 88·51.

A. A. ELDRIDGE.

Polymerisation of the methyl esters of higher unsaturated fatty acids. VIII. Polymerisation of methyl linolenate and linoleate. IX. Hydrogenation of the methyl esters assumed to be

intrapolymerised [cyclic monomerides]. K. Kino (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, **16**, 127—132, 133—135; cf. this vol., 602).—Me linoleate and linolenate, obtained from linseed and sesamé oils through the Pb salts and bromides, are heated in H_2 at 290—300° for varying times. Distillation of the product at 6—7 mm. removes monocarboxylic esters, which from the I val. and mol. wt. are considered to contain *cyclo*butane derivatives, formed by intramol. condensation, the proportion increasing with time of heating, and being less for the linoleate than for the linolenate. The residue from the distillation, which increases with time of heating, consists mainly of dimeride from Me linoleate, but contains higher polymerides in the case of Me linolenate.

IX. More H_2 is absorbed in the catalytic hydrogenation of the above monocarboxylic esters than that calc. from the I val., the velocity of absorption diminishing after the quantity corresponding with the I val. has been absorbed. The ester $C_{19}H_{31}{\cdot}CO_2Me$ (A., 1930, 1272) after reduction gives an acid having the same m. p. as arachidic acid, the theoretical quantity of H_2 to reduce the assumed *cyclo*butane ring being absorbed. The ester $C_{21}H_{33}{\cdot}CO_2Me$ (*loc. cit.*) is not completely reduced, the resulting acid after repeated purification having a lower m. p. than behenic acid. A. A. Levi.

Conversion of erucic acid into brassidic acid by nitrous acid. G. Rankoff (J. pr. Chem., 1931, [ii], **131**, 293—300).—Smooth isomerisation of erucic acid, $Me{\cdot}[CH_2]_7{\cdot}CH{:}CH{\cdot}[CH_2]_{11}{\cdot}CO_2H$, into brassidic acid, $Me{\cdot}[CH_2]_{18}{\cdot}CH{:}CH{\cdot}CO_2H$, occurs when it is treated in 30% HNO_3 with 0·2 of its wt. of $NaNO_2$ at 54—58°. With larger quantities of $NaNO_2$ oxidation affords by-products which prevent crystallisation of the product and under such conditions were isolated arachidic (*n*-eicosoic acid), brassylic, $HO_2C{\cdot}[CH_2]_{11}{\cdot}CO_2H$, and *n*-nonoic acids, and a nitrogenous substance which affords *n*-nonoic acid on steam-distillation. J. W. Baker.

Lignoceric acid and lignoceryl alcohol from "sulphate soap." H. Sandqvist, J. Gorton, and E. Bengtsson (Ber., 1931, **64**, [*B*], 2172—2174).—Extraction of the Na salts from "Tallol" with Et_2O, ligroin, etc. removes phytosterols and lignoceryl alcohol, $C_{24}H_{50}O$, which are separated from one another by fractional crystallisation and destruction of the unsaturated sterols by treatment of their acetates in $CHCl_3$ with an excess of Ac_2O and conc. H_2SO_4. Treatment of the sulphate soap with H_2O leaves the sterols in solution, whereas the lignoceryl alcohol is found in the filter residue. After removal of the alcohol by Et_2O, the remaining Na salts yield lignoceric acid identical with the product obtained by oxidising the alcohol. For lignoceric acid and its Me ester the m. p. 80·3—81° after softening at 77° and 58—59·8°, respectively, are recorded, whereas synthetic *n*-tetracosoic acid and its Me ester have m. p. 85° and 60°, respectively. Lignoceryl alcohol, m. p. 76°, and its acetate, m. p. 56°, are compared with synthetic *n*-tetracosanol, m. p. 77·5°, and its acetate, m. p. 57°. H. Wren.

Optical rotation of lactic acid. W. D. Bancroft and H. L. Davis (J. Physical Chem., 1931, **35**, 2508—2529).—Sarcolactic acid should be designated *l*-(+)-lactic acid to show that, although its dil. aq. solutions are dextrorotatory, the lævorotations of its salts and esters show it to be the *l*-form of lactic acid. As in the case of malic acid (A., 1930, 892), there is a fourth tautomeric modification involved. The evidence indicates this to be a dextrorotatory ethylene oxide form. The equilibria involving the anhydride or lactide are reached slowly, whilst that between the normal and the ethylene oxide forms is reached rapidly. The changes in rotation shown by solutions of sarcolactic acid on concentration or dilution can then be satisfactorily interpreted. L. S. Theobald.

Lævulic acid. II. Vapour pressure of alkyl esters (C_1—C_6). H. A. Schuette and M. A. Cowley (J. Amer. Chem. Soc., 1931, **53**, 3485—3489).—Equations are derived expressing temp.–v. p. relationships for the Me, Et, Pr, Pr^β, Bu, Bu^β, *iso*amyl, n-*amyl*, b. p. (calc.) 253·2°/760 mm., and n-*hexyl*, b. p. (calc.) 266·8°/760 mm., esters of lævulic acid. The entropies of vaporisation indicate that all these esters are associated. Other physical data are recorded. H. Burton.

Oxidation by ozone. Preparation of ι-hydroxydecoic acid by oxidation of undecenyl acetate. M. Mottier (Helv. Chim. Acta, 1931, **14**, 1080—1090).—Details are given for the prep. of ι-hydroxydecoic acid in about 80% yield by ozonolysis of Δ^κ-undecenyl acetate and subsequent hydrolysis with H_2O in presence of air. The effects of temp. and time of heating on the decomp. of the ozonide by H_2O and AcOH are studied. Decomp. of the ozonide with alkali gives mainly aldehydic condensation products one of which is probably the aldol (*semicarbazone*, m. p. 71—72°) derived from 2 mols. of ι-hydroxydecaldehyde. H. Burton.

Preparation of ethyl oxalate. P. W. Jewel and J. S. Butts (J. Amer. Chem. Soc., 1931, **53**, 3560—3561).—Cryst. oxalic acid (1 kg.) is heated with EtOH (2 litres) until dissolved, and the mixture distilled at 80°/25 mm. until the vapour temp. is 60°. The residue is heated with EtOH (2 litres) for 3 hr., H_2O and EtOH are removed as above, the resultant product is dried, and then distilled. The yield of Et oxalate is about 85%. H. Burton.

Additive components of ethyl sodiomalonate and related compounds. N. E. Holden and A. Lapworth (J.C.S., 1931, 2368—2375).—When benzylideneacetophenone is heated in C_6H_6 with Et sodiomethylmalonate, Et α-methylcinnamate and Et sodiobenzoylacetate are produced. This cannot be explained by the hypothesis advanced by Thorpe (*ibid.*, 1900, **77**, 923) and by Michael and Ross (this vol., 67), which overlooks the possibility of exchange of positions of H and CN or H and CO_2Et; it is, however, capable of interpretation on the basis of analogy with well-known reactions which are consistent with electrochemical conceptions of the behaviour of sodio-derivatives of weak acids or ψ-acids. F. R. Shaw.

Di*iso*propylmalonic acid and its derivatives. F. C. B. Marshall (J.C.S., 1931, 2336—2338).—The

prep. of *Et diisopropylmalonamate*, m. p. 62° (from the Ag salt and EtI); *Et*, b. p. 246·2°/751 mm., *Et H*, m. p. 66°, and *Me diisopropylmalonate*, m. p. 32°; and diisopropylmalonic acid, m. p. 198° (from Me ester), which is converted by $SOCl_2$ into *diisopropylacetyl chloride*, b. p. 63°/15 mm. (*anilide*, m. p. 148—149°) (cf. A., 1908, i, 602), is described.

F. R. SHAW.

Electrolysis of hydrogen esters of unsaturated dicarboxylic acids. P. KARRER and M. STOLL (Helv. Chim. Acta, 1931, **14**, 1189—1194).—Electrolysis of Na Et fumarate in presence of MeOH and NaOAc gives no muconate (cf. Bloch, Diss., München, 1902); the main product is an ester, b. p. 98—101°/12 mm., hydrolysed by 10% KOH to fumaric acid and an oil. In absence of NaOAc, the same ester and a trace of Me muconate are produced. *Me H muconate*, m. p. 163°, prepared by partial hydrolysis of the Me_2 ester, does not undergo the Kolbe synthesis when electrolysed as the K salt in presence of aq. MeOH and KOAc; the main reaction is hydrolysis.

H. BURTON.

Digitalonic acid and the corresponding trihydroxymethoxyglutaric acid. H. KILIANI (Ber., 1931, **64**, [*B*], 2027—2028; cf. A., 1916, i, 493).—The isolation of trihydroxymethoxyglutaric acid, m. p. 122°, $[\alpha]_D$ −27·4° in H_2O, from the products of the action of HNO_3 (*d* 1·4) on digitalonolactone is effected through the Ca and Zn salts. A ketonic acid is formed in considerable amount as by-product.

H. WREN.

Action of potassium cyanide on potassium mannosaccharate. H. KILIANI (Ber., 1931, **64**, [*B*], 2018—2026; cf. A., 1928, 741).—The view that the attack of KCN on K mannosaccharate occurs between the ββ′-C atoms requires modification, since the acids, $C_7H_{10}O_{10}$, are converted by boiling HI into adipic and unsaturated C_6 acids instead of butane-αβδ-tricarboxylic acid and when boiled in H_2O lose CO_2 (indicating thus the presence of the $C(CO_2H)_2$ group) and yielding an unknown *acid*, $C_6H_{10}O_8$ or $C_6H_8O_7$, analysed as the *mono-* and *penta-hydrated Ca* salts. An improved method for the isolation of the $C_7H_{10}O_{10}$ acids is described. H. WREN.

Preparation of ellagic acid. M. NIERENSTEIN (Helv. Chim. Acta, 1931, **14**, 912).—Attention is directed to the author's method (J.C.S., 1921, **119**, 279) of prep. of ellagic acid, the Ac_4 derivative of which has m. p. 343—346° and not 317—319° (cf. this vol., 351). H. BURTON.

Polymerisation of acetaldehyde. W. H. HATCHER and B. BRODIE (Canad. J. Res., 1931, **4**, 574—581).—The polymerisation to paracetaldehyde of MeCHO alone or in C_6H_6 in presence of H_3PO_4 has been followed dilatometrically. At low concentrations the reaction is of the third order, but at high concentrations the reaction velocity increases with time. The velocity is directly proportional to the quantity of catalyst. Powdered glass has a slight variable influence on the reaction, but it is considered to be without theoretical significance. The equilibrium concentration of paracetaldehyde is 94·3% for the partial depolymerisation in presence of H_3PO_4.

J. D. A. JOHNSON.

αβ-Ethylenic straight-chain aldehydes. R. DELABY and S. GUILLOT-ALLÈGRE (Compt. rend., 1931, **192**, 1467—1469).—β-Alkylacraldehydes are obtained by oxidation with CrO_3 of the corresponding alcohols, obtained by the isomerisation of alkylvinylcarbinols under the influence of PBr_3. Optimum conditions for oxidation are described. β-*Ethylacraldehyde* [Δ^{α}-*pentenal*], b. p. 125° (*semicarbazone*, m. p. 180°; p-*nitrophenylhydrazone*, m. p. 115°; β-ethylacrylic acid, m. p. 4°); β-*propylacraldehyde*, b. p. 150—152° (*semicarbazone*, m. p. 175—176°; p-*nitrophenylhydrazone*, m. p. 139°; β-*propylacrylic acid*, m. p. 33°); β-butylacraldehyde, b. p. 165—167° (*semicarbazone*, m. p. 169°; p-*nitrophenylhydrazone*, m. p. 154°), and β-iso*amylacraldehyde* (impure), b. p. 76—79°/13 mm. (*semicarbazone*, m. p. 179°; p-*nitrophenylhydrazone*, m. p. 152—156°), are described.

G. DISCOMBE.

Conjugated double linkings. XIX. Hexadienal and octatrienal. R. KUHN and M. HOFFER (Ber., 1931, **64**, [*B*], 1977—1979; cf. A., 1930, 1406).—The isolation of homogeneous hexadienal and octatrienal from the products of the action of piperidine on a mixture of croton- and acet-aldehyde is readily effected through the $NaHSO_3$ *compounds*. Hexadienal can be distilled unchanged in NH_3 and the crude material is readily purified by the action of NH_3 in Et_2O (whereby crotonaldehyde, aldol, etc. are precipitated) and subsequent distillation; it has b. p. 173—174° (corr.)/754 mm., 64—66°/11 mm., d_D^{22} 0·9087 [*oxime*, m. p. 159·5—160·5° (corr., partial decomp.); *phenylhydrazone*, m. p. 101—102° (corr.)]. Octatrienal, m. p. 55°, readily becomes polymerised to a yellow, amorphous mass even in an indifferent gas. The aldehydes readily reduce Fehling's and Ag solution. The green coloration with Schiff's reagent, imputed to octatrienal (*loc. cit.*), is due to an impurity.

H. WREN.

Oxygen absorption by fission products of the hexoses and active catalysts thereof. L. AHLSTROM and H. VON EULER (Z. physiol. Chem., 1931, **200**, 233—245).—The rate of oxidation of dihydroxyacetone, glyceraldehyde, and methylglyoxal increases with rising p_H between 6·5 and 8. Methylglyoxal is much more slowly oxidised, but the rate is considerably increased in presence of hæmin. Oxidation of glyceraldehyde is slightly stimulated by $CuSO_4$ and not inhibited by KCN. Dihydroxyacetone and glyceraldehyde show stimulation by hæmin in pyridine, further increased by KCN. Mesohæmin ester produces slight stimulation, deuteroporphyrin ester inhibition. $FeSO_4$ produces an increase in rate, $Fe_2(SO_4)_3$ none. Mesoporphyrin hydrochloride shows inhibition with glyceraldehyde. Pyruvate oxidation is strongly stimulated by $FeSO_4$.

J. H. BIRKINSHAW.

Action of thiocarbimides on oximes. C. V. GHEORGHIU (Ann. Sci. Univ. Jassy, 1931, **16**, 389—458).—A more detailed account of work previously reviewed (A., 1927, 229). H. BURTON.

Detection of acetone in presence of acetaldehyde. L. KLINC (Arh. Hemiju, 1931, **5**, 212—216).—The Scott–Wilson reagent, for both $COMe_2$ and MeCHO, can be made sp. for $COMe_2$ by adding 5 c.c.

of the reagent to the solution examined, allowing the ppt. to form, adding a few c.c. of H_2O, and evaporating to half vol. 5 c.c. of Scott–Wilson acid mixture are then added, and the solution is distilled through a boiling 30% KOH solution into 5 c.c. of Scott–Wilson reagent, when a ppt. indicates the presence of $COMe_2$. Should the MeCHO content exceed 2 mg., 2 c.c. of 3% H_2O_2 should be added to the original solution together with the reagent, and the mixture is at once distilled through KOH into fresh reagent.

R. TRUSZKOWSKI.

Reductions with lead–sodium [alloys]. I. F. FICHTER and I. STEIN (Helv. Chim. Acta, 1931, **14**, 1205—1211).—Alloys containing 10—30% Na reduce $COMe_2$ in dil. H_2SO_4 solution at 45° to pinacol and small quantities of one or more unstable Pb *iso*propyls.

F. L. USHER.

Chemistry of the three-carbon system. XXVII. Homomesitones, $C_{10}H_{18}O$ and $C_8H_{14}O$. G. A. R. KON and E. LETON (J.C.S., 1931, 2496—2507).—The action of alkaline condensing agents on $COEt_2$ gives no homomesitones (cf. A., 1928, 1218), but evidently a cyclic *compound*, b. p. 124—128°/12—18 mm.; acid agents behave similarly. The expected condensation products, *δ-methyl-ε-ethyl-Δ^{δ}-hepten-γ-one*, b. p. 80°/10 mm. (*semicarbazone*, m. p. 153°), and *δ-methyl-ε-ethyl-Δ^{ϵ}-hepten-γ-one*, b. p. 74°/10 mm. (*semicarbazone*, m. p. 109°), are obtained synthetically from the corresponding acids. $COMePr^{\alpha}$, in presence of NaOEt, undergoes condensation to a mixture of αβ and βγ isomerides of ξ-methylnonen-δ-ones, in the proportion of 3 : 1, *i.e.*, *ξ-methyl-Δ^{ϵ}-*, b. p. 90—92°/16 mm., and *ξ-methyl-Δ^{η}-nonen-δ-one*, b. p. 94°/18 mm., which may also be obtained from the corresponding acids. The homomesitone condenses with Et malonate to give 1-*methyl*-4-*ethyl*-1-n-*propyl*cyclo*hexane*-3 : 5-*dione*, m. p. 106°. The action of acid condensing agents on $COMePr^{\alpha}$ gives crude ketones with branched chains, but synthesis from the corresponding acids is required to give pure products: *δ-methyl-γ-ethyl-Δ^{γ}-* (αβ), b. p. 83°/14 mm. (*semicarbazone*, m. p. 123°), and *δ-methyl-γ-ethyl-Δ^{δ}-hepten-β-one* (βγ), b. p. 69°/11 mm. (*semicarbazone*, m. p. 154°).

The equilibria and mobilities of the foregoing have been determined under standard conditions. The great influence of the α-alkyl substituent in retarding mobility and also in shifting the equilibrium towards the βγ-form is shown. It is indicated that *cis–trans*-isomerism affects the equilibration of CMeEt:CMe·COMe and its βγ-isomeride, and the change between the two forms of the βγ-isomeride passes through the αβ-ketone.

F. R. SHAW.

Mono-methyl and -ethyl ether of dihydroxy-acetone. I. S. NEUBERG (Biochem. Z., 1931, **238**, 459—460).—By oxidation of α-Me and -Et ethers of glycerol with hypobromite the corresponding ethers of dihydroxyacetone are obtained, the m. p. of the 2 : 4-dinitrophenylhydrazones being 175° and 171°, respectively. The same reaction may be carried out biochemically by fermentation with *Acetobacter suboxidans*.

P. W. CLUTTERBUCK.

[Reasons for the difference in the behaviour of analogous compounds of bivalent cobalt, nickel, and copper containing diacetyldioxime.] S. PONZIO (Ber., 1931, **64**, [*B*], 2346).—A reply to Thilu and Heilborn (this vol., 938).

H. WREN.

Dioximes. LXXVIII. G. LONGO (Gazzetta, 1931, **61**, 575—583).—*αγ-Diamino-αβγ-trioximinopropane*, m. p. 154° [Ni salt, $C_3H_6O_3N_5)_2Ni$], is prepared by the reaction $CH_2(CN)_2 \xrightarrow{O_3} NC{\cdot}C(:NOH){\cdot}CN \longrightarrow H_2N{\cdot}[C(:NOH)]_3{\cdot}NH_2$. With Ac_2O it gives the substance $O{<}^{C}_{N:C{\cdot}C(NH_2):N{\cdot}OAc}$, m. p. 193—194° (cf. Wieland, A., 1930, 482). Dicyanoglyoxime, m. p. 145° (decomp.) [trihydrate, m. p. 98—99°; *Ac_2* derivative, m. p. 181—182°; *Bz* derivative, m. p. 143—144° (decomp.); *Bz_2* derivative, m. p. 225° (decomp.); *Na* salt; *Ag* salt], prepared by the action of KCN on dichloroglyoxime, reacts with NH_2OH giving *αδ-diamino-αβγδ-tetraoximinobutane*, m. p. 181—182° (decomp.) [Ac_6 derivative, darkens at 190°, m. p. 230° (decomp.)].

E. E. J. MARLER.

Bromonitroso-derivatives of oximino-compounds. I. DE PAOLINI (Gazzetta, 1931, **61**, 551—557).—The following radicals are classified with regard to their favourable effect on the reaction $CRR'{:}NOH \longrightarrow CRR'Br{\cdot}NO$ (C_nH_{2n+1}, RC_nH_{2n}, CO_2Et) > (COC_nH_{2n+1}, Bz) > (C_6H_4R, CO_2H, CN). Class 3 completely inhibits the reaction. The anomaly of the formation of a bromonitroso-derivative by the form of α-oximinopropionic acid which has additive properties is explained by suggesting a ψ-acid structure –(OH)C:O (A., 1918, ii, 4), the ordinary form of the acid which forms no bromonitroso-derivative being a true carboxylic acid.

E. E. J. MARLER.

Ferricyanide method for the determination of reducing sugars. Modification of the Hagedorn–Jensen–Hanes technique. A. C. HULME and R. NARAIN (Biochem. J., 1931, **25**, 1051—1061).—This modification gives a linear relation between the amount of sugar and the amount of ferricyanide reduced over a range of 0·2—3·0 mg. in the case of dextrose, lævulose, and invert-sugar, and of 0·2 to 3·5 mg. in the case of maltose. In a mixture of sugars the ferricyanide-reducing power of one sugar is unaffected by the presence of others. Invert-sugar prepared by acid hydrolysis of sucrose has a slightly higher reducing value than a mixture of equal amounts of dextrose and lævulose. Sucrose inverted by HCl hydrolysis gives accurate results. The results are high when citric acid is used.

S. S. ZILVA.

Hydrazones and osazones of sugars. E. VOTOČEK and F. VALENTIN (Arh. Hemiju, 1931, **5**, 155—162).—The sugar of which a given hydrazone is a derivative can be identified by distilling the hydrazone with 12% HCl, when the production of furfuraldehyde indicates the presence of pentose, and of methylfurfuraldehyde methylpentose, whilst neither is evolved by hexoses. This reaction can be applied to determine whether the pentose or methylpentose component of a disaccharide is responsible for its reducing action. Lactosephenylosazone exhibits mutarotation in MeOH, whilst the rotation of the phenylosazone of anhyd. lactose is constant. *p*-Nitrobenzaldehyde can conveniently be substituted for PhCHO in the regeneration of sugars from their hydrazones, in view of the greater insolubility of its

hydrazone. Fructosephenylmethylosazone yields the corresponding phenylosazone on heating with excess $NHPh{\cdot}NH_2$, whilst with *p*-bromophenylmethylhydrazone a mixed osazone is obtained. The mutarotation of osazones is not due to tautomerism between the dihydrazone and azo-forms, as fructosephenylmethylosazone, which does not possess a labile H atom, exhibits mutarotation.

R. Truszkowski.

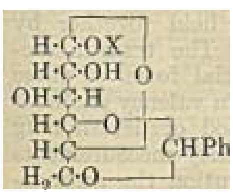
***X*-Ray examination of arabinose, xylose, and rhamnose.** E. G. Cox (J.C.S., 1931, 2313—2323).—*X*-Ray examination, by which unit cells and space-groups have been determined, indicates that β-*l*-arabinose and α-*d*-xylose [the latter described by Wherry (A., 1919, i, 65) as monoclinic] are orthorhombic, bisphenoidal, space-group The space-group of *d*-rhamnose hydrate is C_2^3. Possible structures for arabinose and xylose are suggested and a tentative suggestion as to the configuration of the mols. in the cryst. state is put forward.

F. R. Shaw.

Alterations in the rotation and mutarotation of dextrose. I. Effect of concentrating [solutions]. H. N. Naumann (Biochem. Z., 1931, **239**, 434—440).—When aq. solutions of pure dextrose are conc. (even slightly) at atm. pressure mutarotation occurs and persists for 3—4 hr. Concentration on the water-bath does not cause reduction in the final val. of the rotation. Concentration under reduced pressure causes mutarotation similar to that produced at atm. pressure. When evaporation is carried out under reduced pressure the temp. should not exceed 40° after the solution has become syrupy.

W. McCartney.

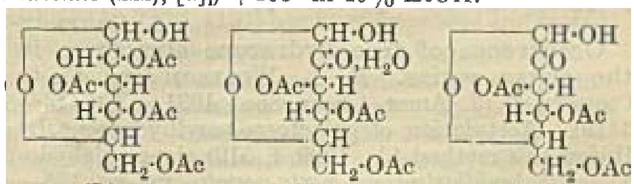
Benzylideneglucose and its application to syntheses; 1-benzoylglucose. L. Zervas (Ber., 1931, **64**, [*B*], 2289—2296).—Interaction of dextrose and PhCHO in presence of anhyd. $ZnCl_2$ gives a mixture from which 4 : 6-*benzylidene*-α-d-*glucose* (I; X=H) m. p. 188° (corr.), $[\alpha]_D^{22}$ −4·0° in MeOH (equilibrium). It exhibits downward mutarotation and reduces Fehling's solution slowly when cold unless excess of alkali is present, rapidly when hot. According to conditions it affords a *phenylhydrazone*, m. p. 181° (corr.), or *phenylosazone*, decomp. 210° (corr.). With alkali and 1 mol. of Me_2SO_4 it gives benzylidenemethylglucoside, identical with that derived from PhCHO and β-methylglucoside. Acetylation of benzylideneglucose yields a mixture from which β-*benzylideneglucose triacetate*, m. p. 201° (corr.), $[\alpha]_D^{22}$ −51·7° in $CHCl_3$, is isolated, converted by catalytic hydrogenation into a glucose triacetate, which further yields β-glucose penta-acetate. Benzylideneglucose is sol. in aq. NaOH to a *Na* derivative (I; X=Na), $[\alpha]_D$ −19·1° (initial val.), which slowly decomposes in aq. solution, but regenerates α-benzylideneglucose if immediately acidified with AcOH. With Me_2SO_4 it affords benzylidenemethylglucoside and with Ac_2O almost exclusively β-benzylideneglucose triacetate. It is transformed by BzCl in anhyd. $CHCl_3$ into 1-*benzoyl*-4 : 6-*benzylidene*-β-*glucose*, m. p. 208° (corr.), $[\alpha]_D^{22}$ −44·2° in $COMe_2$, catalytically hydrogenated to 1-*benzoyl*-β-*glucose*, m. p. 193° (corr.), $[\alpha]_D^{22}$ −26·8° in H_2O (*tetra-acetate*, m. p. 145° (corr.); $[\alpha]_D^{21}$ −26·6° in $CHCl_3$), which is hydrolysed by technical emulsin to BzOH.



(I)

H. Wren.

Crystalline acetates of glucosone and the products of their transformation. K. Maurer and W. Petsch (Ber., 1931, **64**, [*B*], 2011—2017; cf. A., 1929, 428).—Treatment of oxyglucal tetra-acetate in anhyd. Et_2O with Cl_2 followed by agitation of the product with $NaHCO_3$ and a little H_2O leads to the separation of glucosone hydrate tetra-acetate (I), whilst the filtrate when preserved deposits *glucosone hydrate triacetate* (II), m. p. 76°, $[\alpha]_D^{19}$ +104·2° to +84·2° in 40% EtOH in 14 days, which reduces cold Fehling's solution and yields glucosazone after treatment with NaOH and $NHPh{\cdot}NH_2$. It is transformed by P_2O_5 at 18° or in $CHCl_3$ at 0° into *glucosone triacetate* (III), $[\alpha]_D^{21}$ +105° in 40% EtOH.

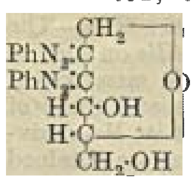


(I.) (II.) (III.)

Examination of the substances by Zerevitinov's method shows the evolution of the expected vol. of CH_4 when *s*-tetrachloroethane is used as solvent, whereas high results are obtained in pyridine (in which the rotation rapidly sinks to 0°) owing to the production of diacetylkojic acid; the change occurs also in aq. solution containing 1—2% of pyridine.

H. Wren.

Unsaturated reduction products of sugars. XVII. Products of the dismutation of sugars. M. Bergmann and L. Zervas (Ber., 1931, **64**, [*B*], 2032—2034; cf. this vol., 939). Re-examination of the phenylosazone $C_{18}H_{22}O_3N_4$ or $C_{18}H_{20}O_3N_4$ (*loc. cit.*) shows that the second formula is correct and that the substance is identical with the osazone obtained from the product of the action of hypobromite on styracitol. The annexed formula is therefore established and also the persistence of oxyglucal in the product of the hydrolysis of hydroxyglucal tetra-acetate.



H. Wren.

Dicarbonyl sugars. II. New oxidation product of dextrose. B. Helferich and N. M. Bigelow (Z. physiol. Chem., 1931, **200**, 263—276; cf. A., 1929, 1280).—Treatment of triacetyl-β-methylglucoseenide (I) with $Pb(OAc)_4$ in C_6H_6 gives *penta-acetyl*-β-*methylgluconoside* (II), m. p. 146—149° (decomp.), $[\alpha]^{20}$ −85·9°. (II) on shaking with H_2O yields *tetra-acetylgluconose* (III), m. p. 103—106° (slow heating), $[\alpha]_D^{20}$ −39·8°. (III) is also formed as by-product in the prep. of (I), with a *substance*, m. p. 88—90°. (III), after 10 min. hydrolysis with 0·2*N*-NaOH, affords *gluconose* (a syrup) (*bis*-p-*nitrophenylhydrazone*, m. p. 121—126°). Catalytic hydrogenation of (I) gives triacetyl-β-methyl-*d*-*iso*rhamnoside (IV) and a

small amount of a *product*, $[\alpha]_D^{20}$ $-49\cdot0°$. Hydrolysis of (IV) in $CHCl_3$ with Na in MeOH yields β-methyl-*d*-*iso*rhamnoside, which when hydrolysed by 5% H_2SO_4 affords *iso*rhamnose (V). Acetylation of (V) with Ac_2O and NaOAc gives β-*tetra-acetyliso*rhamnose (VI), sinters at 142°, m. p. 147°, $[\alpha]_D^{20}$ $+21\cdot3°$. (VI) is also obtained by catalytic hydrogenation of β-tetra-acetylglucoseen. J. H. BIRKINSHAW.

Ring structure of di*iso*propylidenegalactose. P. A. LEVENE and G. M. MEYER (J. Biol. Chem., 1931, **92**, 257—262).—*Trimethyl*-d-*galactose* iso*propylidene ether*, b. p. 105°/0·3 mm., $[\alpha]_D^{20}$ $-31\cdot4°$ in MeOH, obtained by methylation of *d*-*iso*propylidenegalactose (A., 1925, i, 1043), is hydrolysed by acid to *trimethyl*-d-*galactose*, $[\alpha]_D^{20}$ $-4\cdot3°$ in MeOH, which is oxidised by Br and converted into *trimethyl*-δ-*galactonolactone*, $[\alpha]_D^{20}$ $+46\cdot8°$ in H_2O (*Na* salt, $[\alpha]_D^{25}$ $+29\cdot4°$ in H_2O). From the dextrorotation of the lactone and the rate of its formation from the free acid, mono- and di-*iso*-propylidenegalactose possess a pyranose structure. A. COHEN.

Occurrence of true hydrazone structures in the sugar series. M. L. WOLFROM and C. C. CHRISTMAN (J. Amer. Chem. Soc., 1931, **53**, 3413—3419).—Acetylation of galactosephenylhydrazone by Hofmann's method (A., 1909, i, 519) gives aldehydo-*galactosephenylhydrazone penta-acetate*, m. p. 135—136°, $[\alpha]_D^{27}$ $+41\cdot7°$ in pyridine (cf. *loc. cit.*), also formed from *aldehydo*-galactose penta-acetate or its alcoholate (A., 1930, 1023) and NHPh·NH_2. The α-*phenyl*-α-*benzylhydrazone*, m. p. 128—129°, $[\alpha]_D^{28}$ $+91°$ in pyridine, α-*phenyl*-α-*methylhydrazone*, m. p. 138—139°, $[\alpha]_D^{28}$ $+27\cdot3°$ in pyridine, and the p-*nitrophenylhydrazone*, m. p. 194—195° (corr.; decomp.), $[\alpha]_D^{28}$ $+21\cdot2°$ in $CHCl_3$, of *aldehydo*-galactose penta-acetate are also prepared by both methods. The hydrazones are assigned open-chain structures. H. BURTON.

Carbohydrates and polysaccharides. XXXVI. Structure of the lævan synthesised by the action of *B. subtilis* on sucrose. H. HIBBERT and F. BRAUNS (Canad. J. Res., 1931, 4, 596—604).—The lævan obtained by the action of *B. subtilis* on sucrose is identical with that obtained using *B. mesentericus* (this vol., 827), its physical properties and those of the lævulose obtained by hydrolysis, of its Me_3 derivative, of the 1 : 3 : 4-trimethylfructofuranose obtained by hydrolysis of the latter, and of lævan triacetate being in agreement with those recorded for the lævan obtained using the latter culture. The necessity for the use of an ash-free lævan in methylation experiments is emphasised, the presence of 0·5% of ash leading to a methylated product insol. in $CHCl_3$ or MeI. J. D. A. JOHNSON.

Strophanthin. XXIV. Isomeric hexahydrodianhydrostrophanthidins and derivatives. W. A. JACOBS, R. C. ELDERFIELD, A. HOFFMANN, and T. B. GRAVE (J. Biol. Chem., 1931, **93**, 127—138).—Catalytic reduction (Adams) of oxidodianhydrostrophanthidin ethylal in EtOH gives mainly α-*hexahydro-oxidodianhydrostrophanthidin ethylal* (I), m. p. 128—129°, $[\alpha]_D^{25}$ $+21°$ in 95% EtOH, hydrolysed by dil. AcOH to α-*hexahydrodianhydrostrophanthidin* (II), m. p. 178—180° after softening at about 112°, $[\alpha]_D^{25}$ $+41°$ in $CHCl_3$ (*oxime*, m. p. 258—260°, formed only with difficulty); (II) reacts in the aldehydic and the lactol forms. (I) is isomerised (not homogeneously) by HCl in EtOH. Clemmensen reduction of (II) affords a *mixture*, m. p. 196—202°, of octahydrotrianhydrostrophanthidins (cf. A., 1925, i, 566), whilst the *Bz* derivative, m. p. 213—215° (*oxime*, m. p. 242—243°), of (II) gives, similarly, indefinite products. Oxidation of (II) with Kiliani's CrO_3 solution in AcOH yields mainly a *dilactone* (III), $C_{23}H_{32}O_4$, m. p. 192—194°, $[\alpha]_D^{26}$ $+19\cdot4°$ in $CHCl_3$, and a little of the isomeric hexahydrodilactone (IV), m. p. 265—267°, previously described (A., 1926, 73); (III) is converted into (IV) by HCl in AcOH. Re-investigation of the reduction of the dianhydrodilactone, $C_{23}H_{26}O_4$ (*loc. cit.*), shows that (IV) and an *isomeride*, m. p. 196—199° (from EtOH), 204° (from Et_2O), $[\alpha]_D^{25}$ $+18°$ in $CHCl_3$, are produced. Catalytic reduction (Adams) of anhydrodihydrostrophanthidin (*Bz* derivative, m. p. 190—192°) in EtOH proceeds with difficulty, giving *dihydroanhydrodihydrostrophanthidin*, m. p. 217—219°, $[\alpha]_D^{29}$ $+28°$ in pyridine, converted by EtOH containing 5% of HCl into *dihydro-oxidodianhydrodihydrostrophanthidin ethylal*, m. p. 174—176°, $[\alpha]_D^{25}$ $-108°$ in $CHCl_3$. This is hydrolysed to *dihydrodianhydrodihydrostrophanthidin*, m. p. (indef.) 247° after softening above 215°, and reduced catalytically (Pt or Pd) to β-*hexahydro-oxidodianhydrostrophanthidin ethylal*, m. p. 131—132°, $[\alpha]_D^{24}$ $+13\cdot4°$ in EtOH. Hydrolysis of this affords β-*hexahydrodianhydrostrophanthidin* (V), m. p. 155—156° after softening, $[\alpha]_D^{22}$ $+20°$ in $CHCl_3$ [*oxime*, m. p. 262° after softening; *Bz* derivative, m. p. 209—211° (*oxime*, m. p. 252°)], which also reacts in aldehydic and lactol forms. Oxidation of (V) (as II) gives mainly IV.

The results of Windaus *et al.* (A., 1926, 73) on the reduction of dianhydrostrophanthidin could not be confirmed. H. BURTON.

Structure of highly-polymerised compounds. K. H. MEYER and H. MARK (Ber., 1931, **64**, [*B*], 1999—2002).—The authors and Staudinger agree in the view that highly-polymerised, natural materials consist of long, chain-like mols. held together by normal, chemical main valencies. The term macromols. scarcely expresses the special form of these structures. The length of the main valency chains is controversial; Staudinger's method of determining mol. wt. by extrapolition of viscosity measurements does not find acceptance. In solution the arrangements are very complicated and, in general, neither homogeneous micelles nor isolated main valency chains are present. It is beyond doubt that, owing to the marked action of the solvent, the dissolved particles differ from the micelles in the solid state and the propriety of speaking of "dissolved micelles" is doubtful. Causes other than cracking are operative in causing dependence of viscosity of solutions on temp. Staudinger's criticisms of changes in the authors' point of view and his historical treatment of the subject are discussed. H. WREN.

Starch. XXV. Diamylose and tetra-amylose; triamylose and hexa-amylose. H. PRINGSHEIM, A. WEIDINGER, and H. SALLENTIEN (Ber., 1931, **64**, [*B*], 2117—2125).—Mainly a re-investigation of the substances in consequence of the criticisms of Miekeley

(A., 1930, 1414), in agreement with whom the val. $[\alpha]_D^{20}$ + 148° in H_2O for α-tetra-amylose is accepted. The substance loses H_2O and EtOH of crystallisation very slowly and on desiccation yields a product of approx. const. wt. with the composition $C_6H_{10}O_5,0{\cdot}5H_2O$. Diamylose has $[\alpha]_D$ +136° in H_2O, the val. being unchanged by intensive desiccation. Under like conditions, α-hexa-amylose has $[\alpha]_D$ +136°. Repeated crystallisation of diamylose from H_2O leads to its conversion into tetra-amylose. This effect is not due to the heating in H_2O. Tetra- and di-amylose when cryst. from aq. EtOH retain about 2% of EtOH, the presence of which is not betrayed by cryoscopic determinations of mol. wt.; it must therefore be firmly combined in the mol. It is removed when aq. solutions of the carbohydrates are boiled or when the substances are intensely desiccated. Tetra-amylose then remains as tetra-amylose, whereas di- is converted into tetra-amylose. Similarly, α-amylosan is stabilised by a slight EtOH content. Miekeley's production of two acetates from tetra-amylose is due to degradation by either method resulting in diamylose acetate, hydrolysed to diamylose, which is converted by H_2O into tetra-amylose. Re-examination of the difference between tri- and β-hexa-amylose is rendered difficult by the sparing solubility in H_2O, which is too small to permit direct determination of mol. wt. A difference between $[\alpha]_D$ for these compounds similar to that now established between di- and tetra-amylose has been noted. Triamylose acetate, $[\alpha]^{20}$ +120° in $CHCl_3$, and β-hexa-amylose acetate, $[\alpha]^{20}$ +143° in $CHCl_3$, differ distinctly in solubility in PhMe. The acetate of the hexa-compound appears to be present in AcOH and PhOH as that of the tri-substance. In C_6H_6 hexa-amylose acetate persists, whereas the triamylose derivative gives uncertain vals. In camphor the triamylose derivative behaves non-uniformly, whereas the hexa-amylose compound exhibits the corresponding mol. wt. In $C_{10}H_8$ and dioxan the hexa- is transformed into the tri-compound. In $CHBr_3$ the triacetate passes into the hexa-stage or further in very dil. solution, whereas the hexa-acetate remains in a much greater state of aggregation. Hexa-amylose is almost tasteless and "dark," whereas triamylose tastes sweet and "bright." Tetra- and di-amylose are almost equally sweet, but the former is "brighter" and the latter "darker."

H. WREN.

Starch. XXVI. New polyamyloses. H. PRINGSHEIM, A. WEIDINGER, and P. OHLMEYER (Ber., 1931, 64, [*B*], 2125—2130).—α-Tetra-amylose, dried over P_2O_5 at 78°, passes in boiling formamide into α-allo*amylosan*, $C_6H_{10}O_5$, $[\alpha]_D^{20}$ +139° in H_2O; β-allo*amylosan*, $[\alpha]^{20}$ +146° in pyridine–H_2O (7 : 3), is derived similarly from β-hexa-amylose. The substances show the typical polyamylose property of giving with org. solvents, *e.g.*, C_2HCl_3, additive products sparingly sol. in H_2O. The iodo-product of the α-series is depicted, whereas that of the β-compound could not be obtained homogeneous. When heated with H_2O both compounds pass into the colloidal state. α-allo*Amylosan acetate*, $[\alpha]_D^{20}$ +112° in $CHCl_3$, and β-allo*amylosan acetate*, $[\alpha]_D^{20}$ +124° in $CHCl_3$, both trimeric in dioxan, are described. β-Hexa-amylose, dried until const. in wt., has $[\alpha]^{20}$ +159° in H_2O, increased to +172° by further heating, and subsequently remaining const. After crystallisation from H_2O or aq. EtOH, $[\alpha]_D^{20}$ sinks to +159° and cannot again be raised by further heating. Similar observations are recorded for α- and β-*iso*amylosan, but not for the amylosans. α-Amylosan is very faintly sweet, almost tasteless, whereas β-amylosan is decidedly sweet. α-Amylosan is transformed by AcBr into acetobromomaltose, converted by Ag_2CO_3 in EtOH into maltose hepta-acetate, m. p. 178—179°, $[\alpha]_D^{20}$ + 76° in $C_2H_2Cl_4$; β-amylosan behaves similarly, but yields the biose acetate in smaller amount. The amylosans and *iso*amylosans are not fermented by the α-glucosidase of yeast, the β-glucosidase of emulsin, or malt amylase; takadiastase affects the β-compounds much more readily than those of the α-series.

H. WREN.

Iodometric determination of starch by Paloheimo's method. L. PALOHEIMO and I. PALOHEIMO (Biochem. Z., 1931, 238, 391—400).—The authors' method (A., 1930, 1167) has been improved and tested under various conditions. P. W. CLUTTERBUCK.

Use of the Pulfrich photometer in the iodometric determination of starch. L. PALOHEIMO and I. ANTILA (Biochem. Z., 1931, 238, 401—407).—Comparative determinations were carried out, using the simplified spectrophotometer of Heilmeyer and Krebs (A., 1930, 1201) and the authors' dilution method (*ibid.*, 1167). The former is simpler in that standard solutions are not used, but if a colour-filter is employed instead of the standard, the methods are equally simple. P. W. CLUTTERBUCK.

Plant colloids. XXX. Phosphorus-containing degradation products of potato-starch. M. SAMEC [with S. SELISKAR and V. ZITKO] (Kolloidchem. Beih., 1931, 33, 449—459).—An examination of several methods of isolating derivatives of starch rich in P indicates that the best yield is obtained by the procedure of Northrop and Nelson (A., 1916, i, 373). Experiments with one of these derivatives showed its mol. size and P content to lie between the vals. for a compound of H_3PO_4 with a di- and a tri-saccharide. Electrometric and conductometric titration gave two discontinuities in the neutralisation curve, as with H_3PO_4, and the same behaviour is shown by potato-amylopectin. E. S. HEDGES.

Glycogen. II. Preparation of glycogen from yeast, and identity of glycogen from different sources. III. Nature of the carbohydrate constituents of the cell membrane of yeast. K. M. DAOUD and A. R. LING (J.S.C.I., 1931, 50, 365—368T, 379—382T).—II. The method of preparing glycogen from yeast is much the same as that described by Ling, Nanji, and Paton (A., 1925, i, 1011) up to the stage at which the mannan is precipitated with Fehling's solution. The filtrate from the Cu cloth is then rendered slightly acid with HCl and the Cu removed by dialysis in running H_2O for 6 days. The final product was a white powder containing 1·59% of ash; $[\alpha]_D$ (corrected for ash)+179°. The authors have compared glycogen prepared from yeast by Harden and Young's method (J.C.S., 1902, 81, 1224; 1912, 101, 1928); prepared from yeast by their own method; prepared from liver, and prepared from

horse-flesh. They conclude that glycogen from different sources is identical, and that the differences in [α], opalescence of solutions, and coloration with I are probably to be explained by differences in the degree of esterification with H_3PO_4 and of polymerisation.

III. Repeated extraction of dried yeast with boiling 2% NaOH yielded an insol. residue, having moisture 12·95, ash 7·2, protein 13·6, carbohydrate (by difference) 66·16%. The nitrogenous matter is of the nature of protein; chitin is absent. The carbohydrate constituents of yeast-cell membrane are glycogen and mannan, partly esterified with phosphoric and silicic acids and thus rendered insol. Glycogen and mannan are probably the only reserve polysaccharides of the plasma, and they are utilised in building up the membrane of the yeast-cell, this being in accordance with Becker's observation on the thickening of the yeast-cell membrane in a highly conc. wort.

Action of Grignard reagent (magnesium methyl iodide) on cellulose. F. C. Wood (J.S.C.I., 1931, **50**, 257—258T).—Hydrocellulose dried over P_2O_5 at room temp., or ordinary cotton cellulose dried at 120°, does not react with MgMeI in Et_2O at room temp. or in $NPhMe_2$ at 120°. It is very difficult to free the material from Mg; as much as 15% of MgO was found in one sample ashed. If any compound be formed it is of the additive type and does not involve the elimination of gaseous hydrocarbon.

Production and solubility of different highly hydrolysed cellulose acetates. A. Deripasko (Cellulosechem., 1931, **12**, 254—263).—Secondary cellulose acetate sol. in $COMe_2$ is obtained from the primary (sol. in $CHCl_3$) material by treatment of the acetylation product with H_2O or dil. AcOH at const. temp. This process is described as hydrolysis. When insufficient H_2O to convert the residual Ac_2O into AcOH is added, a secondary acetate richer in OAc than the original primary acetate is obtained, but with larger amounts of H_2O a product poorer in OAc is formed. The OAc content also falls with increasing time of hydrolysis. High OAc content is accompanied by low H_2SO_4 content and *vice versa*, and the higher OAc content is ascribed to the greater solubility or the quicker decomp. of the cellulose sulphuric ester present. The stability of secondary acetates increases with decreasing H_2SO_4 content. Hydrolysis with larger amounts of H_2O gives products of high viscosity. When $7\frac{1}{2}$% instead of 15% of H_2SO_4 is used as catalyst in preparing the primary acetate the effect of concentration of the hydrolysis mixture on the viscosity of the secondary acetate is the same, but the rate of hydrolysis is very slow and must be accelerated by the addition of more H_2SO_4. Secondary acetates are sol. in $COMe_2$ when the yield of AcOH is between 60 and 49%. Technical cellulose acetates are manufactured by nearly identical processes and have nearly the same chemical composition and solubility. Factors governing the solubility in different solvents (H_2SO_4 content, particle size, etc.) are discussed, and results of an investigation of solubility by titrating $COMe_2$ solutions of the acetates with org. liquids that have no solvent power for the acetate show that this varies with the OAc content. B. P. Ridge.

Lignin. III. Sulphonation in the hydroaromatic series. Preparation of *cyclo*hexanol-*o*-sulphonic acid. IV. Reaction of phenolic derivatives with acetic anhydride–acetic acid–sulphuric acid. H. Friese.—See this vol., 1286, 1289.

Lignin. Action of bromine on lignin from pine wood. A. Friedrich and E. Pelikan (Biochem. Z., 1931, **239**, 461—472; B., 1926, 151).—When pine-wood lignin is brominated 30% of its OMe content is lost, and since no elimination of OMe takes place, it follows that rearrangement occurs. The OMe groups which do not undergo this change must be in a different form of combination from those which do. Four bromination products can be isolated. Of these, two, which constitute 90% of the yield, are similar in composition but differ in their solubility in AcOH. The other two also contain Br and OMe, but differ in composition from the chief products. Of the Br taken up by lignin only 28% is firmly bound; any Br above this amount is removed by alkylation, and when the alkylated lignin is again brominated the amount of Br taken up is less than that originally absorbed. W. McCartney.

Pine-wood lignin. B. Rassow and H. Gabriel (Cellulosechem., 1931, **12**, 249—254; cf. this vol., 1041).—Lignin is most probably formed by the condensation of coniferyl alcohol and aldehyde, and is therefore aromatic. The presence of an aromatic complex explains the fact that lignin has a higher C content than has cellulose. On this assumption, and from certain analytical results, a structural formula for glycol-lignin is deduced (corresponding with $C_{30}H_{34}O_{10}$) which shows that this substance should have 3 OMe groups, mol. wt. 554, and a OMe content of about 17%, and the experimentally determined values for the C, H, O, and OMe contents of this substance are in agreement with the calc. vals. Extraction of the wood with numerous solvents and examination of the extracts and residues by means of the phloroglucinol test show that it is impossible to effect complete separation of the substance sensitive to this reaction, and it is therefore highly probable that lignin is identical with this substance. By treatment of wood with cuprammonium solution a product much richer in lignin can be obtained. Glycerol gives a red coloration with phloroglucinol, but this may be distinguished from that given by lignin by its behaviour towards NaOH and conc. H_2SO_4.
B. P. Ridge.

Lignin, coniferyl alcohol, and saligenin. K. Freudenberg, F. Sohns, W. Dürr, and C. Niemann (Cellulosechem., 1931, **12**, 263—276).—The results of optical and *X*-ray investigations of wood and cellulose in connexion with the ultimate structure and morphology of wood fibres and lignin show that the earlier conceptions of the structure of lignin are justified. In the formation of lignin two stages are assumed, first condensation of (on the average) 12 mols. of hydrated γ-3 : 4 dihydroxyphenyl-αβ-propylene glycol to form a chain in which the free phenolic groups may be methylated, and, secondly, conversion of these chains into larger aggregates by polymeris-

ation or condensation, which occurs as a result of chemical action or of a *post-mortem* process. The assumed structure—especially its aromatic and permutoid character—is supported by the results of investigations with coniferyl and salicylyl alcohols. The formation of cellulose is also discussed.

B. P. RIDGE.

Action of magnesium ethyl bromide on chloroacetdiethylamide. S. P. TI (Compt. rend., 1931, **192**, 1462—1466).—The reaction product of MgEtBr and $CH_2Cl·CO·NEt_2$ (this vol., 77) is diethyl-β-hydroxy-β-ethylbutylamine (obtained also from $NHEt_2$ and the corresponding chlorohydrin) (*acetate*, b. p. 97—98°/13 mm.; *phenylurethane*, m. p. 78°; *picrate*, m. p. 130—131°), dehydrated by $SOCl_2$, PCl_5, and 48% HBr to *diethyl-γ-methyl-Δ^{β}-pentenylamine*, b. p. 169° (*picrate*, m. p. 74°; *chloroplatinate*, m. p. 142—143°; *chloroaurate*, m. p. 100—102°), and *diethyl-β-ethyl-Δ^{α}-butenylamine* decomposed at once to $CHEt_2·CHO$ and $NHEt_2$.

G. DISCOMBE.

Synthesis of methionine. G. BARGER and T. E. WEICHSELBAUM (Biochem. J., 1931, **25**, 997—1000).—The product of interaction of Et sodiophthalimidomalonate and β-chloro-α-methylthiolethane was hydrolysed with NaOH to the phthalamidomalonic acid and then with HCl to methionine. The yield was 58% against 6% obtained by Strecker's method (A., 1929, 175).

S. S. ZILVA.

Resolution of synthetic methionine. W. WINDUS and C. S. MARVEL (J. Amer. Chem. Soc., 1931, **53**, 3490—3494).—The *formyl* derivative, m. p. 99—100°, of *dl*-methionine (A., 1930, 1026) (*Bz* derivative, m. p. 143—145°) is resolved by brucine into *d*-, $[\alpha]_D^{25}$ $+10·62\pm0·5°$ in H_2O (*brucine* salt, m. p. 144—145°), and l-*formylmethionines*, $[\alpha]_D^{25}$ $-10·0\pm0·5°$ in H_2O. These are hydrolysed by 10% HCl to *d*-, $[\alpha]_D^{25}$ $+8·12—8·76\pm0·5°$ in H_2O, and l-*methionine*, $[\alpha]_D^{25}$ $-7·5$ to $-8·11\pm0·5°$ in H_2O (p-*tolylcarbimide* derivative, m. p. 157—158°).

H. BURTON.

Fungus poisons. I. Muscarine. I. F. KOGL, H. DUISBERG, and H. ERXLEBEN (Annalen, 1931, **489**, 156—192).—A physiological method of determining muscarine, based on its influence on the heart-beats of the frog, is described. With its aid pure muscarine is isolated, new steps in the purification being the removal of other bases by filtration through permutit, and precipitation and crystallisation of its salt with the radical $[(NH_3)_2Cr(SCN)_4]'$, analysis of which indicates the formula $[C_8H_{18}O_2N]^+$ for the muscarine ion. The *chloroaurate* is also described. Muscarine is unaffected by $0·1N$-NaOH in N_2, or by H_2 and PtO_2–Pt at room temp.; it is stable to air at p_H 9·8, but not at p_H 4·0. It contains an OH group [*benzoylmuscarine chloroplatinate*, m. p. 256—257° (decomp.)], and gives the Schiff and Angeli–Rimini aldehyde reactions. The Hofmann degradation (Ag_2O on the chloride) gives NMe_3, an unidentified volatile substance, m. p. 70°, and d-αβ-*dihydroxy*-n-*valeric acid*, m. p. 72°, $[\alpha]_D^{20}$ $+180·7°$ in H_2O [p-*phenylphenacyl* ester, m. p. 207°; identified by direct comparison (mixed m. p. and $[\alpha]_D$) with the *l*-isomeride]. Muscarine is therefore considered to be $OH·CHEt·CH(CHO)·NMe_3·OH$ or $CHO·CH(OH)·CHEt·NMe_3·OH$, probably the former on account of its stability to alkalis; the formation of a carboxylic acid in the Hofmann degradation is due to the oxidising action of the Ag_2O. *dl*-αβ-Dihydroxy-*n*-valeric acid (p-*phenylphenacyl* ester, m. p. 207°), obtained by oxidation of Δ^{α}-pentenoic acid with $AgClO_3$–OsO_4 (cf. A., 1930, 1271), was resolved by means of its brucine salt, but only the l-*acid*, m. p. 72° (*brucine* salt, $[\alpha]_D^{20}$ $-260·8°$ in $CHCl_3$; p-*phenylphenacyl* ester, m. p. 207°), was obtained optically pure. β-*Methyl-αβ-dihydroxybutyric acid*, m. p. 94° (p-*phenylphenacyl* ester, m. p. 182°), was prepared by the action of boiling $0·4N$-KOH on Et dimethylglycidate (this vol., 604), and *αγ-dihydroxybutane-β-carboxylic acid*, m. p. 167°, obtained by reduction of Et hydroxymethyleneacetoacetate with Na and EtOH, were also synthesised for comparison.

H. A. PIGGOTT.

Hydrolysis of chitin by hydrochloric acid. I. L. ZECHMEISTER and G. TOTH (Ber., 1931, **64**, [*B*], 2028—2032).—When chitin is treated for 15 hr. at 20° with aq. HCl saturated at 0° the yields are approx. 25% of acetylglucosamine, 15% of material insol. in H_2O, but sol. in dil. acids, and 60% of intermediate fractions of complex composition which immediately give horny, amorphous products. Mild acetylation of them in pyridine yields a mixture of cryst. acetates of which the simplest member is a biose octa-acetate, $C_{28}H_{40}O_{17}N_2$, m. p. 305° (corr.), $[\alpha]_D$ $+55°$ in AcOH, probably identical with the chitobiose octa-acetate of Bergmann and others (this vol., 250) and characterised by free solubility in cold $CHCl_3$. More complex cryst. acetates sparingly sol. in cold $CHCl_3$ and with lower $[\alpha]_D$ have been isolated.

H. WREN.

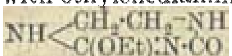
Formation of glycine from serine. B. H. NICOLET (Science, 1931, **74**, 250; cf. this vol., 638).—The mechanism is discussed. No glycine has been detected when cysteine is hydrolysed with alkali.

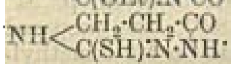
L. S. THEOBALD.

Physico-chemical behaviour of polypeptides derived from $l(+)$-alanine. E. ABDERHALDEN and W GOHDES (Ber., 1931, **64**, [*B*], 2070—2073).—$l(+)$-Alanine polypeptides have been prepared from $l(+)$-alanine and $d(+)$-α-bromopropionyl chloride. Compounds more complex than *d*-α-bromopropionyl-di-*l*-alanyl-*l*-alanine are extraordinarily voluminous and gelatinous and, after desiccation, swell to some extent in H_2O. The penta- and hexa-peptides are obtained exclusively as strongly swollen, hydrated gels from H_2O or aq. NH_3; this behaviour is not shown by the corresponding glycine peptides. They are markedly hygroscopic and retain $1H_2O$ which cannot be removed by desiccation in high vac. without alteration to the polypeptide. Marked diminution in solubility is exhibited by the tetrapeptide; the penta-compound is sparingly sol. and the hexapeptide completely insol. in H_2O. Decrease in solubility is accompanied by increase in colloidal properties which predominate in the case of the pentapeptide and are exclusive with the hexa-derivative. The colloidal particles are negatively charged. The following vals. are recorded for $[\alpha]_D^{20}$ in $2N$-HCl; *l*-alanine, $+14·5°$; *l*-alanyl-*l*-alanine, $-37·6°$; di-*l*-alanyl-*l*-alanine, $-77·5°$; tri-*l*-alanyl-*l*-alanine, $-115°$; tetra-*l*-alanyl-*l*-alanine, $-133°$.

H. WREN.

***cis–trans* Isomerism in ethyl carbethoxythiocarbamate. Synthesis of four-, five-, six-, and seven-membered heterocyclic compounds from ethyl carbethoxythiocarbamate.** P. C. GUHA and N. C. DUTT (Proc. XV Indian Sci. Cong., 1928, 157).—Et carbethoxythiocarbamate, m. p. 144°, is converted by boiling with dil. aq. HCl into a form, m. p. 44°; with ethylenediamine the latter gives

 and the former gives



CHEMICAL ABSTRACTS.

Guanidine and nitrous acid. I. W. D. BANCROFT and B. C. BELDEN (J. Physical Chem., 1931, **35**, 2684—2688).—Treatment of a cold, acid solution of guanidine with N_2O_3 yields cyanamide. The product obtained after a 73% conversion contained no carbamide, cyanide, or dicyanodiamide.

L. S. THEOBALD.

Extension of Michael's reaction. P. C. GUHA and M. N. CHAKLADAR (Proc. XV Indian Sci. Cong., 1928, 150).—Compounds, *e.g.*, $CS(NRNa){\cdot}CH(CO_2Et)_2$, formed from thiocarbimides and Na derivatives of Et acetoacetate, malonate, and cyanoacetate are easily decomposed by acids to yield compounds of the general formula NHR·CSMe, CO_2, and alcohol. Carbimides afford compounds NHR·COMe.

CHEMICAL ABSTRACTS.

Isomerism of hydrocyanic acid. L. REICHEL and O. STRASSER (Ber., 1931, **64**, [*B*], 1997—1999).—Comparison of the absorption spectra of *iso*amyl cyanide and -carbylamine and HCN in *n*-heptane shows that the acid exists mainly in the nitrile form.

H. WREN.

Valency problem of boron. VI. Valency manifestations of boron in boron tri-*p*-anisyl, tri-*tert*.-butyl, and tri-*sec*.-propyl. Possible existence of mixed boron trialkyls. E. KRAUSE and P. NOBBE (Ber., 1931, **64**, [*B*], 2112—2116).—*Boron tri-p-anisyl*, m. p. 128° (vac., corr.), from Mg, *p*-bromoanisole, and BF_3 in Et_2O, forms an additive *product*, $C_{21}H_{24}O_3NBr$, m. p. 191° (decomp.), with NH_3, combines with pyridine and Na, and is converted by air into boron tri-*p*-anisyl oxide. BF_3 and Mg-*tert*.-BuCl in Et_2O afford *B tri-*tert.*-butyl*, b. p. 71°/12 mm., readily oxidised by air, which does not unite with Na and gives a non-cryst. *ammonate* which loses NH_3 at about 85°/atm. It is transformed by regulated oxidation into tert.*-butylboric acid*, m. p. 113° (corr.), stable to light and air. *B tri-*sec.*-propyl*, b. p. 33—35°/12 mm., resembles the *tert*.-butyl derivative. BPhO and MgEtBr react vigorously and the product when distilled gives BEt_3 and BPh_3. The prep. of suitable mixed B trialkyls appears possible, but there is a very pronounced tendency towards the the production of symmetrical compounds.

H. WREN.

Applications of thallium compounds in organic chemistry. VI. Thallium and dialkylthallium derivatives of tetra-acetylethane and tetra-acetylpropane. R. C. MENZIES and E. R. WILTSHIRE (J.C.S., 1931, 2239—2243).—*Thallium, dimethylthallium*, and *diethylthallium tetra-acetylethane* decompose when heated, are sol. in H_2O, but not in organic solvents, and hence belong to the type of salts (cf. Sidgwick and Brewer, A., 1926, 71), whereas thallium and *dimethylthallium tetra-acetylpropane*, m. p. 98°, behave as chelate compounds. The decreased stability of the non-alkylated compound as compared with the alkylated one may be due to a diminution of the labile co-ordinating capacity of the metal in the latter case.

F. R. SHAW.

Reaction between tin trimethyl hydroxide and methyl iodide. T. HARADA (Bull. Chem. Soc. Japan, 1931, **6**, 240—241).—The compound $(SnMe_3)_3OI,H_2O$, previously obtained from $SnMe_3OH$ and $SnMe_3I$ (A., 1925, i, 1254; 1927, 685), is also formed from $SnMe_3OH$ (2 mols.) and MeI (1 mol.) in Et_2O (cf. A., 1930, 1565); conductivity measurements indicate that it is a salt.

H. BURTON.

Hydrocarbons, benzylidene*cyclo*hexane, and 1-benzyl-Δ^1-*cyclo*hexene. D. KURSANOV (Ber., 1931, **64**, [*B*], 2297—2301).—PhCHO and Mg *cyclo*hexyl bromide afford phenyl*cyclo*hexylcarbinol with considerable amounts of $CH_2Ph{\cdot}OH$. The K derivative of the carbinol and CS_2 afford *K* cyclo*hexylbenzyl xanthate*, $C_6H_4{\cdot}CH(CH_2Ph){\cdot}O{\cdot}CS_2K$ (corresponding *Pb* salt), transformed by MeI in C_6H_6 into the *Me* ester, m. p. 54—55°. The last-named compound decomposes at 160—175°/15 mm. into *benzylidene*cyclo*hexane*, b. p. 117—118·5°/10 mm., the structure of which is confirmed by its oxidation to *cyclo*hexanone and BzOH. The hydrocarbon differs from the isomeric product, b. p. 127·2—128·4°/15 mm., derived from $CH_2Ph{\cdot}OH$ and *cyclo*hexene, and P_2O_5, which must therefore be regarded as benzyl-Δ^1-*cyclo*hexene (cf. A., 1915, i, 789).

H. WREN.

Catalytic hydrogenation of aromatic hydrocarbons under high pressure and high temperature. I. KAGEHIRA (Bull. Chem. Soc. Japan, 1931, **6**, 241—254).—Hydrogenation of aromatic hydrocarbons in presence of 8% of their wt. of reduced Ni is studied. C_6H_6 at 200°/76 atm. (all pressures quoted are the initial pressures at 0°) gives an almost quant. yield of *cyclo*hexane. Similarly, Ph_2 at 200°/95 atm. affords di*cyclo*hexyl (I), but at 250°/95 atm. phenyl*cyclo*hexane is produced [by dehydrogenation of (I)]. $C_{10}H_8$ at 200°/91 atm. yields tetrahydronaphthalene, reduced further at 160°/91 atm. to a mixture of 90% of *cis*- and 10% of *trans*-decahydronaphthalenes. Decahydroacenaphthene is obtained at 200°/94 atm., but at 270°/102 atm. tetrahydroacenaphthene results. Anthracene at 200°/97 atm. gives a mixture of octa- (1 pt.), solid (m. p. 60·5—61°) *tetradeca*- (3 pts.), and liquid (b. p. 150—155°/13 mm.) *tetradeca*-hydro-derivatives (2 pts.), whilst phenanthrene (containing a trace of a S compound) at 260°/83 atm. affords only 6% of tetrahydrophenanthrene. This is reduced at 175°/87 atm. to mainly octa- (II) and a little tetradeca-hydrophenanthrene (III); (III) is obtained from (II) in 13% yield at 160°/77 atm. Pyrene is reduced at 300°/82 atm. to hexahydropyrene, which at 210°/92 atm. gives decahydropyrene, converted at 240°/107 atm. into a mixture of isomeric *hexadecahydropyrenes*, m. p. 87—88° and b. p. 162—166°/9·5 mm.

H. BURTON.

Nitration of benzene. P. S. VARMA and K. A. JOSHI (Proc. XV Indian Sci. Cong., 1928, 151).—The

presence of Sn during nitration of C_6H_6 by HNO_3 in absence of H_2SO_4 slightly increases the yield of $PhNO_2$.
CHEMICAL ABSTRACTS.

Diphenyl series. C. COURTOT and C. C. LIN (Bull. Soc. chim., 1931, [iv], **49**, 1047—1065).—Sulphonation of 4 : 4′-dibromodiphenyl with $ClSO_3H$ in $CHCl_3$ affords 4 : 4′-*dibromodiphenylene*-2 : 2′-*sulphone*, m. p. 315°, and 4 : 4′-*dibromodiphenyl*-3-*sulphonic acid* (Ca and Na salts; *chloride*, m. p. 131°; *amide*, m. p. 200°); with $ClSO_3H$ alone at 60°, 42% of 4 : 4′-dibromodiphenylenesulphone, 41·5% of 4 : 4′-*dibromodiphenyl*-3 : 3′-*disulphonic acid* (*Na* salt; *diamide*, m. p. 332°), and 12·5% of 4 : 4′-*dibromodiphenyl*-3 : 3′-*disulphonyl chloride*, m. p. 210°, are obtained. Sulphonation with H_2SO_4 at 80° for 4 hr. yields the same disulphonic acid; with 16% oleum, 21% of 4 : 4′-dibromodiphenylenesulphone, 21% of an isomeric *sulphone*(?), sinters about 450°, and 45% of the 3 : 3′-disulphonic acid; and with 30% oleum, 73% of the 3 : 3′-disulphonic acid and 13·5% of a 4 : 4′-*dibromodiphenylenesulphonedisulphonic acid* (?3 : 6) (*Na* salt). 4 : 4′-Dibromodiphenylenesulphone, m. p. 315°, is not identical with the product obtained by bromination of diphenylene sulphide and oxidation (A., 1928, 896), and since with 22% aq. NH_3 in presence of Cu_2Cl_2 at 250° for 10 hr. it is converted into 4 : 4′-diaminodiphenylenesulphone, m. p. 327—328° (Ac_2 derivative, m. p. 406—407°; Bz_2 derivative, m. p. 413—414°), affording diphenylenesulphone on diazotisation and decomp. with EtOH, the latter must be the 3 : 3′-Br_2-derivative. 75% yields of diphenyl are obtained by Job and Reich's method from PhBr and Mg in presence of $FeCl_3$, and a 95% yield of 4 : 4′-dibromodiphenyl on aq. bromination.

The following are obtained from the corresponding benzidinesulphonic acids by the Sandmeyer reaction; yields of 95—98% for the I-, 80—85% for the Br-, and 65—70% for the Cl-derivatives are obtained: 4 : 4′-*dichloro-acid* (Na salt; *dichloride*, m. p. 148°; *diamide*, m. p. 308°), 4 : 4′-*dibromo*- (Na salt; *dichloride*, m. p. 190°; *diamide*, m. p. 296°), and 4 : 4′-*di-iodo-diphenyl*-2 : 2′-*disulphonic acid* (*dichloride*, m. p. 232°; *diamide*, m. p. above 400°); 4 : 4′-*dichloro*- (Na salt; *dichloride*, m. p. 172°; *diamide*, m. p. 286—287°), 4 : 4′-dibromo-, and 4 : 4′-*di-iodo-diphenyl*-3 : 3′-*disulphonic acid* (Na salt; *dichloride*, m. p. 254°; *diamide*, m. p. 316°); 4 : 4′-*dichloro*- (Na salt; *chloride*, m. p. 104°; *amide*, m. p. 189°), 4 : 4′-dibromo-, and 4 : 4′-*di-iodo-diphenyl*-3-*sulphonic acid* (Na salt; *chloride*, m. p. 157°; *amide*, m. p. 192°).
R. BRIGHTMAN.

Action of aliphatic oxides on aromatic compounds. Preparation of substituted dibenzyls. R. A. SMITH and S. NATELSON (J. Amer. Chem. Soc., 1931, **53**, 3476—3479).—Addition of ethylene oxide (1 mol.) to a mixture of $AlCl_3$ (1 mol.) and C_6H_6 (6 mols.) gives dibenzyl (65%) and β-phenylethyl alcohol (5%) (cf. A., 1925, i, 1278). 4 : 4′-Dibromodibenzyl is prepared similarly from PhBr in 70% yield. Propylene oxide and C_6H_6 afford α-methyldibenzyl (46%) and α-phenyl*iso*propyl alcohol (8%); with PhBr 32% of 4 : 4′-*dibromo-α-methyldibenzyl*, m. p. 95°, is produced.
H. BURTON.

Action of bromine on substituted ethylenes. F. ARNDT and L. LORENZ (Ber., 1931, **64**, [*B*], 2073—2075; cf. this vol., 234).—A reply to Bergmann (A., 1930, 1569; this vol., 949).
H. WREN.

Naphthalene model. N. NAKATA (Ber., 1931, **64**, [*B*], 2059—2069).—Measurements of the dipole moments of a series of derivatives show that only the α-positions in the $C_{10}H_8$ mol. are truly aromatic. Substituents in the β-position are in aliphatic or less markedly aromatic union, thus explaining the difference between 2 : 3-dihydroxy- and other *o*-dihydroxy-naphthalenes. Centrosymmetry, ascribed to the $C_{10}H_8$ mol., is exhibited by 1 : 5-difluoro-, 1 : 4-dichloro-, 1-bromo-5-nitro-, and 1 : 7-dichloronaphthalenes but the possession of a small moment by 2 : 6-dichloronaphthalene is remarkable. The following observation appear new: *α-naphthalenediazonium fluoborate*, decomp. 110°; *β-naphthalenediazonium fluoborate*, decomp. 116°; 2-*fluoronaphthalene*, m. p. 58°; 2 : 8-dichloronaphthalene, m. p. 134° (modified prep.); 1 : 5-*naphthalenebisdiazonium fluoborate*, decomp. 190°, and 1 : 5-*difluoronaphthalene*, m. p. 70°; 1-*bromonaphthalene-2-diazonium fluoborate*, decomp. 98—99°, and 1-*bromo-2-fluoronaphthalene*, m. p. 49°; 1-bromo-2-iodonaphthalene, m. p. 94°; 2-*chloro*-1-*bromonaphthalene*, b. p. 110°/21 mm., m. p. 60°.

The observation that 2 : 6-dichloronaphthalene has a finite dipole moment has led to unsuccessful attempts to resolve the naphthoic acids and naphthylamines into optically active components, during which the following substances have been prepared: *brucine α-naphthoate* (+H_2O), m. p. 182° (decomp.), $[\alpha]_D$ −27·0° in $CHCl_3$, and *brucine β-naphthoate*, m. p. 139° (decomp.), $[\alpha]_D$ −13·7° in $CHCl_3$; *quinine β-naphthoate*, decomp. 130—131°, $[\alpha]_D$ −152·9° in $CHCl_3$; *α-naphthylamine camphorsulphonate*, m. p. 186°, $[\alpha]_D$ +23·4° in EtOH, and *β-naphthylamine camphorsulphonate*, m. p. 200°, $[\alpha]_D$ +29·2° in EtOH; *α-naphthylamine bromocamphorsulphonate*, m. p. 219°, $[\alpha]_D$ +60·6° in $COMe_2$, and *β-naphthylamine bromocamphorsulphonate*, m. p. 192°, $[\alpha]_D$ +38·1° in EtOH.
H. WREN.

Dihydro-derivatives of 1- and 2-methylnaphthalene. V. VESELY and J. KAPP (Coll. Czech. Chem. Comm., 1931, **3**, 448—455).—Reduction of 1-$C_{10}H_7Me$ (I) by Na and 96% EtOH is only partial. The product, when treated with Br in $CHCl_3$, gives ar-*dibromo*-5 : 6 : 7 : 8-*tetrahydro*-1-*methylnaphthalene*, m. p. 86—87°, and a liquid mixture of dibromide and unchanged (I). When this mixture is distilled in steam, partial removal of HBr occurs. The dibromide (? the cryst. portion), when treated with Zn in boiling MeOH, followed by MeOH saturated with HCl, gives an autoxidisable mixture (II) of *ar*-dihydro-1-methylnaphthalenes, b. p. 116—117°/11 mm. Reduction is proved to have affected the *ar*-nucleus because (II) gives hemimellitic acid on oxidation with $KMnO_4$. (II) contains 10% of 6 : 8-dihydro-1-methylnaphthalene, isolated as $Hg(OAc)_2$ compound, m. p. 160—162°, whilst the remainder, being oxidised by $Hg(OAc)_2$ to liquid glycols, is either the 5 : 6- or 7 : 8-dihydro-derivative. 2-$C_{10}H_7Me$, however, affords more 5 : 8-dihydro-derivative; by similar treatment ar-*dibromo*-5 : 6 : 7 : 8-*tetrahydro*-2-*methylnaphthalene* (III), m. p. 90—91°, was obtained, which gives a mixture of *ar*-dihydro-2-methylnaphthalenes, b. p. 107—108°/

14 mm., giving benzene-1 : 2 : 4-tricarboxylic acid on oxidation; this mixture contains 58% of 6 : 8-dihydro-derivative (IV), isolated as $Hg(OAc)_2$ compound, m. p. 124—126°. When regenerated from the latter by conc. HCl, (IV) provides (III) on bromination.

2-Methyl-α-naphthylamine, when treated with Na in amyl alcohol, gives 2-*methyl*-5 : 6 : 7 : 8-*tetrahydro-α-naphthylamine*, b. p. 158—161° (*hydrochloride*; *Ac* derivative, m. p. 185—186°), which, when diazotised and warmed in dil. H_2SO_4, gives 2-*methyl*-5 : 6 : 7 : 8-*tetrahydro-α-naphthol*, m. p. 41—42°, in poor yield.
R. S. CAHN.

1 : 5- and 1 : 8-Dimethylnaphthalene. V. VESELÝ and F. ŠTURSO (Coll. Czech. Chem. Comm., 1931, **3**, 430—431).—Mg 1-methyl-5-naphthyl bromide (prepared from Mg activated by MeI) with Me_2SO_4 in presence of N_2 gives 1 : 5-*dimethylnaphthalene*, m. p. 77—78° (*picrate*, m. p. 137—138°). 1 : 8-*Dimethylnaphthalene*, an oil (*picrate*, m. p. 141 142°), is similarly prepared. R. S. CAHN.

2 : 8-Dimethylnaphthalene. V. VESELY and A. MEDVEDEVA (Coll. Czech. Chem. Comm., 1931, **3**, 440—447).—7-Methyl-α-naphthol could not be converted into 1-chloro-7-methylnaphthalene. When 2-methylnaphthalene-8-sulphonic acid is heated with conc. H_2SO_4 at 100° for 1·5 hr., poured into H_2O, and treated successively with $NaNO_2$ and conc. HNO_3, first at room temp., and then at 100°, 2 : 4-*dinitro*-7-*methyl-α-naphthol* (I), m. p. 166—166·5°, is obtained, which with *p*-toluenesulphonyl chloride in $NPhMe_2$ or $NPhEt_2$ at 100° gives 8-*chloro*-5 : 7-*dinitro*-2-*methylnaphthalene*, m. p. 155·5—156°. This with Et sodiomalonate in Et_2O yields *Et_2* 5 : 7-*dinitro*-2-*methylnaphthalene*-8-*malonate*, m. p. 103—106°, converted by H_2SO_4 in Ac_2O into 5 : 7-*dinitro*-2-*methylnaphthalene*-8-*acetic acid*, m. p. 160—176° (decomp.), which when heated in pyridine at 40°, loses CO_2 to form 5 : 7-*dinitro*-2 : 8-*dimethylnaphthalene*, m. p. 163—165·5°. Reduction of this by $SnCl_2$ and alcoholic HCl at 100° gives a poor yield of 5 : 7-*diamino*-2 : 8-*dimethylnaphthalene*, m. p. 114—116° (hydrochloride), which on diazotisation in aq. EtOH affords 2 : 8-*dimethylnaphthalene*, m. p. 84—85° (*picrate*, m. p. 114—117°). (I) is partly reduced by $SnCl_2$ (3 mols.) and alcoholic HCl at room temp. to 3-*nitro*-4 : 6-*dimethyl-α-naphthylamine*, m. p. 151—153° (*perchlorate*; *Ac* derivative, m. p. 220—222°), and 4-nitro-1 : 7-dimethyl-β-naphthylamine (not obtained pure). The former amine, when diazotised and treated with EtOH, gives 2-*nitro*-1 : 7-*dimethylnaphthalene*, m. p. 56·5—58°, reduced by Fe and AcOH to 1 : 7-*dimethyl-β-naphthylamine*, an oil (*Ac* derivative, m. p. 207—208°). The diazonium salt of this base, when treated with EtOH, gives a *substance*, m. p. 42—43°, and, when decomposed by dil. H_2SO_4, gives 1 : 7-*dimethyl-β-naphthol*, m. p. 138—140°. This does not couple with diazotised *p*-nitroaniline; the constitutions of this and the preceding substances are thus established.

[With M. J. PAC.] 7-Methyl-α-naphthol, NaOAc, NH_4Cl, and Ac_2O at 270° give 7-methyl-α-naphthylamine. R. S. CAHN.

[Polynuclear, aromatic hydrocarbons and their derivatives. IX. Constitution of anthracene.] O. DIELS and K. ALDER (Ber., 1931, **64**, [*B*], 2116—2117; cf. Clar, this vol., 1044).—The authors have shown previously (this vol., 848) that anthracene and 9 : 10-dibromoanthracene add crotonic and maleic acids or their anhydrides etc. in the 9 : 10-position and have interpreted the reaction with respect to the constitution of anthracene.
H. WREN.

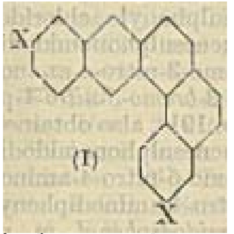
Synthesis of anthracene homologues. III. 2 : 3 : 6 : 7-Tetramethylanthracene. G. T. MORGAN and E. A. COULSON (J.C.S., 1931, 2323—2331).—2 : 3 : 6 : 7-*Tetramethylanthracene* (I), m. p. 308°, and -*anthraquinone* (II), m. p. 338°, have been synthesised by independent methods. (*a*) 3 : 4-*Dimethylbenzoyl chloride*, b. p. 188°/140 mm. (*anilide*, m. p. 108°), condenses alone by Friedel–Crafts reaction to form (II) in small yield, and with ψ-cumene to give 2 : 4 : 5 : 3′ : 4′-*pentamethylbenzophenone*, m. p. 90°, which on pyrolysis affords 2 : 3 : 6 : 7-*tetramethyl*-9-*anthrone*, m. p. 271—272° (when boiled with Ac_2O gives a *substance*, m. p. 233—234°, a complex containing 1 mol. each of 2 : 3 : 6 : 7-tetramethylanthrone and 2 : 3 : 6 : 7-tetramethylanthranyl acetate), readily oxidised to give (II), and reduced by Na to 2 : 3 : 6 : 7-*tetramethyl*-9 : 10-*dihydroanthracene* (III), m. p. 217—219°. (*b*) Condensation of *p*-benzoquinone with βγ-dimethyl-$\Delta^{\alpha\gamma}$-butadiene affords 2 : 3 : 6 : 7-*tetramethyl*-$\Delta^{2:6}$-*octahydroanthraquinone*, m. p. 202—203°, which can be transformed into an *isomeride*, m. p. 307°, the constitution of which is discussed. When O_2 is passed through an alcoholic suspension of this compound, (II) is formed. (II) is reduced by Al powder to 2 : 3 : 6 : 7 : 2′ : 3′ : 6′ : 7′-*octamethyl*-10 : 10′-*dihydroanthranol*, m. p. 319°, and by Na in amyl alcohol to (III), which is dehydrogenated with Se to (I). (I) is contained in the heavy neutral oils of low-temp. tar and can be oxidised to (II). F. R. SHAW.

Anthracene series. Halogenation and nitration. P. S. VARMA and A. SUBRAMANYAM (Proc. XV Indian Sci. Cong., 1928, 151).—Mono- and di-iodoanthraquinone are obtained by the action of $NaNO_2$ and fuming H_2SO_4 on anthracene and I.
CHEMICAL ABSTRACTS.

Synthesis of 4-methylphenanthrene. C. B. RADCLIFFE, I. R. SHERWOOD, and W. F. SHORT (J.C.S., 1931, 2293—2297).—4-Methylphenanthrene, prepared by dehydrogenation with Se of the product of the action of MgMeI on 4-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (from β-naphthyl bromomethyl ketone and Et sodiomalonate), is identical with methanthrene obtained from podocarpic acid either by distillation with zinc dust (Oudemans, A., 1874, 73) or by dehydrogenation with Se. Each hydrocarbon is oxidised to 4-methylphenanthraquinone (*quinoxaline* derivative, m. p. 177°). F. R. SHAW.

Polynuclear aromatic hydrocarbons and their derivatives. X. Naphtho-2′ : 3′ : 3 : 4-phenanthrene and its quinones. E. CLAR and H. D. WALLENSTEIN (Ber., 1931, **64**, [*B*], 2076—2082).—1-*Bromo*-2 : 7-*dimethylnaphthalene*, m. p. 48°, is prepared from the hydrocarbon and Br in CS_2, whilst 1-*iodo*-2 : 7-*dimethylnaphthalene*, m. p. 62°, is obtained by means of I and HIO_3 in boiling AcOH. Treatment of the compounds with Na or Cu powder regenerates the hydrocarbon with possibly a little

tetramethyldinaphthyl. The action of $AlCl_3$ on 2 : 7-$C_{10}H_6Me_2$ or its bromo-derivative yields fluorescent products from which a perylene derivative could not be isolated. 2-$C_{10}H_7Me$ and Cl_2 at 250—286° afford 2-$C_{10}H_7$·CH_2Cl (transformed by Na into αβ-di-2-naphthylethane dehydrogenated by Pt–C to αβ-di-2-naphthylethylene) and much tar; analogous results are obtained with 2 : 7-$C_{10}H_6Me_2$.


(I)

Distillation of the tars with Zn dust yields, respectively, 2′ : 3′-*naphtho-3 : 4-phenanthrene* (I; X=H), m. p. 261° (*dipicrate*, m. p. 213°) and 7 : 7′-*dimethyl-2′ : 3′-naphtho-3 : 4-phenanthrene* (I; X=Me), m. p. 228° (*monopicrate*), neither of which could be dehydrogenated according to Zelinski. The hydrocarbons are oxidised by CrO_3 in AcOH to mixtures of mono- and di-quinones from which 3 : 4-*phthalylphenanthrene*, m. p. 240—241° after darkening, and *dimethyl-3 : 4-phthalylphenanthrene*, m. p. 294° after darkening, are isolated. H. Wren.

Influence of substitution on the oxidation of side-chains in the benzene nucleus. P. S. Varma and P. B. Panicker (Proc. XV Indian Sci. Cong., 1928, 150—151).—In the *p*-series (C_6H_4MeX) the order of decreasing degree of oxidation by neutral aq. $KMnO_4$ is: X=CO_2H, NO_2, Br, Cl, OMe, I, NHAc, and in the *o*-series: NO_2, CO_2H, Br, Cl, NHAc, I.

Chemical Abstracts.

Principle of induced alternate polarity in relation to the reactions of derivatives of *p*-dichlorobenzene and other compounds with sodium methoxide. T. de Crauw (Rec. trav. chim., 1931, **50**, 753—792).—Numerous examples of the replacement of Cl and NO_2 in chloronitro- and nitrobenzenes under the influence of NaOMe are discussed with reference to the theory of alternate polarities; the steric effect is discussed particularly. The effects of various groups on the replacement of Cl in numerous substituted chlorobenzenes are also discussed.

p-$C_6H_4Cl_2$ and BzCl in presence of $AlCl_3$ at 150—170° give 2 : 5-*dichlorobenzophenone* (I), m. p. 88° [*oxime*, m. p. 135° (rapid heating), 207° (slow heating), converted by conc. H_2SO_4 into 2 : 5-*dichlorobenzanilide*, m. p. 122°]. 2 : 5-*Dichloroacetophenone* (II) has b. p. 251°/756 mm., m. p. 14°, when regenerated from its *oxime*, m. p. 130°. Reduction of 2 : 5-dichloronitrobenzene by Lapworth and Pearson's method (J.C.S., 1921, **119**, 765) gives 2 : 5-*dichlorophenylhydroxylamine* (III), m. p. 93°, oxidised by $K_2Cr_2O_7$ and dil. H_2SO_4 to 2 : 5-*dichloronitrosobenzene* (IV), m. p. 101°. 2 : 5-*Dichlorothiophenol*, m. p. 24° (*Pb* salt), prepared by the xanthate method, is similarly oxidised to 2 : 5 : 2′ : 5′-*tetrachlorodiphenyl disulphide*, m. p. 129°. Chlorination of acet-*o*-toluidide by methods other than Chattaway and Orton's gives a mixture of 3- and 5-chloro-derivatives; 3-*chloro-o-toluidine* (*Ac* derivative, m. p. 110°) has b. p. 252—254°/750 mm., m. p. 9°. 2-Acetamidodiphenyl and Cl_2 in AcOH give (after hydrolysis) 3-, m. p. 15° (*Ac* derivative, m. p. 97°), 4′-, m. p. 71° (*Ac* derivative, m. p. 122°), and 5-*chloro-2-aminodiphenyls*, m. p. 54° (*Ac* derivative, m. p. 125°), converted by the usual method into 2 : 3-, b. p. 172°/30 mm., 2 : 4′-, b. p. 191°/30 mm., and 2 : 5-*dichlorodiphenyls* (V), b. p. 182°/3 mm. NH_2Ph and (IV) in AcOH afford 2 : 5-*dichloroazobenzene*, m. p. 64°, reduced by Zn dust and alkali to 2 : 5-*dichlorohydrazobenzene*, m. p. 74°. This is converted into 2 : 5-*dichlorobenzidine*, m. p. 95°, and thence into (V).

The action of NaOMe on numerous 2 : 5-dichlorobenzene derivatives, including the following, is described (the products formed are given in parentheses): I (2 : 5-*dichlorobenzhydrol*, m. p. 66°); II (2 : 5-*dichlorophenylmethylcarbinol*, b. p. 222°/757 mm., and a *compound* $C_{16}H_{12}OCl_4$, m. p. 157°); III (2 : 5 : 2′ : 5′-tetrachloroazoxybenzene and a little 2 : 5 : 2′ : 5′-*tetrachlorohydrazobenzene*, m. p. 124° [also formed by reduction of the *tetrachloroazobenzene*, m. p. 189°]); IV (tetrachloroazoxybenzene); V (5-*chloro-2-hydroxy-*, m. p. 46°, and 2-*chloro-5-hydroxy-diphenyl*, m. p. 63°); 2 : 5-dichlorobenzenesulphonic acid (5-*chlorophenol-2-sulphonic acid*, decomp. about 150°); 2 : 5-dichlorobenzonitrile (5-*chloro-2-methoxybenzonitrile*, m. p. 101°); 2 : 5-dichlorotoluene (mainly 6-chloro-*m*-cresol). The action of NaOMe on polyhalogenobenzenes is reinvestigated. H. Burton.

Mechanism of nitration with nitrates. G. Bacharach and W. Breckstone (Ber., 1931, **64**, [*B*], 2136; cf. Menke, A., 1925, i, 386, 655).—Diacetylorthonitric acid, $(OH)_3N(OAc)_2$, b. p. 45°/15 mm., isolated by the action of Ac_2O on $Cu(NO_3)_2,3H_2O$ whereby $Cu(OAc)_2$ is also produced, is the active agent in Menke's nitration process. The conversion of NH_2Ph into *p*- and *o*-nitroacetanilide is described.

H. Wren.

Derivatives of anilinesulphonyl chloride and aminothiophenol. J. Pollak, R. Pollak, and E. Riesz (Monatsh., 1931, **58**, 118—128).—*Anilinedisulphonyl chloride*, m. p. 94—95° (*dianilide*, m. p. 280°), is obtained with difficulty from sulphanilic acid or PhNHAc and $ClSO_3H$ (Jarsch and Nadel, Diss., Vienna, 1929).

[With A. E. Wittels.] Chloroacetanilide (I), when heated with $ClSO_3H$ (II) at 60° for 2 hr., gives *chloroacetanilide*-p-*sulphonyl chloride* (III), m. p. 112° (*anilide*, m. p. 187°), which with NH_3 gas yields the *sulphonamide*, m. p. 216°, with liquid or warm conc. aq. NH_3 *glycylanilide*-p-*sulphonamide*, m. p. 259°. (III), when heated with AcOH, Ac_2O, NaOAc, and Zn dust, gives *p*-acetylmercaptoacetanilide, and with Zn dust and 10% HCl at 100° *p*-acetamidophenyl disulphide. When (I) and (II) are heated at 150° for 3 hr., anilinetrisulphonyl chloride is obtained, hydrolysis accompanying sulphonation. The SH group in acetylmercaptoacet-*p*-toluidide (IV) [obtained by reductive acetylation of acet-*p*-toluididesulphonyl chloride (*amide*, m. p. 242°)] is in the *o*-position, since this substance is also formed by reductive acetylation of *p*-nitrotoluene-*o*-sulphonyl chloride. Chloroacet-*p*-toluidide (V), when heated with (II) at 60° for 2 hr., gives the o-*sulphonyl chloride*, m. p. 87° (*amide*, m. p. 231°), which on reductive acetylation yields (IV). (V), when heated with (II) and NaCl at 150° for 3 hr., gives the same *p*-toluidinedisulphonyl chloride (VI) as *p*-toluidine or acet-*p*-toluidide; this chloride, on reductive acetylation, gives 4-*acetylmercapto-1 : 5-dimethylbenzthiazole* (VII), m. p. 86—87°, which, when

warmed with Me_2SO_4 and subsequently with *p*-dimethylaminobenzaldehyde and a little piperidine, gives 4-*acetylmercapto*-1-(p-*dimethylaminostyryl*)-2 : 5-*dimethylbenzthiazolium methosulphate* (VIII), violet, m. p. 205—206°. The position of the second SO_3H group in (V) is confirmed by the transformation of (V) into 4-chlorotoluene-2 : 5-disulphonyl chloride. (VII) was also prepared from *p*-toluidinedisulphonyl chloride by treatment first with Zn dust and 20% HCl, and then with Ac_2O or AcCl.

[With A. NADEL.] *o*-Toluidine, when heated with (II) and NaCl at 120—130° for 1 hr., gives the 3 : 5-*disulphonyl chloride*, m. p. 153° (*anilide*, m. p. 188°).

R. S. CAHN.

Preparation of *p*-chloroaniline. K. H. HASAN (Proc. XV Indian Sci. Cong., 1928, 158).—Chattaway and Orton's method is criticised.

CHEMICAL ABSTRACTS.

Lability of fluorine in 4-fluoro-3-nitroaniline. A replacement of fluorine by the ethoxyl group in acid solution. H. H. HODGSON and J. NIXON (J.C.S., 1931, 2272—2274).—The mechanism of the above replacement is discussed. Diazotisation of 4-fluoro-3-nitroaniline gives 2-nitrobenzene-4-diazo-1-oxide, decomp. 178° (*ibid.*, 1915, **109**, 645), brominated to 6-*bromo*-2-*nitrobenzene*-4-*diazo*-1-*oxide*, decomp. 185°, which gives 4-chloro-6-bromo- and 4 : 6-dibromo-2-nitrophenol (also obtained by the action of $CuSO_4$ and KBr on 2-nitrobenzene-4-diazo-1-oxide) by the Sandmeyer reaction, 6-bromo-2-nitrophenol when heated with KOH in EtOH, and 6-*bromo*-4-*iodo*-2-*nitrophenol*, m. p. 85°, when heated with KI and a little $CuSO_4$. 4-Fluoro-3-nitroaniline diazotised in EtOH and H_2SO_4 gives *o*-nitrophenetole, reduced to *o*-phenetidine hydrochloride, which is oxidised by Caro's acid to o-*nitrosophenetole*, m. p. 93°.

A. A. LEVI.

Substituted quaternary azonium iodides. V. Molecular state of phenyl-dimethyl-, -methylethyl-, -diethyl-, -methylbenzyl-, and -propylbenzyl-azonium iodides in solution. B. K. SINGH and M. R. SUD (Proc. XV Indian Sci. Cong., 1928, 148).—For all except phenylethylazonium iodide the degree of dissociation is greater in EtOH than in H_2O. That in H_2O, but not in EtOH, increases with increasing formula wt.; the degree of dissociation increases with dilution in both solvents.

CHEMICAL ABSTRACTS.

Condensation of β-naphthylamine with oxalyl derivatives. G. GALLAS and G. BERMUDEZ (Anal. Fís. Quím., 1931, 29, 464—469).—When β-naphthylamine is heated with $(COEt)_2$ at 150—200° or refluxed with $(COCl)_2$ in CS_2 derivatives of β-naphthyloxamic acid are obtained. Aceto-β-naphthylamide and $(COCl)_2$ with $AlCl_3$ in CS_2 yield (?)2-*acetamidoacenaphthenequinone*, m. p. 232° (*base*, m. p. 196°, yielding *quinoxaline*, m. p. above 250°, with *o*-phenylenediamine), and a *substance*, m. p. 181°.

R. K. CALLOW.

Diphenyl series. X. Bromination of 4-*p*-toluenesulphonamidodiphenyl. F. BELL (J.C.S., 1931, 2338—2343; cf. A., 1930, 904).—Bromination of 4-*p*-toluenesulphonamidodiphenyl in pyridine gives 3 : 5-dibromo- (this vol., 629), and in $CHCl_3$ 3 : 4′-dibromo-4-*p*-toluenesulphonamidodiphenyl, converted (*a*) by HNO_3 in AcOH into 3 : 4′-*dibromo*-5-*nitro*-4-p-*toluenesulphonamidodiphenyl*, m. p. 229°, hydrolysed to the amino-compound, and (*b*) by Br in pyridine into 3 : 5 : 4′-*tribromo*-4-p-*toluenesulphonamidodiphenyl*, m. p. 218°, which gives with *p*-toluenesulphonyl chloride 3 : 5 : 4′-*tribromo*-4-*di*-p-*toluenesulphonamidodiphenyl*, m. p. 274°, also obtained from the tribromoaminodiphenyl and *p*-toluenesulphonyl chloride. Bromination of 3-nitro-4-*p*-toluenesulphonamidodiphenyl in AcOH gives 5 : 4′-dibromo-3-nitro-4-aminodiphenyl, and in pyridine gives 3-*bromo*-5-*nitro*-4-p-*toluenesulphonamidodiphenyl*, m. p. 191°, also obtained by nitration of 3-bromo-4-*p*-toluenesulphonamidodiphenyl, and hydrolysed to 3-bromo-5-nitro-4-aminodiphenyl (A., 1928, 996). 4′-Nitro-4-aminodiphenyl gives 4′-*nitro*-4-p-*toluenesulphonamidodiphenyl*, m. p. 144°, which with Br in pyridine gives 3 : 5-*dibromo*-4′-*nitro*-4-p-*toluenesulphonamidodiphenyl*, m. p. 274°, and in AcOH gives 3-*bromo*-4′-*nitro*-4-*p*-*toluenesulphonamidodiphenyl*, m. p. 144°, converted by HNO_3 in AcOH into 3-*bromo*-5 : 4′-*dinitro*-4-p-*toluenesulphonamidodiphenyl*, m. p. 250°. 2-*p*-Toluenesulphonamidodiphenyl with Br in pyridine gives 3 : 5-*dibromo*-2-*p*-*toluenesulphonamidodiphenyl*, m. p. 118°, hydrolysed to 3 : 5-dibromo-2-aminodiphenyl (A., 1927, 236). 4′-Bromo-4-*p*-toluenesulphonamidodiphenyl with HNO_3 in AcOH gives 4′-*bromo*-3 : 5-*dinitro*-4-p-*toluenesulphonamidodiphenyl*, m. p. 233°. A. A. LEVI.

Diazotisation of difficultly diazotisable amines. S. KRISHNA and R. L. BHATIA (Proc. XV Indian Sci. Cong., 1928, 152).—Pyridine is used as solvent.

CHEMICAL ABSTRACTS.

Organic sulphur-nitrogen linking. VI. E. RIESZ, R. POLLAK, and R. ZIFFERER (Monatsh., 1931, **58**, 147—169; cf. A., 1930, 1573).—The quinonoid formula for the products of oxidation of arylthiolarylamines (*i.e.*, substances of the type Ar·S·NHAr′) by CrO_3 is supported by the fact that these products are formed only when an oxidisable substituent is present in the *o*- or *p*-position of the Ar′ nucleus. A quinone has been obtained from a substance not containing a NO_2 group; hence this group does not take part in the reaction, and, consequently, the valency of the S atom is unchanged. In attempts to elucidate the mechanism of the oxidation in cases in which unimol. quinonoid compounds are not formed, a number of substances were prepared and oxidised. If Ar′ is replaced by an aliphatic radical, no oxidation takes place. If Ar′ is replaced by CH_2Ph (or a substitution product of this), oxidation gives the disulphide $(ArS\cdot)_2$; this reaction doubtless occurs by way of the arylidenethiolamines, ArS·N:CHAr′, since such compounds have been found also to oxidise to form disulphides. No cases were found, when *p*-, or *p*- and *o*-non-oxidisable constituents were present, in which oxidation takes a simple course. Oxidation by PbO_2 in Et_2O or C_6H_6 takes place only when CrO_3 is also effective, and is considered to be due to production of free radicals with subsequent linking of two mols. in two points of each. Many types of product are possible. Attempts to cause the free radicals to react with diazomethane were unsuccessful. Two of the possible bimol. types were synthesised, but found to differ from the oxidation products.

4-Chloro-2-nitro-1-chlorothiolbenzene (I) and p-aminodiphenylamine in Et_2O at 0° give N-4-*chloro-2-nitrophenylthiol*-N'-*phenyl*-p-*phenylenediamine*, reddish-brown, m. p. 104°, which with $Na_2Cr_2O_7$ in AcOH yields N-4-*chloro-2-nitrophenylthiol*-N'-*phenylbenzoquinonedi-imine*, dark red, m. p. 140—150°. o-Aminodiphenylamine and (I) afford similarly N-4-*chloro-2-nitrophenylthiol*-N'-*phenyl*-o-*phenylenediamine*, red, m. p. 122°, and *N-4-chloro-2-nitrophenylthiol*-N'-*phenyl*-o-*benzoquinonedi-imine*, reddish-brown, m. p. 140—142°. p-Aminobenzyl alcohol and (I) give p-(4-*chloro-2-nitrophenylthiolamino)benzyl alcohol*, reddish-yellow, m. p. 154°, which is decomposed by oxidation. *N-p*-Tolylthiolaniline and 30% H_2O_2 in hot AcOH yield a bimol., brown substance, $C_{26}H_{24}N_2S_2$, m. p. 187—190°. p-Chlorothioltoluene and p-aminophenol in dry Et_2O form 4-N-p-*tolylthiolaminophenol*, red, m. p. 68°, yielding on oxidation N-p-*tolylthiolbenzoquinoneimine*, red, m. p. 104°. Shaking (I) in Et_2O with 40% aq. NH_2Me gives 4-*chloro-2-nitrophenylthiolmethylamine*, yellow, m. p. 74°, stable to H_2O_2 and CrO_3, even on warming. Ethylenediamine affords similarly *di-(4-chloro-2-nitrophenylthiol)ethylenediamine*, yellow, m. p. 185—186°, stable to CrO_3 and H_2O_2. Nitrophenylthiol-glycine and -*dl*-leucine esters, chloronitrophenylthiol-*dl*-leucine ester, and chloronitrophenylthiol-leucylglycine and its ester are also stable to H_2O_2 and $Na_2Cr_2O_7$ in AcOH, even on warming. (I) and $CH_2Ph\cdot NH_2$ in Et_2O yield 4-*chloro-2-nitrophenylthiolbenzylamine*, yellow, m. p. 104°, which is unchanged by H_2O_2, but on long heating with CrO_3 in AcOH gives 4-chloro-2-nitrophenyl disulphide (III). Benzylidene-4-chloro-2-nitrophenylthiolamine is stable to CrO_3 in cold AcOH, but when heated gives (III). 4-Chloro-2-nitrophenylthiolamine (IV) and p-dimethylaminobenzaldehyde give the p-*dimethylaminobenzylidene* derivative, red, m. p. 157°, similarly oxidised to the disulphide. 5-Bromo-*m*-4-xylidine and (I) in Et_2O give 5-*bromo*-N-4'-*chloro-2'-nitrophenylthiol*-m-4-*xylidine*, yellow, m. p. 157°; this is oxidised by warm H_2O_2 or CrO_3 in AcOH, but no products were isolated. N-4'-*Chloro-2'-nitrophenylthiolaminoacetophenone*, yellowish-orange, has m. p. 196°. (IV) and picryl chloride in EtOH (with or without NaOAc) give *di-(4-chloro-2-nitrophenylthiol)imide*, yellow, m. p. 232° (cf. A., 1918, i, 537).

The following substances were prepared for comparison with the bimol. oxidation products of 4'-chloro-2'-nitrophenylthiolaniline and similar substances. *NN'*-Di-(4'-chloro-2'-nitrophenylthiol)-*o*-phenylenediamine and pyrocatechol, with or without P_2O_5, at 110° or 150° give a dark, insol. product with too low a C content. 2 : 2'-Dinitrodiphenyl disulphoxide and warm NH_2Ph give a dark product, which was different from the *substance*, $C_{24}H_{18}O_4N_4S_2$, bluish-violet, m. p. 190°, obtained by oxidation of p-nitrophenylthiolaniline with CrO_3 in AcOH.

o-Phenylenediamine, p-toluenesulphonyl chloride, and NaOAc in boiling EtOH form p-*toluenesulphonyl*-o-*phenylenediamine*, m. p. 114°, which with HNO_2 affords 1-p-*toluenesulphonylbenztriazole*, m. p. 133°.

R. S. CAHN.

***cyclo*Hexanonephenyl*cyclo*hexylthiosemicarbazone.** R. STOLLÉ and F. HANUSCH (Ber., 1931, **64**, [*B*], 1979—1980; cf. A., 1930, 1427).—The by-product, m. p. 157°, obtained during the action of *s*-di*cyclo*hexylhydrazine on phenylthiocarbimide in Et_2O (*loc. cit.*) is probably cyclo*hexanonephenyl*cyclo*hexylthiosemicarbazone*, $C_6H_{10}{:}N\cdot N(C_6H_{11})\cdot CS\cdot NHPh$; its production is ascribed to the partial oxidation of the hydrazine to its peroxide during the change. Its prep. from *cyclo*hexylhydrazine, *cyclo*hexanone, and phenylthiocarbimide is described. H. WREN.

Benzene- and naphthalene-azo-*o*-coumaric acids. D. CHAKRAVARTI (J. Indian Chem. Soc., 1931, **8**, 391—396).—When a dil. alkaline solution of a benzene- or naphthalene-azocoumarin is boiled with a little HgO, the first-formed coumarinate undergoes inversion to the coumarate (cf. A., 1930, 913); the following *o*-coumaric acids are prepared : *benzeneazo*- (I), decomp. 205°; o-, decomp. 223°, m-, decomp. 213°, and p- (II), decomp. 236°, -*nitrobenzeneazo*-; *naphthalene-α*- (III), decomp. 198—200°, and -β-*azo*-, decomp. 210°; *benzeneazo*-β : 5-*dimethyl*-, decomp. 186°. *Diphenylbisazodicoumarin*, not melted at 280° (from coumarin and tetrazotised benzidine in alkali), is similarly converted into *diphenylbisazodi*-o-*coumaric acid* (IV), decomp. 315°. *Naphthalene-α*- and -β-*azocoumarins* have m. p. 217° and 271°, respectively. (I), (II), (III), and (IV) are also prepared from *o*-coumaric acid and the requisite diazonium salt in alkali. Benzeneazocoumarin is reduced by $SnCl_2$ and HCl to 6-aminocoumarin. With conc. acids the azo-*o*-coumaric acids become more deeply coloured, probably owing to the formation of a salt of the quinonephenylhydrazone form.

H. BURTON.

New azo dyes. E. JUSA and E. RIESZ (Monatsh., 1931, **58**, 137—146).—Azo dyes, having also the properties of vat dyes, and isomerides of naphthol-AS have been prepared.

[With L. STEINHARDT.] When 6-mercaptocarbethoxy-β-naphthol is boiled with aq. KOH and $CH_2Cl\cdot CO_2K$, β-*naphthol*-6-*thioglycollic acid*, m. p. 156°, is obtained; this on prolonged treatment with $ClSO_3H$ at room temp. gives a dark *substance*, which, since it is sol. in H_2O and is reduced by $Na_2S_2O_4$, appears to contain SO_3H groups and a thionaphthene ring. This product dyes animal fibres dark brown shades (fast to washing and boiling, but not to alkalis), gives a ppt. with metallic salts, and is oxidised by $K_3Fe(CN)_6$ solution to a less sol. compound, which dyes animal fibres bluish-green. Both dyeings give light reddish-brown shades when coupled with diazotised p-nitroaniline. β-Naphthol-3-carboxyl chloride with 2-aminoanthraquinone in $PhNO_2$ at 160° gives the 2-*anthraquinonylamide*, m. p. 275—280°, which dyes cotton yellowish-brown and gives fast red shades when treated with diazotised p-nitroaniline. Anthraquinone-2-sulphonyl chloride with 2-aminoanthraquinone yields a *substance*, $C_{28}H_{14}O_6N_2S$, m. p. 335—338°, which dyes cotton fast dark brown shades. Salicoyl-α- and -β-naphthylamides (the α-compound has m. p. 187°, lit. 182—183°), give azo dyes sensitive to alkali. 4-p-*Nitrobenzeneazosalicoyl-α*- and -β-*naphthylamides* have m. p. 264—265° and 274—275°, respectively. The N-*Bz* derivative of 3-amino-β-naphthol, m. p. 231°, with

diazotised *p*-nitroaniline gives a light red *azo* compound fast to chlorine when coupled on the fibre. 3-Benzamido-β-naphthol has no affinity for cotton.

R. S. CAHN.

Action of diazonium salts, nitrous acid, and hypochlorous acid on *O*-alkylhydroxylamines. A. B. BOESE, jun., L. W. JONES, and R. T. MAJOR (J. Amer. Chem. Soc., 1931, 53, 3530—3541).—Treatment of *O*-methylhydroxylamine with *p*-nitrobenzenediazonium chloride (I) gives MeOH, HCl, and *p*-nitrophenylazide. (I) converts *ON*-dimethylhydroxylamine into N-p-*nitrobenzeneazo*-N-*methoxymethylamine*, m. p. 66°, hydrolysed by conc. HCl at 70° to N_2, *p*-nitrophenol, and *ON*-dimethylhydroxylammonium chloride. N-p-*Nitrobenzeneazo*-N-*ethoxyethylamine*, m. p. 38°, -*methoxy*iso*propylamine*, m. p. 67° (hydrolysed to *O*-methyl-*N*-*iso*propylhydroxylammonium chloride), and -*benzyloxybenzylamine*, m. p. 100°, are obtained from (I) and the requisite *ON*-dialkylhydroxylamines. *N*-Methoxyamylamine and HNO_2 give the N-*nitroso*-derivative, b. p. 83—84°/15 mm., hydrolysed by conc. HCl to diethylcarbinol (3 : 5-*dinitrobenzoate*, m. p. 97°), CH_2O, and N_2, and reduced catalytically (Adams) in AcOH to MeOH and amylamine. The N-*nitroso*-derivatives of *N*-methoxymethylamine and *N*-ethoxyethylamine have b. p. 59—60°/30 mm. and 56—57°/15 mm., respectively; these behave similarly to the above NO-derivative on hydrolysis and reduction. Catalytic reduction (Adams) of these NO-derivatives in EtOH–HCl gives the original *N*-alkoxyalkylamine hydrochloride and NH_4Cl. *O*-Methylhydroxylamine and HNO_2 give MeOH and N_2O; the changes are: $NH_2OMe+HNO_2 \longrightarrow HO{\cdot}N{:}N\,OMe \longrightarrow MeOH+N_2O$. HOCl converts *N*-ethoxyethylamine and *N*-methoxyamylamine into *O*-ethylacetaldoxime and *O*-methyldiethyl ketoxime, respectively. The p-*nitrophenylhydrazone* of $COEt_2$ has m. p. 144.°

H. BURTON.

Catalytic reactions of *cyclo*hexanol at active charcoal. T. BAHR (Ber., 1931, 64, [*B*], 2258—2265).—At 250—300° *cyclo*hexanol is mainly dehydrated by active C (Baeyer) in N_2 to *cyclo*hexene; some dehydrogenation to *cyclo*hexanone and a little to PhOH is observed so that the issuing gas contains H_2. *cyclo*Hexane appears to be due to secondary change, probably union of *cyclo*hexane with nascent H. Slight union of *cyclo*hexene and mol. H_2 is observed at C at 300°. At 350—400° the dehydrogenating effect of active C is more pronounced; production of *cyclo*hexene and *cyclo*hexane is diminished, and the formation of *cyclo*hexanone and PhOH is increased, accompanied by that of a larger proportion of products of higher b. p., including diphenylene oxide and triphenylene. Ph_2O and diphenylene oxide are obtained from PhOH and active C at 300—400°. The results with birch C are similar to those with Baeyer C, but the latter has the greater catalytic activity. $CH_2Ph{\cdot}OH$ and birch C at 300° afford PhCHO, PhMe, and H_2O.

H. WREN.

Hydrogenation of phenol. V. E. TISCHTSCHENKO and M. A. BELOPOLSKI (J. Appl. Chem., Russia, 1930, 3, 1159—1173).—Liquid-phase hydrogenation of PhOH to *cyclo*hexanol is best effected at 155—160°/10—15 atm., a Ni catalyst obtained by igniting Ni formate being used.

CHEMICAL ABSTRACTS.

Lignin. III. Sulphonation in the hydro-aromatic series. Preparation of *cyclo*hexanol-2-sulphonic acid. H. FRIESE (Ber., 1931, 64, [*B*], 2103—2108).—*cyclo*Hexene does not react with H_2SO_4 (mol. ratio 1 : 1) in cold AcOH but addition of Ac_2O to the mixture causes the production of cyclo*hexanol-2-sulphonic acid* (*Ba* and *Na* salts). It is stable towards boiling H_2O, but converted by 25% H_2SO_4 at 150° into an oil of high b. p. derived from primary *cyclo*hexanol (under similar conditions, anisole-*o*-sulphonic acid affords unchanged material, PhOMe, and a little PhOH). The Na salt and KCN yield a nitrile incompletely hydrolysed by 33% HCl to hexahydrosalicylic acid, m. p. 109—111°. *cyclo*Hexene and H_2SO_4 in AcOH at 100° (in absence of Ac_2O) yield *cyclo*hexyl acetate, also derived from the hydrocarbon and AcOH in absence of mineral acid by heating under pressure. *cyclo*Hexene and H_2SO_4 react vigorously to from a dark resin, insol. in H_2O. Sulphonation therefore occurs only in presence of all three components. *cyclo*Hexanol can be sulphonated under similar conditions, but the reaction is complicated by the formation of sulphoacetic acid; since *cyclo*hexene is found as a by-product, it is probable that the primary change is dehydration of the alcohol. *cyclo*Hexene oxide is converted by Ac_2O–AcOH–H_2SO_4 into the monoacetate of *o*-*cyclo*hexane-1 : 2-diol, b. p. 238—241°, hydrolysed to *cis*-*cyclo*hexanediol, m. p. 102—104°; sulphonation of the glycol does not occur.

H. WREN.

Steric transformation of alkoxides. W. HÜCKEL and H. NAAB (Ber., 1931, 64, [*B*], 2137—2141).—*cis*-Decahydro-α-naphthol becomes isomerised when heated in the form of its Na derivative in xylene to *trans*-decahydro-α-naphthol, m. p. 63°, the change corresponding with the racemisation of Na amyloxide by heat. The second *trans*-decahydro-α-naphthol, m. p. 49°, is similarly isomerised to the compound, m. p. 63°, whereas the latter remains unchanged. Isomerisation at the point of junction of the rings does not occur when the alcoholic OH is in the β-position to the C atom 9. The Na derivatives of the *cis*-decahydro-β-naphthols, m. p. 105° and 17°, respectively, yield a mixture containing about 80% of the Na derivative of *cis*-decahydro-β-naphthol, m. p. 105°, and about 20% of that of the substance m. p. 17°; *trans*-decahydro-β-naphthol is not produced. In the *trans*-β-series the Na compounds of the isomeric decahydro-β-naphthols, m. p. 75° and 53°, respectively, yield almost exclusively that of the naphthol, m. p. 75°; *cis*-decahydro-β-naphthol is not produced. In the α-series, the transformation is invariably accompanied by the formation of *trans*-α-ketodecahydronaphthalene in amount which varies, since the ketone is further converted into acids and auto-condensation products. In the β-series the secondary changes occur so much more rapidly that the formation of ketone cannot be established; pre-added ketone is destroyed in less time than is necessary for the isomerisation.

H. WREN.

Phenols of coal tar. O. KRUBER and A. SCHMITT (Ber., 1931, 64, [*B*], 2270—2277).—The initial material

is the residue from the technical distillation of crude cresols. Isolation of *p*-ethylphenol is effected by sulphonation at 100° of the fraction of b. p. 215—218°, removal of xylenol, hydrolysis of the sulphonic acid, and treatment of the phenols with NaOH and $CH_2Cl\cdot CO_2H$. The Na *p*-ethylphenoxyacetate is cryst. from H_2O and decomposed with aq. NaOH at 275°/120 atm. *m*-Ethylphenol is isolated after fractional treatment with aq. NaOH of the product of b. p. 215—218°, through *m*-ethylphenoxyacetic acid, m. p. 76—77°. Technical isolation of *m*-ethylphenol is effected through the corresponding K sulphonate. *p*-Ethylphenol is obtained by sulphonation at 103°, fission of the sulphonates with superheated steam, and collection of the product volatile at 110—130°, followed by re-sulphonation and purification of the Na salt of the sulphonic acid.

The residue, b. p. 227—230°, from the xylenol distillation contains 1 : 3 : 5- and 1 : 2 : 4-xylenol, *iso*-ψ-cumenol [2 : 3 : 5-trimethylphenol] and 3-methyl-5-ethylphenol. *iso*-ψ-Cumenol, m. p. 95—96°, b. p. 233°/760 mm., gives a dibromo-compound, m. p. 152°, *benzoate*, m. p. 50°, *phenylurethane*, m. p. 174°, *phenoxyacetate*, $C_{11}H_{14}O_3$, m. p. 128°, and *Me ether*, b. p. 214—216°/755 mm. *3-Methyl-5-ethylphenol* has m. p. 55°, b. p. 232·5—234·5°/760 mm. (*benzoate*, m. p. 40°; *phenylurethane*, m. p. 152°; *phenoxyacetate*, m. p. 95°). The *Me ether*, b. p. 210°/752 mm., is oxidised by $KMnO_4$ to *5-methoxyisophthalic acid* ($+H_2O$), m. p. 270°, obtained also from 5-methoxy-*m*-xylene. 2 : 3 : 5 : 6-Tetramethylphenol accompanies indole in the fractions of b. p. above 240°. H. WREN.

Replacement of bromine in bromophenols by the nitro-group. I. 2 : 4 : 6-Tribromo-3-nitro- and -3-chloro-phenol. Some cases of group migration. H. H. HODGSON and E. W. SMITH (J.C.S., 1931, 2268—2272; cf. this vol., 958).—*m*-Nitrophenol by an improved process gives 3 : 4-, and 2 : 5-dinitrophenol, converted by Br respectively into 2 : 4-*dibromo*-3 : 6-*dinitrophenol*, m. p. 137°, and 2 : 6-*dibromo*-3 : 4-*dinitrophenol*, m. p. 142°, the latter being also obtained by the action of HNO_3 on 2 : 4 : 6-tribromo-3-nitrophenol. Action of HNO_3 on 3-chloro-2 : 4 : 6-tribromophenol, or of Br on 3- or on 5-chloro-2-nitrophenol, gives 3-*chloro*-4 : 6-*dibromo*-2-*nitrophenol*, m. p. 90°, converted by reduction and diazotisation into (*a*) 2 : 3-dichloro-4 : 6-dibromophenol (A., 1930, 1033), and (*b*) into 3-*chloro*-4 : 6-*dibromo*-2-*iodophenol*, m. p. 105°, both also obtained by reduction, diazotisation, and bromination of 3-chloro-2-nitrophenol. Similarly 5-chloro-2-nitrophenol yields 3 : 6-*dichloro*-2 : 4-*dibromo*-, m. p. 98°, and 3-*chloro*-2 : 4-*dibromo*-6-*iodophenol*, m. p. 93°. 3-Chloro-2 : 6-dibromo-4-nitrophenol, when reduced to 3-*chloro*-2 : 6-*dibromo*-4-*aminophenol*, m. p. 168°, and diazotised gives 3-*chloro*-2 : 6-*dibromo*-4-*iodophenol*, m. p. 102°, also obtained by reduction, diazotisation, and bromination of 3-chloro-4-nitrophenol. A. A. LEVI.

Antipyretic action of *p*-acetamidophenylurethanes. R. F. B. COX, C. R. ECKLER, and R. L. SHRINER (J. Amer. Chem. Soc., 1931, **53**, 3498—3501).—The following alkyl *p*-acetamidophenylcarbamates are prepared from the *p*-NO_2 derivatives (this vol., 709) by catalytic reduction (Adams) in AcOH and subsequent acetylation: *Me*, m. p. 193°; *Et*, m. p. 198°; *Pr*, m. p. 175°; *Pr*$^\beta$, m. p. 164°; *Bu*, m. p. 170·5°; *Bu*$^\beta$, m. p. 165°; sec.-*Bu*, m. p. 177°; sec.-*amyl*, m. p. 165°; n-*hexyl*, m. p. 158°; n-*heptyl*, m. p. 162°, and sec.-*octyl*, m. p. 197·5°. None of these esters has an antipyretic action as great as that of NHPhAc or aminopyrin, and none of them possesses hypnotic activity. H. BURTON.

Interaction of nitroaminophenols with sulphonyl chlorides. F. BELL (J.C.S., 1931, 2343—2353; cf. this vol., 629).—Picramic acid with *p*-toluenesulphonyl chloride (1 mol.) in pyridine gives the *pyridine* salt of 2 : 4-dinitro-6-*p*-toluenesulphonamidophenol, m. p. 203° (Ac derivative, m. p. 190°), both hydrolysed to 2 : 4-*dinitro*-6-p-*toluenesulphonamidophenol*, m. p. 191° (*Ac acetate*, m. p. 174°), also obtained by nitration of 2-*p*-toluenesulphonamidophenol. Picramic acid in pyridine with *p*-toluenesulphonyl chloride (2 mol.) gives *anhydro*-2 : 4-*dinitro*-6-p-*toluenesulphonamidophenylpyridinium hydroxide*, m. p. 249° (decomp.), purified by decomp. of the *chloride*, m. p. 174°, or *nitrate*, m. p. 161° (decomp.), with boiling NaOAc. 2-*p*-Toluenesulphonamidophenyl *p*-toluenesulphonate by mononitration gives the 5-*nitro*-derivative (I), m. p. 159°, hydrolysed to 5-nitro-2-aminophenol, or its p-*toluenesulphonate*, m. p. 188° (*Ac* derivative, m. p. 189°, also obtained in small yield by nitration of 2-acetamidophenyl *p*-toluenesulphonate, and hydrolysed by acid to the nitroaminophenyl *p*-toluenesulphonate, or by alkali to the nitroaminophenol). The nitroaminophenol is reconverted into a mixture of the *p*-toluenesulphonate and (I) by *p*-toluenesulphonyl chloride in pyridine. 2-*p*-Toluenesulphonamidophenyl *p*-toluenesulphonate by more intense nitration gives the 3 : 5-*dinitro*-derivative, m. p. 188°, hydrolysed to 3 : 5-*dinitro-2-aminophenol*, m. p. 218° [p-*toluenesulphonate* (II), m. p. 186°; *Ac* p-*toluenesulphonate* (III), m. p. 205°; *Ac acetate*, m. p. 180°]. The Ac acetate gives 3 : 5-*dinitro-2-acetamidophenol*, m. p. 171°, converted by *p*-toluenesulphonyl chloride into (III), or by β-naphthoyl chloride into 3 : 5-*dinitro*-2-β-*naphthamidophenyl* β-*naphthoate*, m. p. 185°, hydrolysed to 3 : 5-*dinitro*-2-β-*naphthamidophenol*, m. p. 200°. 3-Nitro-2-aminophenol gives a p-*toluenesulphonate* (IV), m. p. 136° [*Ac* derivative (V), m. p. 134°]. 3-Nitro-2-acetamidophenol gives (*a*) a *p*-toluenesulphonate, hydrolysed to (IV), and further acetylated to (V), and (*b*) a β-*naphthoate*, m. p. 177°, which with warm NaOH gives 3-*nitro*-2-β-*naphthamidophenol*, m. p. 140°. 4-Nitro-2-aminophenol gives a p-*toluenesulphonyl* p-*toluenesulphonate*, m. p. 132°, nitrated to 3(?) : 4-*dinitro*-2-p-*toluenesulphonamidophenyl* p-*toluenesulphonate*, m. p. 154° (*pyridine* salt, m. p. 124°, hydrolysed to the *dinitro-2-aminophenol*, which gives a *mono*-p-*toluenesulphonyl* derivative, m. p. 165°). 5-Nitro-2-acetamidophenol gives a β-*naphthoyl* β-*naphthoate*, m. p. 213°, hydrolysed to a mixture of the original, and 5-*nitro*-2-β-*naphthamidophenol*, m. p. 282° (VI). 5-Nitro-2-acetamidophenol with β-naphthoyl chloride gives a little (VI), and a β-*naphthoate*, m. p. 167°, which is converted into (VI) by treatment with warm NaOH. 2-*p*-Toluenesulphonamidophenyl acetate gives a mixture of (*a*) the 5-*nitro*-derivative, m. p.

178°, hydrolysed to 5-nitro-2-aminophenol, or to 5-*nitro*-2-p-*toluenesulphonamidophenol*, m. p. 188° (β-*naphthoate*, m. p. 188°, hydrolysed to the *p*-toluenesulphonyl derivative), which gives (I) with *p*-toluenesulphonyl chloride; and (*b*) the 3-*nitro*-derivative, m. p. 122°, hydrolysed to 3-nitro-2-aminophenol. 3-*p*-Toluenesulphonamidophenyl *p*-toluenesulphonate is nitrated to the 4 : 6-*dinitro*-derivative, m. p. 158°, hydrolysed to 4 : 6-dinitro-3-aminophenol, m. p. 227°, and converted by pyridine and subsequent treatment of the HCl solution of the product with boiling NaOAc into *anhydro*-4 : 6-*dinitro*-3-p-*toluenesulphonamidophenylpyridinium hydroxide*, m. p. 263°, also obtained as follows. *m*-Chloroaniline and *p*-toluenesulphonyl chloride give p-*toluenesulphon*-3-*chloroanilide*, m. p. 135°, nitrated to a mixture of 1-*chloro*-4-*nitro*-5-p-*toluenesulphonamidobenzene*, m. p. 135° (hydrolysed to 5-chloro-2-nitroaniline, m. p. 124°), and 1-*chloro*-2 : 4-*dinitro*-5-p-*toluenesulphonamidobenzene*, m. p. 158°, hydrolysed to 5-chloro-2 : 4-dinitroaniline, m. p. 174°, and converted by pyridine and boiling NaOAc into the above anhydro-compound. Less energetic nitration of 3-*p*-toluenesulphonamidophenyl *p*-toluenesulphonate gives the 4-*nitro*-derivative, m. p. 114°, hydrolysed to 4-nitro-3-aminophenol. 4-Benzylideneaminophenol on nitration gives a small yield of 2 : 4-dinitro-4-aminophenol, which gives with *p*-toluenesulphonyl chloride in pyridine, and treatment of the product with HCl, 2 : 6-*dinitro*-4-p-*toluenesulphonamidophenylpyridinium chloride*, m. p. 205°, converted by hot NaOAc into *anhydro*-2 : 5-*dinitro*-4-p-*toluenesulphonamidophenylpyridinium hydroxide*, m. p. 243°.

A. A. LEVI.

Separation of cresols : properties of pure *m*-cresol. G. DARZENS (Compt. rend., 1931, **192**, 1657—1659).—Separation of mixtures of *m*- and *p*-cresol is effected by treatment of the mixture in an org. solvent with anhydrous NaOAc with vigorous stirring, when only the *m*-cresol forms a compound. The complex $2m\text{-}C_6H_4Me\cdot OH,5NaOAc$ is collected and decomposed by H_2O, and the *m*-cresol recovered. *p*-Cresol is separated from the filtrate by treatment with powdered oxalic acid. Further purification of *m*-cresol is effected by fractional crystallisation of the benzoate, followed by hydrolysis. Pure *m*-cresol has m. p. 11·8°, b. p. 200°/752 mm., 98°/17 mm. (benzoate, m. p. 56°; acetate, m. p. 12°); Raschig nitration index 184%.

G. DISCOMBE.

Addition of phenols to the ethylenic linking. II. Action of phenols on allyl alcohol, allyl acetate, vinyl acetate, and allyl ethers. J. B. NIEDERL, R. A. SMITH, and M. E. McGREAL (J. Amer. Chem. Soc., 1931, **53**, 3390—3396).—*m*-Cresol and allyl alcohol in presence of conc. H_2SO_4 (cf. this vol., 346) give 4-*iso*propenyl-*m*-cresol, also formed similarly from allyl acetate, Et allyl ether, and diallyl ether, and when m-*tolyl* iso*propenyl ether*, b. p. 188—189° (from K *m*-tolyloxide and *iso*propenyl bromide), is treated with H_2SO_4 in AcOH. *o*-*iso*Propenylphenol is obtained similarly using PhOH and the above allyl compounds, whilst PhOH and vinyl acetate give *o*-vinylphenol. The reactions can be explained by the mechanism previously suggested (*loc. cit.*).

H. BURTON.

Alkyl and arylsulphonyl derivatives of *o*-aminophenols. L. C. RAIFORD and O. GROSZ (J. Amer. Chem. Soc., 1931, **53**, 3420—3426).—3-Bromo-5-amino-*p*-cresol yields the same N-*carbethoxy*-O-*benzoyl* derivative, m. p. 142°, no matter in which order the groups are introduced. Diacylation gives isomeric derivatives when 1 of the acyl groups is SO_2R and the other contains CO or CO_2R, depending on the order of introduction. No rearrangements occur during hydrolysis of these isomerides. It is considered that the repulsion energy of atomic kernels (Latimer, A., 1930, 9) cannot be the sole factor in the migration of acyl groups between N and O in *o*-aminophenols.

The following derivatives of 3-bromo-5-amino-*p*-cresol are described : N-*benzenesulphonyl*, m. p. 157°; N-β-*naphthalenesulphonyl*, m. p. 174·5°; N-*carbethoxy*-, m. p. 83°; N-*carbomethoxy*-, m. p. 112—112·5°; ON-*Bz*$_2$, m. p. 166°; ON-*dibenzenesulphonyl*, m. p. 230°; N-*Bz*-O-*benzenesulphonyl*, m. p. 114°; O-*Bz*-N-*benzenesulphonyl*, m. p. 172°; N-*Ac*-O-*benzenesulphonyl*, m. p. 116—116·5°; O-*Ac*-N-*benzenesulphonyl*, m. p. 156—157°; N-*carbethoxy*-O-*benzenesulphonyl*, m. p. 115—115·5°; O-*carbethoxy*-N-*benzenesulphonyl*, m. p. 144—145°; ON-*di*-β-*naphthalenesulphonyl*, m. p. 141—142°; N-*benzenesulphonyl*-O-β-*naphthalenesulphonyl*, m. p. 123°; O-*benzenesulphonyl*-N-β-*naphthalenesulphonyl*, m. p. 126°; N-*carbomethoxy*-O-2-*chloro*-5-*nitrobenzenesulphonyl*, m. p. 151°; ON-*di*-2-*chloro*-5-*nitrobenzenesulphonyl*, m. p. 221°; ON-*dibutanesulphonyl*, m. p. 78·5°; ON-*di*-2-*nitro*-p-*toluenesulphonyl*, m. p. 175—176°; ON-*di*-p-*bromobenzenesulphonyl*, m. p. 130—131°, and ON-*di*-3 : 4-*dichlorobenzenesulphonyl*, m. p. 114°. Et *o*-hydroxyphenylcarbamate gives a *benzenesulphonyl* derivative, m. p. 78·5—79°, whilst *o*-benzenesulphonamidophenol and $ClCO_2Et$ afford an oily product.

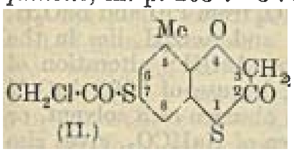
H. BURTON.

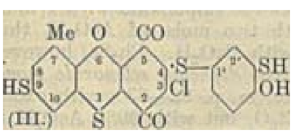
Stereochemical studies on hydronaphthalene and derivatives. I. Catalytic reduction of β-naphthol under high temperature and pressure. II. Catalytic oxidation-reduction of hydronaphthalenes and sesquiterpenes. S. KIMURA (Mem. Coll. Sci. Kyoto, 1931, **A**, **14**, 173—193; cf. A., 1928, 285). I. β-Naphthol is reduced by H_2 in presence of Ni at 130—150°/63 atm. to *ac*- (I) (59·3%) and *ar*-tetrahydro-β-naphthol (II) (40·7%); the amount of (II) is thus increased at high pressure (cf. A., 1923, i, 105). At 160°/73 atm., the products are (I) (47·2%), (II) (51·6%), and β-decalol (III) (1·2%), whilst at 190°/57 atm., (I) (41·5%), (II) (43·2%), (III) (8·4%), and hydronaphthalenes (6·9%), are formed. Reduction of (II) at 180°/58 atm. gives a mixture of liquid (*A*) (containing 85% of *cis* and 15% of *trans*) and *cis*-*cis*-, m. p. 105°, -decahydro-β-naphthols, whilst (I) is reduced more difficultly at 200—270°/65 atm. to hydronaphthalenes (37%) and liquid decahydro-β-naphthol (consisting of 24·2% of *cis* and 75·8% of *trans*). The results suggest that the unsubstituted ring in β-naphthol is the more activated under high pressure and temp. When *A* is kept in presence of H_2 and Ni at 240—260°/100 atm. a mixture of *cis*-*trans*- and *trans*-*trans*-decahydro-β-naphthols is obtained together with a little decahydronaphthalene (*cis* *trans*).

II. When 1 : 2-dihydronaphthalene is passed over palladised asbestos at 250—300° in CO_2, $C_{10}H_8$ and

1 : 2 : 3 : 4-tetrahydronaphthalene (IV) are produced. Similarly *cis*-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-octahydronaphthalene at 200—220° affords (IV) and *trans*-decahydronaphthalene (formed by rearrangement of the *cis*-form at high temp.). These results indicate that a hydronaphthalene containing one double linking in each ring will yield $C_{10}H_8$ and (IV), whilst (IV) and decahydronaphthalene will be the products when both double linkings are in one ring. The formation of cadalene and decahydrocadalene from the sesquiterpene from Japanese cedar oil, and the conversion of octa- into a mixture of tetra- and deca-hydrocadalenes support the structures previously assigned (J. Chem. Soc. Japan, 1930, **51**, 518) to the sesquiterpene and the octahydrocadalene. H. BURTON.

Hydroxy- and amino-thiophenols. R. POLLAK, E. RIESZ, and J. RIESZ (Monatsh., 1931, **58**, 129—136).—Chloroacetyl-*p*-thiocresol [prepared from *p*-thiocresol, aq. Na_2CO_3, and $CH_2Cl{\cdot}COCl$ (I)], when heated with conc. aq. NH_3 at 50—55°, gives *glycyl*-p-*thiocresol*, m. p. 117°, and, when heated with chloranil on the water-bath, gives *tetra*-p-*tolylthiolbenzoquinone*, m. p. 203°. 3 : 5-Dimercapto-*o*-cresol, when boiled with (I), gives 5-*methyl-2-keto-7-(chloroacetylmercapto)benzthioxin* (II), m. p. 195°, and with chloranil yields 3-*chloro-9-mercapto-2 : 5-diketo-4-(3′-methyl-4′-hydroxy-5′-mercaptophenyl)-7-methylphenoxthin* (III), decomp. above 250°. *o*-Aminophenol and (I) give, when boiled, o-*chloroacetamidophenylchloroacetate*, m. p. 120°. 2 : 4-Dinitrothiophenol (prepared by reduction of the disulphide with dextrose and NaOH) is reduced by Zn dust and HCl in warm AcOH to the diamino-compound, which, when treated with chloranil in AcOH, yields a *substance*, $C_{42}H_{17}O_8N_6S_3Cl_5$, giving a light yellow vat and dyeing wool grey. Zinc *p*-toluidine-2 : 5-dimercaptide with chloranil in EtOH gives a *substance*, $C_{45}H_{27}O_8N_2S_6$, reddish-violet. Of the two last-mentioned products the former is considered to consist of thiazine and quinone rings joined by NH groups, whilst in the latter the rings are joined by S and the CO groups are replaced by OH. R. S. CAHN.





Bactericidal properties of monoethers of dihydric phenols. I. Monoethers of resorcinol. E. KLARMANN, L. W. GATYAS, and V. A. SHTERNOV (J. Amer. Chem. Soc., 1931, **53**, 3397—3407).—The following resorcinol mono-alkyl and -aralkyl ethers are prepared from resorcinol and the appropriate bromide in presence of either xylene or alcoholic KOH (the figures in parentheses are the PhOH-coeff. determined by Reddish's method with *B. typhosus* and *Staph. aureus*, respectively): Me (1·3, 1·2); Et (3·6, 3·0); Pr (6·9, 5·4); Bu, b. p. 130°/5 mm. (20, 18); n-*amyl*, b. p. 140°/5 mm. (38, 36); sec.-*amyl*, b. p. 138°/5 mm. (26, 31); n-*hexyl*, b. p. 145°/5 mm. (46, 125); cyclo*hexyl*, b. p. 160°/6 mm. (18, 20): n-*heptyl*, b. p. 160°/5 mm. (21, 330); n-*octyl*, b. p. 170°/5 mm. (2·3, 580); n-*nonyl*, b. p. 171°/4·5 mm. (3·4, 650); *benzyl*, b. p. 200°/5 mm., m. p. 69·2° (21, 16); *p-chlorobenzyl*, b. p. 235°/13 mm., m. p. 76° (61, 38); *β-phenylethyl*, b. p. 202°/6 mm., m. p. 44° (35, 39); *γ-phenylpropyl*, b. p. 202°/5·5 mm. (34, 89). *Resorcinol Ph ether*, b. p. 150°/4·5 mm. (40, 37), is obtained by diazotisation of *m*-aminodiphenyl ether. The activity of the *n*-alkyl ethers towards *B. typhosus* reaches a max. at C_6 and then decreases, but with *S. aureus* it increases with length of the C chain. The *sec.*- have smaller activities than the *n*-alkyl compounds (which are similar to nuclear substituted resorcinols). H. BURTON.

Preparation and bacteriological study of *sym.* organic sulphides. F. DUNNING, B. DUNNING, jun., and W. E. DRAKE (J. Amer. Chem. Soc., 1931, **53**, 3466—3469).—*Sulphides* of the type of 4 : 4′-dihydroxydiphenyl sulphide are prepared (the m. p. are given in parentheses) from the following phenols and SCl_2 in CCl_4 or Et_2O; resorcinol (165—167°); *m*-cresol (142·5°); *p*-chlorophenol (173°); *p*-bromophenol (180°), and thymol (152·5—153·5°). The sulphides (except that from resorcinol) are approx. 10 times as toxic towards *S. aureus* as the phenols from which they are derived. *o*-Substituted phenols and *m*- and *p*-substituted phenols containing a *m*-orienting substituent would not react with SCl_2. H. BURTON.

Lignin. IV. Reaction of phenolic derivatives with acetic anhydride–acetic acid–sulphuric acid. H. FRIESE (Ber., 1931, **64**, [*B*], 2109—2112).—Mono- and di-hydric phenols and their ethers, like PhOEt, are quantitatively converted by $AcOH–Ac_2O–H_2SO_4$ into the corresponding sulphonic acids. Sulphoacetic acid is produced when more H_2SO_4 is present than is necessary for 1 mol. of substance. Phloroglucinol yields triacetyltriketohexamethylene, m. p. 156°. The presence of a CHO group alters the nature of the reaction. Piperonal affords a bluish-violet condensation product, free from S, divisible into different fractions. Vanillin gives a brownish-red compound, insol. in H_2O and containing not more than traces of S. Cinnamaldehyde yields partly a resin free from S and partly sulphonic acids of undetermined structure. Furfuraldehyde or its diacetate affords black, brittle products. H. WREN.

Composition of sitosterol. H. SANDQVIST and E. BENGTSSON (Ber., 1931, **64**, [*B*], 2167—2171).—Quantitative hydrolysis of the acetates of sitosterol and dihydrositosterol from Swedish "tallol" leads to the formulæ $C_{29}H_{49}{\cdot}OAc$ and $C_{29}H_{51}{\cdot}OAc$ and hence to the formulæ $C_{29}H_{49}{\cdot}OH$ and $C_{29}H_{51}{\cdot}OH$ for the non-acetylated products, in contrast to the generally accepted compositions, $C_{27}H_{45}{\cdot}OH$ and $C_{27}H_{47}{\cdot}OH$. Experiments with cholesteryl acetate establish the validity of the method provided that the requisite time is allowed for complete acetylation and hydrolysis. Since the C_{27} formula for sitosterol appears to be based on analyses and determinations of mol. wt. and also on analogy to cholesterol, a sterol from soya bean, rich in γ-sitosterol and free from stigmasterol, and a technical sterol have been similarly examined. Only the dihydrositosterol (and cholesterol) appear absolutely uniform; of the others, only the γ-sitosterol from soya bean can have a formula

simpler than C_{29} but scarcely as low as C_{27}. Natural dihydrositosterol and sitosterol have the formulæ $C_{29}H_{52}O$ and $C_{29}H_{50}O$, respectively. H. WREN.

Stereochemical structure. III. Glycols derived from *d*(−)-mandelic acid. R. ROGER and W. B. McKAY (J.C.S., 1931, 2229—2238; cf. this vol., 487).—α(+)-Tolylhydrobenzoins differ little in sp. rotation from (+)triphenylethylene glycol. Various criteria indicate that the substances are similar in stereochemical structure, although the tolylhydrobenzoins contain a new asymmetric C atom, which is therefore considered to have a weak rotatory power. *r*-Benzoin with Mg *o*-tolyl bromide gives α-r-o-, m. p. 154—155°, and with Mg *m*-tolyl bromide, α-r-m-*tolylhydrobenzoin*, m. p. 135—137°. *d*(−)-Benzoin with the appropriate Grignard reagent gives α-d(−)-o-, m. p. 113—115° (and *r*-benzoin), α-d(+)-m-, m. p. 106—108°, and α-d(+)-p-*tolylhydrobenzoin*, m. p. 120—121°. Et *r*-mandelate similarly gives *α-phenyl-ββ-di-*m-*tolylethylene glycol*, m. p. 132—134°, whilst Et *d*(−)-mandelate gives d(+)-*α-phenyl-ββ-di-*p-*tolylethylene glycol*, m. p. 149—150°. A. A. LEVI.

Condensation of olefinic acids and benzene rings. E. FOURNEAU and P. M. BARANGER (Bull. Soc. chim., 1931 [iv], 49, 1161—1172).—With the object of obtaining esters of therapeutic value in treating leprosy, undecenoic and hydnocarpic acid have been condensed with C_6H_6 and some of its derivatives in presence of $AlCl_3$. None of the substances prepared had any therapeutic value. The esters of olefinic acids afford higher yields than the free acids and the yields increase with the distance between the double linking and the CO_2H group. Derivatives of C_6H_6 containing *p*-directing substituents give better yields than C_6H_6 itself. The following are described: ω-phenylundecoic acid, b. p. 225°/16 mm. (*amide*, m. p. 57°; *Et* ester, b. p. 170—190°/14 mm.), depositing crystals, m. p. 19—20°, when kept at −10°, and ω-1-*phenylundecoic acid*, b. p. 198°/15 mm. (*amide*, m. p. 79°; *Et* ester, b. p. 190—207°/14 mm.); the esters are obtained in 50% yield; ethyl ω-phenylundecoate is also obtained from ethyl ω-bromoundecoate; p-*methoxyphenylundecenoic acid*, b. p. 220°/0·9 mm. (*Et* ester, yield 85% from anisole, b. p. 193°/1·7 mm.), converted by HI (*d* 1·7) and AcOH into p-*hydroxyphenylundecoic acid*, b. p. 220°/1·5 mm., a weak disinfectant; *phenyldihydrohydnocarpic acid*, m. p. 43—44° (*Et* ester, b. p. 195°/1·5 mm.); p-*methoxyphenyldihydrohydnocarpic acid*, b. p. 220°/1·5 mm. (*Et* ester, yield 80% from PhOEt, b. p. 220°/1·7 mm.).

The following dicarboxylic acids are obtained similarly: p-*methoxyphenylbutylmalonic acid*, m. p. 144·5° (*Et* ester, b. p. 209°/20 mm., yield 30% from Et allylmalonate), converted at 160—170° into p-*methoxyphenylvaleric acid*, m. p. 65°; *phenylenediundecoic acid* (*Et₂* ester, b. p. 245°/2 mm.); *Et* 4-*carboxymethylphenylundecoate*, b. p. 220—230°/2 mm. (yield 18% from phenylacetic acid and ethyl undecenoate in CS_2), the *Th* salt of which on distillation at 300—500°/45 mm. affords the ketones, $C_6H_4<\substack{[CH_2]_{10}\\CH_2}>CO$ and $C_6H_4<\substack{[CH_2]_8\\CH_2}>CO$ (*semicarbazones*, m. p. 226° and 205°, respectively). Stoll, by distillation of the Ce salt at 10 mm., has obtained a ketone, $C_{15}H_{26}O$, b. p. 180—195°/9 mm. (*semicarbazone*, m. p. 199—201°). Et undecenoate and β-phenylpropionic acid in CS_2 in presence of $AlCl_3$ similarly afford *Et* p-*β-carboxyethylphenylundecoate*, b. p. 270°/3 mm. Undecenyl acetate and $CH_2Ph{\cdot}CN$ in presence of $AlCl_3$ yield 4-*cyanomethylphenylundecyl acetate*, m. p. 72°; 4-*cyanomethylphenylundecoic acid*, m. p. 123—124°, is similarly obtained from undecenoic acid. Attempts to hydrolyse the above nitriles failed. *X*-Ray examination indicates that the mols. of the last acid are oriented parallel to one another in reticular planes 10·82 Å. apart, and the mode of packing accounts for its resistance to hydrolysis and cyclisation. R. BRIGHTMAN.

Oxidation of organic compounds with peracetic and perbenzoic acids. B. A. ARBUSOV (J. pr. Chem., 1931, [ii], **131**, 357—372).—The view of Boeseken and Schneider (this vol., 207) that the mechanisms of oxidation of org. compounds by AcO_2H and BzO_2H are essentially different is criticised, and it is suggested that the divergent results obtained are a consequence of the conditions of reaction. The cause of the formation of $PhIO_2$ from PhI and BzO_2H, and of $PhI(OAc)_2$ from PhI and AcO_2H, lies in the readier acylation of PhIO by AcOH; alteration of the reaction conditions, *e.g.*, by use of 90% AcO_2H in conc. Et_2O solution, or in absence of a solvent, or in dil. aq. solution in presence of $NaHCO_3$, gives rise to $PhIO_2$ with AcO_2H also. On the other hand, oxidation of PhI with BzO_2H in Et_2O saturated with BzOH gives *iodosobenzene dibenzoate*, m. p. 159—160°, which is also formed by action of BzOH on $PhI(OAc)_2$ in Et_2O. $(CH_2Ph)_2S$ gives the sulphoxide with 1 mol., and the sulphone with two mols. of AcO_2H, thus behaving exactly as with BzO_2H. Ph_2Se, however, resembles PhI and gives *diphenyl selenoxide monoacetate*, $Ph_2Se(OH){\cdot}OAc$, m. p. 82—83°, with excess of AcO_2H in much Et_2O, but with 90% AcO_2H in conc. solution, or with BzO_2H, Ph_2SeO_2 is formed. Oxidation of PPh_3 with AcO_2H in Et_2O gives $POPh_3$ in 93·8% yield. H. A. PIGGOTT.

Allylic rearrangement in reaction between cinnamyl chloride and magnesium. H. GILMAN and S. A. HARRIS (J. Amer. Chem. Soc., 1931, **53**, 3541—3546).—The Grignard reagent (*A*) from cinnamyl chloride reacts mainly as Mg α-phenylallyl chloride, since treatment with CO_2 gives α-phenyl-Δ^{β}-butenoic acid, m. p. 23—24° (*anilide*, m. p. 97—98°, obtained from *A* and phenylcarbimide). This acid is converted by warming with acid or alkali into methylatropic acid (cf. A., 1927, 875), and is reduced catalytically (Adams) to α-phenylbutyric acid. Methylatropic acid is also formed by hydrolysis of the product from *A* and $ClCO_2Et$. The formation of *A* is presumed to involve transformation of cinnamyl into α-phenylallyl radicals. H. BURTON.

Erlenmeyer synthesis of amino-acids. J. LAMB and W. ROBSON (Biochem. J., 1931, **25**, 1231—1236).—Glacial AcOH is substituted for Ac_2O in the reduction stage of the synthesis by HI and red P introduced by Harington and McCartney (A., 1927, 961). A drastic reduction of the amount of HI leads to the reduction of the unsaturated compound without the

loss of Bz radical from the NH_2 group; the oxazolone yields the benzamido-acid by this treatment. If HI is present in sufficient quantity the reduction is also accompanied by the removal of the Bz group, with the consequent production of the α-amino-acid and also of other groups if the reaction is prolonged. Oxazolone can also be made to yield the α-NH_2-acid in this way. Good yields have been obtained by this method in the prep. of the following compounds: benzoylphenylalanine, phenylalanine, tyrosine, α-benzamido-*p*-methoxycinnamic acid, benzoyl-*p*-methoxyphenylalanine. S. S. Zilva.

Conversion of ethyl *l*-α-chloroformoxyphenylacetate into lævorotatory and dextrorotatory ethyl phenylchloroacetate. J. Kenyon, A. G. Lipscombe, and H. Phillips (J.C.S., 1931, 2275—2282; cf. this vol., 480).—Pyridine is without influence on the sign of rotation of the product of interaction of Et *l*-mandelate and PCl_5 or PCl_3. Et l-mandelate in quinoline with $COCl_2$ in PhMe gives Et l-α-*chloroformoxyphenylacetate*, (I), b. p. 72—74°/<0·1 mm., and a little l-α-*carbethoxybenzyl carbonate*, b. p. 195—200°/<0·1 mm., the corresponding *dl*-compound, b. p. 182—184°/<0·1 mm., being obtained by interaction of Et *dl*-mandelate and (I). (I) corresponds in structure with the intermediate pyridine compound assumed in the interaction of $SOCl_2$ and Et *l*-mandelate in pyridine (*loc. cit.*), and, with the products obtained from it, has the expected sign of rotation. Et *l*-mandelate with AcCl, BzCl, or *p*-toluenesulphinyl chloride gives *Et* l-α-*acetoxy-*, b. p. 147°/13 mm., *Et* l-α-*benzoyloxy-*, b. p. 134—135°/<0·1 mm., and *Et* l-α-*toluenesulphinoxy-phenylacetate*, b. p. 136—139°/<0·1 mm., respectively. The same substances are obtained with some racemisation from the interaction of (I) and the Na salts of the corresponding acids, some unchanged ester and some di-*p*-tolyldisulphoxide being also obtained with Na *p*-toluenesulphinate. The toluenesulphinoxy-compound also arises from the interaction of Et *l*-mandelate and Et *p*-toluenesulphinate. With pyridine (I) gives Et *d*-phenylchloroacetate, whilst when heated alone it gives the *l*-compound. Et *dl*-phenylchloroacetate and Na *p*-toluenesulphinate give dl-α-*carbethoxybenzyl*-p-*tolylsulphone*, m. p. 112—113°, hydrolysed to *dl*-α-carboxybenzyl-*p*-tolylsulphone, m. p. 169—170° (decomp.), both being converted into benzyl-*p*-tolylsulphone. Et *d*-phenylchloroacetate gives similarly *d*+*dl*-α-carbethoxybenzyl-*p*-tolylsulphone, m. p. 111—112°. Et *l*-mandelate gives a *urethane*, b. p. 165—166°/<0·1 mm. The corresponding *dl*-compound has m. p. 97° (cf. A., 1899, i, 52). A. A. Levi.

Hydrogen sulphite compounds of naphthalene derivatives. Abnormal reaction between sodium hydrogen sulphite and 2 : 3-hydroxynaphthoic acid derivatives. R. Lantz and G. Mingasson (Compt. rend., 1931, **192**, 1664—1666, and Bull. Soc. chim., 1931, [iv], **49**, 1172—1180).—1-Nitroso-β-naphthol-3-carboxylic acid and $NaHSO_3$ yield a compound which on acidification yields 1-nitroso-β-naphthol-4-sulphonic acid, eliminating the CO_2H group. In a similar manner, treatment of 1-benzeneazo-β-naphthol-3-carboxylic acid with $NaHSO_3$ causes loss of the carboxyl group. A hydrogen sulphite compound of 1-nitroso-β-naphthol 3-carboxylanilide could not be obtained as described by Battegay and others (A., 1924, i, 722) by the action of $NaHSO_3$ on the Na compound in aq. solution, but by working in EtOH a product was obtained apparently containing 1 mol. of NO-derivative and 1 mol. of SO_2. On acidification this gives the original NO-derivative without loss of the CO·NHPh group. G. Discombe.

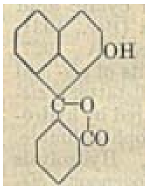
Formation and transformation of cyclic acid imides. W. Hückel and H. Müller (Ber., 1931, **64**, [*B*], 1981—1990).—Contrary to Sircar (A., 1927, 756) the thermal decomp. of the NH_4 salts of *cis*- and *trans*-hexahydrophthalic acid yields Willstätter's *cis*-hexahydrophthalimide, m. p. 137°, prepared by hydrogenation of phthalimide or tetrahydrophthalimide. The preps. are unchanged by distillation. Hydrolysis with cold alkali hydroxide gives homogeneous *cis*-hexahydrophthalic acid, whereas the *trans*-acid is formed at 100°. The action of Ac_2O or AcCl on *cis*- or *trans*-hexahydrophthalamic acid yields the *cis*-imide and a *substance* $C_{16}H_{20}O_3N_2$, m. p. 167°, possibly identical with Sircar's compound, m. p. 164°, and a small amount of a dye. The compound of m. p. 167° decomposes when distilled in a vac., is hydrolysed by cold and hot alkali hydroxide to *cis*- and *trans*-hexahydrophthalic acid, decolorises $KMnO_4$ and Br, but does not absorb H_2. Dissolution in Na_2CO_3 and precipitation with acid affords the monobasic *acid*, $C_{16}H_{22}O_4N_2$, m. p. 210—212°, cautiously hydrolysed to *cis*-hexahydrophthalic acid. *Me* cis-*hexahydrophthalamate* and *Me* trans-*hexahydrophthalamate* have m. p. 77° and 93—94°, respectively. *cis*-Hexahydrophthalic anhydride is converted by NH_2Ph in C_6H_6 into cis-*hexahydrophthalanilic acid*, m. p. 170—171°, transformed by AcCl into the cis-*anil*, m. p. 134°. trans-*Hexahydrophthalanilic acid*, m. p. 223—224°, and the corresponding trans-*anil*, m. p. 193—194°, are described. Protracted heating caused isomerisation of the *trans*- to the *cis*-anil. Hydrolysis of the *trans*-anil yields the *trans*-anilic acid, whereas the *cis*-anil with aq. $Ba(OH)_2$ at 90° yields a mixture of *cis*- and *trans*-anilic acid, the latter being the sole product with conc. aq. or alcoholic NaOH. *meso*Dimethylsuccinic anhydride and NH_3 in Et_2O give meso*dimethylsuccinamic acid*, m. p. 165—167°, converted by AcCl into a product, m. p. 70—100°, whereas the *imide*, obtained by hydrogenation of dimethylmaleimide has m. p. 66—72°. r-*Dimethylsuccinamic acid*, m. p. 148—149°, and *r*-dimethylsuccinimide, m. p. 105—106°, are described. Cautious hydrolysis of the amic acids or imides gives dicarboxylic acids of the corresponding configuration. The following vals. for the hydrolysis consts. at 0° and 25° are recorded: succinimide 39·4, 248; *r*-dimethylsuccinimide, 30, 204; *cis*-hexahydrophthalimide, 79·9, 322; dimethylmaleimide, 5216, 19,550; tetrahydrophthalimide, 16,300, (38,000). H. Wren.

Synthesis of the *d*- and *l*-3 : 4-dihydroxyphenylalanines. C. R. Harington (Biochem. J., 1931, **25**, 1028—1031).—β-3 : 4-Diacetoxyphenyl-α-acetamidoacrylic acid, obtained by condensation of protocatechualdehyde with acetylglycine in presence of Ac_2O and NaOAc, is reduced by $PdCl_4$ and H_2. The

brucine salts of the resulting β-3 : 4-diacetoxyphenyl-α-acetamidopropionic acid are then obtained, the l-isomeride by crystallisation from EtOH and the *d*-isomeride from the mother-liquor.

S. S. ZILVA.

Condensation of β-naphthol with phthalic anhydride. L. F. FIESER (J. Amer. Chem. Soc., 1931, **53**, 3546—3560).—Phthalic anhydride and β-naphthol in presence of $AlCl_3$ at 250° give a yellow *compound* (I) (probably with the annexed structure), $C_{18}H_{10}O_3$, m. p. 198° (*Et ether*, m. p. 163°), and not a hydroxynaphthanthraquinone (G.P., 298,345); the structure assigned to (I) by Rieche and Fruhwald (this vol., 1060) does not explain many of the reactions now described. (I) is converted by aq. NaOH into a *Na* salt $C_{18}H_{11}O_4Na$, by PCl_5 and $POCl_3$ into a *chloride* $C_{18}H_9O_2Cl$, m. p. 165°, and by MgPhBr into a *compound* $C_{24}H_{16}O_3$, m. p. 247° (*diacetate*, m. p. 224°). Oxidation of (I) with alkaline $KMnO_4$ affords *benzhydrol*-2 : 3 : 2′-*tricarboxylic acid* 2′-*lactone* (*Me_2* ester, m. p. 149°), which passes at 214° into an *anhydride*, m. p. 205°. The lactone is oxidised further to *benzophenone*-2 : 3 : 2′-*tricarboxylic acid dilactone*, m. p. 230° (*Me* ester, m. p. 186·5°), decarboxylated in presence of 0·5% of Cu powder at 300° to the dilactone of benzophenone-2 : 2′-dicarboxylic acid [Me_2 ester, m. p. 82° (lit. 86°)], which is reduced ultimately to diphenylmethane-2 : 2′-dicarboxylic acid, m. p. 250° (lit. 254·5°).



Phthalic anhydride and β-naphthyl Me ether in presence of $AlCl_3$ and $C_2H_2Cl_4$ at 100° give o-2-*hydroxy*-1-*naphthoylbenzoic acid*, m. p. 155° [*Me* ester, m. p. 131°; *Me ether*, m. p. 196° (*Me* ester, m. p. 109°), is the main product when reaction is carried out at room temp.], the *lactone*, m. p. 195°, of which is converted by $AlCl_3$ in hot C_6H_6 into (I). *Phenyl*-2-*hydroxy*-1-*naphthylmethane*-2′-*carboxylic acid* (*lactone*, m. p. 147°; *Me ether*, m. p. 196°) has m. p. 187°. β-Naphthyl Me ether and BzCl in presence of $AlCl_3$ and $C_2H_2Cl_4$ at 25° afford 1-*benzoyl*-β-*naphthol* (53%), m. p. 142°, and its *Me ether* (22%), m. p. 127°; the former is converted by $AlCl_3$ and NaCl at 200° into 4-hydroxybenzanthrone. Me *o*-α-naphthoylbenzoate with $AlCl_3$ and NaCl at 130° yields 10% of the compound, m. p. 177°, described in B., 1930, 706. Phthalic anhydride and leucoquinizarin in presence of $AlCl_3$ at 250° give (probably) 5 : 7 : 12 : 14-*tetrahydroxypentacene*-6 : 13-*quinone* [*tetra-acetate*, m. p. 315° (decomp.)].

H. BURTON.

Action of *o*-phthaloyl chloride on phenyl and thiophenyl acetates. W. KNAPP (Monatsh., 1931, **58**, 176—182).—Attempts to prepare thiophenolphthalein were unsuccessful. *o*-Phthaloyl chloride, PhSAc, and $AlCl_3$ in CS_2 give *as*.-diphenyl dithiophthalate, m. p. 101°; this constitution, previously considered improbable (A., 1927, 970), is favoured by the fact that $KMnO_4$ in warm AcOH gives, not the *s*-disulphone, but two *substances*, m. p. 142—144° and 105—106°, respectively, both decomposed by conc. H_2SO_4, one of which is probably the *as*.-disulphone. *o*-Phthaloyl chloride, PhOAc, and $AlCl_3$ in CS_2 give a little phenolphthalein, *s*-diphenyl phthalate, and a gum. The formation of both *s*- and *as*-derivatives from phthaloyl chloride is difficult to explain.

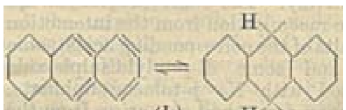
R. S. CAHN.

Synthesis of derivatives of arylacetic and β-arylpropionic acids. J. HOCH (Compt. rend., 1931, **192**, 1464—1466).—Arylacetic acids are obtained from benzyl halides through the nitriles, the β-arylpropionic acids through benzylmalonic esters. 2 : 4-Dimethylbenzyl chloride and 2 : 4 : 6-*trimethylbenzyl chloride*, m. p. 37°, b. p. 119°/15 mm., are obtained by the action of $CH_2Cl·OEt$ on *m*-xylene or mesitylene in presence of $SnCl_4$, *o*-methylbenzyl bromide by the action of HBr on *o*-methylbenzyl Et ether, and β-p-*tolylethyl bromide* from β-p-*tolylethyl Et ether*, b. p. 105°/14 mm., prepared by the action of $C_2H_4Br·OEt$ on Mg *p*-tolyl bromide.

m-4-*Xylylacetonitrile*, b. p. 146°/19 mm., *mesitylacetonitrile*, m. p. 79°, b. p. 150—155°/15 mm., β-2 : 4 : 6-*trimethylphenylpropionic acid*, m. p. 113°; *Et* 2 : 4-*dimethylbenzylmalonate*, b. p. 186—188°/13 mm., *Et* o-*xylylmalonate*, b. p. 180—182°/15 mm., *Et* 2 : 4 : 6-*trimethylbenzylmalonate*, m. p. 36°, b. p. 195—197°/15 mm., and *Et* β-p-*tolylethylmalonate*, b. p. 192—194°/17 mm., are also described.

G. DISCOMBE.

Polynuclear, aromatic hydrocarbons and their derivatives. XI. Constitution of anthracene. E. CLAR (Ber., 1931, **64**, [*B*], 2193—2200; cf. Diels and Alder, this vol., 848).—Study of the reaction of anthracene and its derivatives with unsaturated acid anhydrides leads to the conclusion that the Armstrong–Hinsberg constitution is inadequate to explain the changes, which can be interpreted by the author's equilibrium formula (I). 9 : 10-*endo*-Anthracene-αβ-succinic anhydride, m. p. 258—259°, from the components in boiling $C_6H_4Me_2$, dissociates into maleic anhydride and anthracene at 260—270°. 9 : 10-endo-2-*Chloroanthracene*-, m. p. (indef.) 213—217°, and -2 : 3 : 6 : 7-*dibenzanthracene*-αβ-*succinic anhydride*, m. p. 298° (slight decomp.), are similarly obtained. In boiling $PhNO_2$, maleic anhydride and the requisite derivative afford 9 : 10 : 1′ : 4′-endo-7 : 7′-*dimethyl*-2′ : 3′-*naphtha*-1 : 2-*anthracenedi*-αβ-*succinic anhydride*, m. p. 308° (decomp.) after darkening at 300°, and 9 : 10-endo-9 : 10-*dichloroanthracene*-αβ-*succinic anhydride*, m. p. 258—259°. The last-named compound is converted by boiling quinoline into 9 : 10-dichloroanthracene. In it the Cl atoms have been rendered so mobile that reaction occurs with $AlCl_3$ and C_6H_6 or *m*-xylene, leading to 9 : 10-diphenylanthracene, m. p. 248°, and 9 : 10-*di*-m-*xylylanthracene*, m. p. 290°. In the former action, a reddish-brown *hydrocarbon*, $C_{26}H_{14}$, m. p. 335° after softening at 330°, is occasionally produced, apparently an iso*rubicene*.



(I.)

H. WREN.

Bicoloured phthaleins. A. THIEL (Z. physikal. Chem., Bodenstein Festband, 1931, 352—356).—The α-naphtholphthaleins and the homologues of phenolphthalein, but not phenolphthalein itself, exhibit two

colour changes; the first results in the production of the orange or yellow primary quinonoid anion and the second in that of the deeply coloured meriquinonoid anion. The effect can usually be observed only in EtOH solution, on account of the slight solubility of the phthaleins. The α-naphtholphthaleins prepared according to Schulenburg and Sorensen, respectively, differ in their reactivity with conc. alkali and in their absorption spectra; the former substance is probably an *oo'*- and the latter a *pp'*-compound.

H. F. GILLBE.

Synthesis of 2-hydroxy-4 : 5-dimethoxybenzoic acid. F. S. H. HEAD and A. ROBERTSON (J.C.S., 1931, 2432—2433; cf. this vol., 841).—2-Hydroxy-4 : 5-dimethoxybenzaldehyde, m. p. 107° (this vol., 73), gives an *acetate*, m. p. 95°, which is oxidised by $KMnO_4$ in $COMe_2$ to 2-*acetoxy*-4 : 5-*dimethoxybenzoic acid*, m. p. 166°, hydrolysed to 2-hydroxy-4 : 5-dimethoxybenzoic acid, m. p. 213—214° (decomp.).

A. A. LEVI.

Opianic acid. II. Esterification of opianic acid and internal condensation of certain of its esters. P. SCHORIGIN, V. ISSAGULANZ, and V. BELOV (Ber., 1931, 64, [B], 1931—1935).—Anhydrous K opianate is converted by CH_2PhCl in C_6H_6 at 100° into *benzyl α-opianate*, m. p. 82—83° in 60% yield. *Benzyl ψ-opianate*, $C_6H_2(OMe)_2{<}{\begin{matrix}CH(O{\cdot}CH_2Ph)\\CO\end{matrix}}{>}O$, m. p. 94—95°, is derived from opianic acid and $CH_2Ph{\cdot}OH$ at 100—110°. Analogously, anhydrous K opianate and $CH_2Cl{\cdot}CO_2Et$ in C_6H_6 afford *Et carbethoxymethyl α-opianate*, m. p. 87—88°, transformed by NaOEt into Et ψ-opianate, unaffected by anhyd. oxalic acid or pyridine, but transformed by Na in xylene into 7 : 8-*dimethoxyisocoumarin*-3-*carboxylic acid*, m. p. 264—265°, and Et ψ-opianate. Benzyl α-opianate is converted by pyridine at 160—170° into 7 : 8-*dimethoxy*-2-*phenylisocoumarin*, m. p. 132—133°, and a substance, m. p. 235—238°.

H. WREN.

Condensation of monochloromethyl ether with ethyl phenylmalonate. M. G. RAO and J. L. SIMONSEN (Proc. XV Indian Sci. Cong., 1928, 149).—The product $(CO_2Et)_2CPh{\cdot}CH_2{\cdot}OMe$, when treated with 50% KOH, affords atropic acid, or with 10% alcoholic KOH it affords methyltropic acid.

CHEMICAL ABSTRACTS.

Action of sulphuric acid and bromine on ethyl benzylidenediacetoacetate. B. M. GUPTA and S. C. ROY (Proc. XV Indian Sci. Cong., 1928, 158).—Et α-bromo-αα'-diacetyl-β-phenylglutarate, m. p. 131°, was obtained.

CHEMICAL ABSTRACTS.

Bromination of dehydrodeoxycholic acid. T. NOGUCHI (Z. physiol. Chem., 1931, 200, 48—50).—Bromination gives a *bromo*- (+½EtOAc), m. p. 172° (froths at 100—105°), and a *dibromo-dehydrodeoxycholic acid* (+½EtOAc), m. p. 160—165° (decomp.) (froths at 146—147°). The dibromo-acid is debrominated by aq. $Ba(OH)_2$ to hydroxydiketocholenic acid (+½AcOH), m. p. 248° (decomp.).

J. H. BIRKINSHAW.

Bile acids. XXXI. M. SCHENCK (Z. physiol. Chem., 1931, 200, 41—47; cf. this vol., 841).—Oxidation of *iso*bilianic acid oxime lactone with alkaline $KMnO_4$ eliminates the NOH group yielding the ketolactonetricarboxylic acid, decomp. 245°. 90% H_2SO_4 at 100° produces from the oximinoamino-acid an inversion *product*, decomp. 258°, which has lost the NOH group.

J. H. BIRKINSHAW.

Manufacture of substituted salicylic acids. I. G. FARBENIND. A.-G.—See B., 1931, 917.

Manufacture of 6-halogeno-3-aminodiphenylmethane-2'-carboxylic acids and substitution products and derivatives. NEWPORT CO.—See B., 1931, 918.

Inhibitory action of anthracene in the autoxidation of benzaldehyde. H. L. J. BÄCKSTRÖM and H. A. BEATTY.—See this vol., 1245.

Autoxidation of benzaldehyde. II. Action of catalysts. G. RAYMOND.—See this vol., 1248.

ε-Phenylpentadienal. V. ALEXA (Ber., 1931, 64, [B], 2250—2252).—ε-Phenylpentadienal, conveniently prepared by the fractionation of the residues from the technical production of cinnamaldehyde, is converted into the corresponding azine, m. p. 228°, and into di-ζ-phenylhexatrienyl ketone, m. p. 189—190°. *ε-Pentadienylideneindene*, m. p. 182—183°, and *ε-pentadienylideneindan*-1 : 3-*dione*, m. p. 167—168°, are described.

H. WREN.

Acids derived from diphenyl-4-aldehyde. D. H. HEY (J.C.S., 1931, 2476—2479; cf. A., 1921, i, 417).—Diphenyl-4-aldehyde (improved prep.; cf. A., 1906, i, 589) is oxidised by $KMnO_4$ in Na_2CO_3 to diphenyl-4-carboxylic acid, which by prolonged action with NaOAc and Ac_2O gives p-*phenylbenzylidene diacetate*, m. p. 131° (also obtained from the aldehyde with Ac_2O and a little H_2SO_4), and *diphenylyl-4-acrylic acid*, m. p. 223—224° (*Et* ester, m. p. 87°), also obtained during the prep. of, and by heating, p-*phenylbenzylidenemalonic acid*, m. p. 215° (decomp.), obtained from diphenyl-4-aldehyde and malonic acid. The above diphenylylacrylic acid gives *αβ-dibromo-β-4-diphenylylpropionic acid*, m. p. 196—197° (decomp.), converted by prolonged action of KOH in EtOH into *diphenylyl-4-propiolic acid*, m. p. 175—176°.

A. A. LEVI.

[Preparation of phenylglyoxal.] M. HENZE (Z. physiol. Chem., 1931, 200, 232).—1 mol. of $CH_2Bz{\cdot}OH$ requires theoretically 2 mols. of $Cu(OAc)_2$ and produces 1 mol. of Cu_2O, not as previously stated (cf. this vol., 843). Heating facilitates the reaction.

J. H. BIRKINSHAW.

Action of phenylglyoxal on acetoacetic acid. M. HENZE and R. MÜLLER (Z. physiol. Chem., 1931, 200, 101—107; cf. this vol., 843).—Na acetoacetate and phenylglyoxal afford $COPh{\cdot}CH(OH){\cdot}CH_2{\cdot}COMe$ (I), m. p. 59—60°, oxidised by $FeCl_3$ or $Cu(OAc)_2$ to the *triketone* (Cu salt, m. p. 206°), deep red with $FeCl_3$. Oxidation of (I) with alkaline $KMnO_4$ gives pyruvic and glyoxylic (p-*nitrophenylhydrazone*, m. p. 158°) acids. $COMe{\cdot}CH(OH){\cdot}CH_2{\cdot}COMe$ gives the corresponding *triketone* (*Cu* salt, sublimes at 190° and decomposes at 223°). Oxidation of acetylacetone with alkaline $KMnO_4$ at low temp. yields pyruvic acid.

J. H. BIRKINSHAW.

Wandering of groups during bromination. M. G. S. RAO, C. SRIKANTIA, and M. S. IYENGAR (Proc. XV Indian Sci. Cong., 1928, 158—159).—Wan-

dering of the NO_2 group on bromination of 5-nitro-4-methoxy-β-resorcylaldehyde is recorded.

CHEMICAL ABSTRACTS.

3-Acenaphthyl ethyl ketone (3-propionylacenaphthene). K. DZIEWONSKI and J. MOSZEW (Bull. Acad. Polonaise, 1931, **A**, 158—164).—Acenaphthene and propionyl chloride in presence of $AlCl_3$ and CS_2 give a substance, m. p. 122—123° (picrate, m. p. 129°), and 3-*propionylacenaphthene* (I), m. p. 69—70° (*picrate*, m. p. 109°; *phenylhydrazone*, m. p. 107°; 4-*NO_2* derivative, m. p. 164—165°; *oxime*, m. p. 185—186°, converted by HCl in AcOH and Ac_2O into the *propionyl* derivative, m. p. 150—151°, of 3-aminoacenaphthene). Oxidation of (I) with $Na_2Cr_2O_7$ in AcOH affords 3 : 3'-*dipropionyldiacendione*, $\left[EtCO{\cdot}C_{10}H_5{<}{}^{C}_{CO}\right]_2$, m. p. 286° (decomp.), and (mainly) 4-*propionylnaphthalic anhydride*, m. p. 152—153° (*bisphenylhydrazone*, m. p. 192—193°). 4-*Propionylnaphthalimide* has m. p. 221—222°.

H. BURTON.

Anthracene derivatives. VII. E. DE B. BARNETT, N. F. GOODWAY, and L. H. W. SAVAGE (Ber., 1931, **64**, [*B*], 2185—2194).—2-*Chloro*-10-p-*dimethylaminophenylanthrone*, m. p. 128° according to the rate of heating, and 3-*chloro*-10-p-*dimethylaminophenylanthrone*, m. p. 190—195° (decomp.), are derived from the respective chloro-10-bromoanthrones and $NPhMe_2$. *o*-3' : 4'-Dichlorobenzoylbenzoic acid is reduced by Zn dust and NH_3 to o-3' : 4'-*dichlorobenzylbenzoic acid*, m. p. 146°, converted by conc. H_2SO_4 at room temp. into 2 : 3-dichloroanthrone. Unlike 2- and 3-chloro- or 1 : 4- and 1 : 5-dichloro-anthrone, the 2 : 3-compound is converted by aq. KOH and CH_2PhCl into *benzyl* 2 : 3-*dichloro*-10-*benzylanthranyl ether*, m. p. 165°. Br in CS_2 transforms 2 : 3-dichloroanthrone into 2 : 3-*dichloro*-10-*bromoanthrone*, m. p. 165° (decomp.), converted by $NPhMe_2$ into 2 : 3-*dichloro*-10-p-*dimethylaminophenylanthrone*, decomp. about 140°, and by piperidine into 2 : 3 : 2' : 3'-*tetrachlorodianthraquinone*, m. p. above 300°. Treatment of 2 : 3-dichloro-10-bromoanthrone with $AlCl_3$ in C_6H_6 affords 2 : 3-*dichloro*-10-*phenylanthrone*, m. p. (indef.) 155° (2 : 3-*dichloro*-10-*phenylanthranyl acetate*, m. p. 177°); 1 : 4-*dichloro*-10-*phenylanthrone*, m. p. 188°, and 1 : 4-*dichloro*-10-*phenylanthranyl acetate*, m. p. 187°, are similarly prepared. 1 : 4-*Dichloro*-10-*phenyl*-9-*benzylidene*-9 : 10-*dihydroanthracene* has m. p. 163°. Phthalic anhydride, PhOMe, and $AlCl_3$ afford *o*-*p*'-methoxybenzoylbenzoic acid reduced by Zn dust and NH_3 to *o*-*p*'-methoxybenzylbenzoic acid, m. p. 117°, dehydrated by 90% H_2SO_4 at room temp. or by 80% H_2SO_4 at 50° to 2-*methoxyanthrone*, m. p. 100°. 2-*Methoxyanthranyl acetate*, m. p. 157°, 10-*bromo*-2-*methoxyanthrone*, decomp. about 120°, and 2-*methoxy*-10-p-*dimethylaminophenylanthrone*, m. p. (indef.) 123° (decomp.), are described. 2-Methoxyanthraquinone, m. p. 196°, is prepared by oxidising the anthrone with CrO_3 in boiling AcOH. Reduction of 3-methoxyanthraquinone with Cu powder at 40° affords 3-methoxyanthrone, from which 10-*bromo*-3-*methoxyanthrone*, decomp. 107—108°, 3-*methoxy*-10-p-*dimethylaminophenylanthrone*, m. p. 146—148° (decomp.) after blackening at 135°, and 3 : 3'-*dimethoxydianthraquinone*, m. p. 298°, are derived. Phthalic anhydride and veratrole yield *o*-3' : 4'-dimethoxybenzoylbenzoic acid, whereas prolongation of the action leads to o-4-*hydroxy*-3-*methoxy*- (or, less probably, o-3-*hydroxy*-4-*methoxy*-) -*benzoylbenzoic acid*, m. p. 207°, derived also from the dimethoxybenzoylbenzoic acid and $AlCl_3$ in CS_2. o-3' : 4'-*Dimethoxybenzylbenzoic acid*, m. p. 119°, is converted by 80% H_2SO_4 at 50° into 2 : 3-dimethoxyanthrone, m. p. 134° (2 : 3-dimethoxyanthranyl acetate, m. p. 172°). o-2' : 5'-*Dimethoxybenzylbenzoic acid*, m. p. 124·5°, and 80% H_2SO_4 at 55° yield 1 : 4-*dihydroxyanthrone*, decomp. 185—195° (corresponding *triacetate*, m. p. 203°, and *tri*-p-*nitrobenzoate*, decomp. about 285°, but not completely molten below 300°).

H. WREN.

Dihydropyrocatechol or ***cyclo*****hexane-1 : 2-dione.** E. URION (Compt. rend., 1931, **192**, 1662—1664).—Divinyl glycol heated with reduced Cu at 280° yields cyclo*hexane*-1 : 2-*dione* (20% yield), m. p. 104·5°, sublimes at 97°/10 mm. (*dihydrate*, m. p. 78—79°; *dioxime*, m. p. 148—149°; *bisphenylhydrazone*, m. p. 143°; *dibromide*, m. p. 153—154°; *monophenylurethane*, m. p. 135°; *quinoxaline*, m. p. 73—73·5°; *semicarbazone*, m. p. 280°). Its production from divinyl glycol is explained by the intermediate formation of adipaldehyde, followed by ring-closure and dehydrogenation. In aq. solution the diketone is in equilibrium with the enolic form; a *sodio*-derivative, $C_6H_8O_2Na_2,2C_6H_8O_2$, is described.

G. DISCOMBE.

Mixed benzoins. VII. Maximal catalytic reduction. J. S. BUCK and W. S. IDE (J. Amer. Chem. Soc., 1931, **53**, 3510—3513).—Catalytic reduction (Adams) of benzoin, *o*-chlorobenzanisoin, and *o*-chlorobenzveratroin in EtOH (sometimes containing HCl) at about 70° gives, in each case, αβ-dicyclohexylethane and a *compound* (? αβ-*di*cyclo*hexylethylene glycol*), $C_{14}H_{26}O_2$, m. p. 193—194°, re-solidifying with m. p. 200° (*Ac* derivative, m. p. 133°). Similar reduction of *p*-dimethylaminobenzoin, *p*-dimethylaminobenzanisoin, and *o*-, *m*-, and *p*-chloro-*p*'-dimethylaminobenzoins affords, in each case, 4-*dimethylamino*-αβ-*di*cyclo*hexylethane*, b. p. 170°/9 mm. (*picrate*, m. p. 148—150°). Anisoin, benzanisoin, piperoin, and *o*-chlorobenzpiperoin were reduced similarly to the corresponding hydrobenzoins.

H. BURTON.

Oxidation of nitrobenzylamines. G. GALLAS, V. M. VIVALDI, and P. MORENO (Anal. Fís. Quím., 1931, **29**, 458—463).—When *p*-nitrobenzylamine is oxidised by H_2O_2 in AcOH and the product distilled in steam, there separates from the residue o-*hydroxy*-p'-*nitrobenzildianil*, m. p. 225°, which is hydrolysed by HCl to give p-*hydroxy*-p'-*nitrobenzil*, m. p. 172° [*quinoxaline*, m. p. 250° (darkens 210°), with *o*-phenylenediamine; *bisphenylhydrazone*, m. p. 198°]. Similarly, *p*-nitrobenzyl-*p*-toluidine yields p-*hydroxy*-p'-*nitrobenzildi*-p-*tolil*, m. p. 232°.

R. K. CALLOW.

Haloform reaction. III. Trihalogenoacetyl derivatives of mesitylene, durene, and ***iso*****durene.** A. R. GRAY, J. T. WALKER, and R. C. FUSON (J. Amer. Chem. Soc., 1931, **53**, 3494—3498; cf. A., 1930, 1291).—The following are prepared by the action of Na hypohalite on the requisite Ac compound: *di*(*trichloroacetyl*)-, m. p. 95—95·3° (all m. p. are corr.), and *di*(*tribromoacetyl*)-, m. p. 160—161·5°, -*mesitylenes*;

trichloroacetyl- (I), b. p. 158·5—159·5°/7 mm., *tribromoacetyl-*, m. p. 83·8—84·3°, *di(trichloroacetyl)-*, m. p. 134·8—135·2°, and *di(tribromoacetyl)-* m. p. 180·5° (decomp.). -iso*durenes*; *trichloroacetyl-* (II), m. p. 107—107·5°, and *tribromoacetyl-* (III), m. p. 102—102·5°, *-durenes*. These derivatives are generally stable to cold alkali; (I), (II), and (III) are not affected by 40% NaOH at 95—100°. H. BURTON.

Supposed exceptions to the rules for the substitution of benzene derivatives. K. VON AUWERS and E. RISSE (Ber., 1931, **64**, [*B*], 2216—2222).—Contrary to Simonis (A., 1927, 154), the product obtained by the action of cinnamyl chloride on resorcinol Et_2 ether is 2 : 4-diethoxychalkone, m. p. 90·5°, identical with the substance derived from 2 : 4-diethoxyacetophenone and PhCHO. It is hydrolysed by $AlCl_3$ to 2-hydroxy-4-ethoxychalkone, m. p. 104°, and oxidised by $KMnO_4$ in alkaline solution to 2 : 4-diethoxybenzoic acid, m. p. 99°. Similarly, Simonis' 2 : 6- is 2 : 4-dimethoxychalkone, m. p. 78—79°, identical with that derived from 2 : 4-dimethoxyacetophenone and PhCHO and converted by $AlCl_3$ into 2-hydroxy-4-methoxychalkone, m. p. 107—107·5°. The product from *as-o*-xylenyl Me ether and cinnamyl chloride is identified as *2-methoxy-4 : 5-dimethylchalkone*, m. p. 78°, since it is oxidised to *2-methoxy-4 : 5-dimethylbenzoic acid*, m. p. 142·5—143·5° (hydrolysed by $AlCl_3$ to 4 : 5-dimethylsalicylic acid, m. p. about 199°), and is also obtained from 2-methoxy-4 : 5-dimethylacetophenone and PhCHO. The condensation of resorcinol Me_2 ether with phenylpropiolyl chloride affords small amounts of a product, m. p. 135—136°, which, in agreement with Simonis, is not identical with 7-methoxyflavone and does not give typical flavone reactions.

Isomerisation of *m*-tolyl propionate by $AlCl_3$ at 130° affords 2-hydroxy-4-methylpropiophenone, m. p. 41·5—42·5° (p-*nitrophenylhydrazone*, m. p. 204—205°). H. WREN.

Photochemistry of tetrabenzoylethylene. II. H. VON HALBAN and K. RAST (Z. physikal. Chem., Bodenstein Festband, 1931, 303—308).—The behaviour of tetrabenzoylethylene when exposed to light is much more complex than was postulated by Andres (Diss., Strassburg, 1911). The yellow compound *B* produced by the action of light yields on further exposure a colourless, very sparingly sol. *compound D*, m. p. 300° (decomp.), which yields a fluorescent solution and contains 1 atom of O more than *B*. In acid solution, in the dark, *B* is converted into a colourless *monohydrate C*, but in neutral solution a faintly yellow *compound E*, m. p. 155°, probably isomeric with *C*, is formed. Treatment of *C* with NaOEt yields two *compounds*; one is isomeric with *C* and the other is very similar to *D*, but has m. p. 230·5°, whilst its solution in pyridine is extremely light-sensitive. When tetrabenzoylethylene is covered with CS_2 the greater part dissolves, but within a few min. the solution sets to a jelly; if the solvent is removed by suction a soft white substance remains which is completely unchanged by sunlight, but appears to be otherwise identical with the original compound (mixed m. p.). On heating at 140°, or recrystallising from any solvent other than CS_2, the original compound is obtained. The solubility relationships indicate a transition temp. between 20° and 78°. H. F. GILLBE.

Isomeride of anhydrobisdiketohydrindene (di-indone). W. M. FISCHER and G. WANAG (Annalen, 1931, **489**, 97—106).—iso*Di-indone*,

$C_6H_4{<}{}^{CO}_{CO}{>}CR\cdot C{\ll}{}^{CH-}_{C_6H}{>}CO$ (I; R=H), yellow, m. p. 330° [*Na* (dark green), and *Ag* salts; *Br*- (+$CHCl_3$), m. p. 285°, and *Br*$_3$- (unstable), m. p. 287° (decomp.), derivatives], is found among the products of the self-condensation of 1 : 3-indandione by alkali (even of glass), and of the decomp. by acid of Et 1 : 3-indandione-2-carboxylate. It is best obtained by heating 1 : 3-indandione with pyridine at 120°, or from the Na salt of the -2-carboxylate and AcOH, or, better, AcOH+Ac_2O. It is converted into di-indone by dil. aq. alkalis at the b. p. Interaction of its Na salt with MeI in MeOH gives a *Me* derivative, m. p. 252°, which, on account of its greenish-yellow colour and stability to alkaline hydrolysis, is regarded as a *C*-Me compound (I; R=Me). The Ag salt gives with cold 2*N*-HNO_3 or -H_2SO_4 an orange-yellow substance, m. p. 281°. A *substance*, $C_{27}H_{14}O_4$, m. p. 337°, probably

$C_6H_4{<}{}^{CO}_{CO}{>}C{:}C{<}{}^{C_6H_4}_{CH}{\gg}C\cdot CH{<}{}^{CO}_{CO}{>}C_6H_4$, is also formed by action of pyridine on 1 : 3-indandione at 120° (cf. A., 1927, 669). H. A. PIGGOTT.

Organic sulphur-nitrogen linking. VII. R. POLLAK, E. RIESZ, and J. RIESZ (Monatsh., 1931, **58**, 170—175; cf. this vol., 1284).—The quinonoid formula for the unimol. oxidation products of arylthiolarylamines is confirmed by synthesis of two typical examples. 4-Chloro-2-nitrothiolbenzene (I), quinonechloroimide, and Na_2CO_3 in cold aq. EtOH afford *N*-4-chloro-2-nitrophenylthiolbenzoquinoneimine. *p*-Thioltoluene and β-thiolnaphthalene give similarly the corresponding *p*-tolyl- and *β-naphthylthiolbenzoquinoneimine*, respectively, the latter (red) having m. p. 128°. The first two imines were identical with oxidation products. A similar experiment with quinonedichlorodi-imine gave the disulphide, which was also obtained on treating (I) with NaOCl. *N*-1-Anthraquinonylthiolaniline (II), when oxidised with $Na_2Cr_2O_7$ in AcOH, gives a black bimol. *substance*, $C_{40}H_{24}O_4N_2S_2$, giving a non-oxidisable vat. (II) itself gives a similar vat. 1-Bromothiolanthracene and *as*-dimethyl-*p*-phenylenediamine in cold C_6H_6 give p-N-1-*anthraquinonylthiolaminodimethylaniline*, brown, m. p. 196°, which with HNO_3 in AcOH gives N-1-*anthraquinonylthiol-N'-methylbenzoquinonedi-imine methonitrate*, red, m. p. 177°, which dyes wool and cotton mordanted with tannin bright red, but is destroyed by vatting. R. S. CAHN.

Stereochemistry of phenylquinones. Preparation and resolution of 2-3′-bromo-2′ : 4′ : 6-trimethylphenyl-5-methyl-*p*-benzoquinone-3 : 6-diacetic acid. XVIII. D. W. HILL and R. ADAMS (J. Amer. Chem. Soc., 1931, **53**, 3453—3461).—Mesitylene and *p*-toluquinone in presence of $AlCl_3$ below 5° give 2-2′ : 4′ : 6′-*trimethylphenyl-5-methylquinol* (I), m. p. 134—135° (all m. p. are corr.) (*diacetate*, m. p. 138—139°), oxidised by *p*-benzoquinone

in 95% EtOH to 2-2′ : 4′ : 6′-*trimethylphenyl*-5-*methyl*-p-*benzoquinone*, m. p. 129°. (I) and Br in CCl_4 afford 3 : 6-*dibromo*-2-3′-*bromo*-2′ : 4′ : 6′-*trimethylphenyl*-5-*methylquinol*, m. p. 148—149° (*diacetate*, m. p. 137—138°), oxidised as above to 3 : 6-*dibromo*-2-3′-*bromo*-2′ : 4′ : 6′-*trimethylphenyl*-5-*methyl*-p-*benzoquinone* (II), m. p. 137—138°. The 5′-*nitro*-derivative, m. p. 205—206°, of (II) is reduced catalytically (Adams) to 3 : 6-*dibromo*-2-3′-*bromo*-5′-*nitro*-2′ : 4′ : 6′-*trimethylphenyl*-5-*methylquinol*, m. p. 178—179°, which is converted by successive reduction (Sn+HCl) and oxidation (as above) into 3 : 6-*dibromo*-2-3′-*bromo*-5′-*amino*-2′ : 4′ : 6′-*trimethylphenyl*-5-*methyl*-*quinol*, m. p. 223°, and -p-*benzoquinone*, decomp. 135—140°. Stable salts could not be prepared from this aminoquinone and optically active acids. (II) is converted by NaOH in aq. MeOH into 3 : 6-*dihydroxy*-2-3′-*bromo*-2′ : 4′ : 6 *trimethylphenyl*-5-*methyl*-p-*benzoquinone*, m. p. 282° (decomp.) [*brucine*, m. p. 185—190° (decomp.), and *strychnine*, m. p. 194—200° (decomp.), salts], which could not be resolved. Et sodiocyanoacetate and (II) give *Et* 2-3′-*bromo*-2′ : 4′ : 6′-*trimethylphenyl*-5-*methyl*-p-*benzoquinone*-3 : 6-*dicyanoacetate*, m. p. 205—206°, which on alkaline hydrolysis affords either the corresponding 3 : 6-*dimalonic*, m. p. 160—165° (decomp.), or 3 : 6-*diacetic acid*, m. p. 220—223°. The diacetic acid is resolved by morphine into d-, m. p. 198—200°, $[\alpha]^{20}$ +34·7° in MeOH, and l-*forms*, m. p. 205—207°, $[\alpha]_D^{20}$ −18·8° in MeOH. This resolution is in accordance with the prediction of *X*-ray data (cf. A., 1930, 1588). 2-3′-*Bromo*-2′ : 4′ : 6′-*trimethylphenyl*-5-*methylquinol*-3 : 6-*diacetic acid* has m. p. 242—245° (decomp.).

H. BURTON.

Action of aldehydes on naphthaquinones. H. RAUDNITZ and G. PULUJ (Ber., 1931, **64**, [*B*], 2212—2216).—Treatment of α-naphthaquinone with *iso*valeraldehyde and other aldehydes and HCl in AcOH at 100° (cf. J.C.S., 1896, **69**, 1356, 1363) yields small amounts of intensely coloured substances containing Cl and sol. in alkali carbonate. The hypothesis that their production is due to reduction by the aldehyde of the quinone to the quinol and subsequent condensation is established by the observation that they are formed in good yield from 1 : 4-dihydroxynaphthalene. The products are tetrahydroxydinaphthylalphyl- (or -aryl-)methyl chlorides, the colour of which is explained on the basis of Pfeiffer's theory. They dissolve in alkali hydroxide to intensely bluish-violet solutions, the colour of which gradually fades; acidification with dil. H_2SO_4 ppts. the quinone hydrate. The following *compounds* are derived from 1 : 4-dihydroxynaphthalene: with *iso*valeraldehyde, $C_{25}H_{23}O_4Cl$; with heptaldehyde, $C_{27}H_{27}O_4Cl$; with *n*-butaldehyde, $C_{24}H_{21}O_4Cl$; with propaldehyde, $C_{23}H_{19}O_4Cl$; with crotonaldehyde, $C_{24}H_{19}O_4Cl$; with PhCHO, $C_{27}H_{19}O_4Cl$; with salicylaldehyde, $C_{27}H_{19}O_5Cl$. β-Naphthaquinone is reduced by *iso*valer- or hept-aldehyde to β-dinaphthaquinol, isolated as the tetra-acetate, m. p. 185—187°. 2-Hydroxy-α-naphthaquinone and *iso*valeraldehyde afford *iso*-β-lapachol (cf. *loc. cit.*).

H. WREN.

Anthraquinonesulphonic acids. H. E. FIERZ-DAVID (J. pr. Chem., 1931, [ii], **131**, 373—374).—A criticism of Lauer (B., 1931, 751). 1 : 6- and 1 : 7-Disulphonic acids are formed as by-products during β-monosulphonation (cf. Krebser, Diss., Zurich, 1925, 9). The conversion of anthraquinonedisulphonic acids into the corresponding dichloroanthraquinones by Ullmann's method is quant. only at high dilutions.

H. A. PIGGOTT.

Anthraquinonesulphonic acids. K. LAUER (J. pr. Chem., 1931, [ii], **131**, 375).—A reply to Fierz-David (preceding abstract) reaffirming the results already published.

H. A. PIGGOTT.

1-Methylanthraquinone series. F. MAYER and O. STARK (Ber., 1931, **64**, [*B*], 2003—2010).—The prep. is described of 3-methylphthalic acid from *o*-toluidine through *o*-oximinoacetotoluidide, 7-methylisatin, 2-amino-*m*-toluic acid and its *Me* ester, b. p. 151°/18 mm., and *Me* 2-*cyano*-m-*toluate*, b. p. 284°, m. p. 68—70°. With C_6H_6 and $AlCl_3$, 3-methylphthalic anhydride yields a mixture of 6- and 3-methyl-*o*-benzoylbenzoic acids, transformed by conc. H_2SO_4 at 100° into 1-methylanthraquinone, m. p. 171°. Similarly, with PhMe the anhydride gives a mixture of 6- and 3-methyl-*o*-*p*′-toluylbenzoic acids, converted into a non-separable mixture of 1 : 6- and 1 : 7-dimethylanthraquinone. 3- and 6-Methyl-*o*-2′ : 5′-dimethylbenzoylbenzoic acid and 1 : 5 : 8-*trimethylanthraquinone*, m. p. 146—147° (reduced by Zn dust and NH_3 to the corresponding *anthrone*, m. p. 125° after softening at 80°), are described. 3-Methylphthalic anhydride and quinol in presence of $AlCl_3$ and NaCl at 160—190° give 5 : 8-*dihydroxy*-1-*methylanthraquinone*, m. p. 238—238·5° (*diacetate*, m. p. 224°); shortened heating leads to 3- or 6-*methyl*-o-2′ : 5′-*dihydroxybenzoylbenzoic acid*, m. p. 230—231°. The anthraquinone derivative is converted by $Na_2S_2O_3$ and NH_3 at 135—140° into 5 : 8-*diamino*-1-*methylanthraquinone*, m. p. 205°. 5 : 8-*Ditoluidino*-1-*methylanthraquinone* has m. p. 219—220°. The following substances are obtained from 3-methylphthalic anhydride and the requisite phenol: 5 : 8-*dihydroxy*-1 : 7(or 1 : 6)-*dimethylanthraquinone*, m. p. 171—172° (*diacetate*, m. p. 234°); 5 : 6 : 8(or 5 : 7 : 8)-*trihydroxy*-1-*methylanthraquinone*, m. p. 272—274° (*triacetate*, m. p. 182—184°), also derived from 5 : 8-dihydroxy-1-methylanthraquinone and $Pb(OAc)_4$ in AcOH and conversion of the diquinone into the triacetate; 5 : 7-*dihydroxy*-1-*methylanthraquinone*, m. p. 285—286° (*diacetate*, m. p. 165—166°); 5 : 6(or 7 : 8)-*dihydroxy*-1-*methylanthraquinone*, m. p. above 310° and m. p. 206—207°. 4-Methylphthalic anhydride and *p*-xylene yield 4-(or 5)-*methyl*-o-2′ : 5′-*dimethylbenzoylbenzoic acid*, m. p. 151°, whence 1 : 4 : 6-*trimethylanthraquinone*, m. p. 143°. Oxidation of 6-diethylacetyl-2 : 5-dimethylbenzoic acid with hypochlorite gives a *product*, $C_{16}H_6O_3Cl_2$, m. p. 215°, oxidised by HNO_3 to 4 : *o*-*dichloro*-3 : 6-*dimethylphthalic acid*, m. p. 207°, which with quinol affords 6 : 7-*dichloro*-1 : 4-*dihydroxy*-5 : 8-*dimethylanthraquinone*, m. p. 209—210° (*diacetate*, m. p. 221—222°). 3 : 6-Dimethylphthalic acid and PhMe give successively 2 : 5-*dimethyl*-6-p′-*toluylbenzoic acid*, m. p. 180°, and 1 : 4 : 6-trimethylanthraquinone, m. p. 143°. 2 : 5-Dimethylbenzoic acid is converted through its chloride by condensation with *p*-xylene into di-*p*-xylyl ketone,

b. p. 197°/19 mm., which passes by loss of H_2O into 1 : 4 : 6-trimethylanthracene, m. p. 227°; on oxidation, the hydrocarbon gives a 1 : 4 : 6-trimethylanthraquinone, m. p. 227° (Elbs, m. p. 184°). One of the above methods of prep. is therefore accompanied by wandering of a Me group. 4-Methylphthalic anhydride and *m*-xylene give a mixture of 3- and 5-methyl-*o*-2′ : 4′-dimethylbenzoylbenzoic acid, transformed into 1 : 3 : 7-*trimethylanthraquinone*, m. p. 128—129°, and 1 : 3 : 6-trimethylanthraquinone, m. p. 192°. The following compounds are derived from 3 : 6-dimethylphthalic anhydride and the requisite phenol: 5 : 8-*dihydroxy*-1 : 4-*dimethylanthraquinone*, m. p. 252—253° (*diacetate*, m. p. 181—182°); 5 : 8-*dihydroxy*-1 : 4 : 7-*trimethylanthraquinone*, m. p. 218° (*diacetate*, m. p. 196—198°); 5 : 7 : 8-*trihydroxy*-1 : 4-*dimethylanthraquinone*, m. p. 227—228° (*diacetate*, m. p. 192°); 5 : 6 : 7-*trihydroxy*-1 : 4-*dimethylanthraquinone*, m. p. 243° (*diacetate*, m. p. 203°).

H. Wren.

Retene. I. Synthesis of retene derivatives. M. T. Bogert and T. Hasselstrom (J. Amer. Chem. Soc., 1931, **53**, 3462—3466).—Retene and AcCl in presence of $AlCl_3$ and CS_2 give *acetylretene* (I), m. p. 99—99·5° (all m. p. are corr.) (*picrate*, m. p. 142—143°; *oxime*, m. p. 167—168°; *phenylhydrazone*, m. p. 202°; *dinitro*-derivative, m. p. 215—216°), oxidised by CrO_3 in AcOH to *acetylretenequinone*, m. p. 213—214° (decomp.) (*quinoxaline*, m. p. 196—197°, from *o*-phenylenediamine). (I) condenses with benzaldehyde and *p*-nitrobenzaldehyde in alcoholic NaOEt, forming *cinnamoyl*-, m. p. 154·5—155·5°, and p-*nitrocinnamoyl*-, m. p. 188—189°, -*retene*, respectively. *Acetylretenesemicarbazone*, m. p. 248·5—249·5° (decomp.), and NaOEt at 190—200° give *ethylretene*, m. p. 54—55° (*picrate*, m. p. 145—146°), oxidised to *ethylretenequinone*, m. p. 205·5—206·5°. H. Burton.

Manufacture of 4-halogeno-1-amino-9-anthrones and substitution products and derivatives. Newport Co.—See B., 1931, 918.

Manufacture of *o*-aminocarboxylic esters of the anthraquinone series. I. G. Farbenind. A.-G. —See B., 1931, 918.

Manufacture of 1-hydroxy- and 1-alkoxy-anthraquinone-3-carboxylic acids and derivatives. I. G. Farbenind. A.-G.—See B., 1931, 918.

Cantharidin from *Mylabris pustalata*. B. H. Iyer and P. C. Guha.—See B., 1931, 993.

Pinabietic acid in Canada balsam. J. Ranedo and M. L. Navarro (Anal. Fís. Quím., 1931, **29**, 425—430).—The distillate from Canada balsam collected at 250—300°/55 mm. yields an acid, m. p. 177—178°, in 0·6% yield. It is not identical with any of the substances described by Tschirch and Bruning (A., 1900, i, 679), but resembles pinabietic acid (Aschan, A., 1921, i, 669). It absorbs $2H_2$ on catalytic hydrogenation, yielding a *compound*, m. p. 161—162°.

R. K. Callow.

Physodalic acid. G. Koller and K. Locker (Monatsh., 1931, **58**, 209—212).—Physodalic acid from *Parmelia physodes* is identical with capraric acid (cf. A., 1899, i, 381), since it has the same formula, crystal form, and constituent groups, gives an Ac derivative and an anilide, decomp. 260°, and when heated with Zn dust and NaOH at 100° yields orcinol and 3 : 5-dihydroxy-*p*-tolualdehyde. R. S. Cahn.

Strophanthin. XXII. Correlation of strophanthidin and periplogenin with digitoxigenin and gitoxigenin. W. A. Jacobs and R. C. Elderfield. **XXIII. Ring II of strophanthidin and of related aglucones.** W. A. Jacobs and E. L. Gustus (J. Biol. Chem., 1931, **92**, 313—321, 323—344; cf. this vol., 827).—XXII. Heating Me *iso*periplogonate with MeOH containing HCl gives *Me anhydro*isoperi*plogonate*, m. p. 225—226°, which on catalytic hydrogenation yields two isomeric *Me deoxy*isoperi*plogonates*: I (less sol.), m. p. 251—252°, $[\alpha]_D^{24}$ −44°, and II (more sol.), m. p. 192—193·5°, $[\alpha]_D^{25}$ −40·5° (free *acid*, m. p. 206—208°). The free acid with aq. HCl affords *γ-deoxy*isoperiplogonic *acid*, m. p. 225—226°, $[\alpha]_D^{5}$ +70±2° (*Me* ester, m. p. 180—181°). These derivatives of periplogenin are identical with those obtained from digitoxigenin.

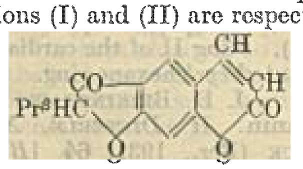
XXIII. An improved yield of Me_2 undephanthontriacidate (I) from Me_2 anhydro*iso*strophanthonate was obtained by oxidation with O_3. A better yield of duodephanthondiacid (II) was obtained by substituting piperidine for 0·1*N*-NaOH in its prep. The Me_2 ester of (II) when treated with N_2H_4 yields the *ketazine*, m. p. 184°. Catalytic reduction of (II) gives the *hydroxy-acid*, $C_{21}H_{30}O_7$, m. p. 234°, or the *dilactone*, $C_{21}H_{28}O_6$, m. p. 253°. Reduction of the Me_2 ester of (II) gives the *dilactone monomethyl* ester, m. p. 240°. (II) when heated with Ac_2O and AcCl gives the unsaturated *lactone anhydride* (III), $C_{21}H_{24}O_5$, m. p. 242°. Hydrogenation of (III) affords a saturated *deoxy-acid anhydride* (IV), $C_{21}H_{30}O_5$, m. p. 173°. (IV) gives a saturated *triacid*, softens above 120° (*Me*$_3$ ester, m. p. 62°). Heating (I) with Ac_2O and AcCl at 80° gives an unsaturated *lactone*, $C_{24}H_{30}O_8$, m. p. 199°. Oxidation of Me anhydro*iso*periplogonate with O_3 yields *Me undeplogondiacidate* (V), m. p. 182—184°, which with Ac_2O and AcCl at 80° affords the unsaturated *lactone*, $C_{23}H_{30}O_6$, m. p. 235—236°. Saponification of the saturated lactone Me_2 ester, $C_{25}H_{36}O_7$ (previously described), with pyridine and aq. NaOH gives the saturated *triacid*, $C_{23}H_{34}O_8$ (VI), effervesces at 225° (+$\frac{1}{2}H_2O$) [*Me*$_3$ ester (VII), m. p. 199°], hydrolysis with aq. NaOH+EtOH, giving the dibasic *lactone acid*, froths at 258°. Oxidation of (VII) with CrO_3 in AcOH affords the *keto-ester*, m. p. 220° (*oxime*, m. p. 210°). Me_2 β-*iso*strophanthate forms *Me*$_2$ β-iso*strophanthonate* (VIII), m. p. 248—250° (*oxime* froths at 190°, remelts at 215—217°). (VIII) forms an anhydro-compound identical with that from the α-ester. The chief product of hydrogenation of Me_2 anhydro-α-*iso*strophanthonate is the sparingly sol. Me_2 deoxy*iso*strophanthonate, revised $[\alpha]_D$ +8°. The other isomeride is oxidised by CrO_3 in AcOH to the dibasic *acid*, $C_{25}H_{34}O_{10}$, m. p. 191—193° (anhydride, m. p. 256°). Ring II of the cardiac aglucones must be a substituted *cyclo*hexane ring.

J. H. Birkinshaw.

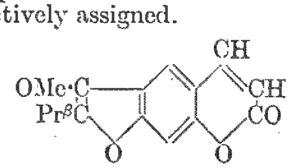
Constitution of alkannin. H. Dieterle, A. Salomon, and E. Nosseck (Ber., 1931, **64**, [*B*], 2086—2090; cf. this vol., 1063).—The isolation of cryst. alkannin, m. p. 120°, from alkanet root is

described. The composition $C_{15}H_{14}O_4$ is confirmed by the analysis of a *diacetate*, $C_{15}H_{12}O_4Ac_2$, m. p. 147°, and of *dihydroalkannin tetra-acetate*, $C_{15}H_{12}O_4Ac_4$, m. p. 120°. Distillation of alkannin with Zn dust yields 2-methylanthracene. Ozonisation in $CHCl_3$ yields a *compound*, $C_{13}H_8O_8$, m. p. 138—139°, regarded as a dihydroxynaphthoquinonedicarboxylic acid (*diacetate*, m. p. above 360°), which loses CO_2 when heated above its m. p. Further ozonisation gives an aldehyde, $C_{11}H_6O_5$, characterised by a *phenylhydrazone*, m. p. 168—169°, whilst subsequent ozonisation affords oxalic acid. The behaviour of alkannin towards O_3 differs from that of 5 : 8-*dihydroxy*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydroanthraquinone*, m. p. 118° (prepared through the *diacetate*, m. p. 120—122°, derived from diacetylnaphthazarin and piperylene at 100°), which gives an *acid*, $C_{13}H_8O_8$, m. p. 211° (decomp.), and 5 : 8-*dihydroxy-2-methyl*-1 : 2 : 3 : 4-*tetrahydroanthraquinone*, m. p. 150° (from diacetylnaphthazarin and isoprene). Sublimation of the 1-Me compound yields a *substance*, $C_{13}H_8O_3$, m. p. 240°, whereas alkannin affords 5 : 8-dihydroxy-1-methylanthraquinone, m. p. 237°, and a *substance*, $C_{12}H_{10}O_3$, m. p. 140°. Treatment of alkannin in AcOH with H_2 in presence of Pd–C gives a tetrahydro-derivative from which 2H is removed by atm. oxidation giving *dihydroalkannin*, m. p. 130°. Alkannin is considered to be a 5 : 8-dihydroxy-1-α-methyl-Δ^{β}-butenyl-1 : 4-naphthaquinone. H. WREN.

Constitution of peucedanine and oreoselone. E. SPÄTH, K. KLAGER, and C. SCHLÖSSER (Ber., 1931, **64**, [*B*], 2203—2211).—Peucedanine, $C_{15}H_{14}O_4$, is converted by HCl in EtOH–H_2O into oreoselone, $C_{14}H_{12}O_4$, m. p. 177—178°; both are optically inactive. In alkaline solution in presence of Pd–C oreoselone absorbs 2H giving *dihydro-oreoselonic acid* $C_{14}H_{16}O_5$, m. p. 173—174°, transformed at 200—220°/0·04 mm. into *dihydro-oreoselone*, $C_{14}H_{14}O_4$, m. p. 170—171°. *Me dihydro-oreoselonate*, m. p. 95—97°, is derived from the acid and diazomethane. Peucedanine suspended in MeOH absorbs 4H in presence of Pd–C yielding a product which foams when distilled in vac., giving a substance, $C_{14}H_{14}O_3$, m. p. 126°, free from OMe. Oreoselone is not dehydrogenated by Pd at 180°. Dihydro-oreoselonic acid is oxidised in faintly alkaline solution by $KMnO_4$ at room temp. to much oxalic and succinic acid. Succinic acid is also obtained by oxidation with HNO_3, whereas styphnic acid, readily derived from oreoselone and HNO_3, is not derived from the dihydro-acid. Oreoselone is oxidised by $KMnO_4$ in alkaline solution to α-hydroxy*iso*butyric acid, whereas when a smaller proportion of the oxidising agent is used the product is 4 : 6-*dihydroxybenzene*-1 : 3-*dicarboxylic acid*, identified as *Me* 4 : 6-*dimethoxybenzene*-1 : 3-*dicarboxylate*, m. p. 149—150°. To oreoselone and peucedanine the constitutions (I) and (II) are respectively assigned.



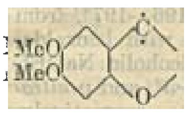
(I.)



(II.)

5-Nitro-2 : 4-dihydroxybenzoic acid is converted by diazomethane in MeOH into *Me 5-nitro-2 : 4-dimethoxybenzoate*, m. p. 147°, reduced by $Na_2S_2O_4$ to *Me 5-amino-2 : 4-dimethoxybenzoate*, m. p. 84°. This is diazotised and transformed into *Me 5-cyano-2 : 4-dimethoxybenzoate*, m. p. 116—117°, hydrolysed to 4 : 6-*dimethoxybenzene*-1 : 3-*dicarboxylic acid*, m. p. 272° (decomp.) (*Me* ester, m. p. 147—148°). Assuming that nitration of β-resorcylic acid actually occurs in the 5-position (cf. von Hemmelmayr, A., 1904, i, 319) it follows that the 2 : 4-dihydroxybenzene-1 : 3-dicarboxylic acid of Waitz (A., 1911, i, 541) is the 4 : 6-dihydroxy-acid. This is shown to be the case; von Hemmelmayr's acid is decarboxylated to 4-nitroresorcinol, which is converted successively into its Me_2 ether, 4-aminoresorcinol Me_2 ether, and 4-*cyano*-1 : 3-*dimethoxybenzene*, m. p. 95—96°, hydrolysed to 2 : 4-dimethoxybenzoic acid, m. p. 106°. Oxidation of the dibenzylidene derivative of 2 : 4-dimethoxy-1 : 5-diacetylbenzene (Eykman and others, A., 1905, i, 359) with $KMnO_4$ affords 4 : 6-dimethoxybenzene-1 : 3-dicarboxylic acid (Me ester, m. p. 150°). H. WREN.

Deguelin. III. Orientation of the methoxy-groups in deguelin, tephrosin, and rotenone. E. P. CLARK (J. Amer. Chem. Soc., 1931, **53**, 3431—3436).—The hydroxydimethoxybenzoic acid previously obtained (this vol., 841) by oxidising dehydrodeguelin is the 2-hydroxy-4 : 5-dimethoxy-acid,



since when heated with NH_2Ph it gives 3 : 4-*dimethoxyphenol*, m. p. 79—80° (3 : 5-*dinitrobenzoate*, m. p. 158°), also prepared from 4-aminoveratrole. Since deguelin, tephrosin, and rotenone are inter-related (this vol., 491, 1065), the annexed grouping occurs in all these compounds. H. BURTON.

Rotenone. XIV. Relation of optical activity of rotenone derivatives to the structure of tubaic acid. H. L. HALLER and F. B. LA FORGE (J. Amer. Chem. Soc., 1931, **53**, 3426—3431).—Of the two asymmetric centres in rotenone, one disappears during the prep. of dehydro-derivatives, whilst the other is lost during isomerisation to *iso*-derivatives. The formation of deoxy-acids (A., 1928, 1017) by fission of a lactone group during catalytic reduction also involves the disappearance of an asymmetric centre, which, however, does not occur during hydrolytic fission. The above (and other evidence) supports the view that the structure proposed by Takei *et al.* (this vol., 847) for tubaic acid is incorrect and that the tubaic acid structure does not occur in rotenone.

When rotenonic acid, m. p. 206°, $[\alpha]_D^{20}$ +45° (all rotations are in $CHCl_3$), is heated with EtOH–KOH, racemisation occurs. dl-*Rotenonic acid*, m. p. 184°, is reduced catalytically (Adams) in AcOEt to the dihydro-derivative, m. p. 194° (also formed from dihydrorotenonic acid, $[\alpha]^{20}$ +67°, and EtOH–KOH), is oxidised by alkaline H_2O_2 to hydroxyrotenonic acid, and isomerised by acid to dl-β-*dihydrorotenone*, m. p. 171°. The last-named is oxidised by alkaline $K_3Fe(CN)_6$ to dehydro-β-dihydrorotenone. Clemmensen reduction of rotenone and *iso*rotenone gives *deoxyisorotenone*, $C_{23}H_{24}O_5$, m. p. 165—166°, $[\alpha]_D^{20}$ −113·2°. The following vals. of $[\alpha]_D^{20}$ are also recorded: rotenol, −77·3°; dehydrodihydrorotenol,

$-8 \cdot 05°$; dihydroderritol Me ether, $-32 \cdot 8°$, and dihydrorotenone, $-123 \cdot 2°$. Dihydrorotenolic, dehydrodihydrorotenolic, methylderritolic, and dehydrodihydrorotenonic acids, β-dihydrorotenolone, and *iso*derritol are optically inactive. H. BURTON.

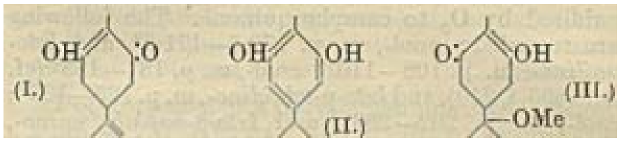
Resins and resin substances. VIII. β-Amyrin from Manila elemi resin. V. A. ROLLETT (Monatsh., 1931, **58**, 113—117; cf. B., 1930, 623).—β-Amyrin (I) is probably unsaturated, because ozonolysis of it and its benzoate (II) yields substances which appear to be stable molozonides. Ozonolysis of (I) in $CHCl_3$ at room temp. gives amorphous substances of progressively increasing O content. (II) gives similarly an amorphous *substance* (III), $C_{37}H_{54}O_6$, m. p. 196—215° (decomp.), and a cryst. *substance*. In AcOH (II) gives unchanged material, together with a cryst. *substance*, $C_{37}H_{54}O_6$, m. p. 225—235° after decomp. from 140—160° [regarded as identical with (III)], which on hydrolysis gives much (I). R. S. CAHN.

Phytosterols and abietic acid as parents of the optically active components of petroleum. N. D. ZELINSKI and N. S. KOSLOV (Ber., 1931, **64**, [*B*], 2130—2135).—Betulin heated with $AlCl_3$ yields about 66% of a liquid condensate partly volatile with steam. The fractions of lower b. p. from the volatile portion appear to be saturated and free from aromatic hydrocarbons, whereas hydrogenation of the fractions of higher b. p. in presence of Pt–C at 200—220° indicates the presence of unsaturated and aromatic hydrocarbons. The product not volatile with steam gives a dextrorotatory hydrocarbon fraction when distilled under diminished pressure. Similarly, abietic acid is converted by heating with $AlCl_3$ into hydrocarbons fractions of which are markedly dextrorotatory, the activity appearing to be due to an unsaturated hydrocarbon. The products appear rich in aromatic hydrocarbons of varying b. p. American colophony and $AlCl_3$ also yield hydrocarbons. H. WREN.

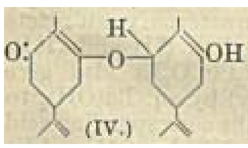
Plant colouring matters. XXXV. Constitution of β-carotene and β-dihydrocarotene. P. KARRER and R. MORF (Helv. Chim. Acta, 1931, **14**, 1033—1036).—Comparison of the amounts of geronic acid obtained by ozonolysis of β-carotene (I) and β-dihydrocarotene with the quantity obtained from β-ionone under similar conditions indicates that each of the former compounds contains two β-ionone groups per mol. and supports the sym. formula (A., 1930, 1422) for (I). The sp. rotation of α-carotene in C_6H_6 varies considerably with the wave-length. H. BURTON.

Taraxanthin, a new xanthophyll with 4 oxygen atoms. R. KUHN and E. LEDERER (Z. physiol. Chem., 1931, **200**, 108—114).—Dandelion (*Taraxacum officinale*) blossoms yield a mixture of xanthophylls from which by fractional adsorption on $CaCO_3$ there was isolated *taraxanthin*, $C_{40}H_{56}O_4$, m. p. 184—185·5° (corr.), $[\alpha]^{22}_{6439}$ +204°, adsorption max. 501, 468·5 mμ. J. H. BIRKINSHAW.

Autoxidation of αβ-unsaturated ketones. II. W. TREIBS (Ber., 1931, **64**, [*B*], 2178—2184; cf. this 94).—The hydroxy-acid $C_{10}H_{18}O_3$, m. p. 112—114°, obtained by the autoxidation of piperitone (*loc. cit.*) is prepared in approx. the same yield by the action of H_2O_2 in presence of KOH and MeOH. Carvone is transformed by H_2O_2 into a diketone, $C_{10}H_{14}O_2$, sol. in alkali hydroxide, and insol. products (see below). The diketone behaves as a monobasic acid and is not precipitated from alkaline solution by



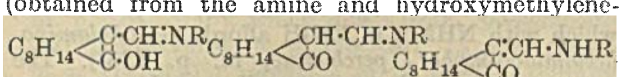
CO_2. With Ac_2O in presence and absence of catalysts it affords a *monoacetate*, $C_{12}H_{16}O_3$, b. p. 154—156°/16 mm. Benzoylation or methylation could not be effected. It yields a monosemicarbazone. It is transformed by $FeCl_3$, $ZnCl_2$, or H_2SO_4 into an isomeric *substance*, $C_{10}H_{14}O_2$, m. p. 130—132° (*dibenzoate*, m. p. 80°; *Me₂ ether*, b. p. 142°/20 mm.). Mild oxidising agents give a yellow ppt. with its aq. solutions and it is very readily autoxidised, particularly in alkaline solution. The relationships of diketone (I) and dihydroxy-isomeride (II) are shown. Particularly when the oxidation of carvone is effected slowly, the formation of the diketone is accompanied by that of (1) a viscous *liquid*, $C_{11}H_{18}O_3$, b. p. 150—160°/17 mm., d^{20}_{15} 1·067, which yields MeI and resin under the action of HI and immediately decolorises $KMnO_4$ and hence probably has the constitution (III) and (2) a cryst. *substance*, $(C_{10}H_{13}O)_2O$ or $(C_{10}H_{14}O)_2O$, m. p. 154°, the yield of which increases as that of the diketone decreases; it is therefore regarded as a secondary product from carvone and the diketone, although it could not



be produced by condensation of these substances. Since it gives a *monoacetate*, a *monosemicarbazone*, m. p. 220° (decomp.), is unsaturated towards $KMnO_4$, and resinified by HI, it probably has the constitution (IV). H. WREN.

Isomerisation of linalool to camphor under the action of aluminium. J. V. VINOGRADOVA (Ber., 1931, **64**, [*B*], 1991—1997).—The action of Al powder in the presence of a trace of $HgCl_2$ on linalool at 160—200° gives a mixture of dipentene (30%), traces of myrcene or linaloolene, camphor (about 2%), borneol (0·8%), dimyrcene (22%), resin (15%), and H_2O (8·5%). The products are optically inactive or of activity opposite to that of the initial material. Under similar conditions, geraniol affords dipentene and camphorene, but not camphor or borneol. H. WREN.

Mechanism of mutarotation of primary amino-derivatives of *d*-methylenecamphor. T. HAYASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, **16**, 200—203; cf. J.C.S., 1909, **95**, 171).—The mutarotation of derivatives of aminomethylenecamphor (obtained from the amine and hydroxymethylene-



(I.) (II.) (III.)

camphor) is ascribed to the process: I (enol) ⟶ II ⟶ III (keto). In two cases the rotation passes through a max., whilst in others it reaches a lower

const. val. through two stages. Fractionation of the solute after mutarotation gives forms corresponding with (I) and (III), the enolic form giving by ozonolysis a peroxide, which yields camphoric anhydride when heated, whilst the ketonic forms give oximes, and are oxidised by O_3 to camphorquinone. The following are recorded: enol-, m. p. 170·5—171·5°, and *keto-anilino-*, m. p. 108—110°; enol-, m. p. 187—188° (cf. A., 1895, i, 250), and *keto-p-toluidino-*, m. p. 125—126°; *enol-*, m. p. 202—203°, and *keto-β-naphthylamino-*, m. p. 171—173°; *enol-*, m. p. 192—193°, and *keto-p-nitroanilino-*, m. p. 151—152°; and *enol-*, m. p. 186—187°, and *keto-carbazolacridonylamino-methylene-camphor*, m. p. 235—236°, and >295° (geometrical isomerides). Et *p*-aminobenzoate and NHPhMe condensed with hydroxymethylenecamphor give a di-(carbethoxyanilino)-, m. p. 187—188°, and a di-(methylanilino)-derivative, m. p. 124° (cf. *loc. cit.*), respectively. A. A. LEVI.

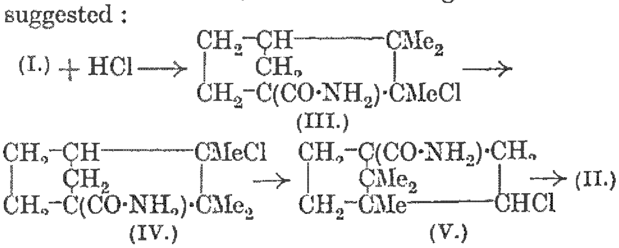
Camphor betaines. I. H. RUPE and W. FLATT (Helv. Chim. Acta, 1931, **14**, 1007—1033).—Dimethylaminocamphor (I) (convenient method of prep. given) (*perchlorate*, m. p. 229—230°) heated with $CH_2Cl·CO_2Et$ gives camphoryltrimethylammonium chloride (II) [corresponding *perchlorate*, m. p. 233°, prepared from $HClO_4$ and (II) or the quaternary salts from (I) and MeI or Me_2SO_4] and *Et* N-*camphoryl*-N-*methylaminoacetate* (III), b. p. 163·5°/10 mm. (*hydrochloride*, m. p. 159°); the initial quaternary salt reacts with a further mol. of (I) yielding (II) and (III). Methylaminocamphor and $CH_2Cl·CO_2Et$ also give (III), hydrolysed (in 1 case only) by aq. $Ba(OH)_2$ to the *Ba* salt, m. p. 233—235°, of the corresponding acid and converted by HNO_2 into the NO-derivative of Et *N*-camphorylaminoacetate (A., 1903, i, 44). MeBr and (III) at 100° afford camphoryltrimethylammonium bromide and $CH_2Br·CO_2Et$. *Me* N-*camphoryl*-N-*methylaminoacetate*, b. p. 159°/11 mm. (*hydrochloride*, m. p. 155°), is prepared from $CH_2Cl·CO_2Me$ and (I) or methylaminocamphor. (I) and $CH_2Br·CO_2Et$ at room temp. give *camphoryldimethylcarbethoxymethylammonium bromide* (corresponding *perchlorate*, m. p. 74°), converted by moist Ag_2O into the *betaine*,

$C_{10}H_{15}O·NMe_2·CH_2·CO_2$, m. p. 198° (*perchlorate*, m. p. 232°). (I) and $CH_2Br·CH_2·OH$ at 100° afford *camphoryldimethyl-β-hydroxyethylammonium bromide*, converted by AgOH into the corresponding *hydroxide* (*chloroaurate*, m. p. 117—118°) and by successive treatment with conc. HCl and $HClO_4$ into *camphoryldimethylvinylammonium perchlorate*, m. p. 237—238° (corresponding *chloroaurate*, m. p. 213—218°) (also formed by the action of AgOH on camphoryldimethyl-β-bromoethylammonium bromide and subsequent treatment with $HClO_4$), and a trace of a substance (*perchlorate*, m. p. 130°). Aminocamphor and $CH_2Cl·COCl$ in C_6H_6 and pyridine give *chloroacetamidocamphor* (IV), b. p. 194°/13 mm., 114°/0·007 mm., which with $NHMe_2$ in EtOH affords *dimethylaminoacetamidocamphor* (*perchlorate*, m. p. 228°). The quaternary bromide (corresponding *perchlorate*, m. p. 135°) from this and $CH_2Br·CO_2Et$ is converted by AgOH into the *betaine*,

$C_{10}H_{15}O·NH·CO·CH_2·NMe_2·CH_2·CO_2$, m. p. 248° (crystallographic data given) (*perchlorate*, m. p. 217°). (IV) and NMe_3 in EtOH afford the *chloride*, $C_{10}H_{15}O·NH·CO·CH_2·NMe_3Cl$, m. p. 224° (corresponding *perchlorate*, m. p. 110°, and *chloroaurate*, m. p. 175°), converted by AgOH into the corresponding hydroxide.

The sp. rotations and dispersion of many of the above compounds are discussed. H. BURTON.

Camphor and terpenes. VII. Replacement of the 2 : 6-rearrangement in the camphor series, [and interpretation of] racemisation of optically active camphene derivatives and conversion of *d*- into *l*-camphor derivatives by the camphene rearrangement of type 2. J. HOUBEN and E. PFANKUCH (Annalen, 1931, **489**, 193—224).—The action of HCl on *d*-camphene-1-carboxylamide (I) (cf. this vol., 558) gives *2-chlorocamphane-4-carboxylamide*, $[\alpha]^{20}$ +36° in EtOH (V), converted by aq. K_2CO_3 into *camphene-4-carboxylamide* (II), m. p. 164—165° [previously "camphene-2-carboxylamide" (A., 1926, 1252); the corresponding *acid*, m. p. 158—159°, $[\alpha]_D$ −83·3°, is obtained from "*d*-6-hydroxycamphane-2-carboxylic acid" (now 2-hydroxycamphane-4-carboxylic acid) through the corresponding *chloro*-derivative, m. p. 147—148°; a number of related substances previously described need correspondingly altered numeration]. Addition of HCl to (I) is quant. (this vol., 558), yet 2-chlorocamphane-2-carboxylamide cannot be isolated, and does not itself undergo rearrangement in cresol to (V), but slowly loses HCl and gives camphene-1-carboxylamide. The Meerwein 2 : 6- change of the Cl atom is therefore excluded, and the following mechanism is suggested:



The change of (III) into (IV) is a normal pinacone rearrangement without ring isomerisation (type 2) and is postulated to occur without change of optical structure, although it may be accompanied by a change of sign. It is responsible for the racemisation of *iso*bornyl chloride (*e.g.*, in *m*-cresol) in which the equivalence of the 1 : 4-positions masks the structural change involved. The constitution of (II) is proved by conversion of the corresponding dihydro-acid (A., 1926, 1251) into its *chloride*, m. p. 40°, b. p. 110—112°/19 mm., which is not acted on by PCl_5 at 140°, and therefore lacks an α-H atom. It is confirmed by reduction of (V) with H_2 and Pd–$BaSO_4$ to the *dihydro*-derivative, m. p. 126—130°, which is degraded by NaOMe and Br in MeOH to the (*methyl*)*urethane*, m. p. 74—75°, of *4-aminodihydrocamphene* (*hydrochloride*) (hydrolysis with KOH in MeOH); the NH_2 compound gives with HNO_2 *4-hydroxydihydrocamphene*, m. p. 133—134°, b. p. 105°/30 mm. (*acetate*, b. p. 104—105°/12 mm.), the tertiary nature of which is proved by its stability to oxidation by CrO_3–AcOH. *4-Aminocamphene*, m. p. 135°, $[\alpha]^{19}_D$ −90° in EtOH [*hydrochloride*, m. p. above 290°; *methylurethane*,

m. p. 73—74°; *Ac* derivative, m. p. 141° (H_2 derivative, m. p. 153—154°)], is similarly prepared, but is not readily reduced. Its urethane and AcH_2 derivatives are hydrolysed by acids to *d*-camphor.

An example of the optical inversion that may accompany this rearrangement is the successive conversion of *l*-camphor-4-carboxylic acid, m. p. 238—240° (best purified by means of its *amide*, m. p. 207—208°), into l-4-*aminocamphor*, m. p. 230—232° (CO_2Me, m. p. 117°, and *Ac*, m. p. 122—123°, derivatives), l-4-*hydroxycamphor*, m. p. 250° (*oxime*, m. p. 212°; *semicarbazone*, m. p. 236—238°; *Ac* derivative, b. p. 132°/11 mm.) [with an unsaturated *acid*, $C_{10}H_{16}O_2$, m. p. 155—158° (*lactone*, m. p. 142°)], and l-4-(*hydroxycamphene-1-carboxylamide* (oxime and HNO_2), m. p. 201—203° (decomp.) (H_2 derivative, m. p. 138—140°), which when evaporated with conc. HCl gives *d*-camphor-4-carboxylic acid. Further, the rearrangement of camphor dichloride (A., 1924, i, 188) gives, not 2 : 6-, but 2 : 4-dichlorocamphane, for the (4-)chlorocamphene obtained by elimination of HCl from the product gives with $CCl_3{\cdot}CO_2H$ at 60—70° dl-4-*chloro*iso*borneol*, m. p. 235—236°, oxidised by CrO_3–AcOH to dl-4-*chlorocamphor*, m. p. 198—199° [*oxime*, m. p. 158—160°; *semicarbazone*, m. p. 260—264° (decomp.)], identified by its prep. from 4-aminocamphor, and also by conversion into its 3-*oximino*-derivative, m. p. 174—175° (decomposed by PCl_5 in $CHCl_3$ with formation of HCN), and dl-4-*chlorocamphorquinone*, m. p. 219—220°, which with H_2O_2 in AcOH gives 3-chlorocamphoric anhydride. *d*-2-*Hydroxycamphane-4-carboxylic acid*, $[\alpha]^{20}$ +15·7°, is obtained by not too prolonged heating of *d*-camphene-1-carboxylic acid with $CCl_3{\cdot}CO_2H$ at 60—70°. The $\cdot CO_2Me$ derivative, b. p. 136—137°/16 mm. (*hydrochloride*), of camphorimine is readily decomposed to camphor by acids. H. A. Piggott.

Action of hydrazine hydrate on camphoric anhydride. V. Alexa and G. Gheorghiu (Bull. Soc. chim., 1931, [iv], **49**, 1112—1119).—When treated with 2 mols. of N_2H_4,H_2O in EtOH and heated at 120° camphoric anhydride is converted into *camphoric dihydrazide*, $\begin{matrix}CH_2{\cdot}CMe(CO{\cdot}NH{\cdot}NH_2)\\ CH{-}CH(CO{\cdot}NH{\cdot}NH_2)\end{matrix}\!\!>\!CMe_2$ [$+H_2O$, lost at 100°, m. p. 126° (sinters at 118°); anhyd., m. p. 158—160°], yielding the corresponding dihydrazone, m. p. 273°, with PhCHO and converted by heating at 150° into N-*aminocamphorimide*, m. p. 156° [*picrate*, $+H_2O$, m. p. 128° (anhyd., m. p. 112—115°); hydrochloride; picrolonate], which with PhCHO and 3 : 4-dihydroxybenzaldehyde yields *benzylidene*-N-*aminocamphorimide*, m. p. 106°, and 3 : 4-*dihydroxybenzylidene*-N-*aminocamphorimide*, m. p. 195—197°. The basic properties of the aminocamphorimides in contrast to the acidic hydrazides, $\cdot CO{\cdot}NH{\cdot}NH{\cdot}CO\cdot$, and the absence of analogy with the dihydroxyphthalazines in the absorption spectra of *N*-aminocamphorimide, establish the constitution of phthalhydrazide and its derivatives.

R. Brightman.

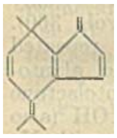
Silver camphorcarboxylate. Silver organosols. M. Picon (Compt. rend., 1931, **192**, 1660—1662, and J. Pharm. Chim., 1931, [vii], **14**, 273—281).—Ag camphorcarboxylate, precipitated in H_2O (Na salt and $AgNO_3$) and dried over P_2O_5, is sol. in C_6H_6, $CHCl_3$, and CS_2, from which another form separates. This retains solvent tenaciously, and is sol. only in $CHCl_3$, from which, by evaporation, a solid similar to the H_2O ppt. is obtained. The aq. solution is converted into a colloidal solution by the action of traces of H_2S in impure H_2, the latter always containing small quantities of O_2 or S. G. Discombe.

Polyterpenes and polyterpenoids. LV. Alantolactone. L. Ruzicka and P. Pieth (Helv. Chim. Acta, 1931, **14**, 1090—1103; cf. this vol., 734).—The so-called *iso*alantolamide is an additive *compound* (I), m. p. 233°, of NH_3 (1 mol.) and *iso*alantolactone (2 mols.). Thermal decomp. of (I) regenerates only a small amount of the lactone (cf. this vol., 360). Technical "helenin" is separable by repeated fractional crystallisation from EtOH into alantolactone, *iso*alantolactone, and dihydro*iso*alantolactone (II), m. p. 167·5—168°, $[\alpha]_D^{20}$ +72° in EtOH (also obtained by reduction of Na *iso*alantolate with Na and EtOH). Hydrolysis of the ozonide of (II) gives the keto-lactone (III), $C_{14}H_{20}O_3$, m. p. 198—199°, previously described (*loc. cit.*, where the m. p. is given as 203—205°), reduced (Clemmensen) to a *monocarboxylic acid*, $C_{14}H_{24}O_2$, b. p. 130—133°/0·1 mm., and (mainly) 9-methyl-3-ethyl-*cis*-decahydronaphthalene, $[\alpha]_D^{20}$ −2·64° (cf. this vol. 1303) [dehydrogenated by Se at 380° to 2-ethylnaphthalene (cf. Hansen, this vol., 1065)]. Treatment of the glycol (IV) obtained by reduction of tetrahydroalantolactone with Na and EtOH or by catalytic reduction of the glycol, $C_{15}H_{26}O_2$ (*loc. cit.*), with 33% HBr in AcOH, elimination of HBr from the resulting dibromide with $NPhMe_2$ at 190°, and catalytic reduction of the unsaturated hydrocarbon (freed from traces of Br by Na and K at 150°) gives a product, b. p. about 135°/12 mm., dehydrogenated by Se at 295—330° to a hydrocarbon, $C_{15}H_{18}$ [a dimethyl*iso*propylnaphthalene (?)] (*picrate*, m. p. 114°, not identical with cadalene picrate). The same hydrocarbon is obtained when (IV) is reduced with red P and HI and then dehydrogenated. Alternative formulæ for the above lactones are discussed (cf. *loc. cit.*; Hansen, *loc. cit.*).

[With (in part) J. A. van Melsen.] Hydrolysis of the ozonide of an incompletely hydrogenated impure alantolactone and oxidation of the product with $KMnO_4$ in $COMe_2$ gives mainly a *monocarboxylic acid*, $C_{15}H_{22}O_5$ (*Me* ester, b. p. 190—200°/0·4 mm.), and a little (III). H. Burton.

Polyterpenes and polyterpenoids. LVI. Azulene. LVII. Guaiol. L. Ruzicka and A. J. Haagen-Smit (Helv. Chim. Acta, 1931, **14**, 1104—1122, 1122—1132).—LVI. Dehydrogenation of guaiene with S at 180—240° (cf. A., 1926, 299) gives an azulene (designated S-*guaiazulene*) (I), blue, b. p. 167—168°/12 mm. (*picrate*, m.p. 121—122°; *styphnate*, m. p. 105—106°), which differs from Se-*guaiazulene* (II), bluish-violet, b. p. 170—171°/13 mm. (*picrate*, m. p. 114—115°; *styphnate*, m. p. 98—99°) (obtained by dehydrogenation of guaiene with Se). Catalytic reduction (Adams) of (I), which is identical with kessazulene (A., 1928, 616), gives *decahydro*-S-*guaiazulene*, colourless, b. p. 132—134°/12 mm., dehydro-

genated by Se to (II), whilst *decahydro*-Se-*guaiazulene*, b. p. 130—131°/13 mm., is dehydrogenated by S to a mixture of products containing a little (II). Elemazulene (III), violet-blue (*picrate*, m. p. 110°; *styphnate*, m. p. about 87°), is obtained in 1% yield by dehydrogenating elemene with Se. *Decahydrochamazulene* has b. p. 119—120°/12 mm. The above decahydroazulenes have approx. the same values for d_4^{15} and n_D^{15}, indicating that they possess similar ring systems. (I), (II), (III), and chamazulene (IV), when oxidised with 4% $KMnO_4$ at room temp., consume 17—19 O per mol. and all give AcOH and oxalic acid; $COMe_2$ and *iso*butyric acid are produced from (I), (II), and (III). When the oxidation is



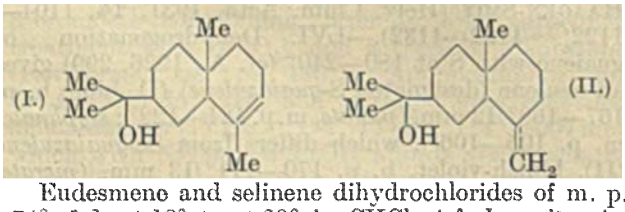
carried out at 100° (bath), (I), (II), and (III) consume 26—27 O per mol. Ozonolysis of (I) gives $COMe_2$, AcOH, HCO_2H, and *iso*butyric acid. The annexed structure is suggested as a possible azulene formula. The absorption spectra of (I) and (IV) are not identical.

[With H. A. Boekenoogen and H. W. Huyser.] The parachors of (I), (II), (III), and (IV) are practically identical (495·3±1·3).

LVII. The (*a*) neutral and (*b*) acidic hydrolysis products of the ozonide of guaiol contain (*a*) a doubly-unsaturated oxide (V), $C_{15}H_{22}O$, b. p. 140—141°/15 mm., a *compound* (VI), $C_{15}H_{26}O_3$, m. p. 218°, $[\alpha]_D$ +7·16° in AcOH (also obtained when guaiol is oxidised with $KMnO_4$ in aq. $COMe_2$), and lactonic products, and (*b*) lactonic and acidic products corresponding with $C_{15}H_{24}O_3$ and $C_{15}H_{26}O_4$, respectively. (VI) contains 2 *tert.*-OH groups and when treated with boiling EtOH–NaOH or with Zn dust and AcOH at 60—70° gives (V). Catalytic reduction (Pt-black) of (V) in AcOEt affords an *oxide*, $C_{15}H_{26}O$, b. p. 138—139°/12 mm. Guaiene is reduced catalytically (Adams) in *cyclo*hexane to *tetrahydroguaiene*, b. p. 126—128°/12 mm., whilst guaiol yields similarly *dihydroguaiol*, m. p. 79—80°, and a mixture of hydrogenated sesquiterpene and sesquiterpene alcohol.

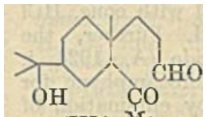
H. Burton.

Polyterpenes and polyterpenoids. LVIII. Relation between eudesmol and selinene. LXI. Proof of identity of machilol with eudesmol. L. Ruzicka, D. R. Koolhaas, and A. H. Wind (Helv. Chim. Acta, 1931, **14**, 1132—1151, 1178—1186).—LVIII. Eudesmol (*A*), m. p. 82—83°, $[\alpha]_D$ +31·3° in $CHCl_3$ (impure benzoate), is shown to consist of a mixture of α- (I) and β-eudesmol [to which formula (II) is now assigned (cf. A., 1927, 569)]. Selinenol (Semmler and Risse, A., 1913, i, 66) is (I), since dihydroselinenol and dihydroeudesmol are identical.



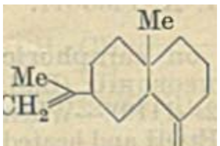
(I.) (II.)

Eudesmene and selinene dihydrochlorides of m. p. 74°, $[\alpha]_D$ +18° to +20° in $CHCl_3$ (cf. *loc. cit.*; A., 1913, i, 885), are identical; eudesmene dihydrochloride, m. p. 79—80°, is considered to be a structural isomeride. A new *selinene dihydrochloride*, m. p. 52°, $[\alpha]_D$ −70° in $CHCl_3$, is now described. The alcohol, m. p. 78—79°, $[\alpha]_D$ +38° in $CHCl_3$, obtained from this and aq. $Ca(OH)_2$ does not depress the m. p. of *A* [the variation in physical data is ascribed to the different ratios of (I) to (II) in the alcohols], and is reduced catalytically (as is *A*) to dihydroeudesmol, m. p. 85—86°, $[\alpha]_D$ +17° in $CHCl_3$. Contrary to a previous statement (A., 1927, 569), a dihydrochloride could not be obtained from the hydrocarbon prepared from eudesmol (m. p. 79—80°) and conc. H_2SO_4 in EtOH. The neutral hydrolysis products from the ozonide of *A* contain a hydroxyketoaldehyde, $C_{15}H_{26}O_3$ (probably III) (*semicarbazone*, m. p. about 145°), which is derived from (I), and 5-*keto*-9-*methyl*-3-β-*hydroxy*iso*propyldecahydronaphthalene*, m. p. 119—120°, which arises from (II), whilst the acidic products contain



(III.)

an acid (III, where CHO=CO_2H) (*Et* ester, b. p. about 167°/0·15 mm.), dehydrated by hot HCO_2H to the corresponding *iso*propylidene derivative (*Et* ester, b. p. about 125°/0·08 mm.). Ozonolysis of 3 dihydroeudesmenes obtained (*a*) from dihydroeudesmol and MgPhBr, (*b*) from dihydroeudesmyl chloride and MeOH–KOH, and (*c*) from dihydroeudesmyl chloride and NH_2Ph gives 3-*acetyl*-5 : 9-*dimethyldecahydronaphthalene* (IV), b. p. 145—147°/12 mm., $[\alpha]_D$ +5·2° (*semicarbazone*, m. p. 206—208°; *picrate* of aminoguanidine compound, m. p. 175—176°), in each case; 3-keto-5 : 9-dimethyldecahydronaphthalene (*semicarbazone*, m. p. 215—217°; *picrate* of aminoguanidine compound, m. p. 207—209°) is obtained from (*c*) (and from "dihydroselinene" prepared by method *c* from dihydroselinenyl chloride), whilst the acidic products consist of a mixture of ketomonocarboxylic and



(V.)

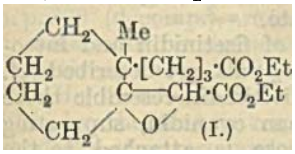
dicarboxylic acids. The results show that the dihydroeudesmenes are mixtures of isomerides. (IV) and MgMeI give dihydroeudesmol. Ozonolysis of selinene (V) gives 5-*keto*-3-*acetyl*-9-*methyldecahydronaphthalene*, b. p. 123—125°/0·2 mm. (*disemicarbazone*, m. p. 222°), the *benzylidene* derivative, m. p. 170°, of which is oxidised by successive treatment with O_3 and CrO_3 in AcOH to 5-keto-9-methyldecahydronaphthalene-3-carboxylic acid (*Me* ester, b. p. 153—155°/0·25 mm.).

LXI. Machilol (A., 1921, i, 732) is shown by ozonolysis experiments to consist mainly of β-eudesmol; machilol and eudesmol give the same derivatives.

H. Burton.

Polyterpenes and polyterpenoids. LIX. Synthesis of alkylated *trans*-decahydronaphthalenes in connexion with the stereochemistry of sesquiterpenes. LX. Spatial configuration of the decahydronaphthalene ring in sesquiterpenes. L. Ruzicka, D. R. Koolhaas, and A. H. Wind (Helv. Chim. Acta, 1931, **14**, 1151—1171, 1171—1178).—LIX. 2-Methyl*cyclo*hexanone and Et β-iodopropionate in presence of $NaNH_2$ and Et_2O give a mixture of products which, after condensation with Et oxalate in presence of Na and light petroleum, affords some *Et* 2-*methyl*-2-*carbethoxyethyl*cyclo*hexanone*-6-*carboxylate*, b. p. 153—157°/0·3 mm. Hydrolysis

of this (whereby the 6-CO_2H group is eliminated) and subsequent esterification gives *Et 2-methyl*cyclo*hexanone-2-β-propionate*, b. p. about 150°/15 mm., which with $CH_2Br{\cdot}CO_2Et$ and Zn yields *Et 2-methyl-2-carbethoxyethyl*cyclo*hexylideneacetate*, b. p. 130—132°/0·3 mm. 2-Methyl*cyclo*hexanone and γ-iodobutyronitrile in presence of $NaNH_2$ and Et_2O afford a mixture of products which after hydrolysis, esterification, condensation with Et oxalate, further hydrolysis, re-esterification, and final condensation with $CH_2Cl{\cdot}CO_2Et$ in NaOEt affords the *ester* (I), b. p. 148—150°/0·1 mm.


(I.)

Various *trans*-decahydronaphthalenes are prepared by the Clemmensen reduction of their diketo-derivatives, which are obtained usually by the method of Kon and Qudrat-i-Khuda (A., 1927, 150).

[With H. A. Boekenoogen, J. van der Kamp, and P. Nebbeling.] Liquid (*a*) and solid (*b*) Et 1 : 3-diketodecahydronaphthalene-4-carboxylates are obtained from *cyclo*hexenyl Me ketone and Et sodiomalonate (cf. *loc. cit.*). These are hydrolysed by 15% HCl to mixtures of products containing a considerable amount of a keto-acid, $C_{10}H_{16}O_3$ (*semicarbazone*, m. p. 179°). Reduction of these hydrolysis products and purification of the resultant hydrocarbons by heating with K and subsequent treatment with $KMnO_4$, gives *trans*-decahydronaphthalene (from *b*) and a mixture of *cis*- and *trans*-decahydronaphthalenes (from *a*).

[With T. Ausems, A. Baart, and H. J. Wigman.] The product from 2-methyl-Δ^1-*cyclo*hexenyl Me ketone and Et sodiomalonate is hydrolysed, the acidic products [oxidised by NaOBr to 1-methyl-1-carboxymethyl*cyclo*hexane-2-carboxylic acid (*Me_2* ester, b. p. about 140°/12 mm.)] reduced, and the resulting trans-9-*methyldecahydronaphthalene*, b. p. 70—71°/12 mm., purified as above.

[With H. J. Edelmann.] The *carbinol*, b. p. 112—113°/12 mm., from MgMeBr and *trans*-β-ketodecahydronaphthalene is dehydrated with 95% HCO_2H and the resulting product reduced catalytically (Adams) in *cyclo*hexane to trans-2-*methyldecahydronaphthalene*, b. p. 76°/12 mm.

[In part with H. Goedhart.] Et 2-methyl*cyclo*hexanone-6-carboxylate, prepared from 2-methyl*cyclo*hexanone and Et oxalate in NaOEt, is methylated by MeBr and NaOMe to *Et* 2 : 6-*dimethyl*cyclo*hexanone*-6-*carboxylate*, b. p. 112—118°/12 mm., hydrolysed by mineral acids to 2 : 6-dimethyl*cyclo*hexanone, b. p. 62°/12 mm. (*semicarbazone*, m. p. 176°). This is reduced by Na and moist Et_2O to 2 : 6-*dimethyl*cyclo*hexanol*, b. p. 172°/750 mm., 73°/16 mm., dehydrated by $KHSO_4$ at 180—190° to 1 : 3-*dimethyl*-Δ^1-cyclo*hexene* (II), b. p. 124—126°, oxidised by 3% $KMnO_4$ (=3O) to an *acid*, $C_8H_{14}O_3$, b. p. 150—155°/12 mm. Oxidation of (II) with 1% $KMnO_4$ at 0° gives a glycol (not characterised), converted by hot 20% H_2SO_4 into a stereoisomeric 2 : 6-dimethyl*cyclo*hexanone (*semicarbazone*, m. p. 196°). AcCl and (II) in presence of $SnCl_4$ and CS_2 afford (after treatment of the intermediate product with $NPhEt_2$) 2 : 6-*dimethyl*-Δ^1-cyclo*hexenyl Me ketone*, b. p. 90—95°/14 mm. (*semicarbazone*, m. p. 215°), which after condensation with Et sodiomalonate and subsequent hydrolysis gives trans-5 : 7-*diketo*-4 : 9-*dimethyldecahydronaphthalene*, m. p. 166°. This is reduced to trans-4 : 9-*dimethyldecahydronaphthalene*, b. p. 77—78°/12 mm.

[With J. H. van der Hulst.] 2-Methyl-Δ^1-*cyclo*hexenyl Pr ketone (from 1-methyl-Δ^1-*cyclo*hexene and butyryl chloride in presence of $SnCl_4$ and CS_2) is converted by the general method into trans-9-*methyl*-3-*ethyldecahydronaphthalene*, b. p. 97—98°/12 mm.

[With J. de Liver.] trans-5 : 9-*Dimethyl*-3-*ethyldecahydronaphthalene*, b. p. 112—113°/14 mm., is prepared from 2 : 6-dimethyl-Δ^1-*cyclo*hexenyl Pr ketone.

LX. Clemmensen reduction of the various ketodecahydronaphthalenes obtained from eudesmol and its derivatives (this vol., 1302) gives *cis*-decahydronaphthalenes; the *cis*- and *trans*-configurations (above) are assigned from physical data. cis-4 : 9-*Dimethyl*-, b. p. about 85°/12 mm., cis-5 : 9-*dimethyl*-3-*ethyl*-, b. p. about 115—116°/12 mm., and cis-9-*methyl*-3-*ethyl*-, b. p. about 102—103°/12 mm., -*decahydronaphthalenes* are thereby obtained from 3-keto-5 : 9-dimethyl-, 3-acetyl-5 : 9-dimethyl-, and 5-keto-3-acetyl-9-methyl-decahydronaphthalene (III), respectively. The ketones are, therefore, all *cis*-derivatives. The glycol from (III) and MgMeI is dehydrated to a *hydrocarbon*, $C_{15}H_{24}$, b. p. 128—131°/13 mm., reduced catalytically (Adams) to its *tetrahydro*-derivative ("synthetic tetrahydroselinene"), b. p. about 128—130°/12 mm., which, like tetrahydroselinene, is also a *cis*-derivative. The viscosities of the *cis*-decahydronaphthalenes are invariably higher than those of the isomeric *trans*-compounds.

H. Burton.

Sesquiterpenes. I. Sesquiterpenes and sesquiterpene alcohol from Japanese camphor oil. S. Komatsu, H. Fujimoto, and S. Tanaka.—See B., 1931, 993.

Hydroxy-carbonyl derivatives. IV. Preparation of coumarins and 1 : 4-pyrones from phenol, *p*-cresol, quinol, and α-naphthol. A. Robertson, W. Sandrock, and (in part) C. B. Hendry (J.C.S., 1931, 2426—2432; cf. this vol., 962).—The substances obtained when *o*-hydroxy- (I), 2-hydroxy-5-methyl- (II), and 2 : 5-dihydroxy-propiophenone (III) are treated with Ac_2O and NaOAc are identical with the condensation products of Et α-methylacetoacetate with phenol, *p*-cresol, and quinol, respectively; they are, therefore, 1 : 4-pyrones (cf. A., 1914, i, 424). This confirms the generalisation (this vol., 963) that ω-substituted *o*-hydroxyacetophenones yield 1 : 4-pyrones on vigorous acetylation. However, the Simonis reaction, when applied to α-naphthol (IV), gives the naphthacoumarin. *o*-Methoxybenzoyl chloride and Et sodio-α-methylacetoacetate in Et_2O, or *o*-methoxybenzonitrile and MgMeI in Et_2O, give *o*-methoxypropiophenone (*semicarbazone*, m. p. 154°), which with $AlCl_3$ in boiling C_6H_6 yields (I) (*semicarbazone*, m. p. 213°); this, when heated with Ac_2O and NaOAc at 170—180°, affords 2 : 3-dimethyl-1 : 4-benzopyrone. (II) (modified prep.) when heated with Ac_2O and NaOAc at 180—190° yields

2 : 3 : 6-trimethyl-1 : 4-benzopyrone. *p*-Cresol, Et methylacetoacetate, and cold 80% H_2SO_4 give 3 : 4 : 6-*trimethylcoumarin* (non-fluorescent), m. p. 165°. The *Ac* derivative of 6-hydroxy-3 : 4-dimethylcoumarin (modified prep.) has m. p. 159—161°. Quinol, EtCOCl, and pyridine give (III), obtained only in traces by the Nencki reaction. (III), when heated with Ac_2O and NaOAc at 170—180°, yields 6-*acetoxy*-2 : 3-*dimethyl*-1 : 4-*pyrone*, m. p. 139°, hydrolysed by KOH in cold MeOH to the corresponding hydroxypyrone, m. p. 247° after sintering at 241° (lit. 242°). 4-Methyl-α-naphthacoumarin is obtained from (IV) and Et acetoacetate with either cold 84% H_2SO_4, or P_2O_5 at 100° (cf. A., 1910, i, 405); with Et α-methylacetoacetate 3 : 4-*dimethyl*-α-*naphthacoumarin*, m. p. 203—204°, is obtained by both methods. 2-Propionyl-α-naphthol, Ac_2O, and NaOAc, when heated at 180—190° give 2 : 3-*dimethyl*-1 : 4-α-*naphthapyrone*, m. p. 143—144° (green fluorescence in conc. H_2SO_4). R. S. CAHN.

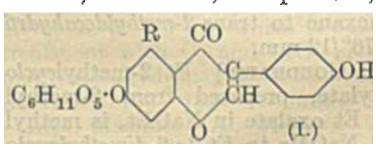
Synthesis of coumarins from phenols and β-ketonic esters using phosphorus pentoxide. II. Coumarins from polyhydric phenols and α-naphthol. D. CHAKRAVARTI (J. Indian Chem. Soc., 1931, 8, 407—411; cf. this vol., 962).—Coumarins are prepared from phenols and the requisite Et acylacetates and α-chloroacylacetates in presence of P_2O_5 or conc. H_2SO_4. The following are described: (*a*) from orcinol: 5-hydroxy-4 : 7-dimethyl- (*Ac* derivative, m. p. 195°); 3-chloro-5-hydroxy-4 : 7-dimethyl- (*Ac* derivative, m. p. 160°); 5-*hydroxy*-3 : 4 : 7-*trimethyl*-, m. p. 250° (*Ac* derivative, m. p. 135°), and 5-*hydroxy*-4 : 7-*dimethyl*-3-*ethyl*-, m. p. 206°, -*coumarins*; (*b*) from pyrogallol: 7 : 8-dihydroxy-4-methyl-; 3-chloro-7 : 8-dihydroxy-4-methyl- (*Ac* derivative, m. p. 197°); 7 : 8-*dihydroxy*-3 : 4-*dimethyl*-, m. p. 270°, and 7 : 8-*dihydroxy*-4-*methyl*-3-*ethyl*-, m. p. 218°, -*coumarins*; (*c*) from phloroglucinol: 3-chloro-5 : 7-dihydroxy-4-methylcoumarin; (*d*) from α-naphthol: 4-methyl-, 3-chloro-4-methyl-, 3 : 4-*dimethyl*-, m. p. 197—199°, 4-*methyl*-3-*propyl*-, m. p. 118°, and 4-*methyl*-3-iso*propyl*-, m. p. 165°, -1 : 2-α-*naphthapyrones*. H. BURTON.

Reduction of quercetin. T. MALKIN and M. NIERENSTEIN (Ber., 1931, 64, [*B*], 1976; cf. A., 1930, 1189).—The investigations of Asahina and Inubuse (this vol., 940) emphasise the distinction between cyanidin chloride and 3 : 5 : 7 : 3′ : 4′-pentahydroxyflavylium chloride. H. WREN.

Synthesis of pyrylium salts of anthocyanidin type. Fisetinidin and luteolinidin chlorides. R. ROBINSON and A. LEÓN (Anal. Fis. Quím., 1931, 29, 415—425; cf. A., 1925, i, 825).—2 : 4-Dihydroxybenzaldehyde yields with BzCl and aq. KOH 2-*hydroxy*-4-*benzoyloxybenzaldehyde*, m. p. 103°, converted by MeI into the 2-*OMe*-derivative, m. p. 85—86°, which yields 4-hydroxy-2-methoxybenzaldehyde on hydrolysis. 2 : 4-Dihydroxybenzaldehyde condenses with ω-3 : 4-triacetoxyacetophenone in dry EtOAc under the action of HCl to give fisetinidin chloride. Catalytic reduction of fisetinidin chloride yields an amorphous material (*Pb* compound) with the colour reactions of catechins. ω-Chloro-3 : 4-dihydroxyacetophenone is prepared by heating pyrocatechol, $CH_2Cl{\cdot}CO_2H$, and $POCl_3$ in PhMe. The Ac_2 derivative is reduced in EtOH solution by Fe and H_2SO_4, with NaI as catalyst, to 3 : 4-dihydroxyacetophenone. Condensation of 3 : 4-diacetoxyacetophenone with the Bz derivative of phloroglucinolaldehyde yields the 5-Bz derivative of luteolinidin chloride, decomp. 182°, which is hydrolysed and converted into luteolinidin chloride by way of the picrate.

The colours of solutions of fisetinidin and luteolinidin chlorides at various p_H vals. are described (cf. A., 1929, 477). Those of fisetinidin resemble those given by cyanin rather than cyanidin, supporting the assumption that glucose is attached to the 5-OH group in cyanin. R. K. CALLOW.

isoFlavone and saponin glucosides in *Soja hispida*. E. WALZ (Annalen, 1931, 489, 118—155).—The glucosides described were isolated from the soya bean after removal of the outer skin, and are found in the fraction sol. both in 90% MeOH and in $COMe_2$. *Genistin*, m. p. 254—256°, $[\alpha]_D^{11}$ −27·7° [Ac_6, m. p. 188°, and Bz_6, m. p. 132°, derivatives; Me_3 *ether* (MeI and K_2CO_3 in MeOH), m. p. 200—205° (decomp.)], is hydrolysed by HCl in aq. MeOH to dextrose and genistein (5 : 7 : 4′-trihydroxy*iso*flavone; cf. A., 1925, i, 1299; 1926, 1253), m. p. 296—298° (decomp.) [Ac_3, m. p. 200—202°, and Bz_3, m. p. 239°, derivatives; *Me*, m. p. 189—191° (5 : 7-*dihydroxy*-4′-*methoxy*iso*flavone* ?), and Me_2, m. p. 139—140°, ethers], identified by fission with boiling 30% aq. KOH to HCO_2H, *p*-hydroxyphenylacetic acid, and phloroglucinol; with 5% KOH the intermediate 2 : 4 : 6-trihydroxyphenyl *p*-hydroxybenzyl ketone can be isolated. Acid hydrolysis of genistin Me_3 ether gives a new *dimethylgenistein*, m. p. 290—293° (7-*hydroxy*-5 : 4′-*dimethoxy*iso*flavone*), which does not give a coloration with $FeCl_3$ and is therefore methylated in position 5, and is hydrolysed by boiling 30% KOH to HCO_2H and 2 : 4-*dihydroxy*-6-*methoxyphenyl* p-*methoxybenzyl ketone* (*oxime*, m. p. 178°); the last-named is stable to alkalis, but is oxidised by alkaline $KMnO_4$ to anisic acid. The glucose residue therefore occupies the 7-position in genistin (I; R=OH). *Daidzin*, m. p. 235°, $[\alpha]^{20}$ −36·4° (Ac_5, m. p. 203°, Bz_5, m. p. 145—150°, derivatives; *Me ether*, m. p. 206°), is separated from genistin by virtue of its greater solubility in aq. EtOH and hot H_2O.



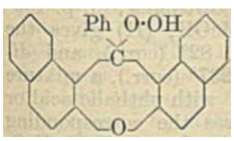
It is hydrolysed to dextrose and *daidzein*, m. p. 315—320° (Ac_2 derivative, m. p. 182°; Me_2, m. p. 154°, and *Me*, m. p. 251°, *ethers*); the latter is a dihydroxy-compound, and on fission with KOH gives HCO_2H and 2 : 4-*dihydroxyphenyl* p-*hydroxybenzyl ketone*, m. p. 192° (*oxime*, m. p. 202—203°). Similarly, methyldaidzein gives 2 : 4-*dihydroxyphenyl* p-*methoxybenzyl ketone*, m. p. 158° (*oxime*, m. p. 220°). The two ketones were identified by synthesis from *p*-hydroxy- and *p*-methoxy-phenylacetonitrile, respectively, by condensation with resorcinol and HCl in Et_2O, and hydrolysis of the iminochlorides. Daidzin is therefore represented by formula I (R=H). Three *saponin-glucosides*, *C*, m. p. 272° (*aglucone*, m. p. 235—236°),

C_1, m. p. 225° (*aglucone*, m. p. 243—245°), and C_2, m. p. 280°, are isolated from the crude genistin by extraction with H_2O; they appear to contain both glucose and pentose residues, and the first is strongly hæmolytic. They are accompanied by alkali-sol. flavone derivatives from which, by acid hydrolysis, *aglucone D*, $C_{15}H_9O_4\cdot OMe$, m. p. 310°, and *aglucone E*, m. p. 306° (decomp.), are isolated; these are converted by alkali into *substances* (probably $PhCO\cdot CH_2Ph$ derivatives), m. p. 159° and 188°, respectively, and HCO_2H; the formation of a green coloration with $FeCl_3$ by the first is regarded as indicating an *o*-dihydroxy-structure, and consequently aglucone *D* is probably a hydroxymethoxy-derivative of 8-hydroxy-*iso*flavone. H. A. PIGGOTT.

Plant colouring matters. XXXVI. Violaxanthin. P. KARRER and R. MORF (Helv. Chim. Acta, 1931, **14**, 1044—1046).—Violaxanthin (I), m. p. 207—208° (corr.) (cf. this vol., 491), and its perhydro-derivative both contain 3 and not 4 OH groups (Zerevitinov). Oxidation of (I) with alkaline $KMnO_4$ in presence of C_6H_6 gives *as*-dimethylsuccinic acid, indicating the presence of the grouping

$CH_2<\begin{matrix}CH(OH)\cdot CH\\ CMe_2—CMe\end{matrix}>C\cdot CH:$. H. BURTON.

Pyrenium salts. XIV. Oxidation of pyrenium salts. F. QUINT and W. DILTHEY (Ber., 1931, **64**, [*B*], 2082—2086).—*Phenylxanthenium perchlorate* suspended in AcOH is oxidised by H_2O_2 to 2-*o-hydroxyphenoxybenzophenone*, m. p. 104°, transformed by distillation with Zn dust into 9-phenylxanthen and a little PhOH. It is converted by KOH and Me_2SO_4 into 2-*o-methoxyphenoxybenzophenone*, m. p. 128—129°, obtained also from *o*-hydroxybenzophenone, *o*-bromoanisole, and Cu powder. Similar oxidation of phenyldibenzoxanthenium perchlorate affords the expected *H peroxide* (I), m. p. 167—168° (decomp.) (also $+ 1C_6H_6$, m. p. 167—168°; $+ 1COMe_2$, m. p. 167—168°; $+ 1C_5H_5N$, m. p. about 127°), reconverted by $HClO_4$ in AcOH into phenyldibenzoxanthenium perchlorate. H. WREN.



(I.)

Synthetical experiments in the chromone group. III. Diflavones. K. C. GULATI and K. VENKATARAMAN (J.C.S., 1931, 2376—2381; cf. this vol., 963).—Resorcinol diacetate, when heated with anhyd. $FeCl_3$ in an atm. of CO_2, gives a poor yield of 4 : 6-diacetylresorcinol (I). With $FeCl_3$ in AcOH, however, it yields *resacetophenone 2-monoacetate*, m. p. 119—120°, also obtained under certain conditions with $AlCl_3$, and transformed by $FeCl_3$ at 180° into (I); under other conditions use of $AlCl_3$ led to a *substance*, m. p. 83—84°, whilst with $ZnCl_2$ at 130° resacetophenone was obtained. (I), Bz_2O, and NaOBz at 180—185° give diflavone and 7-*hydroxy-6-acetylflavone*, m. p. 123°. Anisic anhydride and Na anisate yield similarly 4′ : 4″-*dimethoxydiflavone*, yellow, m. p. 192°, and 7-*hydroxy-4′-methoxy-6-acetylflavone*, m. p. 160—161°; the former flavone with Ac_2O and HI gives 4′ : 4″-*dihydrodiflavone*, m. p. 317° (Ac_2 derivative, m. p. 204—205°). Under similar conditions, however, trimethylgallic anhydride (modified prep.) and Na trimethylgallate give very little 3′ : 4′ : 5′ : 3″ : 4″ : 5″-*hexamethoxydiflavone*, m. p. 134—136° (decomp.), and mostly 7-*hydroxy-3′ : 4′ : 5′-trimethoxy-6-acetylflavone*, m. p. 224—225° (*Ac* derivative, m. p. 156—157°), whilst in the veratryl series only 7-*hydroxy-3′ : 4′-dimethoxy-6-acetylflavone*, m. p. 182° (*Ac* derivative, m. p. 141°), was obtained. (I), NaOAc, and boiling Ac_2O give 3 : 3′-*diacetyl-2 : 2′-dimethyldichromone*, m. p. 261—264°, and 7-*hydroxy-6-acetyl-2-methylchromone*, m. p. 134—135°. Colour reactions are described for the above substances. R. S. CAHN.

1 : 3-Benzdioxin. F. D. CHATTAWAY and H. IRVING (J.C.S., 1931, 2492—2494).—6-*Acetamido-1 : 3-benzdioxin*, prepared from the NO_2-derivative, Na, and Ac_2O at 100°, or from the NH_2-derivative, Ac_2O, and a drop of H_2SO_4, has m. p. 224° (decomp.). 1 : 3-Benzdioxin (modified prep.), m. p. 12·5°, b. p. 210—211°/754 mm., 100·5—101·5°/20 mm., with HNO_3 (*d* 1·5) and a little carbamide gives 6 : 8-*dinitro-1 : 3-benzdioxin* (I), m. p. 135—136°.

[With M. GOEPP.] (I) with CrO_3 in hot AcOH yields 6 : 8-*dinitro-4-keto-1 : 3-benzdioxin*, m. p. 196·5—197·5°, which with boiling 10% NaOH affords CH_2O and 3 : 5-dinitrosalicylic acid, thus proving the constitution of (I). R. S. CAHN.

Dichromylenes and the valency tautomerism of unsaturated systems. A. SCHÖNBERG and S. NICKEL (Ber., 1931, **64**, [*B*], 2323—2327).—In the search for analogues of dixanthylene (A., 1928, 526), it has been observed that tetraphenyl-, tetra-*p*-anisyl-, and octamethyltetra-*p*-aminotetraphenyl-ethylene are not thermochromic and do not suffer fission at the central ethylenic linking when heated with S. The action of xanthion on diphenyldiazomethane yields *oo′-oxidotetraphenylethylene sulphide*, $O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C<\begin{matrix}CPh_2\\S\end{matrix}$, m. p. indef. 185—190° when rapidly heated, transformed by Cu-bronze in boiling PhMe into *oo′-oxidotetraphenylethylene*, $O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C:CPh_2$, m. p. 195—196°, a colourless substance which is reddish-yellow when molten and yields hot, reddish-yellow solutions. 4-Thio-2-phenylchromone is converted by diazomethane in Et_2O–C_6H_6 into *di-γ-2 : 2′-diphenylchromenyl-4 : 4′-dithiolmethylene ether*, $\begin{matrix}CR\cdot S\\CR\cdot S\end{matrix}>CH_2$ (I; R= $C_6H_4<\begin{matrix}^{1}O\cdot CH^{2}\\ _{4}C\cdot CH_{3}\end{matrix}$) m. p. about 182—183° (decomp.) after softening, transformed by Li phenyl into 2 : 2′-*diphenylchromylene* (II), $\left[C_6H_4<\begin{matrix}O\cdot CPh\\C\cdot CH\end{matrix}\right]$, m. p. 224°, yellow crystals which become red when warmed or compressed and melt to a blood-red liquid which becomes yellow when cooled. α-Naphthaflavone is transformed by P_2S_5 into *α-naphtha-4-thioflavone*, m. p. 171—172°, converted by diazomethane into the *compound* (I) ($R=C_{10}H_7<\begin{matrix}^{1}O\cdot CPh\\C\cdot CH\end{matrix}$), m. p. 165°, to a reddish-brown liquid after softening at 164°. H. WREN.

Action of aliphatic diazo-compounds on pyrrole and its homologues. C. D. NENITZESCU

and E. SOLOMONICA (Ber., 1931, **64**, [*B*], 1924—1931).—The products of the action of aliphatic diazo-compounds and ketens on pyrroles appear to be invariably *C* derivatives. Pyrrole, Cu powder, and Et diazoacetate at 100° afford *Et pyrrole-2-acetate*, b. p. 129°/15 mm., hydrolysed to *pyrrole-2-acetic acid*, decomp. 83—84°, which is decarboxylated to 2-methylpyrrole. Similarly, *Et* 2 : 4-*dimethylpyrrole-5-acetate*, b. p. 134°/12 mm., yields successively non-cryst. 2 : 4-dimethylpyrrole-5-acetic acid and 2 : 4 : 5-trimethylpyrrole. 2 : 3 : 4 : 5-Tetramethylpyrrole is derived from Et diazoacetate and 2 : 4 : 5-trimethylpyrrole. Benzoylphenyldiazomethane and pyrrole at 50—60° yield 2 : 5-*bisdiphenylacetylpyrrole*, m. p. 225°. 5-*Diphenylacetyl*-2 : 4-*dimethylpyrrole*, m. p. 169°, also prepared from CPh_2:CO and 2 : 4-dimethylpyrrole, is oxidised by CrO_3 in AcOH to benzophenone; it is also obtained by the successive addition of dimethylpyrrole and diphenylacetyl chloride to MgEtBr in Et_2O. 2 : 4-Dimethylpyrrole and Et diazoacetoacetate give 5-α-*carbethoxypropionyl*-2 : 4-*dimethylpyrrole*, m. p. 109°, transformed into 5-*propionyl*-2 : 4-*dimethylpyrrole*, m. p. 134°, also prepared from 2 : 4-dimethylpyrrole, EtCOCl, and MgEtBr in Et_2O. *Et* 1-*methylpyrrole-2-acetate*, b. p. 137°/26 mm., and 1-*methylpyrrole-2-acetic acid*, m. p. 112°, are described. With a larger proportion of Et diazoacetate, 1-methylpyrrole gives 1-*methylpyrrole*-2 : 5-*diacetic acid*, decomp. above 150° (*Me* ester, m. p. 56°). H. WREN.

Pyridine derivatives. XV. Hydrogenation of [2-]pyridone and its *N*-alkyl derivatives. C. RATH (Annalen, 1931, **489**, 107—118).—2-Pyridone and its *N*-alkyl derivatives are readily hydrogenated at 180—220°/40 atm. in presence of Ni, Cu, or, best, Ni–Cu, to the corresponding tetrahydro-compounds. By interaction of *K* 2-*pyridone*, m. p. 274—276°, with the appropriate alkyl iodide 1-iso*propyl*-, b. p. 145—150°/15 mm., 1-n-*butyl*-, b. p. 148°/10 mm., and 1-n-*octyl*-, b. p. 189°/12 mm., -2-*pyridones* are obtained. The following are obtained by reduction : 2-piperidone [hydrochloride, m. p. 182—183° (lit. 155—160°); $C_5H_9ON,HgCl_2,H_2O$, m. p. 187° (decomp.)]; *N*-methyl- [*hydrochloride*, m. p. 104°; $+HgCl_2,H_2O$, m. p. 119—120°]; N-*ethyl*-, b. p. 109°/12 mm. (*hydrochloride*, m. p. 108°; $+HgCl_2,H_2O$, m. p. 113°); N-*propyl*-, b. p. 121°/14 mm. (*hydrochloride*, m. p. 112°); N-iso*propyl*-, b. p. 127—128°/15 mm. (*hydrochloride*, m. p. 118°; $+HgCl_2$, m. p. 140—141°); N-*butyl*-, b. p. 130—131°/11 mm.; N-n-*octyl*-, b. p. 172°/10 mm., and N-*benzyl*-, b. p. 193°/8 mm., -2-*piperidones*. The alkylpiperidones are hydrolysed by acids or (very readily) by alkalis to the corresponding δ-alkylaminovaleric acids, of which the following appear to be new: δ-*ethyl*-, m. p. 115°; δ-*propyl*-, m. p. 118—119°; δ-iso*propyl*-, m. p. 123—124°; δ-*butyl*-, m. p. 124°; δ-n-*octyl*-, m. p. 139—140°, and δ-*benzyl*-, m. p. 120°, -*aminovaleric acid hydrochlorides*. Hydrogenation of 2-chloro-5-nitropyridine at 150—200°/30 atm. gives the corresponding NH_2-compound only, and of 2-chloro-5-cyanopyridine gives (probably) *di*-(2-*chloro*-5-*pyridylmethyl*)*amine*, m. p. 104°. H. A. PIGGOTT.

Stereochemistry of *N*-phenylpyrroles. XIX. L. H. BOCK and R. ADAMS (J. Amer. Chem. Soc., 1931, **53**, 3519—3522; cf. this vol., 362).—Et acetonylacetoacetate (I) and *p*-aminobenzoic acid in EtOH give, after alkaline hydrolysis, N-p-*carboxyphenyl*-2 : 5-*dimethylpyrrole*-3-*carboxylic acid*, m. p. 277—280° (corr.) (*brucine H* and *strychnine H* salts). N-m-*Carboxyphenyl*-, m. p. 229—233° (corr.) (*brucine H* and *strychnine H* salts), N-o-*tolyl*-, m. p. 184·5—185·5° (corr.), and N-3-*methoxy*-o-*tolyl*-, m. p. 198—199° (corr.), -2 : 5-*dimethylpyrrole*-3-*carboxylic acids* are prepared similarly from (I) and *m*-aminobenzoic acid, *o*-toluidine, and 3-methoxy-*o*-toluidine, respectively. Anthranilic acid and Et αα′-diacetylsuccinate afford N-o-*carboxyphenyl*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylic acid*, m. p. 237—238° (*strychnine* H_2 and *cinchonine* H_2 salts). None of the above pyrroles could be resolved. Optical isomerism in *N*-phenylpyrroles probably resembles that in the Ph_2 series. H. BURTON.

Synthesis of indole derivatives. R. H. F. MANSKE (Canad. J. Res., 1931, **4**, 591—595).—Et α-acetyl-δ-phenoxyvalerate (I) treated in aq. EtOH alkaline solution with PhN_2Cl gives Et α-anilinoimino-δ-phenoxyvalerate, converted by application of the Fischer indole synthesis into *Et* 3-β-*phenoxyethylindole*-2-*carboxylate*, m. p. 135° (corr.), hydrolysed to the corresponding *acid*, m. p. 166—167° (corr.), which is decarboxylated to 3-β-*phenoxyethylindole*, m. p. 99° (corr.). Hydrolysis of (I), followed by treatment with PhN_2Cl in alkaline solution, leads to the γ-phenylhydrazone of η-phenoxy-βγ-diketohexane, m. p. 110° (corr.). *Et* 2-*carbethoxy*-7-*methoxy*-β-(3-*indolyl*)-*propionate* (from Et *cyclo*pentanone carboxylate and diazotised *o*-anisidine), m. p. 95—96° (corr.), is hydrolysed to the corresponding dibasic *acid*, m. p. 232° (loss of CO_2), decarboxylated to 7-*methoxy*-β-(3-*indolyl*)*propionic acid*, m. p. 146° (corr.). The azide of indolylpropionic acid (II) is decomposed by hot H_2O, giving *di*-β-(3-*indolylethyl*)*carbamide*, m. p. 159° (corr.). When boiled with MeOH, (II) gives the corresponding *urethane*, m. p. 82° (corr.), and *di-indolylpropionhydrazide*, m. p. 237° (corr.), a mixture of which (crude) heated at 230° with phthalic acid or anhydride (A., 1929, 698) gives the corresponding phthalimide, converted into the free base by N_2H_4,H_2O. By heating the monophenylhydrazone of 1 : 2-diketo*cyclo*pentane with EtOH and HCl, 2-*ketodihydropentindole*, m. p. 248—249° (corr.), is formed. J. D. A. JOHNSON.

Hydroxyquinoline derivatives obtained by the action of sodium hydrogen sulphite. J. M. KOGAN (Ber., 1931, **64**, [*B*], 2150—2156; cf. A., 1930, 1445).—6-Hydroxyquinoline is coupled with diazotised sulphanilic acid to Na 6-hydroxyquinolinebenzeneazo-*p*-sulphonate, which, with $NaHSO_3$ at $\not>$60—70°, affords the *substance* $C_{15}H_{10}O_4N_3SNa,NaHSO_3$, readily decomposed by NaOH, Na_2CO_3, or $NaHCO_3$. Treatment of 6-hydroxyquinoline hydrochloride with $NaNO_2$ yields 5-nitroso-6-hydroxyquinoline, which with $NaHSO_3$ gives the *compound* $C_9H_6O_2N_2,NaHSO_3$, transformed by aq. H_2SO_4 into 5-*amino*-6-*hydroxyquinoline*-8-*sulphonic acid*; the last-named substance is converted by conc. HCl into the *product* $C_9H_8O_4N_2S,HCl$. H. WREN.

Quinoline derivatives. XXVII. Derivatives of 2-phenyl-3-methylquinoline-4-carboxylic acid.

XXVIII. **4-Amino- and 4-chloro-2-phenyl-3-methylquinoline. XXIX. 4-Amino-2-*p*-tolylquinoline and 4-amino-2-phenylquinoline-4-carboxylic acid. XXX. Derivatives of 2-phenylquinoline-3-carboxylic acid.** H. JOHN [with H. OTTAWA] (J. pr. Chem., 1931, [ii], **131**, 301—308, 309—313, 314—322, 323—330).—XXVII. 2-Phenyl-3-methylquinoline-4-carboxylic acid (this vol., 1167) is converted through its acid chloride into *Me*, m. p. 76°; *Et*, m. p. 51°; β-*chloroethyl*, m. p. 81°; Pr^{a} (*picrate*, m. p. 163°); and β-*diethylaminoethyl* (*picrate*, m. p. 185°), esters: *diethylamide*, m. p. 127° (*hydrochloride*; *sulphate*; *nitrate*; *picrate*); *hydrazide*, m. p. 141° (*hydrochloride*; *sulphate*; *nitrate*; *picrate*, m. p. 215°), converted into iso*propylidene*, m. p. 151°, and p-*amino-α-methylbenzylidene*, m. p. 241°, derivatives, and by HNO_2 into the *azide*. This with boiling H_2O affords s-*bis*-(2-*phenyl*-4-*quinolyl*-3-*methyl*)*carbamide*, m. p. 279° (*hydrochloride*, m. p. above 300°; *picrate*).

XXVIII. NH_3 converts the above acid chloride into the *amide*, m. p. 286° (*hydrochloride*; *sulphate*; *nitrate*; *picrate*), which, with KOBr, yields 4-*amino*-2-*phenyl*-3-*methylquinoline*, m. p. 118° (*Ac* derivative, m. p. 162°; *hydrochloride*, m. p. above 300°; *sulphate*; *nitrate*; *chloroplatinate*), converted by HCl and KNO_2 into 4-*chloro*-, m. p. 97° [*hydrochloride*, m. p. 280° (decomp.); *sulphate*; *nitrate*; *picrate*], together with a little 4-*hydroxy*-, m. p. 267°, -2-*phenyl*-3-*methylquinoline*.

XXIX. Similarly, 2-p-tolylquinoline-4-carboxylic acid gives the acid chloride (*hydrochloride*, m. p. 188°), *Et*, m. p. 54°; β-*chloroethyl*, m. p. 79°; and Pr^{a}, m. p. 32°, esters; *amide*, m. p. 208° (*hydrochloride*; *sulphate*; *nitrate*, *picrate*), and *hydrazide*, m. p. 232—233° (*hydrochloride*; *sulphate*, *nitrate*; and *picrate*, m. p. above 300°), converted by $CH_2Ac\cdot CO_2Et$ into (2-p-*tolyl*-4-*quinolyl*)-3-*methyl*-5-*pyrazolone*, m. p. 305°, and by HNO_2 into the *azide*, decomp. 180°. The last-named is converted by heating in dry C_6H_6 into 2-p-*tolyl*-4-*quinolylcarbimide*, m. p. 206° (decomp.) (hydrolysed by KOH in EtOH to 4-amino-2-*p*-tolylquinoline), by boiling H_2O into s-*bis*-(2-p-*tolyl*-4-*quinolyl*)*carbamide*, m. p. 163° (*hydrochloride*; *sulphate*; *nitrate*; *picrate*), and by hot EtOH into 2-p-*tolyl*-4-*quinolylurethane*, m. p. 98°, hydrolysed by hot HCl (*d* 1·19) to 4-*amino*-2-p-*tolylquinoline*, m. p. 159° (*Ac* derivative, m. p. 195—196°; *hydrochloride*; *sulphate*; *nitrate*; *picrate*, m. p. 255°). Oxidation of 4-amino-2-*p*-tolylquinoline with MnO_2 or CrO_3 and H_2SO_4 affords p-(4-*amino*-2-*quinolyl*)*benzoic acid*, m. p. above 300° (many *salts*).

XXX. By similar methods the acid chloride [*hydrochloride*, m. p. 220° (decomp.)] of 2-phenylquinoline-3-carboxylic acid is converted into its β-*chloroethyl*, m. p. 55°, $CEtMe_2$, m. p. 210°, β-*diethylaminoethyl* (*hydrochloride*, m. p. 102—103°), and CH_2Ph, m. p. 137°, esters; *amide*, m. p. 216° (*hydrochloride*; *sulphate*; *nitrate*; *picrate*); *ethylamide*, m. p. 185° (*hydrochloride*; *sulphate*; *nitrate*; *picrate*); *diethylamide*, m. p. 114° (*hydrochloride*; *sulphate*; *nitrate*; *picrate*); iso*amylamide*, m. p. 86° (*hydrochloride*; *sulphate*; *nitrate*; *picrate*); β-*hydroxyethylamide*, m. p. 150° (*hydrochloride*; *sulphate*; *nitrate*; *picrate*); and β-*benzyloxyethylamide*, m. p. 107°; *urethane*, m. p. 135° (*hydrochloride*; *sulphate*; *nitrate*; *picrate*); 2-*phenyl*-3-*quinolyl*-, m. p. 86° (*hydrochloride*; *sulphate*; *nitrate*; *picrate*), and s-*bis*-(2-*phenyl*-3-*quinolyl*)-, m. p. 236° (*hydrochloride*; *sulphate*; *nitrate*; *picrate*), -*carbamide*; and NN′-(2-*phenyl*-3-*quinolyl*)*ethylenediamine*, m. p. 300° (*hydrochloride*; *sulphate*; *nitrate*; *picrate*).

J. W. BAKER.

Quinoline derivatives. XXXI. 3-Amino-2-phenylquinoline. XXXII. 3-Halogeno-2-phenylquinolines. H. JOHN (J. pr. Chem., 1931, [ii], **131**, 346—353, 354—356).—XXXI [with H. OTTAWA]. 2-*Phenylquinoline*-3-*carboxyhydrazide*, m. p. 212°, prepared either from the corresponding Me ester or acid chloride, condenses with $CH_2Ac\cdot CO_2Et$ with formation of 1-(2′-*phenyl*-3′-*quinolyl*)-3-*methyl*-5-*pyrazolone*, m. p. 237°, and is converted by HNO_2 into 2-*phenylquinoline*-3-*carboxyazide*. The azide is decomposed in boiling C_6H_6 to 3-*carbimido*-2-*phenylquinoline*, m. p. 262° (decomp.), and on hydrolysis, and alcoholysis, respectively, gives s-*di*-(2-*phenyl*-3-*quinolyl*)*carbamide*, m. p. 268°, and 2-*phenyl*-3-*quinolylurethane*, m. p. 115°. 3-Amino-2-phenylquinoline [*methiodide*, m. p. 238°; *ethiodide*, m. p. 212°; *Ac*, m. p. 124°, and Ac_2, m. p. 173° (cf. A., 1923, i, 481), derivatives] is obtained by hydrolysis of the urethane with conc. aq. HCl, or of the carbimide with 30% KOH in EtOH, or by the action of NaOBr on the carboxylamide.

XXXII. 3-Amino- is converted into 3-hydroxy- (63%) and 3-*chloro*-, m. p. 92°, (37%) -2-phenylquinoline by diazotisation in conc. HCl at −14° to −10°, and subsequent heating. 3-*Bromo*-2-*phenylquinoline*, m. p. 86°, is prepared by the Gattermann reaction. Numerous salts are described.

H. A. PIGGOTT.

Syntheses in the carbazole series. Alleged synthesis of 3-nitro-*N*-ethylcarbazole. F. R. STORRIE and S. H. TUCKER (J.C.S., 1931, 2255—2263).—Reduction of 2 : 4-dinitro-*N*-ethyldiphenylamine (I) by $(NH_4)_2S$ or Na trisulphide gives 2-nitro-4-amino-*N*-ethyldiphenylamine (II) [*hydrochloride*, m. p. 183—185° (decomp.)], and not the 4-nitro-2-amino-compound (cf. A., 1904, i, 270). Hence the substance, m. p. 108°, obtained from this amine (*loc. cit.*), is not 3-nitro-*N*-ethylcarbazole (cf. J.C.S., 1923, **123**, 2143). The constitution of (II) is proved by conversion into 4-*chloro*-2-*nitro*-N-*ethyldiphenylamine* (III), which has been synthesised by independent methods. Other reduction products of (I) are described. Reduction affects the 4-NO_2-group also of the *N*-Me homologue. The anomalous behaviour of these substances is possibly due to the tert. nature of the N atom. Syntheses of *N*-methyl- and *N*-ethylcarbazole are recorded.

(I) and Na_2S in aq. EtOH give 2-*nitro*-4-*azoxy*-N-*ethyldiphenylamine* (?), m. p. 152—153°, or *aminoazo*-N-*ethyldiphenylamine* (?), m. p. 194°, according to the experimental conditions. The constitution of the former product is rendered probable by its formation from (I), benzoin, and NaOEt in hot EtOH, but Nisbet's formulation (A., 1927, 1063) of this reaction is criticised. The diazonium sulphate of (II) with Cu-bronze gives no identifiable substance, but the diazonium chloride with Cu-bronze or CuCl gives (III),

red, m. p. 81—82°, also obtained (i) from 1 : 4-dichloro-2-nitrobenzene, NHPhEt, and K_2CO_3 at 205—215°, and (ii) by adding Et_2SO_4 to 4-chloro-2-nitrodiphenylamine, and KOH in boiling $COMe_2$. 2-Nitro-4-amino-*N*-methyldiphenylamine [*hydrochloride*, m. p. 177—178° (decomp.)] and 4-*chloro-2-nitro-N-methyldiphenylamine*, orange-red, m. p. 71—72°, were prepared in the same way as the *N*-Et homologues. *o*-Nitrodiphenylamine, KOH, and Me_2SO_4 in $COMe_2$ yield *o-nitro-N-methyldiphenylamine*, b. p. 205°/15 mm. (and under certain conditions a yellow *substance*, m. p. 172°), which with Sn and HCl in EtOH gives *o-amino-N-methyldiphenylamine*, b. p. 182—184°/15 mm. (*Ac* derivative, m. p. 87—89°; long heating with Ac_2O gives a *substance*, m. p. 118°); this, when diazotised and subsequently heated with aq. NaOH, affords *N*-methylcarbazole. *N*-Ethylcarbazole was similarly prepared from the corresponding *N*-Et compounds. Nitro - 4 - carboxy - 4′ - methyldiphenylamine, when heated with aq. KOH, gives *p*-toluidine and 3-nitro-4-hydroxybenzoic acid. R. S. Cahn.

Phenanthridine series. I. Synthesis of phenanthridine homologues and derivatives. G. T. Morgan and L. P. Walls (J.C.S., 1931, 2447—2456).—Dehydration of acyl-*o*-xenylamines by $POCl_3$ affords smoothly alkyl-, chloroalkyl-, phenyl-, and nitrophenyl-phenanthridines, but fails with formyl-*o*-xenylamine. The nitrophenylphenanthridines are sol. in fairly conc. acids. The corresponding NH_2-compounds (which are diazotisable) give no colour in conc. or dil. AcOH; the *o*- and *p*-, but not the *m*-, compounds give orange-red solutions in dil. mineral acids, owing to tautomerisation to an imino-quinonoid structure; addition of more acid destroys the colour, addition of a proton to the :NH group suppressing the tautomerisation. Acetyl-*o*-xenylamine (2-acetamidodiphenyl), m. p. 120° [prepared from *o*-xenylamine (I) and warm Ac_2O (cf. A., 1927, 236)], when gently boiled with $POCl_3$ for 1 hr., affords 9-methylphenanthridine in 70% yield. Propionyl-*o*-xenylamine gives similarly 9-ethylphenanthridine. (I) and $CH_2Cl\cdot COCl$ in Et_2O give *chloroacetyl-o-xenylamine*, m. p. 98·5°, which with $POCl_3$ yields 9-ω-*chloromethylphenanthridine*, m. p. 134°. Benzoyl-*o*-xenylamine (prepared by the Schotten–Baumann method) gives 9-phenylphenanthridine. (I) with *o*-, *m*-, and *p*-nitrobenzoyl chloride and pyridine at 100° gives o-, m-, and p-*nitrobenzoyl-o-xenylamine*, m. p. 129—131°, 134°, and 158·5°, respectively, which, when boiled with $POCl_3$ for 2—3 hr., afford 9-o-, -m-, and -p-*nitrophenylphenanthridine*, m. p. 122·5°, 172°, and 192°, respectively. These, when reduced with Fe filings in acidified dil. EtOH, give 9-o-, -m-, and -p-*aminophenylphenanthridine*, yellow, m. p. 168·5°, 159—161°, and 197—199° [*Ac* derivatives, ($+0\cdot5C_6H_6$) m. p. anhyd. 185°, 237·5°, (+ ?EtOH) m. p. anhyd. 219°], respectively. The NHAc-derivatives, when treated with Me_2SO_4 in hot $PhNO_2$, give the *methosulphates*, o-, m. p. about 225° (decomp.) after sintering and decomp., m-, m. p. about 209° (decomp.) after becoming yellow at 170°, and p-, $+PhNO_2$, which is lost on recrystallisation from EtOH, decomp. anhyd. 228° after darkening at 170°, respectively; when these are boiled for 1 hr. with 5*N*-HCl and the p_H is subsequently brought to 5 by addition of aq. NH_3, 9-o-, -m-, and -p-*aminophenyl* 10-*methylpyridinium chloride*, m. p. 226° (decomp.) after decomp. from 170°, 222° (decomp.) after decomp. from 160°, and 247° (decomp.) after sintering, respectively, are obtained. R. S. Cahn.

E. Fischer's tetramethylureidine. H. Biltz and P. Nachtwey (Ber., 1931, 64, [*B*], 1974—1976).—Unsuccessful attempts were made to repeat Fischer's prep. of tetramethylureidine from tetramethyluric acid (cf. Gatewood, A., 1925, i, 1189). It is concluded that the compound does not exist and that Fischer's product was somewhat impure dimethylhydantoylmethylamide. H. Wren.

Reactions of some barbituric acid derivatives. J. Bougault and J. Guillon (Compt. rend., 1931, **193**, 463—466).—The action of I and Br on unsaturated derivatives of barbituric acid in aq. $NaHCO_3$ is described. The former causes the addition of HOI followed by elimination of H_2O, giving iodinated lactones. Using Br, allyl derivatives behave similarly, but with other substituted barbituric acids compounds analogous to chloroamides are obtained. E. H. Sharples.

Changes in ultra-violet absorption spectrum of uracil and related compounds under the influence of radiations. F. F. Heyroth and J. R. Loofbourow (J. Amer. Chem. Soc., 1931, **53**, 3441—3453).—Ultra-violet absorption spectra are given for uracil, adenine sulphate, thymus nucleic acid, and 2 : 5-dichloro-4-methylpyrimidine in H_2O. The spectra of these compounds during ultra-violet irradiation show that first of all increased absorption occurs in the low regions adjacent to the absorption band, and then selective absorption gradually disappears. The first change indicates an alteration in constitution (which may be due to some type of intramolecular rearrangement producing an unstable ring), whilst the latter shows that the compounds are either decomposed or polymerised. H. Burton.

Methylcaffeidine. H. Biltz and H. Rakett (Ber., 1931, 64, [*B*], 1970—1974).—Methylation of caffeidine with Me_2SO_4 occurs slowly and incompletely (cf. A., 1928, 906), whereas the compound is readily transformed by MeI into methylcaffeidine, m. p. 98—99°, and *caffeidide hydriodide*, m. p. 247—249° (decomp.); methylcaffeidine perchlorate, m. p. 173°, *chloroaurate*, and the complex *salt*, $[Ag(C_8H_{14}ON_4)]NO_3$, are described. *Caffeidine chloroplatinate*, *chloroaurate*, *fluoborate*, m. p. 219° (decomp.), and *thiocyanate*, m. p. 197° [passing at 160—170° into 2-thiotheobromine, m. p. 298° (decomp.)], have been prepared. The constitution $\begin{array}{l}C(CO\cdot NHMe)\cdot NMe\\ \| \\ C(NMe_2)\text{———————}N\end{array}\!\!>CH$ is assigned to methylcaffeidine, since with MeI it affords the *hydriodide*, $C_9H_{18}O_2N_4,HI$, m. p. 153° (decomp.). Caffeidine is transformed by methyl- or ethyl-carbamide into theobromine, by *s*-dimethylcarbamide into caffeine, and by *s*-diethylcarbamide into 1-ethyltheobromine. H. Wren.

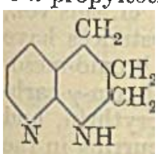
Colour of complex diazoles. III. G. C. Chakravarti (Proc. XV Indian Sci. Cong., 1928, 158).—Since all known coloured condensed pyrrole- and

pyridine-glyoxaline derivatives may be represented as containing a double quinonoid pyrrole or pyridine nucleus, this structure is regarded as the chromophore.
CHEMICAL ABSTRACTS.

Thio-orotic acid. M. BACHSTEZ (Gazzetta, 1931, **61**, 520—527; cf. A., 1930, 781).—Condensation of thiocarbamide with Et oxalacetate gives an unstable *ester* which on rapid saponification yields thio-orotic acid [blackens without melting at 322° (corr.); decomp. 339° (corr.)] (*Na*, *K*, NH_4, *Ag*, Ag_2, Ag_3, and *Pb* salts). Thio-orotic acid in MeOH with gaseous HCl gives the *O-Me* derivative, m. p. 261° (corr., decomp.). MeI and the Ag salt give instead of the *N*-Me derivative of thio-orotic acid the *O*-Me derivative of orotic acid. The S atom is not attacked by chloroacetic acid or by HCl. E. E. J. MARLER.

Synthesis of a pyridazine derivative. R. E. MEYER (Helv. Chim. Acta, 1931, **14**, 1187—1189).—Et *s*-di(benzeneazo)acetonedicarboxylate, m. p. 125°, prepared from Et acetonedicarboxylate and an excess of benzenediazonium chloride, when heated with EtOH passes (by loss of EtOH from the hydrazone form) into *Et 5-benzeneazo-4 : 6-diketo-1-phenyl-1 : 4 : 5 : 6-tetrahydropyridazine-3-carboxylate*, m. p. 164—165° (free *acid*, m. p. 260°). H. BURTON.

Decahydro-1 : 8-naphthyridine and other naphthyridine derivatives. G. KOLLER and E. KANDLER (Monatsh., 1931, **58**, 213—237).—Reduction of 2 : 4-dichloro-1 : 8-naphthyridine with an excess of Na and abs. EtOH gives a poor yield of decahydro-1 : 8-naphthyridine (I), m. p. 119—121°, subliming from 68°/16 mm. (*NO*- and *Bz* derivatives, oils; mixed products obtained by treatment with MeI, oils), together with a substance, probably a partly reduced hydroxy- or methoxy-naphthyridine, which on repeated reduction yields more (I). The structure assigned to (I), in preference to that of 2-amino-3-*n*-propyltetrahydropyridine, is proved because the base cannot be reduced, and because dehydrogenation by Pd affords a base, $C_8H_{10}N_2$, containing a sec. and a tert. N atom, which must be (II). Methylation of (I) gives two methiodides, both of which on degradation yield $NHMe_2$ and a base $C_{10}H_{17}N$; this last base yields NMe_3 on degradation by Emde's method, and must, therefore, be



(II.)

CHMe:C(:CH₂)·CH:CH·CH₂·NMe₂ (III),
CH₂:CH·CH:C(CH₂·NMe₂)·CH:CHMe (IV), or
CH₂:CH·CH:C(CH₂·NMe₂)·CH₂·CH:CH₂ (V);

alternative structures containing the grouping C:CH·NMe₂ are impossible, because of the stability of the base to acids. On catalytic reduction this base absorbs 3 mols. of H_2, and the saturated base thus obtained is shown by synthesis to be β-n-*propyl*-n-*amylamine* (VI). The unsaturated base must, therefore, be (IV) or (V). Methylation of (I), even in the cold, leads to the liberation of NMe_3 and $NHMe_2$; possible mechanisms for this degradation are discussed and considered to favour formula (V) rather than (IV).

(I) and finely-divided Pd at 220° give NH_3 (isolated as *m*-nitrobenzamide), *tetrahydro*-1 : 8-*naphthyridine* (II), m. p. 68—70°, b. p. 140—145°/12 mm. (*picrate*, m. p. 231°; *NO*-derivative, m. p. 79—81°), a little oil, b. p. approx. 80°/12 mm., and an oily residue. (I) gives a *chloroaurate*, m. p. 135°, passing in warm HCl into the monoacidic *salt*, m. p. 166—167°. (I) with MeI and K_2CO_3 in MeOH at room temp. give the *dimethiodide*, m. p. 218°, of a methylated compound derived from (I) by ring fission, and a syrupy *dimethiodide* (?); these salts, singly or mixed, when treated in H_2O with Ag_2O and distilled, yield the *base* (V) [or (IV)], b. p. 82—83°/11 mm. (*picrate*, an oil) (which reduces $AuCl_3$ and resinifies on keeping), together with NMe_3 [chloroaurate, m. p. 257° (decomp.), not as hitherto] and $NHMe_2$. The amorphous *methiodide* of this base, on treatment in H_2O with Ag_2O or Na–Hg, affords NMe_3 and an unsaturated hydrocarbon (resembling acraldehyde in odour), which yields no cryst. derivatives. (V) [or (IV)] in AcOH in presence of PtO_2 absorbs 3 mols. of H_2 to give (VI), b. p. 77—80°/27 mm. (*chloroaurate*, m. p. 158—160°; *methiodide*, decomp. 212°). β-Methyl-*n*-amyl alcohol (prepared by reduction and hydrolysis of Et methyl-*n*-propylacetoacetate with Na and EtOH) with red P and I, first cold and then at 100°, affords the *iodide*, b. p. 53—55°/12 mm., which with Et sodioacetoacetate gives *Et* α-*acetyl*-γ-*methyl*-n-*heptoate*, b. p. 120—124°/12 mm. On reducing and hydrolysing this with Na and abs. EtOH, δ-*methyl*-n-*heptanol*, b. p. 188—193°, and a lower-boiling fraction (possibly hydrocarbons) are obtained. The heptanol with red P and I gives the *iodide*, b. p. 92—95°/13 mm., which with $NHMe_2$ in EtOH at 130—135° forms *dimethyl*-δ-*methyl*-n-*heptylamine*, b. p. 75°/29 mm. [*chloroaurate*, m. p. 47—49°; *methiodide*, m. p. 185° (decomp.), depressed by the methiodide of (VI)]. $Pr^{\alpha}Br$ (prepared by distilling $Pr^{\alpha}OH$ with H_2SO_4 and KBr), b. p. 71°, condenses with Et_2 disodiomalonate to give Et_2 di-*n*-propylmalonate, b. p. 248—249°, which on hydrolysis and loss of CO_2 gives α-*n*-propyl-*n*-valeric acid, b. p. 218°, the Et_2 ester of which, when reduced with Na and abs. EtOH at 100°, affords β-n-*propyl*-n-*amyl alcohol*, b. p. 179°, having an odour of peppermint. This alcohol with red P and I gives the corresponding *iodide*, b. p. 90°/14 mm., which with $NHMe_2$ in abs. EtOH at 130° yields (VI) [*chloroaurate*, m. p. 160—161°; *methiodide*, decomp. 215°; neither m. p. is depressed by admixture with the derivatives of (VI) obtained from the base (V)].

When the *methiodide*, m. p. 212°, of 2 : 4-dimethoxy-1 : 8-naphthyridine is treated with aq. KOH and $K_3Fe(CN)_6$, 2 : 4-*dimethoxy*-8-*methyl*-1 : 8-*naphthyridone*, m. p. 137—138°, distilling at 12 mm., is obtained.
R. S. CAHN.

Formation of semiquinones as intermediary reduction products from pyocyanine and some other dyes. L. MICHAELIS (J. Biol. Chem., 1931, **92**, 211—232).—The titration of pyocyanine (this vol., 684) has been applied to α-hydroxyphenazine and rosinduline. In acid solution (below p_H 4 and 2, respectively) reduction of these dyes proceeds in two separate stages, in each of which one H atom is added. The colour changes are red–green–yellow for α-hydroxyphenazine, and red–violet–yellow for rosinduline, the intermediate colour corresponding with the formation of semiquinones. The latter are not mol. compounds of the oxidised and reduced states,

but true reduction products, resembling free radicals in constitution. A. COHEN.

Basic components of the secretion of the skin of the toad. H. WIELAND, G. HESSE, and H. MITTASCH (Ber., 1931, **64**, [*B*], 2099—2103).—The secretion of *Bufo vulgaris* is freed from neutral and acidic substances, after which extraction of the faintly alkaline solution with Et_2O yields a non-cryst. base isolated as yellow and red *picrates*, m. p. 178°. At about 140° the red passes into the yellow form. In solution the picrates have their individual colours, so that they are not dimorphous, but the colours gradually become identical, showing that an equilibrium has been attained. Analyses of the picrate and *methiodide*, m. p. 209°, indicate the formula $C_{14}H_{18}O_2N_2$ for *bufotenin*. The quaternary NH_4 base, prepared by $Tl(OH)_2$ instead of Ag_2O on account of its strong reducing properties, evolves NMe_3 when heated, leaving an acidic residue; its picrate is identical with the salt of a base isolated by Mittasch from Chinese *Senso*, and now named *bufotenidine*. The latter substance is isolated from this source as the flavianate, decomp. 200°, and is also present in the aq. extracts from *Bufo vulgaris* from which bufotenin has been removed; it gives a *picrate*, m. p. 198°. Bufotenin contains 2 Me groups attached to a tert. N atom. The analogy of bufotenin with hypaphorin (J.C.S., 1911, **99**, 2068) leads to the conclusion that the constitutions $NMe{<}{\substack{C_6H_4\\CH}}{\gg}C{\cdot}CH_2{\cdot}CH(NMe_2){\cdot}CO_2H$ and $NMe{<}{\substack{C_6H_4\\CH}}{\gg}C{\cdot}CH_2{\cdot}CH{<}{\substack{CO\\NMe_3}}{>}O$ are possessed by bufotenin and bufotenidine, respectively. In the red picrate, the acid is attached to the indole-N, whereas in the yellow compound it is united to the tert.-N of the NH_2-acid. H. WREN.

Complex salts of 1 : 2 : 4-triazole. M. BAJ and I. DE PAOLINI (Gazzetta, 1931, **61**, 557—560).—The following complex salts of the type $[M(C_2H_2ArN_3)_2(H_2O)_2]SO_4$ are described: the *Cu*, *Ni*, and *Co* salts of 1-phenyl-1 : 2 : 4-triazole, the *Cu* salt of 1-tolyl-1 : 2 : 4-triazole, and the Cu salt of 1 : 2 : 4-triazole. E. E. J. MARLER.

Condensation of unsaturated compounds with diazomethane. III. R. ROTTER and E. SCHAUDY (Monatsh., 1931, **58**, 245—248; cf. A., 1927, 247).—Carbodi-α-naphthylimide (modified prep.) with diazomethane in Et_2O at 0° during 5—6 days forms 1-α-*naphthyl*-ɔ-α-*naphthylaminotriazole*, m. p. 184°; carbodi-β-naphthylimide, m. p. 144°, and not 145—146° (A., 1886, 1035), with diazomethane in dioxan and C_6H_6 gave, after a few hr., 1-β-*naphthyl*-ɔ-β-*naphthylaminotriazole*, m. p. 199°. R. S. CAHN.

3-Quinolyl methyl ketone. G. KOLLER and H. RUPPERSBERG (Monatsh., 1931, **58**, 238—244).—The constitution previously assigned to 3-acetylquinoline (I) (A., 1929, 937) is correct, because this substance yields an *oximino*-derivative, decomp. 172°, and with *o*-aminobenzaldehyde and KOH in abs. EtOH forms 2 : 3-diquinolyl. When (I) is heated with PhCHO and $ZnCl_2$ in a vac. at 130—140° for 2 hr., it yields 3-*quinolyl styryl ketone*, red, m. p. 123°, which is oxidised by $KMnO_4$ to BzOH and quinoline-3-carboxylic acid. The colourless compound, previously (*loc. cit.*) given this structure, must have another constitution. When treated with MgMeI, (I) yields 3-*quinolyldimethylcarbinol*, m. p. 120—121·5° (*picrate*, m. p. 191°), which can be distilled at 12 mm., and is stable to $KMnO_4$ in $COMe_2$. The *phenylhydrazone*, m. p. 167° (decomp.), of Et 3-acetylquinoline-2-carboxylate, when heated at 180—200° in CO_2, loses EtOH to form 4-*keto*-3-*phenyl*-1-*methyl*-3 : 4-*dihydro*-2 : 3 : 5-*naphthtriazine*, yellow, m. p. 244°. The compound $C_{18}H_{17}O_6N$, obtained from Et_2 acetonedioxalate and *o*-aminobenzaldehyde (*loc. cit.*), must be *Et* γ-(2-*carbethoxy*-3-*quinolyl*)-αγ-*diketobutyrate*, since on hydrolysis with KOH it yields 3-acetylquinoline-2-carboxylic acid, which passes into (I) by loss of CO_2 when sublimed in vac. R. S. CAHN.

Chlorophyll series. VII. Structure from measurements of absorption spectra. J. B. CONANT and S. E. KAMERLING (J. Amer. Chem. Soc., 1931, **53**, 3522—3529).—Absorption spectra of 7 porphyrins, 14 chlorophyll derivatives, and 9 coloured compounds have been determined at the temp. of liquid air by the method previously described (A., 1930, 1341); microphotometric curves of several of the spectra are given. The characteristic phenomenon of a series of narrow sharp bands shown by the porphyrins is not found for the other substances. The chlorins occupy an intermediate position between the porphyrins and coloured substances, being analogous to *cyclo*hexadiene in comparison with C_6H_6 and butadiene; this is considered to support the chlorin formula previously proposed (this vol., 1075). The changes in the spectra of the porphyrins associated with changes in substituents are discussed. H. BURTON.

Constitution and spectra of the porphyrins. II. Spectral properties of porphyrins with substituents in the porphin ring. H. HELLSTROM (Z. physikal. Chem., 1931, **B**, **14**, 9—17; cf. this vol., 784).—The spectra of the following substances have been examined: tetrachloro- and bromo-mesoporphyrin, phylloporphyrin, rhodoporphyrin-γ-carboxylic acid, chloroporphyrin e_6, phylloerythrin, and phæoporphyrin a_5. The ring closure occurring in the last two compounds causes a considerable change in the frequency interval and intensity of the bands. The CO_2H group produces a small shift towards the violet. J. W. SMITH.

Atmospheric dealkylation of aqueous solutions of cresol-blue. W. C. HOLMES and A. R. PETERSON (Stain Tech., 1931, **6**, 79—82).—In slightly alkaline solutions (*e.g.*, at p_H 7·68) some dealkylation occurs at room temp. in a few weeks. At p_H 9 the change is detectable after 1 day. H. W. DUDLEY.

Action of hydroxylamine on mustard oils; formation of dianilino-1 : 2 : 5-oxadiazole. P. C. GUHA and M. N. CHAKLADAR (Proc. XV Indian Sci. Cong., 1928, 157).—Unstable hydroxythiocarbamide derivatives, NHR·CS·NH·OH are decomposed even at room temp., affording 1 : 2 : 5-oxadiazoles with separation of S and H_2O. CHEMICAL ABSTRACTS.

Compounds resembling peptides. XXXIII. Dehydration of amino-acids and a transition to

the pyrrole series. M. BERGMANN, L. ZERVAS, and F. LEBRECHT (Ber., 1931, **64**, [*B*], 2315—2322).—Chloroacetylphenylalanine is converted by pyridine at 100° into the *hydrochloride* of the *betaine*

(I) $NH<^{CH(CH_2Ph)\cdot CO\cdot O}_{CO\text{———}CH_2\cdot NC_5H_5}$, m. p. 205—206° (corr.), transformed by Ac_2O at 80° into the *pyrrole* derivative (II), $NR<^{CH(CH_2Ph)\cdot C\cdot O}_{CO\text{———}C\cdot NC_5H_5}$ (R=Ac), m. p. 159—160° (corr.), from which the Ac group is removed by *N*-NaOH, yielding the *compound*, (II; R=H), m. p. 183—183·5° (corr.) after softening at 177° (*hydrochloride*). Treatment of the hydrochloride of the betaine (I) or of chloroacetylphenylalanine with Ac_2O and pyridine at room temp. yields the azlactone of α-acetamidocinnamic acid, m. p. 152—153°. Chloroacetyl-*l*-tyrosine under similar conditions gives the azlactone of *p*-hydroxyacetyl-α-acetamidocinnamic acid, m. p. 137° (corr.). Chloroacetylglycine is converted by Ac_2O and pyridine into the *pyrrole* derivative $NR<^{CH_2\cdot C\cdot O}_{CO-C\ NC\ H}$ (III) (R=Ac), m. p. 239—240° (corr.), which yields pyridine when heated at 300°; it is transformed by conc. HCl at 100° into the free *base* (III) (R=H), m. p. 200—201° (corr., slight decomp.) [*hydrochloride*, m. p. 243—244° (corr.)]. With pyridine at 100° chloroacetylglycine gives the *betaine*, $^{CH_2-CO-O}_{NH\cdot CO\cdot CH_2}>NC_5H_5,HCl$, m. p. 211—212° (corr.), transformed by Ac_2O at 90° into (III) (R=H). Oxidation of the base (III) (R=H) with H_2O_2 in presence of NH_3 yields *NH_4 oxalylaminoacetate*, m. p. 196—197° (corr.) after softening at 193° (corresponding Ag salt), hydrolysed to $H_2C_2O_4$ and glycine.

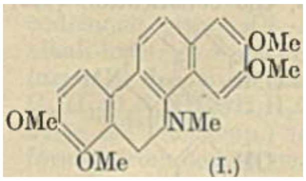
The *compounds* $C_{11}H_{10}O_3N_2$, m. p. 255—256° (corr.) after softening at 243° and partial decomp. at 249°, from chloroacetylglycine, pyridine, and Ac_2O, and $C_{12}H_{12}O_5N_2$, m. p. 180—181° (corr.), from α-bromopropionylglycine, Ac_2O, and pyridine, are incidentally described. H. WREN.

Synthesis of substituted thiazines. S. KRISHNA and M. S. JAIN (Proc. XV Indian Sci. Cong., 1928, 153—154).—6-Chloro-3-nitrobenzenesulphonic acid condenses with aniline to give 4-nitroacetanilide-2-sulphonic acid. If the blue solution in H_2SO_4 is immediately diluted with H_2O, 3-nitrophenothiazine *S*-oxide is precipitated, but if dilution is delayed for 30 min., 3-nitrophenothiazine is obtained and SO_2 is evolved. 3-Nitrophenothiazine is readily reduced to the 3-NH_2-compound, from which, via the diazo-compound, phenothiazine is obtained.

CHEMICAL ABSTRACTS.

Volatility of nicotine. V. L. NAGY (Biochem. Z., 1931, **239**, 324—328).—Nicotine evaporates appreciably when exposed to air at room temp. and is volatile in the vapours of Et_2O, light petroleum, a mixture thereof, or EtOH (96%). W. MCCARTNEY.

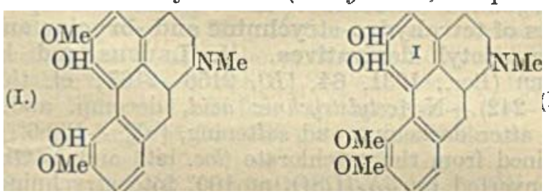
Chelerythrine and sanguinarine. E. SPÄTH and F. KUFFNER (Ber., 1931, **64**, [*B*], 2034—2038; cf. this vol., 854).—Chelerythrine is reduced by Zn dust and dil. HCl to dihydrochelerythrine, m. p. 166—167°, converted by phloroglucinol and H_2SO_4 and subsequently with diazomethane into *tetramethoxy*-N-*methyldihydro*-α-*naphthaphenanthridine* (I), m. p. (vac.) 182—183°. The same product is derived from *hydrosanguinarine*, m. p. (vac.) 188—189°, obtained by reducing sanguinarine nitrate with Zn and HCl. The formation of the same product from chelerythrine and sanguinarine is proof of the analogous structure of the quaternary chelidonium bases and of the similar position of the O atoms attached to the aromatic nuclei. The structure of homochelidonine is more firmly established.



(I.)

Reply is made to von Bruchhausen and Bersch (this vol., 750). H. WREN.

Constitution of corydine, *iso*corydine, and corytuberine. Synthesis of corydine. E. SPÄTH and F. BERGER (Ber., 1931, **64**, [*B*], 2038—2048).—Corytuberine is converted by diazoethane into its amorphous *Et_2 ether*, which is oxidised by $KMnO_4$ to 4-methoxy-3-ethoxyphthalic acid (identified as the *ethylimide*, m. p. 85°), thus showing that the free phenolic groups are not present in the same C_6H_6 nucleus. If corytuberine is treated with that amount of diazoethane required for the essential production of the two monoethyl ethers and the product is energetically oxidised with $KMnO_4$, 4-methoxy-3-ethoxyphthalic acid and 5-methoxy-4-ethoxybenzene-1 : 2 : 3-tricarboxylic acid (*methylimide*, m. p. 160—161°) are formed, thus establishing the constitution (I) for the alkaloid.

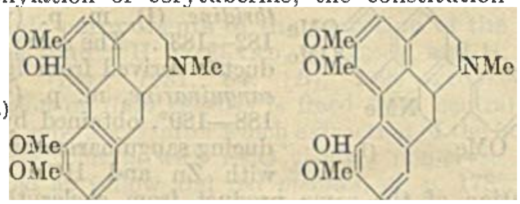


(I.) (II.)

The synthesis of the tricarboxylic acid is effected as follows : opianic acid is converted by fuming HCl at 100° into 2-aldehydo-6-hydroxy-5-methoxybenzoic acid, m. p. 155—156°, and thence by diazoethane into 2-*aldehydo*-5-*methoxy*-6-*ethoxybenzoic acid*. 3-*Nitro*-2-*aldehydo*-5-*methoxy*-6-*ethoxybenzoic acid*, prepared by means of fuming HNO_3 in AcOH, is reduced by $SnCl_2$ to *anhydro*-6-*amino*-4-*methoxy*-3-*ethoxyphthalic acid*, m. p. 162—163° (decomp.). 3-Nitro-2-aldehydo-5-methoxy-6-ethoxybenzoic acid is oxidised by $KMnO_4$ in neutral solution to 6-nitro-4-methoxy-3-ethoxyphthalic acid (*Me* ester, m. p. 86—87°), whence successively *Me* 6-*amino*-4-*methoxy*-3-*ethoxyphthalate*, m. p. 130—131°, *Me* 6-*cyano*-4-*methoxy*-3-*ethoxyphthalate*, m. p. 98—99°, and 5-*methoxy*-4-*ethoxybenzene*-1 : 2 : 3-*tricarboxylic anhydride*, m. p. 150—151° (corresponding *methylimide*, m. p. 160—161°). 4-*Methoxy*-3-*ethoxyphthalmethylimide* has m. p. 136—137°.

Removal of the CH_2O_2: group from bulbocapnine Me ether with phloroglucinol and H_2SO_4 affords the phenolic *base* (II) (+MeOH), m. p. 118—120° with loss of MeOH, which is partly methylated to corydine, identified as the free base and hydrochloride. Since the 2 OH groups of the phenolic base must be situated

in the nucleus (I) and corydine is obtained by partial methylation of corytuberine, the constitution (III)

(III.)  (IV.)

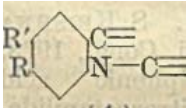
must be ascribed to corydine. This is in agreement with the observation that 3 : 4-dimethoxyphthalic acid is formed by oxidation of corydine or its Et ether. The establishment of the constitution of corydine and the conversion of corytuberine by partial methylation into *iso*corydine enable the constitution (IV) to be assigned to the last-named alkaloid. H. WREN.

Synthesis of sinactine. E. SPÄTH and E. MOSETTIG (Ber., 1931, 64, [*B*], 2048—2050).—Cryptopine is transformed into *r*-tetrahydro*epi*berberine (improved method). The base cannot be resolved into its optically active components by *d*-camphor- or *d*-bromocamphor-sulphonic acid or by tartaric acid in EtOH. Resolution is readily effected by alternate use of *d*- and *l*-tartaric acid in MeOH. The optically active bases have m. p. (vac.) 178—179°, $[\alpha]_D$ ±302° in $CHCl_3$. For natural sinactine Goto and others (A., 1930, 98, 935) record m. p. 175°, $[\alpha]_D$ −312°. H. WREN.

***Strychnos* alkaloids. LXI. Oxidation products of tetrahydro-strychnine and -brucine and their acetyl derivatives.** H. LEUCHS and H. BEYER (Ber., 1931, 64, [*B*], 2156—2167; cf. this vol., 242).—N-*Acetylstrychnic acid*, decomp. about 305° after darkening and softening, $[\alpha]_D^{18}$ +130·6°/*d*, obtained from the perchlorate (*loc. cit.*) and NaOH, is converted by 5*N*-H_2SO_4 at 100° into strychnine; the *methiodide*, m. p. 247—249° (decomp.), and the *Et* ester (as *perchlorate*) are described. It is reduced by H_2–PtO_2 to *dihydro-N-acetylstrychnic acid*, m. p. 245—248° (decomp.) after softening at 240°, $[\alpha]_D^{21}$ +95·0°/*d*, transformed by 5*N*-H_2SO_4 into dihydrostrychnine. The NH_2-acid, $C_{21}H_{22}O_4N_2$, is converted by HCl–EtOH into the *Et* ester, m. p. 178—180° after softening and darkening at 173° [*hydrochloride*; (?) *methiodide*, decomp. 296° after darkening at 220—290°]; it is hydrogenated to the *acid* $C_{21}H_{24}O_4N_2$, m. p. 280—285° (*hydrochloride*, $[\alpha]_D^{20}$ +30·6°; *oxime hydrochloride*; *Ac* derivative).

Brucine is reduced at a Pb cathode to brucidine (50%) and tetrahydrobrucine (30%). Oxidation of the last-named with CrO_3 and H_2SO_4 gives the base $C_{17}H_{20}O_4N_2$, m. p. 245—247° after softening (perchlorate, $[\alpha]_D^{20}$ +76·3°/*d*) (cf. *loc. cit.*), and a trihydrated *substance*, $C_{19}H_{22}O_5N_2$, m. p. 300—305° (decomp.) after softening at 285°, $[\alpha]_D^{20}$ +63·8°/*d* in H_2O (*perchlorate* +H_2O, $[\alpha]^{20}$ +38·8°/*d* increasing greatly when the salt is heated). The NH_2-acid readily absorbs 4H, giving the *compound* $C_{19}H_{26}O_5N_2$, softening above 315°, $[\alpha]_D^{24}$ +69·7°/*d*. The *base* $C_{17}H_{18}O_3N_2$, also obtained by the oxidation of tetrahydrobrucine, has m. p. 298—300° after darkening and softening, $[\alpha]_D^{24}$ +297°/*d* (*perchlorate*, $[\alpha]_D^{24}$ +209·5°/*d*); it is hydrogenated to 2-keto-3-hydroxydihydronucidine. The base $C_{17}H_{20}O_4N_2$ has been converted into its *Ac* derivative (*perchlorate* +H_2O, $[\alpha]_D^{20}$ +64·3°/*d*, passing after protracted heating into the salt of the base $C_{17}H_{18}O_3N_2$), its *methiodide*, m. p. 291—293° (decomp.) after darkening at 285°, and its *oxime hydrochloride*, $[\alpha]_D^{14}$ +74·1°/*d* in H_2O. It is reduced by Na–Hg and H_2O to 2-*keto*-2′ : 3′-*dihydroxynucidine*, m. p. 271—273° (decomp.), $[\alpha]_D$ −33·8°/*d* in H_2O, and by Zn–Hg and 6*N*-HCl to 2-keto-3-hydroxynucidine, m. p. 254° (decomp.), $[\alpha]_D^{21}$ −21·3°/*d* in H_2O. Hydrogenation in presence of PtO_2 affords the *substance* $C_{17}H_{24}O_4N_2$, m. p. 228—230° after softening, $[\alpha]_D^{23}$ +43·4°/*d* in H_2O (*perchlorate* of corresponding *Ac* derivative). Tetrahydrobrucine is converted by Ac_2O and NaOAc into its *Ac_2* derivative, m. p. 125—127° [*hydrochloride*, $[\alpha]_D^{20}$ +95·4°/*d*; *perchlorate* +$2H_2O$, $[\alpha]_D^{20}$ +85°/*d*; *methiodide*, m. p. 285—290° (decomp.)]. The Ac_2 substance is hydrolysed by NaOH to N-*monoacetyltetrahydrobrucine*, m. p. 130—135° [*hydrochloride*, $[\alpha]_D^{20}$ +95·3°/*d*; *perchlorate*, $[\alpha]_D^{20}$ +87·2°/*d*; *methiodide*, m. p. 305° (decomp.)]. H. WREN.

Three new *Strychnos* alkaloids [α- and β-colubrines, ψ-strychnine]. K. WARNAT (Helv. Chim. Acta, 1931, 14, 997—1007).—The mother-liquors from the technical production of strychnine contain 3 new alkaloids: *α-colubrine* (I), $C_{22}H_{24}O_3N_2$ +$4H_2O$, m. p. 184°, $[\alpha]_D^{18}$ −66·4°, −76·5° (H_2O-free) in 80% EtOH (*hydrochloride* +$3H_2O$; *sulphate* +$10H_2O$); *β-colubrine* (II), $C_{22}H_{24}O_3N_2$, m. p. 222°, $[\alpha]_D^{19}$ −107·7° in 80% EtOH (*hydrochloride* +H_2O; *sulphate* +$9H_2O$); and *ψ-strychnine* (III), probably $C_{21}H_{22}O_3N_2$, m. p. 266—268° (decomp.), $[\alpha]_D^{23}$ −43·8° in EtOH, −85·9° in $CHCl_3$ (*hydrochloride* +$2H_2O$; *nitrate*; *NO*-derivative, m. p. 292—294°). Oxidation of (I) and (II) with alkaline $KMnO_4$ (cf. A., 1926, 1263; this vol., 242) and esterification of the acids formed with diazomethane gives *Me_2* N-*oxalyl*-4-, m. p. 163°, and N-*oxalyl-5-methoxyanthranilate*, m. p. 176°, respectively. These esters are synthesised from the requisite Me methoxyanthranilate and oxalic acid at 120—130° with subsequent esterification.



(*A*.)

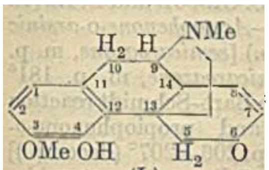
The structure (*A*) is present, therefore, in (I) (where R=OMe and R′=H), (II) (R=H, R′=OMe), strychnine (R=R′=H), and brucine (R=R′=OMe).

Dissolution of (III) in hot MeOH and EtOH gives, on cooling, *methyl*-, m. p. 198—200°, $[\alpha]_D^{23}$ −70·1° in $CHCl_3$, and *ethyl-ψ-strychnine*, m. p. 224—225°, respectively; 1 mol. of H_2O is replaced by 1 mol. of the alcohol, which cannot be removed at 110°. H. BURTON.

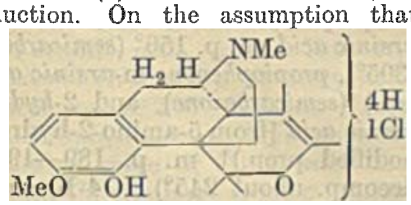
Denigès–Oliver test for morphine. F. BAMFORD (Analyst, 1931, 56, 586—589).—Both morphine and heroin give a red colour in the Denigès–Oliver test. For ordinary work the method of Denigès, using aq. $CuSO_4$, is more convenient, but in the case of extracts prepared from viscera etc. Oliver's modification with a Cu wire gives more definite results. The red colour developed is an intermediate product and is destroyed by an excess of H_2O_2. For 1 mg. of alkaloid the max. colour is produced by dissolving

in 5 c.c. of H_2O, adding 4 c.c. of H_2O_2 (2/3 vol. O), 1 drop of 0·1% $CuSO_4$, and 1—4 drops of conc. aq. NH_3, and diluting the whole to 10 c.c. For qual. work this is matched against a solution of Congo-red (1 in 10^6), and for quant. work a solution of heroin (1 in 10^4). Quinine, if present, may be salted out by Na_2SO_4. If Na K tartrate is used to salt out quinine, the morphine or heroin must be extracted by an immiscible solvent, since tartaric acid interferes with the test. T. McLachlan.

Acid rearrangement of morphine alkaloids. II. Preparation of "true" thebainone, and action of concentrated hydrochloric acid on thebaine. C. Schopf and H. Hirsch (Annalen, 1931, **489**, 224—251).—*Thebainone* (I) (+0·5H_2O), m. p. 151—152° [*hydriodide*, m. p. 258°; *methiodide*, m. p. 223°; *oxime* (+0·5H_2O), m. p. 185—186° (*hydrochloride*, m. p. 290—291°)], is obtained by the gradual addition of thebaine or codeinone to $SnCl_2,2H_2O$ in conc. HCl at room temp., and heating for a short time at 70°, or, in much smaller yield, by reduction of the red halochromic solution of thebaine in conc. HCl with $SnCl_2$ at 70°. That it has the formula assigned (I) is shown by its reduction with Pd–H_2 to dihydrothebainone, and by degradation of its methiodide to 3 : 4 : 6-*triacetoxyphenanthrene*, m. p. 165—167°, which is also obtained by hydrolysis and demethylation of acetylthebaol with HBr and acetylation of the product. Thebainoneoxime also gives this acetoxyphenanthrene on reduction. Codeinone, which is stable to cold conc. HCl, exists in the red solution of thebaine in HCl to the extent of about 7%, and therefore can be responsible for only a small proportion of the thebainone formed on reduction. From the general properties of the solution the existence in it of the substances (II) and (III) (in reversible equilibrium ?) is postulated; these are converted into (I) and metathebainone, respectively, on reduction. On the assumption that (III) is responsible for the halochromism of the solution, these views are supported by approx. polarimetric determinations. The conversion of morphine into *apo*morphine and of thebaine into thebenine is discussed in the light of these results. The reduction of thebaine with $SnCl_2$–AcOH gives methebenine in 59% yield, the course of the reaction being similar to that with HCl (*d* 1·07) except that the OMe group



(I.)



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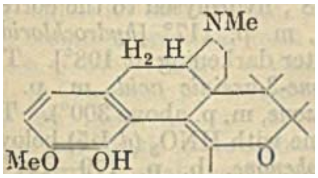


(III.)

migrates from C_6 to C_8 without simultaneous hydrolysis. Avoidance of heating in the reduction of codeinone with $SnCl_2$–HCl leads to formation of an alkali-insol. *base*, $C_{18}H_{20-22}O_3N_2$, m. p. 155—158° (*oxime*, decomp. slowly, 305°). A *compound*, $C_{18}H_{19}O_3N,NH_2OH,H_2O$, m. p. 142—144°, (anhyd.) 210—212° (decomp.) (*hydrochloride*, m. p. 204°), is formed from codeinone and NH_2OH in acid solution. H. A. Piggott.

Composition of oxonitin. E. Spath and F. Galinovsky (Ber., 1931, **64**, [*B*], 2201—2202; cf. this vol., 243).—The OMe content of oxonitin prepared according to Barger (J.C.S., 1915, **107**, 231) is usually somewhat low and falls when the substance is cryst. from $CHCl_3$–Et_2O or other agents. When precipitated by Et_2O from $CHCl_3$–MeOH const. vals. are obtained in good agreement with the formula $C_{32}H_{43}O_{12}N$, which therefore, contrary to Henry and Sharp (this vol., 636), is provisionally maintained. H. Wren.

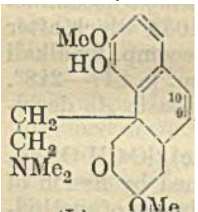
Phenolic alkaloids of *Cocculus trilobus*, D.C. I. H. Kondo and M. Tomita (Arch. Pharm., 1931, **269**, 433—442).—The total alkaloids of *C. trilobus* consist of trilobine, homotrilobine, an amorphous non-phenolic base, and two phenolic bases (*a*) *trilobamine* (I), $C_{31\,(or\,32)}H_{22\,(or\,24)}(\cdot O\cdot)_2(OH)_2(OMe)_2(NMe)_2$, m. p. 195°, decomp. 212°, $[\alpha]_D^{15}$ +356·6° in 2% AcOH [*dihydriodide*, decomp. 264°; *dimethiodide* (+H_2O); amorphous *Me_2 ether*, m. p. 169° (sinters at 130°), from (I) and diazomethane], and (*b*) a *base* (II), $C_{20\,(or\,21)}H_{15\,(or\,17)}O_3(OMe)(NMe)$, m. p. 223°, $[\alpha]_D^{18}$ +190·3° in $CHCl_3$. The product from (I) and Me_2SO_4 is decomposed by 20% NaOH to *dimethyltrilobamine-methylmethine*, amorphous, decomp. 105°, which after further treatment with Me_2SO_4 and decomp. by alkali gives NMe_3 and a N-free substance, m. p. 217—218°. (I) and Ac_2O at 70—80° give a non-basic *Ac* derivative, probably $C_{27\,(or\,28)}H_{20(22)}O_2(OMe)_2(OAc)_2(NMeAc)_2(:C\cdot CH\cdot OAc)_2$, amorphous, decomp. 210—213°, formed by fission of 2 tetrahydro*iso*quinoline rings. Oxidation of methyltrilbaomine with 1% $KMnO_4$ affords 2-methoxy-5 : 4′-dicarboxydiphenyl ether. The absorption spectrum and colour reactions of (I) are similar to those of oxyacanthine and berbamine, probably $C_{31\,(or\,32)}H_{22\,(or\,24)}(\cdot O\cdot)_2(OH)(OMe)_3(NMe)_2$ (this vol., 242); the spectrum of (II) resembles that of menisarine. H. Burton.

Alkaloids of pereiro bark. I. Geissospermine. A. Bertho and G. von Schuckmann (Ber., 1931, **64**, [*B*], 2278—2286).—The finely-powdered bark is extracted with EtOH, the solvent evaporated, and the residue mixed with $Ca(OH)_2$ and H_2O and dried. Extraction of the product with ligroin gives a mixture of bases purified by dissolution in AcOH and precipitation with NH_3. Recrystallisation from aq. MeOH gives *geissospermine sesquihydrate*, $C_{40}H_{48}O_3N_4,1{\cdot}5H_2O$, decomp. 145—147° (corr.) after softening, $[\alpha]_D^{20}$ −101·9° in 96% EtOH. Crystallisation of the sesquihydrate from AcOEt or C_6H_6 yields *geissospermine dihydrate*, m. p. 210—212° (corr., decomp.) after softening at about 160°, $[\alpha]_D$ −108·2° in 96% EtOH. The alkaloid can be cryst. only in the form of its hydrates. In the dihydrate the H_2O

is so firmly combined that normal mol. wt. is observed in freezing C_6H_6 or $CHBr_3$; when preserved, it passes slowly into the sesquihydrate. Both hydrates are derived from the same substance, since they are capable of interconversion, can be cautiously dehydrated whereby $1H_2O$ is shown to be firmly and chemically retained in the mol., and yield the same *sulphate* $X,H_2SO_4,6H_2O$ ($X=C_{40}H_{48}O_3N_4$), decomp. 226° (corr.) after incipient discoloration at 180°, $[\alpha]^{20}$ −84·2° in H_2O, *oxalate*, $X,(CO_2H)_2,5H_2O$, decomp. 193° (corr.), and *dimethiodide*, X,2MeI,$4H_2O$, decomp. 261—262° (corr.) after becoming yellow at 240°, $[\alpha]_D^{20}$ −61·5° in 96% EtOH. Geissospermine contains 1 OMe and a labile, basic NMe group. It cannot be benzoylated or acetylated and does not react with ketonic reagents. The two remaining O atoms are therefore present in bridges or in a masked CO group; the marked heat of hydration indicates the latter possibility. Losses during the recrystallisation of the substance and its sensitiveness towards acid indicate that the third O atom is probably present in a very labile CO·N· group. H. WREN.

Pereirine oxide. M. C. ROSA (Ann. soc. pharm. Chim. Sao Paulo, 1931, 2, 67—84).—Addition of 30% H_2O_2 affords the amine oxide of pereirine; on successive crystallisation the peroxide action disappeared. CHEMICAL ABSTRACTS.

Sinomenine and disinomenine. XXVIII. Hofmann decomposition of dihydrosinomenine. K. GOTO and H. SHISHIDO (Bull. Chem. Soc. Japan, 1931, 6, 229—233).—Dihydrosinomenine methiodide is converted by boiling 16·5% KOH into *dihydrosinomeninemethine* (I), m. p. 173° (sinters at 160°), $[\alpha]_D^{18}$ −84·32° (all rotations are in $CHCl_3$), the methiodide (not characterised) of which similarly gives *7-methoxydehydro-l-thebenone* (II), m. p. 118° (sinters at 113°), $[\alpha]_D^{18}$ −268° [*oxime*, m. p. (decomp.)]. Catalytic reduction ($PdCl_2$–charcoal) of (I) in dil. HCl gives its 9 : 10-*dihydro*-derivative, m. p. 133° (sinters at 123°), $[\alpha]_D$ +2·09°, the methiodide of which is decomposed to *7-methoxy-l-thebenone* (III), m. p. 128° (sinters at 122—123°), $[\alpha]_D^{18}$ −147·66° [*oxime*, m. p. 168° (sinters at 145°); *oximino*-derivative], also prepared by catalytic reduction (as above) of (II). The step-wise inversion of rotation during the change sinomenine ⟶ (III) is explicable by the hypothesis previously suggested (this vol., 1172), which can only be applied to the simplest cases (*i.e.*, thebenone and thebenane series). H. BURTON.



(I.)

Precipitation of alkaloids in gels. B. JONSSON (Svensk farm. Tidskr., 1931, 35, 25—29, 45—49; Chem. Zentr., 1931, i, 2789).—If the alkaloid solution is allowed to diffuse slowly into a gel containing the precipitant, well-formed crystals are obtained. The prep. of the gels from Na silicate, various nitrophenols, and H_3PO_4 is described. A. A. ELDRIDGE.

Benzyloxyphenylarsinic acids. I. E. BALABAN (J.C.S., 1931, 2473—2475).—Attempts to prepare 3 : 4-dihydroxyphenylarsinic acid failed. *o*-Hydroxy-, *o*-amino-, di- and tri-amino-phenylarsinic acids give an olive-green colour with aq. $FeCl_3$. 2 : 4-Dinitrochlorobenzene, CH_2PhCl (I), and aq. KOH at 100° give 2 : 4-dinitrophenyl benzyl ether, m. p. 154° after softening (lit. 150°), reduced by $(NH_4)_2S$ in boiling EtOH in poor yield to 4-nitro-2-aminophenyl benzyl ether, m. p. 92° (crude) [*hydrochloride*, m. p. 220° (decomp.)]. 4-Hydroxyphenylarsinic acid, (I), and NaOH in aq. MeOH at 100° give *4-benzyloxyphenylarsinic acid* (II), m. p. above 300° (*Ba* salt). 3-Nitro-4-hydroxyphenylarsinic acid yields similarly *3-nitro-4-benzyloxyphenylarsinic acid* (*Ba* salt) [not obtained by nitration of (II)], which is reduced by $Fe(OH)_2$ at 80—90° to the corresponding NH_2-*acid*, decomp. about 220° (*Ac* derivative); the NH_2 group could not be replaced by OH; with $CH_2Cl·CO·NH_2$ it gives *3-carbamylmethylamino-4-benzyloxyphenylarsinic acid*, m. p. 215° (decomp.), which did not yield a benz*iso*oxazine derivative. 2-Chloro-5-nitrophenol and $CH_2Ph·OH$ in aq. KOH at 100° give a substance, $C_6H_6O_2NCl$, m. p. 175° (possibly *2-chloro-5 hydroxylaminophenol*), in small yield. R. S. CAHN.

Benzaldehyde-*p*-arsinic acid, arsinic acid derivatives of acylphenylketones and their derivatives. Chemotherapeutic examination of these and other arsinic acids. C. S. GIBSON and B. LEVIN (J.C.S., 1931, 2388—2407).—*Acetophenone-o-arsinic acid*, m. p. 285—286° (decomp.) [*semicarbazone*, m. p. 234—235° (decomp.); *thiosemicarbazone*, m. p. 181° (decomp.)], was prepared by the Bart–Schmidt reaction from *o*-aminoacetophenone, and propiophenone-*o*-arsinic acid [*semicarbazone*, m. p. 206—207° (decomp.)] from *o*-aminopropiophenone. 5-Bromo-2-acetamidoacetophenone, m. p. 160° (modified prep.), gives on hydrolysis *5-bromo-2-aminoacetophenone* (I), m. p. 86—88°, which by the Bart–Schmidt reaction affords a *substance*, $C_8H_7O_2N_2Br$, m. p. 278° (probably *5-bromo-2-nitrosoaminoacetophenone*, but possibly *o-bromo-2-amino-oximinoacetophenone*), and *5-bromoacetophenone-2-arsinic acid*, decomp. incipient at 188° and complete at 291—293° (*Na* salt). The constitution of (I) was proved by conversion (Sandmeyer) into 2 : 5-dibromoacetophenone, m. p. 41°, oxidised to 2 : 5-dibromobenzoic acid. Directions are given for the prep. by analogous methods of *acetophenone-m-arsinic acid*, m. p. 156° (*semicarbazone*, not decomp. at 305°), *propiophenone-m-arsinic acid*, m. p. 212° (decomp.) (*semicarbazone*), and *2-hydroxyacetophenone-5-arsinic acid* [from 5-amino-2-hydroxyacetophenone (modified prep.)], m. p. 189—192° (*semicarbazone*, decomp. about 245°). 4-Bromo-3-nitroacetophenone, m. p. 120° (lit. 116·5°), is unaffected by Na_3AsO_3 in aq. MeOH and is not reduced to the NH_2-compound by Fe and AcOH, or Sn and HCl; with $SnCl_2$ and Ac_2O it yields *4-bromo-3-acetamidoacetophenone*, m. p. 118°, hydrolysed to the corresponding 3-NH_2-compound, m. p. 117° [*hydrochloride*, m. p. 206° (decomp.) after darkening at 198°]. This led to *4-bromoacetophenone-3-arsinic acid*, m. p. 198° (decomp.) (*semicarbazone*, m. p. above 300°). Treatment of *iso*valerophenone with HNO_3 (*d* 1·5) below 0° gives *m-aminoisovalerophenone*, b. p. 179—181°/14 mm. (*di-p-toluenesulphonyl* derivative) (converted into *m-bromoisovalerophenone*, b. p. 153—155°/19 mm., and thence by oxidation into *m*-bromobenzoic acid), together with some o- and p-NH_2-derivatives (con-

verted into the mixed Br compounds and thence into *o*- and *p*-bromobenzoic acid). Acetophenone-*p*-arsinic acid (II) [oxime, m. p. about 188° (lit. 157°, decomp.); *semicarbazone*, froths at 210° without change of colour; *thiosemicarbazone*, m. p. above 290°; *ketazine*, m. p. above 290°; *semioxamazone*, decomp. about 217°; *phenylhydrazone*, yellow, m. p. 225° (decomp.); p-*bromophenylhydrazone*, m. p. 227° (decomp.)] was prepared (*a*) from *p*-aminoacetophenone (obtained from NHAcPh, AcCl, and $AlCl_3$ in CS_2), and (*b*) from aq. Na_3AsO_3 and *p*-bromoacetophenone at 160—170°. The last-mentioned compound was prepared from PhBr, AcCl, and $AlCl_3$; an analogous reaction with *p*-dibromobenzene afforded oily *p*-bromoacetophenone (*semicarbazone*, m. p. 201°). Acetophenone-*p*-dichloroarsine and warm aq. NaOH give *acetophenone*-p-*arsenious oxide*, m. p. above 300°. *m*-Nitroanisole (from *m*-nitrophenol, aq. NaOH, and Me_2SO_4) is reduced by Sn and a trace of graphite in HCl (1 : 1) to *m*-anisidine, the Ac derivative of which with AcCl and $AlCl_3$ in CS_2 affords *4-acetamido-2-hydroxyacetophenone*, m. p. 91° (yield variable, up to 35%), hydrolysed by hot 15% HCl to the corresponding 4-NH_2-compound (III), m. p. 122—123°. A Friedel–Crafts reaction with acet-*o*-anisidide gave only a trace of cryst. material. (III) gives, by the Bart–Schmidt reaction, *2-hydroxyacetophenone-4-arsinic acid*, m. p. 156°. *p*-Acetamidoacetophenone and HNO_3 (*d* 1·5) give the 3-NO_2-compound, m. p. 137°, hydrolysed by boiling conc. HCl to *3-nitro-4-aminoacetophenone*, m. p. 148—149°, and oxidised by $KMnO_4$ to 3-nitro-4-acetamidobenzoic acid. The 4-NH_2-compound, by a modified Bart–Schmidt reaction, affords *3-nitroacetophenone-4-arsinic acid* (IV), m. p. 228—230°; this could not be obtained by nitration of acetophenone-*p*-arsinic acid, which under certain conditions gives carboxyphenyl-*p*-arsinic acid. Reduction of (IV) by $Fe(OH)_2$ and NaOH gives *3-aminoacetophenone-4-arsinic acid*, m. p. above 290° (lit. decomp. 230°), which could not be prepared from 4-bromo-3-aminoacetophenone, Na_3AsO_3, and Cu powder. 3-Bromo-4-aminoacetophenone (prepared by hydrolysis of the NHAc-compound with 20% HCl) gives, by the Bart–Schmidt reaction, *3-bromoacetophenone-4-arsinic acid*, m. p. 190—191° (decomp.) [*semicarbazone* (*Na* salt)]. *4-Acetyldiphenylamine-6'-arsinic acid*, m. p. 205—208°, is obtained (*a*) from *p*-bromoacetophenone, *o*-aminophenylarsinic acid, K_2CO_3, and a trace of Cu powder in boiling amyl alcohol, and (*b*) similarly from *p*-aminoacetophenone and *o*-bromophenylarsinic acid. *Propiophenone*-p-*arsinic acid*, m. p. above 295° (*semicarbazone*), is obtained from *p*-aminopropiophenone. *p*-Acetamido-*n*-valerophenone could not be obtained from NHAcPh, *n*-valeryl chloride or bromide, and $AlCl_3$ in CS_2. n-*Valeryl bromide*, prepared from *n*-valeric acid and PBr_3, has b. p. 64°/66 mm. *n*-Valeryl chloride, PhBr, and $AlCl_3$ in CS_2 yield p-*bromo*-n-*valerophenone*, b. p. 168—169°/20 mm., m. p. 37—38°, which with Na_3AsO_3 in aq. MeOH gives a small amount of a *substance*, m. p. 203°, containing As. The last ketone with HNO_3 (*d* 1·5) and conc. H_2SO_4 at −5° gives *4-bromo-3-nitro*-n-*valerophenone*, m. p. 196—197°, which did not condense with Na_3AsO_3 under the above conditions. By a modified Bart–Schmidt reaction, *p*-aminobenzaldehyde gives *benzaldehyde*-p-*arsinic acid*, m. p. above 280° [*oxime*, m. p. 157° (decomp.); *semicarbazone*, m. p. above 300° (*Na* salt); *thiosemicarbazone*, m. p. above 300°; *phenylhydrazone*, m. p. 186°; p-*bromophenylhydrazone*, m. p. 233° (decomp.); *semioxamazone*, m. p. above 300°].

Many of the above and other arsinic and arsazinic acids have been examined for activity against *T. equiperdum* in mice, but few show marked curative action. Those having the AsO_3H_2 group in the *p*-position to another group are less toxic than their *m*- and *o*-isomerides; the latter are not curative. Acetophenone- and benzaldehyde-*p*-arsinic acid are moderately toxic and slightly curative; their semicarbazones and thiosemicarbazones are less toxic and more curative, but the phenylhydrazones are not curative. R. S. CAHN.

Pyridine derivatives. XVI. *N*-Substituted pyridonearsinic acids. A. BINZ, H. MAIER-BODE, and A. RAST (Z. angew. Chem., 1931, **44**, 835—840; cf. this vol., 1071).—The following *N*-substituted 2-pyridone-5-arsinic acids were prepared by treating the unsubstituted acid and appropriate alkyl halide with KOH in MeOH or H_2O; all products are amorphous: *Bu*$^{\beta}$-, m. p. about 213°; iso*amyl*-, m. p. about 154—155°; *carboxymethyl*-, $+0·5H_2O$ (I) (from $CH_2Cl·CO_2H$) (*Na*$_2$ salt), which on reduction by SO_2 without isolation gives the corresponding *arsenious acid* (II), decomp. about 191° [-*arsenious oxide*, m. p. 230—234° (decomp.)], also obtained from (I) by boiling with As, $CuSO_4$, and aq. KOH, and oxidised to (I) by H_2O_2; *allyl*- (III), m. p. about 154—155°; *acetamido*- (from $CH_2Cl·CO·NH_2$), decomp. from 222°; *CH_2Ph*-, m. p. 227—228°; *acetanilido*- (from $CH_2Cl·CO·NHPh$), decomp. from 240°. The following *N*-substituted derivatives (all amorphous) of 2-pyridone-3-arsinic acid were similarly prepared: *carboxymethyl*-, m. p. above 270° [prepared only by way of the *arsenious oxide* (from $CH_2Cl·CO_2H$, followed by reduction by SO_2), decomp. 231°]; *Bu*$^{\alpha}$- (IV), m. p. 188—189°; *allyl*-, m. p. about 178—179°; *CH_2Ph*-, m. p. about 237—238°, also obtained by diazotisation etc. of 3-amino-2-hydroxypyridine, and by fusion of 2-pyridone with H_3AsO_4; *acetamido*-, decomp. about 262—263°. 3-Amino-4-pyridone, when diazotised in HCl, treated with As in NaOH, and then with hot H_3PO_2 and HI, gives the arseno-compound, which is oxidised by H_2O_2 to *4-pyridone-3-arsinic acid*, cryst. [reduced by warm H_3PO_2 and HI to *4 : 4'-dihydroxy-5 : 5'-arsenopyridine* (*dihydrochloride*, cryst., hydrolysed by H_2O)], from which the following cryst. *N*-substituted derivatives were prepared: *Me*-, decomp. 285° after darkening at 273°; *Bu*$^{\alpha}$-, m. p. 107—108°; *acetamido*-, decomp. about 232°; *CH_2Ph*-, m. p. about 221—222°. The following compounds were prepared by reduction of the corresponding arsinic acids by hot H_3PO_2 and HI: *NN'-di-n-butyl-5 : 5'-arseno-2 : 2'-pyridone*, m. p. 250—251°, large colourless and small yellow crystals (giving cryst. *X*-ray diagram), the former bimol., the latter unimol. in camphor (arsenobenzene is bimol. in camphor); NN'-*diacetamido-3 : 3'-arseno-2 : 2'-pyridone*, decomp. about 267°, cryst. (confirmed by *X*-ray diagram); *1 : 1'-di(carboxymethyl)-5 : 5'-arseno-2 : 2'-pyridone*, m. p. 210—215°. (I)

with thiophenol gives 1-*carboxymethyl* 5-*di(phenylthiol)arseno*-2-*pyridone*, m. p. 176° (aq. solution of Na salt unstable). (II), when oxidised with H_2O_2 and treated with Br, gives 3 : 5-*dibromo*-1-*carboxymethyl*-2-*pyridone*, m. p. 240—241°, and 3-*bromo*-1-*carboxymethyl*-2-*pyridone*-5-*arsinic acid*, $+0{\cdot}5H_2O$, losing H_2O at 125° and decomp. at 250°; the latter was also obtained from 3-bromo-2-pyridone-5-arsinic acid and $CH_2Cl{\cdot}CO_2H$. (I) with warm conc. H_2SO_4 and fuming HNO_3 gives 3-*nitro*-N-*methyl*-2-*pyridone*-5-*arsinic acid*, m. p. above 250°, which when warmed in MeOH with 4% Na–Hg and subsequently acetylated in the cold, affords 3-*acetamido*-N-*methyl*-2-*pyridone*-5-*arsinic acid*, m. p. above 270°.

The toxic doses for most of the above arsinic acids are recorded. Only (III) and (IV) are curative against trypanosomes. R. S. CAHN.

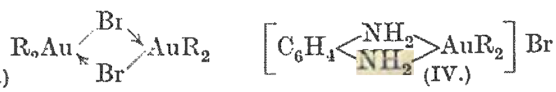
Introduction of arsenic into the coumarin nucleus. I. M. GOSWAMI and H. N. DAS-GUPTA (J. Indian Chem. Soc., 1931, 8, 417—422).—The Bart reaction with 6-aminocoumarin gives *tricoumarylarsine oxide*, m. p. 200° (slight decomp.); the toxicity of its Na salt is determined. 6-Chloromercuricoumarin and $AsCl_3$ give coumarin. H. BURTON.

10-Chloro-5 : 10-dihydrophenarsazine and its derivatives. XV. Monoacyl derivatives. L. A. ELSON and C. S. GIBSON (J.C.S., 1931, 2381—2388; cf. this vol., 501).—5 : 10-Dihydrophenarsazine derivatives, prepared by condensation of the substituted $NHPh_2$ with $AsCl_3$ and by reduction of substituted diphenylamine-6′-arsinic acids in HCl, are homogeneous in the cases hitherto reported and when obtained by reduction of 3-*acetyl*-, -*propionyl*-, and -*butyryl-diphenylamine*-6′-*arsinic acid* (I), (II), and (III), respectively. m-*Acetyldiphenylamine* (IV), however, gives a mixture of 1- and 3-substituted isomerides; the structure of the latter is proved by synthesis from NH_2Ph and 3-bromoacetophenone-4-arsinic acid (V). The structure of the other phenarsazine derivatives described below follows by analogy and because of similar colour reactions. A number of other As compounds were prepared.

m-Bromoacetophenone, *o*-aminophenylarsinic acid, anhyd. K_2CO_3, and a trace of Cu powder in boiling amyl alcohol give (I), m. p. 154°, also obtained similarly from *m*-aminoacetophenone (VI) and *o*-bromophenylarsinic acid. Reduction of (I) (SO_2, I, EtOH, HCl) yields 10-*chloro*-3(or 1)-*acetyl*-5 : 10-*dihydrophenarsazine* (VII), m. p. 268—270° (decomp.) [corresponding 10-*Br*-compound, m. p. 269° (decomp.)]. The 10-Cl-compound with "chloramine-*T*" in cold aq. $COMe_2$ yields 3(or 1)-*acetylphenarsazinic acid*, not decomp. at 290°. *m*-Bromopropiophenone gives similarly (II), m. p. 160°, and 10-*chloro*-3(or 1)-*propionyl*-5 : 10-*dihydrophenarsazine*, m. p. 227° after sintering and darkening, whilst *m*-bromobutyrophenone gives (III), m. p. 125—126°, and 10-*chloro*-3(or 1)-*butyryl*-5 : 10-*dihydrophenarsazine*, m. p. 210°. (V), NH_2Ph, K_2CO_3, and a trace of Cu powder in boiling amyl alcohol afford (VII). K *o*-chlorobenzoate, (VI), and a trace of Cu powder in boiling amyl alcohol yield 3-*acetyldiphenylamine*, m. p. 93°; this condenses with $AsCl_3$, best in PhCl, giving 10-*chloro*-1-*acetyl*-5 : 10-*dihydrophenarsazine*, m. p. 280°, and a mixture, probably containing (VII).

Acetophenone-*p*-arsinic acid with SO_2–HI–HCl gives p-*acetylphenyldichloroarsine*, m. p. 100°, b. p. 212—215°/30 mm., unaffected by Br in CCl_4 at 100°. Addition of phenylarsenious oxide and NaOH to diazotised *p*-aminoacetophenone and warming affords p-*acetyldiphenylarsinic acid*, m. p. 182° [*semicarbazone*, +(?) H_2O, m. p. indefinite]. *p*-Acetylphenylarsenious oxide gives similarly acetophenone-*p*-arsinic acid and a little 4 : 4′-*diacetyldiphenylarsinic acid*, m. p. 194°. Acetophenone-*p*-arsinic acid with Br (1 mol.) in warm $CHCl_3$ gives a *Br* derivative, m. p. 187—190°, and with an excess of Br in boiling CCl_4 gives an impure Br_2 derivative, m. p. 196—198°. R. S. CAHN.

Organic compounds of gold. II. Co-ordination compounds. C. S. GIBSON and W. M. COLLES (J.C.S., 1931, 2407—2416; cf. this vol., 78).—Analyses show that the material previously described as "gold tribromide" (*loc. cit.*) or "auric bromide" (this vol., 1172) is $HAuBr_4,3H_2O$ (I). Because of the facts mentioned below it is suggested that Au^{+++} does not exist; that Au always has a co-ordination no. of 4, and that gold tribromide is $(AuBr_3)_n$ (II), where *n* is at least 2. (II) is almost insol. in dry Et_2O with or without anhyd. HBr, and in H_2O, but sol. in aq. solutions of inorg. bromides. Addition of H_2O to (II) in Et_2O containing anhyd. HBr gives a solution of (I) in Et_2O. (II) does not react with Grignard reagents. The prep. of (I) from Au, for synthetic purposes, is modified. The yield of gold diethyl bromide (III; R=Et) is highest (17·4%) if 6 mols. of MgEtBr are used, but some unchanged (I) and Au are also obtained. An ethylenediamine bromide with aq. HBr gives a quant. yield of (III). *Gold ethylenediaminedi*-n-*propyl bromide* (IV; R=Pr^a) (prepared by the Grignard reagent) becomes violet about 130° and decomp. about 190°, and with aq. HBr gives gold di-*n*-propyl. The analogous *di*-n-*butyl* compound (IV; R=Bu^a), decomp. about 190° (similarly pre-


(III.) (IV.)

pared), gives similarly gold di-*n*-butyl bromide. The following compounds were prepared by adding the appropriate base to aq. $KAuBr_4$: *gold pyridine tribromide*, $C_5H_5N,AuBr_3$, scarlet, decomp. about 150°, which, best with 3 mols. of MgEtBr in Et_2O and pyridine, gives (III), and when recryst. from pyridine gives *gold dipyridinodibromo-bromide*, $[(C_5H_5N)_2AuBr_2]Br$, deep red; gold pyridinetrichloride, giving similarly gold dipyridinodichlorochloride, which at 135° loses pyridine and gives a reddish-yellow substance; *gold quinoline tribromide*, deep red, decomp. above 200°; *gold isoquinoline tribromide*, violet-red plates or brick-red powder; *gold 2-aminopyridine tribromide*, black, decomp. about 160° (probably co-ordinated by the pyridine-N); *gold di-2-pyridylamine tribromide*, scarlet; *gold diethylenediamine tribromide*, $[Au(NH_2{\cdot}C_2H_4{\cdot}NH_2)_2]Br_3$, bright yellow, which with aq. HBr gives $HAuBr_4$; $NHPh_2$ gives a dark green compound containing

2 mols. of base. The above co-ordination compounds are only slowly attacked by aqua regia or aq. SO_2.

R. S. CAHN.

Organic lead compounds. II. Oxidation reactions. P. R. AUSTIN (J. Amer. Chem. Soc., 1931, **53**, 3514—3518).—Oxidation of Pb tri-*p*-tolyl with $KMnO_4$ in $COMe_2$ gives *Pb tri*-p-*tolyl acetate*, m. p. 158—159° (AcOH is presumably formed by oxidation of $COMe_2$ and then reacts with the intermediate hydroxide), which with HCl in EtOH affords *Pb tri*-p-*tolyl chloride*, m. p. 140—141° (from Pb tetra-*p*-tolyl and HCl in $CHCl_3$). Similar oxidation of Pb tri-*o*-tolyl furnishes a product which is converted by HCl into *Pb tri*-o-*tolyl chloride*, m. p. 141—142°, also obtained from Pb tetra-*o*-tolyl and HCl. Mg allyl bromide and $PbPh_3Cl$ give *Pb triphenylallyl* (I), m. p. 76—77°, oxidised by $KMnO_4$ in $COMe_2$ containing a little H_2O to $PbPh_3OH$ (main product) and *Pb triphenyl-βγ-dihydroxypropyl* (II), m. p. 124—125°. (I) and O_3 in light petroleum afford probably Pb triphenyl oxide, since treatment of this with AcOH yields *Pb triphenyl acetate*, m. p. 206—207°. (I) and (II) are converted by HBr in EtOH into $PbPh_3Br$. Definite products could not be obtained by oxidation of Pb triphenyl-*p*-tolyl, tri-*o*-tolyl chloride, and tetra-*o*- and -*p*-tolyl; much unchanged material is recovered. *Pb di*-o-*tolyl dichloride*, m. p. 178—179°, is obtained from Pb tetra-*o*-tolyl and excess of HCl or from Pb tri-*o*-tolyl and conc. HCl in $CHCl_3$.

H. BURTON.

Basic amino-acids of silk fibroin. Determination of basic amino-acids yielded by proteins. H. B. VICKERY and R. J. BLOCK (J. Biol. Chem., 1931, **93**, 105—112).—Ag_2SO_4 is unsuitable for the precipitation of arginine and histidine from protein hydrolysates rich in monoamino-acids owing to the difficulty of maintaining a [Ag˙] adequate for complete precipitation of arginine. Replacement by $AgNO_3$ and the use of Ag_2SO_4 for subsequent re-precipitation and separation of the two bases is recommended. By this method silk fibroin yields 0·74% of arginine, 0·07% of histidine, and 0·25% of lysine (relative proportions approx. as in wool). F. O. HOWITT.

Basic amino-acids of proteins. Chemical relationship between the various keratins. R. J. BLOCK and H. B. VICKERY (J. Biol. Chem., 1931, **93**, 113—117).—The arginine, histidine, lysine, and cystine contents of keratins derived from human hair, sheep wool, goose feathers, snake epidermis, *Plexaurella dichotoma*, *Gorgonia flabellum*, and silk fibroin were determined (preceding abstract). The mol. ratio of the first 3 acids is approx. 1 : 4 : 12 for these keratins; the cystine content is variable. F. O. HOWITT.

Precipitation of proteins and of their degradation products with tannin. H. LUNDIN and J. SCHRODERHEIM (Biochem. Z., 1931, **238**, 1—23).—The effects of acidity, [H˙], particular acid used, amount and nature of precipitant, temp., and presence of EtOH, salts, or sugars on the precipitation by tannin of proteins and protein degradation products as well as on the co-precipitation of substances not directly precipitable from milk, blood, flesh hydrolysate, wort, and beer have been studied and the methods best adapted to the varying conditions and materials have been worked out. Tannin produces no ppt. in normal urine. W. MCCARTNEY.

Electrolyte-free proteins. X. Electrochemical constitutive characterisation of proteins by the Ag activity of their silver salts. E. GOIGNER and W. PAULI (Biochem. Z., 1931, **235**, 271—302; cf. this vol., 856).—The electrochemical differences in the "zwitterion" forms of proteins and in the multivalent negative ions may be studied by a comparison of the activity changes produced by addition of $AgNO_3$ or of AgOH, respectively. In serum-albumin all the negative groups are engaged on addition of $1·7\times10^{-3}N$-AgOH. Egg-albumin shows strong inactivation of Ag. It is practically complete at $1\times10^{-3}N$-$AgNO_3$. Inactivation by gelatin is far behind that of serum-albumin (about 60%). Gelatose shows still weaker inactivation (40%), considerably below that of the simpler NH_2-acids (78%). The somewhat unexpected behaviour of the NH_2-acids may be due to internal metal-complex salt formation. J. H. BIRKINSHAW.

Proteins. I. Importance of ions for the inner stability of the protein molecule (caseinogen). G. ETTISCH and G. SCHULZ (Biochem. Z., 1931, **239**, 48—73).—The behaviour of the protein mol. over a certain p_H range is a reversible function of its electric charge, the space occupied by the mol. increasing with the charge, the process leading to reversible fission of the mol. Increase of p_H beyond this range causes irreversible disintegration of the mol. (chemical action of OH′). The alkali-fixing power of caseinogen is due to the primary ionic reaction and a secondary irreversible slower reaction. The irreversible reaction is not brought about by neutral salts. The viscosity under the action of alkali increases at first and then slowly decreases. The splitting of caseinogen by alkali can be inhibited with NaCl over a p_H range of 7·4—11 but not above this p_H (cf. this vol., 426, 427, 503). P. W. CLUTTERBUCK.

Structure of simple nucleic acid. II. *h*- and *t*-Adenylic acid. H. STEUDEL and R. WOHINZ (Z. physiol. Chem., 1931, **200**, 82—86; cf. A., 1930, 1307).—The plant-(*h*-)nucleic acids (yeast-nucleic acid, *h*-guanylic acid, *h*-adenylic acid, *h*-inosic acid) give 60—75% of the theoretical yield of furfuraldehyde (from the pentose). Animal-(*t*-)inosic acid affords only 8—11% of the theoretical, but the *t*-inosine obtained after hydrolysis and its Ac_3 derivative give 63—70%. Probably the different point of attachment of the H_3PO_4 constitutes the difference between *h*- and *t*-adenylic acid. J. H. BIRKINSHAW.

Synthesis of the histone of the thymus gland. IV. K. FELIX and H. RAUCH (Z. physiol. Chem., 1931, **200**, 27—40; cf. A., 1930, 939).—Histone picrate from the calf's thymus gland was converted by means of HCl in MeOH into the *Me ester hydrochloride*, $[\alpha]_D^{20}$ −95·5°. Comparison with preps. produced in another way and subsequently esterified by MeOH and HCl or by Me_2SO_4 showed that no change occurred in the mol. apart from a conversion of SH into S·S groups. The mol. contains, per 100 atoms of N, 7·5 free esterifiable CO_2H, 5 preformed Me groups attached to N, and a basicity of 20 equivs. (calc. from the Cl content of the ester hydrochloride).

J. H. BIRKINSHAW.

Change of rotatory power of purified egg-albumin as evidence of the mode of combination of acid and alkali with proteins. H. J. ALMQUIST and D. M. GREENBERG (J. Biol. Chem., 1931, **93**, 167—170).—Purified egg-albumin (3·5% aq. solution) has a min. $[\alpha]_D^{25}$ $-30·8$ at p_H 5·04. This val. is not changed by addition of alkali to p_H 11·0, whilst from 11·0 to 12·6 it increases to a max. of $-60·6°$. With addition of acid the rotation rises sharply to $-35·1°$ at p_H 3·15 and then remains const. to p_H 1·72. The change on both sides of the isoelectric point is reversible. At p_H 12·6 the albumin has attained its max. base combination. On the acid side the attainment of a max. at p_H 3·15 is not in agreement with that of max. acid combination, due to a complex change and not to simple ionisation of the protein.
F. O. HOWITT.

Determination of protein by differential opacimetry. P. MOUNIER (Bull. Biol. Pharm., 1931, **2**, 196—197).—The greater part of the protein is precipitated by standard K iodomercurate. The residual protein in the centrifugate is precipitated by a solution of $CCl_3·CO_2H$ and the opacity contrasted with that produced by a known wt. of protein. C. C. N. VASS.

Determination of small quantities of acetylene. W. RIESE (Z. angew. Chem., 1931, **44**, 701—703).—An account of the use of Ilosvay's reagent for the determination of traces of C_2H_2; by a new method of prep. of the reagent, and under the conditions described, 0·0005 vol.-% may be determined.
H. F. GILLBE.

Determination of water. J. LINDNER.—See this vol., 1257.

Halogen determinations. K. HELLER and others. —See this vol., 1257.

Determination of smallest amounts of ethyl alcohol in very dilute solution by a modified micro-Ziesel method. J. B. NIEDERL and B. WHITMAN (Z. anal. Chem., 1931, **86**, 65—68).—The modified procedure for the determination of EtOH as EtI (or KI) is most satisfactory for about 1 mg. of EtOH at a concentration of 0·02%, but can be conducted with a 0·06 mg. sample in 0·001% aq. solution.
E. S. HEDGES.

Determination of ethyl alcohol. M. NICLOUX. —See this vol., 1327.

Electrometric micro-determination of amino-nitrogen. J. ROCHE and (MME.) A. ROCHE (Bull. Soc. Chim. biol., 1931, **13**, 835—840).—By electrometric titration to a definite p_H a more accurate end-point is reached than is possible with indicators. By use of extrapolation methods 0·05 to 5 mg. of NH_2-N can be determined with an accuracy of 1—2%. C. C. N. VASS.

Micro-method for determination of nitro-groups in aromatic compounds. S. MARUYAMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, **16**, 196—199).—Reduction with $TiCl_3$ is employed. The following new compounds are recorded: *6-nitro-2-chlorolepidine*, m. p. 209—209·5°; *5-nitro-6-methoxy-α-lepidone*, m. p. 295° (decomp.); *β-(m-nitroanilino)crotonyl-m-nitroanilide*, m. p. 155°; and *4-chloroquinaldine picrate*, m. p. 176—177°.
A. A. LEVI.

Determination of 2:4-dinitrophenol. A. SUCHIER (Z. anal. Chem., 1931, **85**, 434—435).—The solution is titrated at the b. p. with 0·5*N*-NaOH in presence of phenolphthalein, the end-point being reached when the orange colour becomes red. It is desirable to titrate to a standard tint.
R. CUTHILL.

Micro-determination of cholesterol. M. YASUDA (J. Biol. Chem., 1931, **92**, 303—312).—Okey's method (A., 1930, 1303) is modified in that lipins and excess of digitonin are removed by dissolution in $COMe_2$, and the remaining cholesterol digitonide is dissolved in hot EtOH and filtered from impurity. The residue on evaporation of the EtOH solution is determined by oxidation with $K_2Cr_2O_7$. The results for a number of tissue extracts are about 15% lower than those given by the colorimetric method. A. COHEN.

Action of iodine monochloride on cholesterol. Determination of the iodine value. H. WERNER (Z. Unters. Lebensm., 1931, **61**, 321—337).—I vals. of cholesterol have been determined by a variety of methods, of which Kaufmann's, employing an EtOH solution of NaBr and Br (cf. B., 1926, 447), was found to be the most suitable, the next best being that of Rosenmund and Kuhnhenn (cf. B., 1923, 798A) employing pyridine sulphate dibromide, with Winkler's method (cf. B., 1922, 473A) third in order of merit. Methods involving the use of ICl or IBr (Hanus, Hübl, Wijs) were unsuitable owing to simultaneous substitution. Attempts to determine the relative proportions of substitution and addition by titrating the halogen acid formed were unsuccessful. H. J. DOWDEN.

Colour reaction of adrenaline. B. AZZOLINI (Boll. chim.-farm., 1931, **70**, 665—667).—4—5 c.c. of a neutral solution are acidified with 1 drop of HCl and 2—3 c.c. of EtOH containing 4% of aq. NH_3 are added. In presence of adrenaline in a limiting dilution of 1 : 500,000 a rose-peach coloured ring is obtained, spreading through the solution on shaking and changing to yellowish-brown. R. K. CALLOW.

Detection of organic compounds. IV. Micro-chemical reactions of mezcaline. L. ROSENTHALER (Pharm. Ztg., 1931, **76**, 653—654).—Several reactions of mezcaline (β-3 : 4 : 5-trimethoxyphenylethylamine) are given and the crystal form of some of the ppts. is sketched.

Determination of small amounts of camphor. M. L. NICHOLS and A. STUBBLEFIELD (Z. anal. Chem., 1931, **86**, 30—34).—Camphor affects the surface tension of a mixture of H_2O and EtOH (3 : 1 by weight) in proportion to its concentration. Surface tension measurements by the ring-tensiometer method permit the determination of the camphor content of EtOH solutions containing 0·05—13% of camphor.
E. S. HEDGES.

Potentiometric determination of some compounds precipitable by potassium mercuric iodide. L. MARICQ (Bull. Soc. chim. Belg., 1931, **40**, 361—370).—Stovaine, novocaine, pyramidone, antipyrine, and atophan can be determined potentiometrically by means of an acid solution of HgI_2 in KI.

The first three compounds give complexes of the type HgI_2,X,HI and the last two of the type $HgI_2,2X,HI$. Antipyrine and pyramidone can be determined simultaneously. E. S. HEDGES.

Use of ferric salts for the detection of morphine. L. ROSSI (Anal. Farm. Bioquim., 1930, **1**, 106—110; Chem. Zentr., 1931, i, 2789).—$Fe^{\cdot\cdot\cdot}$ salts (in conc. solution) give with morphine salts (solid) a blue colour. A. A. ELDRIDGE.

Micro-chemistry of stereoisomerides. L. ROSENTHALER (Z. anal. Chem., 1931, **86**, 61—65).—*l*-Ephedrine and ephetonine can be distinguished by microscopical examination of the products formed with picrolonic acid, $NaClO_4$, KCNS, Reinecke's salt, and $Na_3Co(NO_2)_6$. E. S. HEDGES.

Biochemistry.

Production of methæmoglobin and increased respiration by organic dyes. L. MICHAELIS (Biochem. Z., 1931, **239**, 186—188).—The author's paper (this vol., 857) is supplemented.

P. W. CLUTTERBUCK.

Role of copper in hæmoglobin regeneration and in reproduction. H. L. KEIL and V. E. NELSON (J. Biol. Chem., 1931, **93**, 49—57).—In rats with anæmia, due to a diet of whole milk uncontaminated by contact with metals, hæmoglobin regeneration is effected by addition of small amounts of $FeCl_3$ supplemented by $CuSO_4$, but not when supplemented by salts of V, Ti, Mn, Ni, As, Ge, Zn, Cr, Co, Sn, or Hg (cf. A., 1929, 206; this vol., 247). The subnormal reproduction of rats on a milk and Fe diet is corrected by addition of Cu. F. O. HOWITT.

Preparation of nitric oxide-hæmoglobin. H. HARTRIDGE (Analyst, 1931, **56**, 571—572).—NO-hæmoglobin is most readily prepared by adding to blood a dil. solution of $NaNO_2$ and $(NH_4)_2S$ as a reducing agent. On heating a solution of CO-hæmoglobin coagulation commences at about 65°, whereas NO-hæmoglobin changes at 50° to methæmoglobin, which then coagulates. T. MCLACHLAN.

Preparation of standard acid-hæmatin solutions from hæmin. C. A. ELVEHJEM (J. Biol. Chem., 1931, **93**, 203—210).—Hæmin is prepared by the action of conc. AcOH on defibrinated blood at 90° and from it a solution of acid-hæmatin is obtained by dissolving in dil. HCl with the addition of gelatin as protective agent. The hæmoglobin equiv. of such a solution is given by the Fe content, and it may be used as a standard for the colorimetric determination of hæmoglobin or as a means of calibration of the glass standards of the Newcomer method (A., 1919, ii, 179). F. O. HOWITT.

Determination of volatile substances in blood. N. V. LAZAREV, A. J. BRUSSILOVSKAJA, and J. N. LAVROV (Biochem. Z., 1931, **240**, 12—18).—A method for determination of C_6H_6 in air depending on the conductometric titration of the CO_2 formed on burning it in an electric furnace is adapted for determination of hydrocarbons, Et_2O, and $COMe_2$ in blood.

P. W. CLUTTERBUCK.

Relative composition of sea-water and of the blood of *Limulus polyphemus*. M. E. DAILEY, F. FREMONT-SMITH, and M. P. CARROLL (J. Biol. Chem., 1931, **93**, 17—24).—The blood-serum of *L. polyphemus* is isotonic with sea-water, the isotonicity being maintained even when the sea is diluted by heavy rain. The distributions of Cl' and $Na^{\cdot}$ between sea-water and the serum agree with the theoretical Donnan ratio. F. O. HOWITT.

Occurrence of proteolytic enzymes in serum. J. WOHLGEMUTH (Biochem. Z., 1931, **239**, 493—494).—The procedure of Fuchs and von Falkenhausen (this vol., 1080) was unsatisfactory. Their results and their criticism of the work of Yokota (this vol., 641) must be rejected. W. MCCARTNEY.

Physico-chemical properties of the globulin fraction of serum and plasma precipitable by acetic acid. A. ROCHE (Bull. Soc. Chim. biol., 1931, **13**, 962—970).—Addition of 10% AcOH to serum diluted ×10 causes complete precipitation of the globulins at p_H 7·0—7·2, as compared with about p_H 6·0 in the case of plasma. The globulins obtained in this way from serum contain no mucoprotein and give no NH_2-carbohydrate on hydrolysis; the isoelectric point is p_H 5·8—6·0. P. G. MARSHALL.

Determination of the protein composition of blood-serum. J. VON DARANYI and B. VON GÖZSY (Biochem. Z., 1931, **239**, 110—127).—The method described uses 2 c.c. of serum and permits the determination of 4 protein fractions of 4 to 8 sera in 36—48 hr. The results compare favourably with those by the gravimetric method. P. W. CLUTTERBUCK.

Refractometric investigation of serum-protein. VII. Effect of dilution and of ammonium sulphate concentration on the protein fractions of horse-serum. D. VON DESEO (Biochem. Z., 1931, **239**, 329—349; cf. this vol., 1176).—When serum-protein is precipitated with $(NH_4)_2SO_4$ a vol. contraction, probably of the same order as that which occurs when such solutions are mixed with distilled H_2O, takes place and the ppt. contains less $(NH_4)_2SO_4$ than does the mother-liquor. The change in the $(NH_4)_2SO_4$ concentration of the liquid which occurs after the precipitation is due to the binding of H_2O by the ppt. The amount of the protein precipitated varies with the dilution of the serum and the concentration of the $(NH_4)_2SO_4$ used. At the same time the amounts of eu- and pseudo-globulin especially are greatly changed. W. MCCARTNEY.

Precursor of ammonia arising in blood and muscle. J. K. PARNAS (Biochem. Z., 1931, **239**, 18—20).—Criticism of the results and conclusions of Freund and Lustig (this vol., 641).

P. W. CLUTTERBUCK.

Approximate determination of blood-urea by opacimetry. P. MOUNIER (Bull. Biol. Pharm., 1931, **2**, 191—192).—The opacity produced by the

precipitation of the urea as dixanthylcarbamide from 1—2 drops of blood in presence of egg-white and glycerol is compared with that produced by a 0·02% solution of urea. C. C. N. VASS.

Acetylcholine in ox-blood. III. C. BISCHOFF, W. GRAB, and J. KAPFHAMMER (Z. physiol. Chem., 1931, **200**, 153—165; cf. this vol., 1080).—Acetylcholine was isolated from 20 samples of fresh ox-blood by precipitation as the Reinecke salt, conversion into the Au salt, then into the chloride. It was present in all samples examined, the average amount being 27·4 mg. per litre of blood. In 11 cases the physiological test on the blood showed little or no acetylcholine present, although the isolated chloride was physiologically active. The acetylcholine content of blood decreases on keeping according to the method of isolation. J. H. BIRKINSHAW.

Determination of choline in blood. M. MAXIM (Biochem. Z., 1931, **239**, 138—139).—A method for separation of blood-choline as periodide is described, titration of the I liberated therefrom on treatment with HNO_3 giving a measure of the choline content. P. W. CLUTTERBUCK.

Distribution of serum-phosphatide and of cholesterol in the ultra-filtrates obtained by filtration through large-pored collodion filters. S. WENT and L. GORECZKY (Biochem. Z., 1931, **239**, 441—448).—When horse-serum is ultra-filtered through collodion membranes having large pores the P, phosphatide, cholesterol, lecithin, and protein (in its various fractions) contents indicate that in serum the phosphatides and sterols exist in different types of combination with proteins, since the lipin content of the ultra-filtrates is dependent on the protein content and the concentration of cholesterol in them decreases in direct proportion as the protein content decreases. Also, as regards their phosphatide content, the ultra-filtrates can be divided into two groups sharply divided at the point where the euglobulin content falls to zero. In the one group the lecithin content equals that of the original serum and the protein content exceeds 40—50% of the total protein; in the other, the lecithin content is much lower and the protein content falls to zero. Ultra-filtrates which are free from protein contain Et_2O-sol. P equiv. to 30—40% of the total phosphatide but no cholesterol. The lipin content of the ultra-filtrates is independent of the pressure used. W. MCCARTNEY.

Total non-protein-sulphur in whole blood, plasma, and serum, and the glutathione content of blood. I. S. LORANT, N. HAJDU, and W. WEIL (Z. physiol. Chem., 1931, **200**, 121—125).—The non-protein-S in plasma or serum from the blood of healthy persons after a 12-hr. fast is 2·5 mg. per 100 c.c. Since the non-protein-S in whole blood is 6·8 mg. the val. for glutathione-S is 5·42—4·30 mg. for men and 5·30—4·30 mg. for women. J. H. BIRKINSHAW.

Determination of total base in serum. M. CHATRON (J. Pharm. Chim., 1931, [viii], **14**, 236—240, and Bull. Biol. Pharm., 1931, **3**, 290—291).—Serum is heated with H_2SO_4–$HClO_3$ mixture and the residue dissolved in H_2O, neutralised to bromothymol-blue with 0·2N-NaOH, and boiled, neutralising with a known vol. of 0·02N-NaOH if necessary. SO_4'' is determined by Fiske's method. Phosphates are removed by the method of Stadie and Ross (A., 1926, 100). C. C. N. VASS.

Determination of reducing sugars in blood and milk by the Fleury–Boutot method. L. BOUTOT (Bull. Biol. Pharm., 1931, **2**, 177—183).—Proteins are precipitated by $HgSO_4$ and after neutralisation with NaOH the filtrate is freed from excess of Hg by addition of powdered Zn. An excess of Bertrand's alkaline Cu solution is added and the mixture is warmed under definite conditions. The excess of the Cu solution is measured iodometrically and the difference between this val. and the blank measures the amount of reducing sugars present. C. C. N. VASS.

Determination of dextrose in blood. G. RODILLON (Bull. Biol. Pharm., 1931, **2**, 216—219).—After precipitation of proteins with $CCl_3\cdot CO_2H$, the sugar is determined by titration with alkaline $Cu_2Fe(CN)_6$. C. C. N. VASS.

Compensation dialysis *in vivo*; state and character of the blood-serum. C. H. GREENE and M. H. POWER (Proc. Staff Mayo Clinic, 1931, **6**, 123).—Examination of the protein-free dialysates of dog's blood indicated the absence of "labile" dextrose. Only 1—2 mg. of the reducing material per 100 c.c. was non-fermentable. CHEMICAL ABSTRACTS.

Prevention of glycolysis of blood by iodoacetic acid. A. D. MARENZI and W. A. MUNDT (Anal. Farm. Bioquim., 1931, **2**, 100—102).—Addition to dog's blood of $CH_2I\cdot CO_2H$ or its Na salt in the proportion 1 : 2000 prevents glycolysis at 37° for 24 hr. (cf. Lundsgaard, A., 1930, 954, 958). T. H. POPE.

Influence of arsenate on phosphorus exchange and glycolysis in blood. A. E. BRAUNSTEIN (Biochem. Z., 1931, **240**, 68—93).—Addition of arsenate (0·00016—0·005M) to whole blood and erythrocyte suspensions containing dextrose causes a rapid liberation of inorg. PO_4''' from the pyrophosphate and glycerophosphate fractions. The action of serum-phosphatase and the liberation of PO_4''' in non-glycolysing erythrocytes are not affected by arsenate. Addition of arsenate (0·0002—0·007M) increases the rate of disappearance of sugar and formation of lactic acid in whole blood and erythrocytes. PO_4''' exchange and glycolysis are influenced by vanadate in the same way as by arsenate. The hydrolysis of hexosediphosphate by the phosphatase, the formation of methylglyoxal by the *apo*zymase of dried erythrocyte preps., and the activity of the glyoxalase of erythrocytes are not influenced by arsenate. P. W. CLUTTERBUCK.

Determination of lactic acid in tissue and blood. F. MATAKAS (Biochem. Z., 1931, **239**, 417—423).—In the method of Mendel and Goldscheider (A., 1926, 212), which is fairly satisfactory, the HPO_3 can with advantage be replaced by 0·5N-H_2SO_4 and 5% $NaPO_3$ solution. Colorimetric are not necessarily more accurate than titrimetric processes, circumstances determining which is preferable. W. MCCARTNEY.

Enzymes and blood groups. II. F. SCHIFF and G. WEILER (Biochem. Z., 1931, **239**, 489—492;

cf. this vol., 1174).—The agent in human fæces which inactivates the substance A_1 is not affected in 20 hr. (in some cases also in much longer periods) by the following substances at the dilutions given or by $CHCl_3$-H_2O or glycerol: quinine hydrochloride, 0·5%, KCN 0·5%, 30% formalin 1%, thymol 0·1%, atoxyl 0·1%, PhOH 0·1%. Consequently sterile suspensions of fæces in which the activity of the agent remains undiminished can be prepared. The action of the agent on A_1 is not affected by 0·1% solutions of any of the following substances, but is inhibited by KCN (0·5%) or by salicylic acid (0·1%): quinine, cocaine, atoxyl, sympatol (α-4-hydroxyphenyl-β-methylaminoethyl alcohol hydrochloride), PhOH. Probably the agent is a "blood group" enzyme.

W. McCartney.

Serum anaphylaxis. Chemical nature of the anaphylactising substance. Desplanques, Simonnet, and Verge (Ann. Inst. Pasteur, 1931, **48**, 332—338).—Anaphylaxis of guinea-pigs by horse-serum is due to the serum-globulin, serum-albumin being inactive after precipitation of the globulin.

A. Cohen.

Mineral content of the developing avian embryo. W. R. Mankin (Med. J. Austral., 1930, **2**, 41—48).—The Na and K contents of the 4-day embryo are much higher than those of the fully developed chick; for Ca the reverse holds. About the 13th day the Ca increases slightly and the other constituents fall. The H_2O content is closely parallel with the K content.

Chemical Abstracts.

Phosphatides. III. Fatty acids of the ether-soluble phosphatides and of the protagon fraction of brain. E. Klenk (Z. physiol. Chem., 1931, **200**, 51—68; cf. this vol., 251).—The saturated fatty acid fraction of the Et_2O-sol. phosphatides was a mixture of palmitic and stearic acids. The unsaturated fatty acid fraction, on catalytic hydrogenation, yielded, in addition to stearic and behenic, small amounts of palmitic and *n*-eicosoic acid. The last must have arisen from an unsaturated C_{20} acid.

In the protagon fraction the amount of unsaturated fatty acid is small. The chief constituents are palmitic and stearic together with a little nervonic acid. The portion in amide-linking consists of the 4 fatty acids of the C_{24} group: cerebronic, lignoceric, hydroxynervonic, and nervonic acids. Stearic acid was also present, and possibly an acid of higher mol. wt. Apart from the latter the acids present are those recognised as fission products of cerebrosides and sphingomyelins. The acids of the C_{18} and C_{24} series predominate.

J. H. Birkinshaw.

Phosphorus in glycogen. T. C. Taylor and J. J. McBride (J. Amer. Chem. Soc., 1931, **53**, 3436—3440).—Glycogen isolated from rat-liver and sea scallop by Pflüger's method and then subjected to long dialysis contains 0·013—0·24% of P, which is attached to some nitrogenous residue of const. composition.

H. Burton.

Iodine content of commercial desiccated anterior pituitary preparations. K. Closs (J. Pharm. Exp. Ther., 1931, **43**, 131—138).—The accurate determination of I in org. material is discussed and a modification of the micro-method of von Fellenberg (A., 1926, 1052) is given. All but one prep. (with 0·00198—0·00996%) of those examined contained 0·00008—0·00019% I.

F. O. Howitt.

Production of homogeneous skeletal material for analysis of the whole skeleton and the presence in it of small amounts of calcium soaps. F. Fischler, A. Wild, and H. Kaussler (Biochem. Z., 1931, **239**, 213—223).—The bone material is prepared by hydrolysis of the whole animal with 2% KOH and the ratios of Ca : PO_4 : MgO show great constancy in composition. It contains 0·5—1·0% of Ca soaps. The ratios for teeth show a higher PO_4 and MgO val.

P. W. Clutterbuck.

Organic chlorine compounds in animal tissues. W. Hogartz (Z. physiol. Chem., 1931, **200**, 119—120).—The org. Cl compounds are not removed from tissue by simple Et_2O extraction of the powdered dried material (cf. Amer. J. Physiol., 1929, **90**, 375).

J. H. Birkinshaw.

Copper content of human organs. H. Kleinmann and J. Klinke (Arch. path. Anat. Physiol., 1930, **275**, 422—435; Chem. Zentr., 1931, i, 2777—2778).—The livers of prematurely and newly-born infants (up to 3 days old) contained up to 11 times as much Cu as the normal val. Perfusion experiments also showed that the Cu content of the liver is high. PhBr was used instead of $CHCl_3$ in Schonheimer and Oshima's method for the determination of Cu.

A. A. Eldridge.

Loss of weight of the human body during the six hours following death. L. Hébert (Bull. Biol. Pharm., 1931, **2**, 151—152).—The loss is attributed to loss of H_2O and CO_2 by the oxidation of lactic acid produced in the muscle after the heart has ceased to beat.

C. C. N. Vass.

Fission of arcaine by micro-organisms. F. Linneweh (Z. physiol. Chem., 1931, **200**, 115—118; cf. this vol., 1178).—A mixed culture of saprophytic bacteria hydrolysed arcaine to putrescine and urea.

J. H. Birkinshaw.

Pigments of *Haliotis californiensis*. R. Lemberg (Z. physiol. Chem., 1931, **200**, 173—178).—*H. californiensis* yields *A*, green in acid $CHCl_3$ solution, absorption max. at 623 mμ, weaker band at 498 mμ, in neutral solution bands at 555 and 496 mμ; *B*, greenish-blue in acid solution, band at 622 mμ.

J. H. Birkinshaw.

Salts of heavy metals as fixatives. J. J. Sheinin and H. A. Davenport (Stain Tech., 1931, **6**, 131—148).—Heavy metal salts were used for tissue fixation and their precipitating action on albumin and gelatin solutions was studied. Precipitation of proteins is generally influenced by the at. wt. of the cation of an electrolyte. A relatively good protein precipitant is not necessarily a good tissue-hardening agent, but the reverse is true.

H. W. Dudley.

Insect waxes. IV. Coccerin, the wax of the cochineal insect (*Coccus cacti*). M. Becker (Biochem. Z., 1931, **239**, 235—242).—Coccerin is a compound of 1 mol. of cocceryl alcohol, $C_{32}H_{64}(OH)_2$ (*monoacetate*, m. p. 78—79°), with 1 mol. of coccerinic acid, $C_{31}H_{62}(OH)\cdot CO_2H$ (*Et* ester, m. p. 72—73°). The second OH group of the alcohol is very difficult to esterify (cf. this vol., 975).

P. W. Clutterbuck.

Composition of the silk-worm pupa. S. WADA (Acta Schol. Med. Kyoto, 1931, **13**, 201—210).—The material contained H_2O 8·8; the dry substance contained protein 63·2, neutral fats 19·9, unsaponifiable substances 0·8, glycogen 1·2, ash 3·3%. The following NH_2-acids were isolated: glutamic acid 4·17, glycine 1·01, leucine 2·47, alanine 0·78, valine 0·95, *iso*leucine 1·71, *l*-proline 1·85, *dl*-proline 0·4, phenylalanine 1·21, *dl*-aspartic acid 0·11, *l*-aspartic acid 0·26, serine?, tyrosine 1·84, cystine 0·19, tryptophan 1·2, histidine 0·07, arginine 0·15, lysine 0 02, guanine 0·03, adenine 0·03%, hypoxanthine?, choline?

CHEMICAL ABSTRACTS.

Effect of respiratory injury on biophysical properties of the body fluid and digestive fluid of silk-worm larvæ. T. GAMÔ (J. Sci. Agric. Soc. Japan, 1928, 124—149, 177—187).—Changes in p_H and electrical conductivity are recorded.

CHEMICAL ABSTRACTS.

"Kaijo" of cocoons and their sericin particles. H. KANEKO (Bull. Sericult. Japan, 1931, **4**, 2—6).—The physical properties of their sericin solutions are used to characterise the "kaijo" of cocoons. A better "kaijo" gives a greater p_H, and, in an electric field, greater cataphoretic velocity and biuret colour-change in the anodic compartment. H. DAVSON.

Distribution of various forms of nitrogen in wild silk, and in fibroin and sericin of true silk. R. INOUYE and K. SAKAMOTO (Bull. Sericult. Japan, 1931, **4**, 10—12).—The N of wild silks dissolved in conc. HCl is less than that of true silks, whilst humin and amide are the same. More arginine than histidine and lysine is found in each silk. N distribution is similar in fibroin and sericin, also in Yamamai and Tussah silks, and different in *Attacus cynthia* and *Caligula japonica*. H. DAVSON.

Nature of the enzyme secreted by the hatching gland of plagiostomes (*Scylliorhinus canicula*). O. T. YIO (Compt. rend., 1931, **193**, 545—546).—The enzyme resembles trypsin in digesting mixtures of gluten with albumin and gelatin at p_H 7·0—7·2. It is, however, active at a lower temp. (13°). A. COHEN.

Equilibrium between cerebrospinal fluid and blood-plasma. VI. Distribution of sodium between cerebrospinal fluid and blood-serum. M. E. DAILEY (J. Biol. Chem., 1931, **93**, 5—15).—Human serum-Na tends to vary directly with the serum-Cl. The cerebrospinal fluid-Na is generally higher (1·03 : 1) than the serum-Na, whilst the average ratio of serum-Cl to cerebrospinal fluid-Cl is 0·82. Meningitis is associated with a decrease in Cl content and a less marked decrease in Na content of both serum and fluid. Acute changes in the serum by blood dilution are followed by corresponding changes in the cerebrospinal fluid, the change in Na content being proportional to that in Cl.

F. O. HOWITT.

Photometric determinations of different constituents of body-fluids. G. RODILLON (Bull. Biol. Pharm., 1931, **2**, 163—175).—Details for the application of the photometric method for the microdetermination of urea, uric acid, dextrose, Cl′, PO_4''', Ca, and phenols in body-fluids are recorded.

C. C. N. VASS.

Milk secretion. (A) Influence of inanition. (B) Influence of insulin and phloridzin. J. W. GOWEN and E. R. TOBEY (J. Gen. Physiol., 1931, **15**, 45—66, 67—85).—(A) Cows when starved but supplied freely with H_2O secrete milk with a high content of total solids, especially of fat and ash, the increase in protein being usually small. The vol. of milk secreted and the concentration of lactose are decreased. Administration of "parathormone" (1000 units) had no significant effect on the blood or the milk.

(B) Milk secretion is altered by a large dose of insulin sufficient to lower the blood-sugar (500—1200 units) in a manner somewhat similar to that observed during starvation, the chief difference being that the marked rise in total solids, butter-fat, and ash and the fall in rate of secretion are more immediate. Administration of phloridzin during inanition temporarily increases the % of total solids and butter-fat. The results are in conformity with the view that the lactose is derived from the blood-dextrose and that a balance is maintained between the osmotic pressure of the milk and that of the blood. W. O. KERMACK.

Absorption spectrum of bilirubin in various solvents. II. P. MÜLLER and L. ENGEL (Z. physiol. Chem., 1931, **200**, 145—152; cf. this vol., 1082).—Bilirubin in all solvents examined shows a sharply defined absorption band, the position of which varies for each solvent. With increasing alkalinity of the solution the absorption band moves towards the violet, decreases in strength, and becomes less clearly defined. J. H. BIRKINSHAW.

Bile salts in urine. P. MOUNIER (Bull. Biol. Pharm., 1931, 2, 153—160).—Surface tension measurements afford the only means of determining minute quantities of bile in urine. A statistical val. for normal urine has been determined; max. vals. of surface tension are obtained in urine acidified with 0·05*N*-HCl. The presence of bile is shown by an increased surface tension; free org. acids also increase the surface tension, but to a much smaller extent. Hay's test is extremely sensitive, corresponding with a concentration of 0 05 g. of bile salts per litre. Difficulties may be met in urine containing min. concentrations of bile and max. concentrations of keto-acids. C. C. N. VASS.

Distinction between dextrose and lactose in urine. G. RODILLON (Bull. Biol. Pharm., 1931, **2**, 185—187).—Lactose and dextrose are differentiated by means of their osazones. C. C. N. VASS.

Diacetyl, acetylmethylcarbinol, and βγ-butylene glycol in human urine. H. SCHMALFUSS and H. SCHAAKE (Z. physiol. Chem., 1931, **200**, 169—172).—These substances occur in small amounts in the urine of healthy persons. J. H. BIRKINSHAW.

Colorimetric determination of phenols in urine. A. D. MARENZI (Anal. Farm. Bioquim., 1931, **2**, 81—90).—A modification of Benedict and Theis' method (A., 1918, ii, 461) serves for the determination of free PhOH and, after hydrolysis, of conjugated PhOH in urine. Folin and Denis' (A., 1915, ii, 802)

and Goiffon and Nepveux' methods (A., 1924, ii, 706) yield high results. T. H. Pope.

Micro-determination of total urinary nitrogen. G. Rodillon (Bull. Biol. Pharm., 1931, 2, 192—193).—1 c.c. of urine is heated with 1·5 c.c. of H_2SO_4 in presence of $KHSO_4$ and $HClO_3$. After dilution the solution is neutralised to phenolphthalein and the concentration of NH_3 determined by formol titration. C. C. N. Vass.

Determination of total nitrogen in urine. M. Wirbel (Bull. Biol. Pharm., 1931, 3, 325).—Urine is heated with H_2SO_4–$HClO_3$ mixture, the residue dissolved in H_2O, and the NH_3-N determined by formol titration. C. C. N. Vass.

Photometric determination of total and inorganic phosphorus in urine. C. Urbach (Biochem. Z., 1931, **239**, 28—41).—The process depends on examining the P–molybdic acid complexes by means of the step photometer. The method is superior to the colorimetric method in accuracy and rapidity. P. W. Clutterbuck.

Determination of organic phosphorus in urine by means of the step photometer. C. Urbach (Biochem. Z., 1931, **239**, 182—185).—The method is described and claimed to be superior to others in accuracy, rapidity, and in the avoidance of the use of standards. P. W. Clutterbuck.

Anæmias. I. Porphyria and red cell generation. II. Anæmias and liver substance. R. Duesberg (Arch. exp. Path. Pharm., 1931, **162**, 249—279, 280—295).—I. Clinical and experimental anæmias are divided into two classes. Those caused by distilled H_2O injection, phenylhydrazine, and jaundice are marked by an increase in reticulocytes and O_2 consumption, without an increase in porphyrin excretion. Pernicious, sulphonal, and Pb anæmias do not show increased regeneration of blood-cells, whilst porphyrin in the urine increases.

II. Liver preps. have no therapeutic action on anæmias due to experimental bleeding, distilled H_2O, loss of blood, $NHPh\cdot NH_2$, and jaundice. Favourable reactions are observed in anæmias where blood-cell regeneration is inhibited, *e.g.*, pernicious, sulphonal, and Pb anæmias. A. Cohen.

Methæmoglobin formation by antianæmic organ extracts. R. Duesberg and W. Koll (Arch. exp. Path. Pharm., 1931, **162**, 296—306).—Several liver preps. and organ extracts of clinical therapeutic val. in anæmia convert hæmoglobin into methæmoglobin in the presence of O_2 *in vitro*; cyanohæmoglobin is formed by the addition of HCN. Fe, Cu, SH compounds, or disulphides are not responsible for the conversion. A. Cohen.

Production of nutritional anæmia in rats. C. A. Elvehjem and A. R. Kemmerer (J. Biol. Chem., 1931, **93**, 189—195; cf. A., 1928, 790).—In rats weaned at 17 days of age and fed on whole cow's milk *ad libitum*, blood-hæmoglobin decreases to a level of 2—3·5% within 2 weeks, when, if no additions are made to the diet, death ensues. On addition of Fe and Cu to the milk fed to such rats the hæmoglobin returns to normal levels. Such anæmic rats possess a low Mn storage (0·0026—0·0064 mg. per animal). F. O. Howitt.

Ineffectiveness of purified glutamic acid as a supplement to iron in the correction of nutritional anæmia. C. A. Elvehjem, H. Steenbock, and E. B. Hart [with E. van Donk] (J. Biol. Chem., 1931, **93**, 197—201).—Contrary to Drabkin and Miller (cf. this vol., 247; also following abstract) the addition of pure glutamic acid to a diet of whole milk and Fe does not correct nutritional anæmia in the rat. F. O. Howitt.

Hæmoglobin production. III. Relief of anæmia, due to milk diet, by feeding amino-acids and related compounds. D. L. Drabkin and H. K. Miller (J. Biol. Chem., 1931, **93**, 39—48; cf. this vol., 247, 510).—Rats develop anæmia on a diet of either raw or boiled milk. The onset of the disease is retarded by administration of 0·18 mg. Fe per rat per day; this amount is ineffective, either alone or supplemented with leucine, cystine, glycine, α-aminovaleric acid, or glutaric acid, in curing the anæmia once produced. Fe and succinic acid or succinimide are partly effective. Rats receiving milk supplemented with Na glutamate, but not with Fe, are more resistant to anæmia than those receiving Fe alone or Fe and alanine. Glutamic acid (70 mg. per rat per day) stimulates hæmoglobin formation in anæmic rats when administered with as little as 0·05 mg. of Fe. F. O. Howitt.

Blood studies in hæmorrhagic anæmia. H. S. Mayerson and H. Laurens (J. Nutrition, 1931, **3**, 453—463).—The effect of various diets on hæmoglobin production in dogs is recorded. Chemical Abstracts.

Metabolism of cancer tissue. G. Harker (J. Cancer Res. Comm. Sydney, 1931, **3**, 114—118).—A review. C. C. N. Vass.

Tumour immunity. Effects of eu- and pseudo-globulin fractions of anti-cancer sera on tissue cultures. T. Lumsden (J. Path. Bact., 1931, **34**, 349—355).—The euglobulin contains all the antibodies which are specifically toxic to cancer cells and all the heterotoxins which have escaped destruction during fractionation. The pseudoglobulin contains the anti-species bodies. Chemical Abstracts.

Cancer-producing substances of Rous sarcoma. E. Frankel (Z. physiol. Chem., 1931, **200**, 126—132).—Certain dyes of known constitution (Hansa-yellow, lack-orange, and thioindigo colours) adsorb the cancer-producing agent. Except in the case of lack-orange the eluates are active. J. H. Birkinshaw.

Non-enzymic nature of entity transmitting chicken sarcoma. W. Nakahara and H. Yaoi (Gann, 1930, **24**, 318—336).—Repeated freezing (−18° for 20 min. or −75° for 10 min.) and thawing (37° for 5—10 min.) of tissue reduces the tumour-transmitting action of the saline extract of Rous chicken sarcoma tissue or its sediment. If an enzyme-like substance is responsible for the formation of the sarcoma, extracts obtained from disrupted cells should be more active than those obtained from intact cells. Chemical Abstracts.

Capability of serum to dissolve carcinoma lipins. R. Willheim and K. Stern (Biochem. Z., 1931, **239**, 473—483; cf. A., 1930, 1611).—The lipins

which are derived from cancer cells are dissolved by normal sera, whilst cancer sera not only lose this power, but even readily deposit the lipins which they contain. Lipins from different tumours exhibit considerable differences as regards solubility in sera, whereas those from normal cells or from the whole carcinoma tissue do not. It is concluded that, since attempts to separate the lipins into fractions fail, the differences are not due to differing contents of a chemical substance, but to the combination of various constituents to form a physicochemical unit.

W. McCartney.

Experimentally produced changes in the behaviour of serum towards cancer cells. R. Willheim and K. Stern (Biochem. Z., 1931, **239**, 484—488; cf. A., 1930, 1611).—When human carcinoma cells or lipins extracted from human tumours are injected into rabbits and curves of the type previously described are drawn, these are of the same type as those obtained in the case of persons suffering from cancer.

W. McCartney.

Effect of sodium fluoride on the metabolism of tumours. C. Sellei and J. Jany (Biochem. Z., 1931, **239**, 94—99).—Glycolysis in kidney tissue is decreased and respiration but little affected by NaF. The respiration of carcinoma tissue with a high concentration of NaF is similarly effected, but with more dil. solutions (0·001—0·0001*N*) is increased and the glycolysis decreased, the heat coeffs. $W^{O_2}_{CO_2}/W$ and $W_{CO_2}^{O_2}/W_{O_2}$ being similar to those of normal tissue without NaF.

P. W. Clutterbuck.

Cancer chemotherapy. X. Effect of thorium, cerium, erbium, yttrium, didymium, praseodymium, manganese, and lead on transplantable rat tumours. L. C. Maxwell and F. Bischoff [with E. M. Ottery] (J. Pharm. Exp. Ther., 1931, **43**, 61—70).—The lethal dose and the action on cancer tumours of compounds of the above metals have been investigated in rats. All are essentially negative in checking cancer growth.

F. O. Howitt.

Respiratory quotient. Value in diagnosis of diabetus mellitus. M. Wishnofsky and C. S. Byron (Arch. Int. Med., 1931, **48**, 470—477).—Vals. for R.Q. less than 0·88 after the ingestion of dextrose are considered as indicative of diabetus mellitus. Where the presence of glycosuria and hyperglycæmia is inadequate owing to other factors, such as high renal threshold, hypertension, nephritis, or hyperthyroidism, the R.Q. is the ultimate criterion in the diagnosis of diabetus mellitus.

A. Lawson.

Intermediate fat metabolism in diabetes and disorders of the liver. L. Cannavó (Biochem. Z., 1931, **239**, 100—109).—Almost all aliphatic acids are acidogenic and all acids having an even no. of C atoms are very ketogenic. The acidosis caused by acids having an odd no. of C atoms is due to acids (not keto-acids) formed during metabolism. Acidosis is accompanied by increased urinary NH_3. In all the liver cases some ketonæmia and ketonuria were observed.

P. W. Clutterbuck.

"Parathormone" dosage and serum-calcium and -phosphorus in experimental chronic hyperparathyroidism leading to ostitis fibrosa. A. Bodansky and H. L. Jaffe (Proc. Soc. Exp. Biol. Med., 1930, **27**, 797).—On a low Ca intake hypercalcæmia tended to disappear in chronic hyperparathyroidism on a given dose of parathormone; an increase of Ca intake or hormone dosage increased the serum-Ca. The serum-P in chronic hyperparathyroidism in young puppies continued at or rose above the normal high level. The effects of single doses and of prolonged treatment with parathormone are described.

Chemical Abstracts.

Native complement in hyperthyroidism. N. Novick (Arch. Int. Med., 1931, **48**, 462—469).—A method of determining the complement val. by hæmolytic titration is described. In disagreement with the results of Hadjopoulos and Burbank (J. Lab. Clin. Med., 1928, **14**, 131), no increase of complement val. in hyperthyroidism is found. No relationship is apparent by comparing the post-operative and preoperative complement vals. with the basal metabolic rates.

A. Lawson.

Significance of the potassium–calcium ratio and of the inorganic phosphorus and cholesterol of the blood-serum in arterial hypertension. A. A. Weinstein and S. Weiss (Arch. Int. Med., 1931, **48**, 478—499).—Slight improvements in the Fiske–Logan (unpublished) and Taylor methods of determining Ca and K respectively are given, the former being found to give lower vals. than the Kramer–Tisdall or Jansen methods owing to the elimination of org. acids, MgC_2O_4, and excess $C_2O_4H_2$. In the cases examined, the average rise in K is 2·15 mg. per 100 c.c. of serum, this being most marked in hypertension with cardiac involvement. Allowing for factors other than hypertension, no appreciable rise in either Ca or cholesterol levels is found, a fact which does not support the hypothesis that these are fundamental in the development of arterial hypertension. Elevation of the K and cholesterol levels in one group of cases is considered as the result rather than the cause of changes in the cardiovascular system.

A. Lawson.

Blood-cholesterol in acute malaria. R. D'Alessandro (Arch. Farm. sperim., 1931, **52**, 258—268).—Acute malaria is generally accompanied by hypercholesterolæmia, which is intensified during fever in benign tertian or quartan malaria, but the reverse effect occurs in malign tertian malaria or mixed infections including this form.

R. K. Callow.

Significance of cerebrospinal-fluid sugar. E. F. Wahl (Arch. Int. Med., 1931, **48**, 446—461).—A high val. for the cerebrospinal-fluid sugar is not diagnostic of any given disease, but decreasing vals. are obtained as tuberculous and purulent meningitis progress.

A. Lawson.

Pathological physiology of pellagra. I—V. R. H. Turner (J. Clin. Invest., 1931, **10**, 61—70).—Serum-albumin tends to be low owing to digestive disturbance; serum-Ca is abnormal. Plasma-Cl′ and total acids are low.

Chemical Abstracts.

Chemical changes in the blood of the dog in experimental bile peritonitis. A. M. Ziegler and T. G. Orr (J. Exp. Med., 1931, **53**, 865—868).—The changes are similar to those found in experimental

peritonitis. The increase in blood-non-protein- and -urea-N is probably due to increased tissue destruction, and the fall in Cl′ to vomiting.

CHEMICAL ABSTRACTS.

Metabolism in pneumonia. II. Mechanism of retention of chloride. III. Excretion of anions and total base. I. GREENWALD (Arch. Int. Med., 1931, **48**, 418—439, 440—445).—II. Using dogs injected intratracheally with *Pneumococcus*, increase of Cl′ and subsequent retention in the urine is confirmed. Approx. agreement is shown between the retained Cl′ val. and that of the estimated increased body-fluid content.

III. The fact that there is no marked change in the anion–cation balance in pneumonia is confirmed.

A. LAWSON.

Ammonia content of the blood of women during pregnancy, labour and delivery, and childbed. L. STANOJEVIC (Biochem. Z., 1931, **239**, 257—272).—The NH_3 content of the blood of women rises just perceptibly in the 8th and 9th months of pregnancy, but quite distinctly during labour and delivery. During the first few days after delivery the content returns to its normal val. The part of the "mother substance" of the blood-NH_3 which gives up its NH_3 at room temp. seems to decrease during labour and delivery. W. MCCARTNEY.

Colloidal benzoin reaction for the diagnosis of neurosyphilis. G. RODILLON (Bull. Biol. Pharm., 1931, **3**, 313—318).—The flocculation produced by decreasing amounts of cerebrospinal fluid in a colloidal benzoin solution varies with the nature of the disease.

C. C. N. VASS.

Calcium and phosphorus metabolism in a case of non-tropical sprue with associated tetany. A. MARBLE and W. BAUER (Arch. Int. Med., 1931, **48**, 515—532).—Low serum-Ca and -P, the osteoporosis and tetany in sprue are not due to parathyroid deficiency, but to the inadequate absorption of Ca and P from the gastrointestinal tract because of existing diarrhœa. A very low val. of 124 mg. per 100 c.c. for total base in serum is reported.

A. LAWSON.

Relationship of guanidine metabolism and the activity of liver-arginase in tetany after parathyroidectomy in dogs. A. VON BEZNAK and K. SZEOKE (Biochem. Z., 1931, **239**, 159—162).—The activity of liver-arginase is the same for normal and parathyroidectomised dogs and the accumulation of guanidine in tetany of this type cannot arise from arginine. It is probably formed from the choline group of lecithin. P. W. CLUTTERBUCK.

Thrombo-angiitis obliterans (Buerger). VI. Chemistry of the blood. M. FRIEDLANDER and S. SILBERT (Arch. Int. Med., 1931, **48**, 500—506).—The blood in 40 cases shows increases in total ash, total protein, Ca, and cholesterol content. Cl′ and sugar content is normal. A. LAWSON.

Chemical view of pathogenesis of tuberculosis. E. R. LONG (Amer. Rev. Tuberculosis, 1930, **22**, 467—490).—A discussion. CHEMICAL ABSTRACTS.

Plasma-protein, red-cell sedimentation, and serum lability of the blood in tuberculosis. L. R. JONES (Amer. Rev. Tuberculosis, 1931, **23**, 325—332).—The plasma-protein was normal; fibrin was increased in 19 and (of these) globulin in 7 of 20 cases. Albumin was normal in 13 and low in 7 cases. In tuberculosis the average val. of the protein quotient was 1·47 (normal, 2·39). CHEMICAL ABSTRACTS.

Accumulation of iron in tuberculous areas. V. MENKIN and M. F. MENKIN (J. Exp. Med., 1931, **53**, 919—927).—Repeated intravenous injection of $FeCl_3$ is followed by accumulation of Fe in tuberculous areas of the lungs. CHEMICAL ABSTRACTS.

Differential quantitative tuberculin test. J. E. BLAIR and W. J. GALLAND (Amer. Rev. Tuberculosis, 1931, **23**, 1—2). CHEMICAL ABSTRACTS.

Oxygen consumption of tissues from rats fed with a diet deficient in cystine. R. GERSCHMANN (Rev. soc. argentina biol., 1930, **6**, 50—62).—A diet low in cystine diminishes O_2 consumption, glutathione, and oxidation–reduction power of tissues.

CHEMICAL ABSTRACTS.

Role of phosphate in biological oxidations. M. BARMORE and J. M. LUCK (J. Gen. Physiol., 1931, **15**, 97—105).—The rate of oxidation of glyceraldehyde by methylene-blue, α-naphthol-2-sulphonate-indophenol, and phenol-indophenol in presence of borate, phenylalanine, or carbonate at p_H 7·9 is increased by the addition of phosphate, whereas at p_H 4·77 in presence of phthalate buffer no catalytic effect of phosphate appears except in the case of α-naphthol 2-sulphonate-indophenol. Quant. observations on the rate of oxidation of glyceraldehyde by phenol-indophenol in presence of borate buffer over a range of p_H vals. are in agreement with the view that the PO_4''' ion is responsible for the catalysis of oxidation. W. O. KERMACK.

Conservation of rainfall as carbohydrates. W. A. OSBORNE (Nature, 1931, **128**, 378).—In arid countries of high temp. a fraction of the rainfall is locked up in carbohydrate mols. and becomes available for animal life. L. S. THEOBALD.

Regulatory action of yeast in deficient nutrition of rats. T. OSUKA (Biochem. Z., 1931, **239**, 163—171).—When glycogen utilisation is increased, *e.g.*, in bodily activity and when the type of diet influences the formation of glycogen unfavourably (in fat and in protein diets) addition of yeast to the diet increases the formation of glycogen. Yeast slightly decreases liver-glycogen of an animal on a mixed diet, but increases it by several times on a pure fat or protein diet. The fat contents of the fresh liver of rats on a mixed diet with or without addition of yeast are almost identical. On a pure protein diet, yeast causes an increase of body-fat and a slight decrease of liver-fat. On a carbohydrate diet the body-fat is greatly increased and the liver-fat slightly decreased.

P. W. CLUTTERBUCK.

Relation of glycogen to water storage in the liver. E. M. BRIDGE and E. M. BRIDGES (J. Biol. Chem., 1931, **93**, 181—187).—The variation in the glycogen content of the liver of rabbits induced by modifications of diet is accompanied by changes in one or more of the other components, a high glycogen content being associated with a low protein and, to

a smaller extent, fat and H_2O concentration. Thus the glycogen : H_2O ratio is not even approx. const., although the liver-H_2O per kg. body-wt. is fairly steady. Hence changes in body-H_2O are more likely due to changes in the metabolism of fats than that of carbohydrates. F. O. Howitt.

Fate of histidine in the animal organism. E. Abderhalden and S. Buadze (Z. physiol. Chem., 1931, **200**, 87—100).—Administration of *l*-histidine to dogs causes an increase in the total creatinine excreted in the urine, although the N metabolism remains const. Only a portion of the glyoxaline-N of *l*- and *d*-histidine reappears as such in the urine. Glycerol extracts of liver tissue attack *l*- and *d*-histidine. The enzyme has a broad optimum p_H 8—9. By the usual methods for NH_3 determination, the NH_3 recovered does not correspond with complete deamination. With more conc. alkali at 60° the amount of NH_3 obtained indicates a removal of N from the glyoxaline ring. J. H. Birkinshaw.

Methylamine as intermediate product of glycine degradation in the surviving liver. R. Kohn (Z. physiol. Chem., 1931, **200**, 191—208).—Glycine added to blood used for perfusion of the surviving liver of dogs gives rise to NH_2Me, which is detected by the carbylamine reaction, and determined by distillation after removal of NH_3 with HgO. In perfusion experiments only about 1% of the glycine yields NH_2Me. Considerable amounts of NH_2Me are rapidly withdrawn from circulation by the liver. No increase in NH_3 and only a small increase in urea are observed. J. H. Birkinshaw.

Absorption and utilisation of the carbohydrate of *Arctium lappa* as shown by a protein-sparing action on the diet of dogs. J. C. Krantz, jun., and C. J. Carr (J. Pharm. Exp. Ther., 1931, **43**, 187—191).—The drop in N output (7·6%) of dogs fed a protein diet when burdock (*A. lappa*) root is added indicates a protein-sparing action comparable with that of pure inulin (cf. A., 1922, i, 82). F. O. Howitt.

Nitrogen metabolism in infants on graded intake of soya-bean "milk" proteins. E. Tso and F. T. Chu (Chinese J. Physiol., 1931, **5**, 287—294).—In young infants fed on soya-bean "milk" furnishing 120—150 g.-cal. per kg. body-wt., adequate N retention is obtained when 18% of the cals. is provided in the form of protein. On cow's milk feeding, in which 10—14% of the cals. is furnished in the form of protein, 38—42% of the N intake was retained, whilst on soya-bean "milk" in which 8—18% of the cals. was provided as protein 14—30% of the N ingested was retained. At different levels of intake with soya-bean "milk" the ratio of N absorbed to N ingested is approx. const. at 80%, the corresponding figure in the case of cow's milk being 95%. W. O. Kermack.

Salts and protein metabolism. E. Gerhartz (Biochem. Z., 1931, **239**, 404—416).—Administration of $CaCl_2$ or KCl to dogs favours or reduces excretion of N according as there are or are not sufficient salts in the food consumed. The N balance is impaired by administration of PO_4'''. The unfavourable results are probably due to the interference with the electrolyte equilibrium. In case of $CaCl_2$ administration corresponding changes take place in the utilisation of N, but distinct results are not obtained with other salts. W. McCartney.

Influence of growth on a number of constituents of the white rat. A. Chanutin (J. Biol. Chem., 1931, **93**, 31—37).—The variations in the following constituents with age of the animal were studied from birth in normal rats, eviscerated before analysis: total solids, org. (*i.e.*, dry, fat- and ash-free) tissue, org. and wet tissue-creatine, -N, and ash and the Et_2O-extractable substances of the org. tissue. The greatest increase in all the constituents investigated occurred during suckling. Creatine reached a max. in 30—40 days and the fat and ash in 20 days, whilst the N concentration remained const. throughout life. F. O. Howitt.

Normal retention of food-iron during growth and the utilisation of the iron of protein foods. R. C. Miller (Proc. Amer. Soc. Animal Produc., 1928, 21—25).—The Fe content of rats decreases very rapidly during suckling, rapidly rising to a const. val. when solid food is ingested. Meat diet leads to a high, and milk powder to a low, Fe content. Chemical Abstracts.

Significance of minerals in the mixed foods of domestic animals. N. Hansson (Bied. Zentr., 1931, **B**, **3**, 137—173).—Analyses of numerous fodder and other crops show that the essential mineral constituents of animal rations may be ensured by the properly regulated use of these feeding stuffs. Where insufficient grass or hay is available mixtures of bone meal, $CaCO_3$, Na phosphates, and NaCl are satisfactory supplements and cod-liver oil may be used in extreme cases. A. G. Pollard.

Phosphatic limestone and other rock products as mineral supplements. C. Tolle and L. A. Maynard (Proc. Amer. Soc. Animal Produc., 1928, 15—21).—Phosphatic limestone (Ca phosphate 23, $CaCO_3$ 70%), bone meal, and limestone were equally effective as sources of Ca for bone development in rats, but rock phosphate was much less effective. The presence of F causes changes in tooth structure. Chemical Abstracts.

Phosphorus metabolism in embryonic life. I. Invertebrate eggs. J. Needham and D. M. Needham (J. Exp. Biol., 1930, **7**, 317—347).—Considerable differences in P distribution are recorded. Chemical Abstracts.

Effect on abnormal skeletal mineral metabolism of the Ca Mg salts of inositolphosphoric acid together with biologically active plant extracts. B. Bleyer and F. Fischler (Biochem. Z., 1931, **239**, 224—231).—By administration of McCollum's diet to rats, a decrease of total mineral content of the bones and an abnormal composition in individual bone constituents are obtained. Normality is completely restored in 4 weeks by administration of Ca Mg inositolphosphate. P. W. Clutterbuck.

Calcium content of the body in relation to that of the food. H. C. Sherman and L. E. Booher (J. Biol. Chem., 1931, **93**, 93—103).—Ca determinations

were made on the ash of eviscerated rats raised on diets of varying Ca content. With full diets varying only in Ca content the body-Ca varied in accordance with the food-Ca. Rats on a Ca-poor diet increased very slowly in body-wt. and consequently had a higher body-Ca than those on a diet richer in Ca. Hence with a Ca-poor diet the average normal adult body-Ca (1·09% for males and 1·23% for females) was attained at a late age. With certain lower levels of Ca intake the appearance and growth were normal but the bodies were poor in Ca. F. O. Howitt.

Calcium. V. Blood and urine levels after peroral and deep muscular administration of calcium gluconate in man. A. L. Lieberman (J. Pharm. Exp. Ther., 1931, **43**, 139—145).—Whilst there is no direct quant. correlation between the blood- and urine-Ca the latter can serve as a qual. index of the former. Thus a urinary Ca output greater than 10 mg. per hr. indicates a rise of blood-Ca. F. O. Howitt.

Absorption and retention of calcium chloride and phytin. J. C. Forbes and H. Irving (J. Pharm. Exp. Ther., 1931, **43**, 79—83).—When $CaCl_2$ or phytin was fed to young rats on a diet of known Ca content the retention of Ca was of the same order for each salt. F. O. Howitt.

Relationships between parathyroids, calcium metabolism, and bone-growth. E. Bulbring (Arch. exp. Path. Pharm., 1931, **162**, 209—248).—In normal rats, serum-Ca and retention of Ca are not increased by a Ca-rich diet, and the Ca : P ratio varies with the diet-Ca. Parathyroidectomy causes a temporary increase in Ca and P retention in the soft parts, a fall in serum-Ca which is intensified by a Ca-rich diet, and a fall in bone-Ca which is prevented by Ca feeding. "Parathormone" decreases Ca and P retention and Ca and P content of bone, the effects being more marked on Ca-rich, and modified or reversed by Ca-poor, diet. The increased serum-Ca caused by the hormone is most pronounced on a Ca-rich diet. A. Cohen.

Muscle structure and aerobic carbohydrate formation. A. Hahn, H. Belmonte, and H. Niemer (Z. Biol., 1931, **91**, 491—495).—Carbohydrate formation by the frog sartorius muscle immersed in lactate-Ringer solution and in presence of O_2 is reduced to 33% in isotonic and to 13% in hypertonic solution by transverse section of the fibres, whilst longitudinal section gives vals. agreeing with the intact muscle. Thus the non-formation of carbohydrate by pulped muscle is explained (cf. this vol., 258). The process of recovery is also probably dependent on the structure. F. O. Howitt.

Formation of lactic acid in muscular work after removal of the suprarenal glands. A. von Árnay and L. Lengyel (Biochem. Z., 1931, **239**, 128—137).—The formation of lactic acid in 67 muscles taken from adrenalectomised rats during rest, work, after tetanic stimulation, and in rigor is very greatly decreased. P. W. Clutterbuck.

Phosphorylation and production of lactic acid in muscles and organs. B. Tankó (Biochem. Z., 1931, **239**, 318—323; cf. A., 1929, 1106).—When human striped muscle and striped muscle from the pigeon, pig, rat, and guinea-pig are compared as regards phosphorylation, it is found that the process takes place most strongly in pigeon breast-muscle, which also yields most lactic acid from glycogen. In human muscle (from the leg) also phosphorylation usually proceeds rather strongly with production of lactic acid, but in cases where this is not so addition of boiled muscle-juice containing co-enzyme stimulates the process considerably. Phosphorylation and lactic acid production proceed strongly in fresh heart-muscle (dog) and even more strongly in pig heart-muscle, whilst in pig liver the process is less pronounced, although here also phosphorylation can be stimulated by addition of boiled muscle-juice. This juice also causes phosphorylation and lactic acid production in pig abdominal muscle, kidneys, and brain, in which, otherwise, these processes do not occur. W. McCartney.

Insulin and phosphorylation. J. Bodnar and B. Tankó (Biochem. Z., 1931, **239**, 314—317; cf. this vol., 520).—Since it exerts no influence on phosphorylation under physiological conditions (no glycogen or NaF added, low phosphate concentration) in fresh muscle pulp, muscle powder, or muscle powder poor in co-enzyme and since phosphorylation proceeds briskly in the leg muscle of dogs from which the pancreas has been removed, insulin cannot be regarded as a sp. activator of muscle-phosphatase. W. McCartney.

Fate of *p*-chlorobenzoic acid in the animal organism. J. Wührer (Arch. exp. Path. Pharm., 1931, **161**, 719—729).—Na *p*-chlorobenzoate administered to dogs or rabbits is excreted in the urine partly unchanged and partly combined with glycine in the form of p-*chlorohippuric acid*, m. p. 148°. W. O. Kermack.

Poisoning by acetic acid. R. W. Blair (Analyst, 1931, **56**, 596—597).—The symptoms are described. To identify AcOH the stomach and intestines are steam-distilled, the distillate is made just alkaline with NaOH and evaporated, and the AcOH is esterified with EtOH. T. McLachlan.

Behaviour of bees towards honey-dew containing melezitose. F. E. Nottbohm and F. Lucius (Z. Unters. Lebensm., 1931, **61**, 314—321).—A destructive criticism of Elser's statement (cf. *ibid.*, 1930, **60**, 332) that melezitose is non-injurious to bees (cf. B., 1929, 955). H. J. Dowden.

Poisonous action of ingested saponins. A. J. Ewart (Counc. Sci. Ind. Res. Austral., Bull. 1931, **50**, 28 pp.).—The toxic action of saponin and saponin-containing plant extracts on guinea-pigs and stock is described. Ingested saponin is hydrolysed in the alimentary canal and only a small fraction is absorbed. It acts indirectly on the central nervous system. The liver, in affording protection from the toxic effects, undergoes fibrosis. Saponin-containing plants are probably responsible for certain stock diseases. A. Cohen.

Ethyl alcohol. I. Micro-determination. II. Oxidation in a small homeotherm and in a poikilotherm at different temperatures. M. Nicloux (Bull. Soc. Chim. biol., 1931, **13**, 857—918).

—For complete oxidation of EtOH to AcOH a slight excess of standard $K_2Cr_2O_7$ is added to 5 c.c. of the dil. EtOH mixed with 0·5 vol. of 66% H_2SO_4, and the mixture heated in a stoppered bottle at 85° for 1 hr. After cooling, a slight known excess of $Fe(NH_4)_2(SO_4)_2$ is added and the excess titrated with standard $KMnO_4$.

II. With subcutaneous injection of small quantities of EtOH in mice (1 c.c. per kg.), oxidation is rapid and only 3·7% is eliminated by way of the lungs and skin in 2 hr., as opposed to 10% in 8 hr. in the case of larger quantities (about 7 c.c. per kg.). In a frog 24 hr. are required at 30° to effect complete oxidation of a quantity of EtOH which is oxidised in 2 hr. in a mouse, whilst at 12° only 31·3% is oxidised.

P. G. Marshall.

Anæsthetic action of furan. J. F. A. Johnston (J. Pharm. Exp. Ther., 1931, **43**, 85—88).—Inhalation of furan vapour in cats induces an unsuitable type of anæsthesia. F. O. Howitt.

Anæsthetic potency in the *cyclo*-hydrocarbon series. V. E. Henderson and J. F. A. Johnston (J. Pharm. Exp. Ther., 1931, **43**, 89—92).—The anæsthetic potency of *cyclo*hexane is 4·8 times that of *cyclo*propane for anæsthetic concentrations and 3·2 times for fatal concentrations (cf. A., 1929, 1104; 1930, 639). F. O. Howitt.

Reversible coagulation in living tissue. W. D. Bancroft and J. E. Rutzler, jun. (Proc. Nat. Acad. Sci., 1931, **17**, 482—484).—The effect of anæsthetisation is a reversible coagulation of proteins in both plants and animals. In plants there is a preliminary stage of excitation before anæsthetisation sets in. The sensitivity of *Mimosa pudica* can be increased by the addition of peptising agents (*e.g.*, NaCNS) and by coagulating agents (*e.g.*, Na citrate). Bernard's theory of anæsthesia is applicable to plants as well as animals. A. J. Mee.

Physiology of phenol. B. A. Houssay and A. D. Marenzi (Anal. Farm. Bioquim., 1931, **2**, 75—80).—The disappearance of PhOH, after intravenous injection into dogs, from the blood is due to the action of the kidneys and its conjugation (*e.g.*, with H_2SO_4) is a very general action and proceeds rapidly in the small intestine. T. H. Pope.

Action of rarefaction of air on the hæmoglobin and resistance of the erythrocytes in rabbits treated with "pyrodin." F. Heimann (Arch. exp. Path. Pharm., 1931, **161**, 686—691).—The red blood-corpuscles of normal rabbits which have been kept in a partly exhausted chamber have a max. resistance to hæmolysis by hypotonic NaCl solution much above normal and an approx. normal min. resistance. The max. resistance increases further after administration of "pyrodin." The red blood-corpuscles of rabbits which have been poisoned with "pyrodin" have a low hæmoglobin content and a min. resistance above normal. When these rabbits are kept in a partly exhausted chamber, the min. resistance decreases and the max. resistance rises.

W. O. Kermack.

Antipyretic action of *p*-acetamidourethanes. R. F. B. Cox, C. R. Eckler, and R. L. Shriner.—See this vol., 1287.

Influence of cinchophen derivatives on the uric acid excretion in the bile of rabbits. M. Yamagami (Folia Pharmacol. Japon., 1931, **12**, 53—66).—After subcutaneous injection of erycon (0·2 g.) into rabbits the bile-uric acid is considerably increased, but the quantity of bile is practically unaltered. The changes following splanchnectomy and vagotomy are recorded; there is a close connexion between the splanchnic and vagus nerves and uric acid excretion. Chemical Abstracts.

Detection and separation of barbituric acid derivatives in toxicological examination. J. J. L. Zwikker (Pharm. Weekblad, 1931, **68**, 975—983).—The deep blue complex Ba Co compound formed when the extract is treated in MeOH solution with $CoCl_2$ and $Ba(OMe)_2$ is sp. Quant. separation from Et_2O extracts of urine is effected by dissolving the residue after evaporation of Et_2O in H_2O containing pyridine, precipitating a Cu pyridine barbiturate, collecting, washing, and treating with acid. S. I. Levy.

Sensitiveness to alkali as a distinction between choline and acetylcholine. K. Velhagen (Arch. exp. Path. Pharm., 1931, **161**, 697—702).—Acetylcholine is more sensitive to dil. alkali than is choline. This observation is of use in the detection of acetylcholine in cell extracts. W. O. Kermack.

Production of a compound with histamine-like action from histidine by cathode rays. F. Ellinger (Arch. exp. Path. Pharm., 1931, **161**, 703—712).—By irradiation of solutions of histamine hydrochloride or of the solid salt by cathode rays a compound is formed resembling histamine in its actions on the intestine and the uterus (cf. A., 1930, 638, 1472). W. O. Kermack.

Blood-electrolytes during histamine shock in dogs. D. W. Atchley, D. W. Richards, jun., and E. M. Benedict (J. Clin. Invest., 1931, **10**, 1—7).—Concentration of blood, uncompensated lactic acidosis with increase in serum-total base and decrease in serum-HCO_3', increase in serum-inorg. phosphate, and decrease in O_2-saturation are observed.

Chemical Abstracts.

Antagonism between the action of atropine and that of acetylcholine, pilocarpine, and physostigmine on the isolated rabbit's uterus. M. Takahashi (Folia Pharmacol. Japon., 1931, **12**, no. 1, 102—110).—The action of acetylcholine is increased and of pilocarpine decreased. When the action of physostigmine is weak it is not completely inhibited by atropine. Chemical Abstracts.

Action of pilocarpine on the rabbit's blood-sugar. G. Carbonaro and F. Salamone (Arch. Farm. sperim., 1931, **53**, 1—16).—Doses of 0·01—0·05 mg. of pilocarpine per kg. body-wt. exert a hypoglycæmic effect without causing other apparent disturbance; 0·1 mg. per kg. has slight and inconstant effects, whereas 5 mg. exhibit a biphasic effect, namely, primary hyperglycæmia accompanied by the manifestations of general pilocarpine action, followed by hypoglycæmia. From the pharmacodynamic viewpoint pilocarpine must, therefore, be regarded as having amphotropic action. T. H. Pope.

Blood-sugar in animals after administration of morphine and the theoretical basis of the dextrose-insulin treatment of morphinism. G. Anton (Arch. exp. Path. Pharm., 1931, **161**, 646—668).—The rise in blood-sugar which occurs in dogs after the administration of morphine runs parallel with increased blood acidity and is not inhibited by pituitary or ergotamine, but may be reduced by the administration of alkali. W. O. Kermack.

Influence of the nervous system on blood-sugar. II. Action of ergotamine on blood-sugar level and arecoline hyperglycæmia. G. Carbonaro (Arch. Farm. sperim., 1931, **52**, 241—257).—Subcutaneous injection of ergotamine into rabbits causes a considerable hypoglycæmia, due to its paralysing action on the sympathetic. The hyperglycæmia produced by arecoline is prevented by first injecting ergotamine, and the effect of arecoline is, therefore, produced by action on the sympathetic. R. K. Callow.

Toxicological detection of coniine. O. Krayer (Arch. exp. Path. Pharm., 1931, **162**, 342—372).—A forensic study. The similarity in properties of coniine and bases present in putrefied material from a corpse is discussed. Coniine hydrochloride may be separated by micro-sublimation. A. Cohen.

Coniine-like properties of some amines. O. Krayer and W. Koll (Arch. exp. Path. Pharm., 1931, **162**, 373—384).—Coniine cannot be distinguished chemically from a number of volatile basic putrefaction products. The contracting effect on the abdominal muscle of the frog is also possessed by *iso*amylamine, β-phenylethylamine, and pyrrolidine. A. Cohen.

Distribution and excretion of coniine hydrochloride. S. Thaddea (Arch. exp. Path. Pharm., 1931, **162**, 385—394).—The distribution of coniine in guinea-pigs at varying times after administration has been determined quantitatively by micro-sublimation of the hydrochloride. The lethal subcutaneous and oral doses are 4 and 15 mg. per 100 g. body-wt., respectively. Subcutaneously, coniine is quickly and widely distributed in the blood and organs, and 75% of coniine *per os* is absorbed from the gastro-intestinal tract in 45 min. In a few hr. 80—90% of the alkaloid (by either route) is destroyed in the body whilst 10% is excreted in the urine in 24 hr. in quantities increasing in the first 4—5 hr. Traces only are excreted in the fæces. A. Cohen.

Determination of traces of strychnine. W. Koll (Arch. exp. Path. Pharm., 1931, **162**, 307—319).—Strychnine is precipitated in H_2SO_4 solution by neutral phosphomolybdate. The ppt. gives a bluish-violet colour with NH_4 vanadate in conc. H_2SO_4, changing to orange, which serves for the colorimetric determination of the alkaloid ($\pm 3\%$). A. Cohen.

Detection of strychnine in organs. W. Koll (Arch. exp. Path. Pharm., 1931, **162**, 320—341).—EtOH extraction yields only 15—40% of the strychnine content of organs, as shown by colorimetric determination (cf. preceding abstract). This is due to adsorption of the alkaloid on protein and on filters used in manipulation. A method is described whereby proteins are first digested with pepsin and trypsin. Strychnine is then extracted by dil. H_2SO_4 and HCl, and from the latter by $CHCl_3$. Of 2 mg. of strychnine added to 100 g. of tissue, 90% is recovered. An extraction apparatus for solvents heavier than H_2O is described. A. Cohen.

Potentiation of toxicity of strychnine by quinine. R. I. Grantham and J. C. Munch (J. Assoc. Off. Agric. Chem., 1931, **14**, 295—296).—Mixtures of strychnine and quinine cannot be assayed by their toxicity to rats, owing to potentiation of toxicity. The lethal dose of mixtures containing 83% or more of quinine, injected subcutaneously into white rats, is about 1·0 mg. of strychnine per kg. body-wt., the lethal doses of strychnine and quinine being 2·5 mg. and 1000 mg. respectively. W. J. Boyd.

Spermicidal powers of contraceptives. II. J. R. Baker (J. Hyg., 1931, **31**, 189—214).—The toxic effect of pure substances on guinea-pig sperm was determined. The [H$^\cdot$] of acids is the determining factor. Substances which reduce surface tension may be effective. Chemical Abstracts.

Carbon monoxide poisoning. Its detection, and the determination of percentage saturation in blood, by means of the Hartridge reversion spectroscope. R. C. Frederick (Analyst, 1931, **56**, 561—571).—For each instrument a curve must be plotted connecting the span with % saturation. The span for CO-hæmoglobin is plus compared with oxy-hæmoglobin and cannot be confused with that of NO-hæmoglobin, which is negative. T. McLachlan.

Investigation of carbon monoxide poisoning. J. S. Haldane (Analyst, 1931, **56**, 571).—The use of a spectroscope for the determination of CO-poisoning is unnecessary. NO-poisoning may be detected in blood samples taken during life by the presence of methæmoglobin, and in the cadaver by the colour of the clot on boiling. T. McLachlan.

Detection of hydrogen cyanide and its alkali salts in viscera and other products by formation of Prussian-blue. G. Magnin (J. Pharm. Chim., 1931, [viii], **14**, 233—236).—Air is drawn through the substance under investigation and passed over a strip of filter-paper moistened with 5%KOH. The paper is then treated with a few drops of very dil. aq. $FeSO_4$ and a few drops of 10% HCl. The intensity of the blue colour is proportional to the amount of HCN present. 1 part HCN in 1,000,000 parts can be detected by this method. C. C. N. Vass.

Effect of prolonged iodine feeding on the iodine content of animal organs. S. Weiser and A. Zaitschek (Bied. Zentr., 1931, **B**, **3**, 275—297).—Prolonged feeding of KI (35—125 mg. daily) increased the I content of all organs and tissues (but not bones) of goats and their suckling kids. Cessation of I administration decreased the I content of the thyroid gland, blood, milk, liver, bile, spleen, pancreas, and reproductive organs to vals. which remained above normal. In other organs vals. returned to normal. Skin, hair, and hoofs retained an increased I content. Changes in the I contents of the organs of suckling

kids were not always of the same order as those of their dams. A. G. POLLARD.

Iodine tolerance of goats. S. WEISER and A. ZAITSCHEK (Bied. Zentr., 1931, B, 3, 298—301; cf. A., 1930, 495).—For goats of all ages and both sexes the optimum daily dose of I is 1 mg. per kg. live wt. Administration may be continued indefinitely. For milch goats 2 mg. per kg. live wt. was used for several weeks without ill effects.
A. G. POLLARD.

Pharmacology of iodine. I. Action of iodine on cholesterol and ergosterol sclerosis. H. SEEL and G. CREUZBERG (Arch. exp. Path. Pharm., 1931, 161, 674—685).—Sclerosis produced in animals by administration of cholesterol or irradiated ergosterol is favourably influenced by I either in inorg. (KI) or in org. ("Iodotropin") form, the effect being more marked in the case of cholesterol than of irradiated ergosterol. W. O. KERMACK.

Detoxication of phosphorus by sugar. R. SCHOLL (Biochem. Z., 1931, 240, 62—67).—The lethal dose of P when subcutaneously injected into rats is 8 mg. per kg. but increases when inulin is fed to 12—15 mg. per kg. The toxicity of As derivatives is not similarly influenced by a rich carbohydrate diet.
P. W. CLUTTERBUCK.

Effect of intravenous injection of "novarsenobenzol" on blood-nitrogen, -sugar, and -cholesterol. A. LEULIER, J. GATE, and P. LINARD (Compt. rend. Soc. Biol., 1930, 105, 12—13; Chem. Zentr., 1931, i, 2780).—No changes were observed.
A. A. ELDRIDGE.

Effects of varying calcium and phosphorus intake on the œstrus cycle and reproduction in the rat. H. R. GUILBERT and G. H. HART (Hilgardia, 1930, 5, no. 5, 101—118).—A diet containing 0·22% P and Ca : P=4 : 1 fed to female rats from weaning seriously interfered with growth and sexual maturity. In mature rats receiving a diet having 0·18—0·22% P and Ca : P=4 : 1 up to 100 days old, ovulation was irregular or ceased entirely. This proportion of P, however, suffices to maintain a normal œstrus cycle after 110 days of age. With a diet containing Ca : P=8 : 1 ovulation ceased in mature rats. Lowering the Ca content of the ration from 0·82 to 0·22% did not limit growth or reproductive functions. A. G. POLLARD.

Influence of irradiation on the behaviour of silver in the organism. II. Silver in the organs of full-grown rats. L. PINCUSSEN and W. ROMAN (Biochem. Z., 1931, 239, 374—403; cf. this vol., 652).—When Ag (as Ag_2SO_4) is injected in 6- or 12-mg. doses into full-grown male rats the proportions of the three Ag fractions found in the blood, liver, kidneys, spleen, heart, lungs, skin, and hair are independent of the size of the dose, although the total amount of Ag found in these organs is greater when the dose is 6 than when it is 12 mg. The liver retains most, the blood least of the Ag. Except in the liver, where most of the Ag is retained as Ag–protein compound, most of the metal occurs as ionised Ag. Irradiation of the rats after administration of the Ag decreases the amount of the metal recovered in the organs and alters the proportions of the various Ag fractions in them. The magnitude of the decrease depends on the intensity, duration, and type of radiation. Moderate irradiation favours increase in the Ag-protein fraction, strong irradiation leads to increase in the metallic Ag fraction. Clipped rats are more strongly affected by irradiation than are unclipped. W. MCCARTNEY.

Action of *X*-rays on the material of inner secretion and organ poisons. B. TERATA and R. ITO (Folia Pharm. Japon., 1931, 12, no. 1, 67—73).—The effect of adrenaline on blood-pressure is increased by "moderate" *X*-rays but inhibited by "strong" rays; that of pituitrin and thyroid extract is increased, whilst that of histamine and peptone is decreased, by the rays. CHEMICAL ABSTRACTS.

Metabolic changes produced by irradiation. VIII. Effect of irradiation and of insulin on the substances in the organs which affect the sugar content of the blood. L. PINCUSSEN. **IX. Glutathione content of the organs.** L. PINCUSSEN and S. YOKOTA (Biochem. Z., 1931, 239, 290—302, 303—309; cf. this vol., 872).—VIII. From the pancreas, liver, hind-leg muscle, lungs, spleen, and skin of the treated guinea-pigs (donors) extracts were made and injected into other guinea-pigs (the receivers), in which the blood-sugar content was then determined. All the extracts from normal donors living in diffused light reduced the blood-sugar in the receivers, the pancreas extract having the greatest effect. The blood of the donors also always contained agents which altered the blood-sugar in the receivers. Extracts from the organs of donors kept in the dark increased the blood-sugar in the receivers. In donors (especially in those kept in the dark) to which insulin was administered the blood-sugar was reduced, but extracts from these donors increased the blood-sugar in the receivers. Very similar effects were obtained with donors irradiated with a "vitalux" lamp. Irradiation of the donors with various types of light and with heat rays reduced the sugar content of the blood except when the irradiation was by a quartz lamp and was of short duration. In the latter case the blood-sugar was increased whilst if the irradiation lasted longer it was reduced. Extracts from the organs of donors irradiated with the quartz lamp increased or reduced the blood-sugar in the receivers according as the period of irradiation had been short or long. Although in the case of irradiation by quartz and "vitalux" lamps extracts from all the organs of the donors acted alike, in that of the Ne and Na lamps and of the heat rays extracts of different organs had different effects. It is concluded that the effects produced may be attributed to the production and action of a substance similar to adrenaline which acts antagonistically to insulin, and the similarity between the effects of insulin and those of irradiation is emphasised.

IX. In guinea-pigs irradiation with a Hg-vapour lamp appears to cause increase in the glutathione content of the liver, lungs, and muscle, but to have no effect on that of the spleen. In white rats the increases are very distinct in liver and lungs, whilst there is no change in the amount of glutathione in the muscle, but a slight decrease in the amount in

the spleen. In general, the stimulating effect of irradiation on the metabolism has been confirmed.

W. McCartney.

Influence of sweet material on biocatalysis and metabolic processes. II. Action on blood-sugar and liver-glycogen in rabbits. W. Diemair and F. Fischler (Biochem. Z., 1931, **239**, 232—234).—No disturbance occurs in the carbohydrate metabolism of rabbits receiving large doses of saccharin for a long time. P. W. Clutterbuck.

Amylases of malt and potato. H. Borchardt and H. Pringsheim (Biochem. Z., 1931, **239**, 193—200).—The prep. of maltase-free amylases and their characterisation are described.

P. W. Clutterbuck.

Viscosimetric method of estimating enzyme concentration, with special reference to amylase. W. R. Thompson, C. E. Johnson, and R. Hussey (J. Gen. Physiol., 1931, **15**, 1—7).—The viscosimetric method for the determination of enzyme concentration has been improved and applied to the determination of amylase (cf., A., 1923, ii, 271). W. O. Kermack.

Effect of radiations from a mercury arc in quartz on enzymes. II. Effect of ultra-violet radiation on amylase in solution. W. R. Thompson and R. Hussey (J. Gen. Physiol., 1931, **15**, 9—13).—The activity of pancreatic amylase solutions decreases under the influence of the radiation of a quartz–Hg-vapour lamp exponentially with time (cf. A., 1926, 202). The sensitiveness to irradiation is greater than with pepsin solutions.

W. O. Kermack.

Influence of temperature on the formation of reducing material in the autosaccharification of rye meal. S. Pronin (Biochem. Z., 1931, **240**, 94—97).—The max. autosaccharification, expressed as maltose % of the meal starch, is for two kinds of rye meal 46·34 and 52·24%. The process has an optimum temp. zone at 55—64°.

P. W. Clutterbuck.

Amylosynthease. S. Nishimura and T. Minagawa (Proc. Imp. Acad. Tokyo, 1931, **7**, 258—260).—A 1% solution of achroodextrin at p_H 6·2 was treated in the presence of $CHCl_3$ with a filtrate from autolysed yeast. After keeping at 25—26°, a ppt., which formed in 84% yield, was collected, washed with EtOH and Et_2O, and dried; it gave a bluish colour with I. Amylosynthease is destroyed at 60°. It is present in wine, press, and distiller's yeasts, and in *Saccharomyces Biwa* and *Mycoderma*.

C. C. N. Vass.

Disaccharide fission by α-glucosidase. R. Weidenhagen (Z. physiol. Chem., 1931, **200**, 279).—A neutral phosphate extract of the dry prep. of *B. coli* I. used by Myrbäck (this vol., 983) was inactive but a PhMe autolysate hydrolysed weakly both maltose and sucrose. J. H. Birkinshaw.

Contraction constants of enzyme–substrate reactions. M. Sreenivasaya and H. B. Sreerangachar (Nature, 1931, **128**, 585).—The contraction per g.-mol. of substrate is a const. for each enzyme–substrate system; for urea–urease the const. is 24, and for sucrose–invertase, 6. L. S. Theobald.

Role of pectase in the fermentation of coffee. A Perrier (Compt. rend., 1931, **193**, 547—549).—The spontaneous elimination of the undesirable mucilaginous layer on coffee seeds is not due to direct microbic action. It is solubilised by the digestion of its pectins by pectase under favourable temp. conditions arising from simultaneous fermentation occurring in the seed. A. Cohen.

Animal phosphatase and sulphatase. C. Hommerberg (Z. physiol. Chem., 1931, **200**, 69—81).—Enzyme material from different organs shows the same ratio between phosphatase and sulphatase activity. Brain preps. of the pig, calf, and rabbit show no greater activity than those of pig's kidney. Phosphatase but not sulphatase was found in autolysates or eluates. Shaking dry preps. of pig's kidney with H_2O or dil. aq. NH_3 increases their activity. The washed prep. contains less P than the original; when the original P is restored, inhibition is observed. Addition of $MgCl_2$ to the dry prep. activates phosphatase and inhibits sulphatase. The inhibition may be due to the formation of $MgCO_3$ since $CaCO_3$ is present as sulphate acceptor.

J. H. Birkinshaw.

Gluco-sulphatase. T. Soda and C. Hattori (Proc. Imp. Acad. Tokyo, 1931, **7**, 269—270).—In the autolysates of some Japanese snails (*Eulota* spp.) is an enzyme which exerts a sp. hydrolysis of dextrose-monosulphate, optimum p_H 7. C. C. N. Vass.

Presence of a gelatin-liquefying enzyme in crude pepsin preparations. J. H. Northrop (J. Gen. Physiol., 1931, **15**, 29—43).—An amorphous fraction isolated from crude pepsin preps. shows high gelatinase activity, being 400 times as active in liquefying gelatin as is cryst. pepsin. The initial val. of the ratio (decrease in viscosity)/(increase in "formol-N") is much greater in the case of gelatinase than in the case of cryst. pepsin. Its action on caseinogen, edestin, and ovalbumin is relatively weak. It is more stable to alkali than is cryst. pepsin, being inactivated at p_H 11—12 and partly reactivated when its solution is brought back to p_H 6. W. O. Kermack.

Action of trypsin on solutions of monoamino-acids, alone or in mixtures. A. Blanchetiere (Compt. rend., 1931, **193**, 549—550; cf. this vol., 1090).—Under the influence of trypsin at p_H 8·0, NH_2-N slowly decreases in solutions of glycine, alanine, and a mixture of both, alanine showing the greatest loss (10%). The formation of diketopiperazines is demonstrated by the Abderhalden and Kamm reaction.

A. Cohen.

Effect of temperature on the degradation of collagen by pancreatin. F. Stather and H. Machon (Biochem. Z., 1931, **239**, 430—433).—The action of pancreatin in an enzyme mixture from fish viscera on collagen in the presence of borate–HCl buffer exhibits a max. at about 50°. In the absence of the buffer the action also reaches a max. which is shifted towards high temp. as the concentration of the enzyme is increased. W. McCartney.

Influence of heavy metals and metal complexes on proteolytic processes. L. Michaelis and K. G. Stern (Biochem. Z., 1931, **240**, 192—217).—Further

work (cf. this vol., 874) is described on the effect of heavy metals (varying amounts of Hg^{II} salts, complexes containing Zn, Co, Fe, etc.) on the degradation of dissolved organ proteins by tissue proteinase (cathepsin), the process being followed nephelometrically. Certain complex compounds, especially Zn and Fe dipyridyl complexes, accelerate the early stages of degradation more strongly than the same metal in the ionic form. With Fe^{II} and Fe^{III} compounds of varying complex types every effect is obtained from activation to complete inactivation, the valency of the Fe not playing any decisive role. The degradation of gelatin by trypsin is studied in terms of the NH_2-groups liberated. At p_H 8, Zn, Hg, and Mn salts inhibited the enzyme but $FeSO_4$ activated it.

P. W. CLUTTERBUCK.

Effect of oxygen, carbon dioxide, and cysteine on arginase. S. SALASKIN and L. SOLOVIEV (Z. physiol. Chem., 1931, **200**, 259—260).—CO_2 inactivates arginase slightly, O_2 more strongly. Cysteine reactivates the arginase after passage of O_2 or CO_2, but subsequent O_2 treatment again inactivates. Cysteine has no effect. Probably the O_2 oxidises cysteine to cystine, thus destroying the activating effect.

J. H. BIRKINSHAW.

Enzymes and light. XVII. Tyrosinase. L. PINCUSSEN and T. HAMMERICH (Biochem. Z., 1931, **239**, 273—289).—A modification of Raper's method (A., 1926, 977) for the prep. of tyrosinase and of Raper and Wormall's method (A., 1923, i, 1146) for its (micro-)determination are described. Methods are also given for the volumetric determination of 3 : 4-dihydroxyphenylalanine, of this compound and tyrosine together, and of the red intermediate product (colorimetrically) produced by the action of tyrosinase on these two substances. The activity of tyrosinase and the production of the red substance are greatly reduced by irradiation, which also decomposes both compounds, tyrosine particularly in the acid region and dihydroxyphenylalanine particularly in the alkaline. The formation of melanin from the compounds is favoured by the presence of Fe. In a mixture of the two acids containing tyrosinase the dihydroxyphenylalanine content increases at first as a result of the oxidation of the tyrosine and the oxidation of the latter is favoured by the presence of the former. It follows that the production of melanin from tyrosine or similar substances in the skin is not due to the effect of ultra-violet light on tyrosinase.

W. McCARTNEY.

Mitogenetic spectrum analysis. III. Detailed glycolytic spectrum. J. PONOMAREVA (Biochem. Z., 1931, **239**, 424—429; cf. this vol., 1083).—The technique of mitogenetic spectrum analysis is described. Results are tabulated for *B. acidi lact.* from whey; rabbit blood; rabbits' eyes; and an EtOH solution of an active wine yeast from beer wort. In each case five prominent bands comprise the glycolytic spectrum occurring at 1900—1910, 1910—1920, 1940—1950, 1960—1970, and 2170—2180 Å.

W. R. ANGUS.

Action of yeast on fumaric acid. K. P. JACOBSOHN (Biochem. Z., 1931, **239**, 449—455).—When yeast acts on fumaric acid the amounts of CO_2 evolved and lactic acid produced are so small and so slowly formed that there is no ground for supposing that the decarboxylation is other than a very secondary process. The conclusions of Jung and Müller (A., 1922, i, 486) must be rejected. Possibly their yeast was infected.

W. McCARTNEY.

Mechanism of the phosphorylation of sugars by yeast. Changes during the period of total phosphorylation. S. VEIBEL (Biochem. Z., 1931, **239**, 350—373).—When fresh bottom yeast acts on dextrose, NaH_2PO_4, and $NaHCO_3$ in presence of PhMe, hexosemono-, hexosedi-, and trehalosemono-phosphate are produced and can be isolated. At first the ratio of di- to mono-phosphate is less than 1, but rises in about 2 hr. to 1 and in 4 hr. to its max., 1·5. The time at which the ratio reaches its max. coincides with the max. binding of PO_4'''. Between the 4th and the 14th hr. the amount of the diphosphate decreases and that of monophosphate increases, so that after about 8 hr. the ratio is again 1 and elimination of inorg. PO_4''' becomes appreciable. After 14 hr. the amount of monophosphate reaches its max. and the ratio falls to 0·5—0·7, at which val. it remains for the remainder of the experiment. After 32 hr. half of the phosphate used is again in inorg. combination. No trehalosemonophosphate can be detected during the first 4 hr., but appreciable amounts are present after 8 hr. and these increase up to the end (32 hr.). The monophosphate fraction consists chiefly of Robison's ester after 4 hr., but after 8 hr. chiefly of Neuberg's ester. Trehalosemonophosphate crystallises with $7H_2O$ which are lost at 110° and 15 mm. The bearing of the results on the theories of phosphorylation is discussed.

W. McCARTNEY.

Phytochemical production of δε-octanediol from butyroin. S. VEIBEL (Biochem. Z., 1931, **239**, 456—460; cf. Neuberg and Kobel, A., 1926, 96).—δε-Octanediol can be obtained in 43% yield from butyroin by the action of bottom yeast. The product is a mixture of the *meso*-form (m. p. 123—124°) and the *d*-form ($[\alpha]_D^{20}$ +32° at least) (cf. Bouveault and Locquin, A., 1906, i, 783). During the process practically all the butyroin disappears.

W. McCARTNEY.

Function of magnesium in enzymic carbohydrate degradation. H. VON EULER, R. NILSSON, and E. AUHAGEN (Z. physiol. Chem., 1931, **200**, 1—26).—Mg is essential in the yeast fermentation of dextrose, lævulose, and sucrose, the optimum concentration being about 10^{-2} mols. of $MgCl_2$. For varying amounts of co-zymase added to Mg-free *apo*zymase, the rate of fermentation at optimum Mg activation is proportional to the amount of Mg required. Mg is also essential for the production of hexosephosphoric acid. Reduction of methylene-blue occurs in absence of Mg, but is activated by it; reduction of MeCHO proceeds without Mg and its addition has little effect. Inhibition of fermentation by F′ is not due to the withdrawal of Mg. MeCHO reduction is stimulated by NaF in a yeast containing Mg, but is inhibited in a Mg-free yeast. It is definitely activated by MgF_2. The latter produces a slight activation of fermentation by Mg-free yeast.

Methylene-blue reduction is stimulated by muscle-

adenylic acid in presence of hexosediphosphoric acid, but not in absence of the latter or of co-zymase. Adenylic acid activates the fermentation of hexosephosphates but not that of dextrose.

J. H. BIRKINSHAW.

Nomenclature of the catalysts of alcoholic fermentation. C. NEUBERG and H. VON EULER (Biochem. Z., 1931, **240**, 245).—The term holozymase (panzymase) is used for the whole system concerned in alcoholic fermentation; zymase is restricted to the purely enzymic constituents, and *apo*zymase to the holozymase freed from co-zymase, *apo*zymase thus still containing Mg. P. W. CLUTTERBUCK.

Effect of sea-water irradiated with ultra-violet light on the velocity of alcoholic fermentation of dextrose solutions. L. SANZO and F. PIRRONE (Atti R. Accad. Lincei, 1931, [vi], **13**, 613—617).—This fermentation is activated by sea-water only if exposure of the latter is limited, under the conditions employed, to 3 hr. The activity depends partly on the sea-water, considered as a salt solution, and partly on an unknown factor which loses its effect if the irradiated sea-water is either boiled for 20 min. or evaporated to dryness and made up to its original vol. with sterile, distilled H_2O (cf. this vol., 1091).

T. H. POPE.

Action of imine-producing substances on the decomposition of sugar by yeast. Action of co-zymase. I. F. ZUCKERKANDL and L. MESSINER-KLEBERMASS (Biochem. Z., 1931, **239**, 172—181).—Yeast fermentation inhibited by $CH_2I\cdot CO_2H$ or NaF can be reactivated by addition of NH-forming amines, *e.g.*, *p*-phenylenediamine hydrochloride, NH_2Ph hydrochloride, tyrosine. EtOH and glycerol are formed. It is considered that the action is analogous to that of the NH-groups of adenine in the adenine nucleotide of co-zymase.

P. W. CLUTTERBUCK.

Action of halogen derivatives on alcoholic fermentation. P. CAYROL (Compt. rend., 1931, **193**, 446—447).—The sp. inhibition of the alcoholic fermentation of yeast by $CH_2Br\cdot CO_2H$ is compared with that of other halogenated fatty acids. Bromides, bromates, and some halogen-containing hypnotics are inactive. Inhibition is confined to α-halogenated monocarboxylic acids. A. COHEN.

Vital properties of yeast plasma: preparation and biochemical importance of some new yeasts. V. JONAŠ (Biochem. Z., 1931, **239**, 140—158).—The culture and properties of some new yeasts are described and it is claimed that the life of the organism is bound, not with the cell, but with the plasma.

P. W. CLUTTERBUCK.

Yeast fat. I. J. WEICHHERZ and R. MERLANDER (Biochem. Z., 1931, **239**, 21—27).—The presence of valeric acid and probably also of decoic acid is detected. P. W. CLUTTERBUCK.

Glycogen from yeast. Cell membrane of yeast. K. M. DAOUD and A. R. LING.—See this vol., 1277.

Alkaloid content of *Claviceps purpurea* grown on artificial media. H. KREITMAIR and W. KUSSNER (Biochem. Z., 1931, **239**, 189—192).—The presence of alkaloids of ergot in cultures of *C. purpurea* grown on artificial media is detected by chemical and biological methods. P. W. CLUTTERBUCK.

Insensitivity of *Paramecium* to cyanide and effects of iron on respiration. C. S. SHOUP and J. T. BOYKIN (J. Gen. Physiol., 1931, **15**, 107—118).—The rate of respiration of *P. caudatum* is not depressed by KCN at from $N/200$ to $N/10{,}000$, but a slight stimulating action is usually observed. This effect is not related to the p_H of the medium, which, within limits, does not sensibly influence the rate of respiration. Fe^{III} and Fe^{II} salts are usually toxic to *Paramecium* even at low concentrations and in no case stimulate respiration. *Paramecium* probably does not contain a respiratory catalyst containing Fe sensitive to CN'. W. O. KERMACK.

Importance of iron for the growth of fungi. B. B. MUNDKUR (Proc. XV Indian Sci. Cong., 1928, 230).—Fe stimulates the growth of *Fusarium vasinfectum*, Atkinson. CHEMICAL ABSTRACTS.

Dependence of the nitrogen assimilation of some fungi on [H˙]. K. RIPPEL (Arch. Mikrobiol., 1931, **2**, 72—135).—The N-assimilation of fungi was a function of the p_H of the nutrient, but the Robbins effect was not similarly applicable to all fungi. No selective power of assimilation was observed. NH_2-acids are not preferentially assimilated. The position of the growth optima of the fungi examined was to the left of the isoelectric points. A. G. POLLARD.

Decomposition of the various chemical constituents of complex plant materials by pure cultures of fungi and bacteria. S. A. WAKSMAN (Arch. Mikrobiol., 1931, **2**, 136—154).—Certain classes of organisms act on the H_2O-sol. substances, hemicelluloses, and N-complexes of plant tissues, others decompose cellulose, and a few attack lignin. The decomp. of proteins is accompanied by a synthesis of new materials and the extent of decomp. cannot be judged by wt. losses alone. A. G. POLLARD.

Formation of citric acid by moulds. V. Formation of citric from acetic acid. K. BERNHAUER and H. SIEBENAUGER (Biochem. Z., 1931, **240**, 232—244).—The power to form citric acid from acetates (especially NaOAc) is a general one for all strains of *Aspergillus niger* used, in several cases the yield being up to 16% on the AcOH disappearing. EtOH, fumaric, malic, and glycollic acids are all converted into citric acid. P. W. CLUTTERBUCK.

Relation between p_H and citric acid formation by *Aspergillus niger* and *Citromyces glaber*. A. FREY (Arch. Mikrobiol., 1931, **2**, 272—309).—Citric acid production by *C. glaber* is favoured by the buffer action of Ca citrate and by p_H 3—4. Addition of acid to produce p_H 2 inhibits the activity of the organism. For *A. niger* the optimum p_H is 2·0. Inorg. N aids citric acid formation and the addition of $CaCO_3$ to produce p_H 6 favours the production of gluconic acid. Max. yields of citric acid are obtained by partial neutralisation of the acid with $CaCO_3$, while maintaining the $p_H \not< 3$. The temporary reduction of [H˙] during the first 12—24 hr. of growth is ascribed to the transition of inorg. to org. P. A. G. POLLARD.

Mechanism of the synthesis of fats from carbohydrates. P. R. Bohn (Compt. rend., 1931, **193**, 441—442).—The fat content of cells of *Aspergillus niger* increases markedly when the lævulose in the medium is increased from 3 to 40%. Although the N content decreases, the efficiency of the fat synthesis is of the same order as is observed with dextrose (A., 1927, 797). A. Cohen.

Production of a growth regulator by *Aspergillus niger*. P. Boysen-Jensen (Biochem. Z., 1931, **239**, 243—249; cf. this vol., 1091).—*A. niger* produces considerable amounts of the regulator in both solid and liquid nutrient media, of which peptone and hæmoglobin solutions are amongst the best. No regulator is produced by peptic digestion of fibrin, hæmoglobin, or caseinogen, or by *A. niger* when the only N available is inorg. or when solutions of malt extract and ovalbumin form the medium. W. McCartney.

Oligodynamic action of copper. W. Schwartz and H. Steinhart (Arch. Mikrobiol., 1931, **2**, 261—271).—During its growth *Aspergillus niger* takes up Cu from nutrient solutions. The absorption curve is largely independent of the initial concentration of Cu in the nutrient. The max. intake of Cu is reached during the first day's growth and with subsequent growth the Cu content of the mycelium declines. A. G. Pollard.

Influence of calcium and strontium on the catalysis of nitrogen fixation by *Azotobacter*. D. Burk and H. Lineweaver (Arch. Mikrobiol., 1931, **2**, 155—186).—The fixation of N by *Azotobacter* demands 25—50 p.p.m. of Ca or Sr in the medium. The suitability of numerous Ca and Sr salts for this purpose is examined. No other elements can replace Ca or Sr. For the growth of *Azotobacter* in fixed N Ca and Sr are not required provided there is a sufficiency of other elements (*e.g.*, Mg, Ba, Be). The rate of growth of the organism in free N_2 depends on the concentration of the organism present. In this respect the ratio concentration of organism : concentration of Ca is important, but plays no part when the organism grows in fixed N. The action of Ca and Sr is exerted within the cell, but the greater part of the Ca required is probably concerned in metabolic processes and not actually in N fixation. In the latter process Ca may have a catalytic action. A. G. Pollard.

Oxidation–reduction potentials in cultures of *Es. coli*. E. M. Boyd and G. B. Reed (Canad. J. Res., 1931, **4**, 605—613; cf. this vol., 527).—In anaerobic buffered broth cultures free from dextrose the beginning of the logarithmic growth period coincides with a sudden fall in oxidation–reduction potential. In presence of dextrose the fall in potential to the limiting negative val. is more rapid and starts at the same time as the evolution of gas, which suggests that the primary aerobic metabolism gradually becomes anaerobic when dextrose is present. There is also present in the cultures a non-gaseous reversible oxidation–reduction system. R. Cuthill.

Bacteria producing trimethylene glycol. C. H. Werkman and G. Gillen (J. Bact., 1931, **21**, 6—7).—Fermentation of glycerol by certain organisms of the *Coli–aerogenes* group yielded 30% of trimethylene glycol. A. G. Pollard.

Oxidation of alcohols by acetic bacteria as a form of cellular respiration. H. Queré (Compt. rend., 1931, **193**, 445—446).—The O_2 consumption of a type of *B. acetigenum* increases from zero in mineral or dextrose media to vals. in alcoholic media which are inversely proportional to the mol. wt. of the alcohol. The acid fermentation is inhibited by $0{\cdot}0001M$-KCN but not by $0{\cdot}01M$-$CH_2Br{\cdot}CO_2H$. The mechanism of alcohol oxidation is therefore similar to that of respiration. A. Cohen.

Factors influencing the free acidity and p_H of the medium of a lactic–acetic fermentation. V. Bolcato (Giorn. Chim. ind. appl., 1931, **13**, 405—408).—The acidity and p_H developed in a medium undergoing fermentation by the ordinary *Lactobacillus* depend on the contents of buffer salts, colloids, and electrolytes. Buffer salts increase markedly the free acidity and lower the final p_H. Org. compounds having a buffering action and capable of forming colloidal solutions act similarly to salts, but exert also a protective action against the depressing influence of the acids on the organisms. Addition of an electrolyte such as NaCl almost suppresses this protective effect of colloids. It is thus not possible to establish *a priori* the limits of resistance of a micro-organism to acids without a knowledge of the defensive elements—buffer salts and colloids—present in the medium. T. H. Pope.

Reducing substances in milk determine the predominating development of lactic fermentation in milk. P. Mazé and P. J. Maze, jun. (Compt. rend. Soc. Biol., 1930, **105**, 518—519; Chem. Zentr., 1931, i, 2777).—If a gelose test-tube is inoculated with a young culture rich in lactic acid bacteria, cultures separated by a sterile layer (0·5—1 mm. thick) are obtained. On addition of 2—3 drops of 1% methylene-blue solution the layer becomes thicker and nearer to the surface. A. A. Eldridge.

Action of free oxygen on anaerobic lactic acid bacteria. P. Maze and P. J. Mazé, jun. (Compt. rend. Soc. Biol., 1930, **105**, 519—520; Chem. Zentr., 1931, i, 2777).—The sterile layer (preceding abstract) is due to the anaerobic metabolic products becoming converted by the action of O_2 into an antiseptic substance, probably derivatives of lactic acid. A. A. Eldridge.

Biological and chemical studies of the *Lactobacillus* genus with special reference to xylose fermentation. L. Weinstein and L. F. Rettger (J. Bact., 1931, **21**, 4—5).—In the fermentation of pentoses by strains of *L. pentoaceticus* from various sources, max. acid production occurred at 33°, the addition of $CaCO_3$ being necessary. 90—95% of the xylose was destroyed in 14—16 days and the yield of acids was equiv. to 85—92% of the carbohydrate. A. G. Pollard.

Rhamnose-fermenting bacillus. A. Castellani (Ann. Inst. Pasteur, 1931, **48**, 297—305).—"*Bacillus rhamnosifermentans*," isolated from certain pathological human fæces, ferments rhamnose with

evolution of gas. It has no action on several other carbohydrates and glucosides, and is suggested as a means of identifying rhamnose. A. COHEN.

Gaseous fermentation of erythritol by symbiotic bacteria. A. CASTELLANI and D. MACKENZIE (Ann. Inst. Pasteur, 1931, **48**, 306—310).—Mixed cultures of *B. kandiensis* and *B. morgani* ferment erythritol with production of gas containing CH_4 but no CO_2. A. COHEN.

Biological filtration of dilute sucrose solutions. N. W. BARRITT (Biochem. J., 1931, **25**, 1419—1446).—The determination of carbohydrate in terms of O_2 absorption is vitiated by the fact that org. synthesis takes place in the process. The nature of the inoculum also affects the relative amounts of oxidation and synthesis. The org. acids formed during the decomp. of sugar are rapidly destroyed by an efficient filter-bed. Lactic and acetic acids are more rapidly oxidised than sucrose. The formation of oxidised N in presence of org. matter promotes the dehydrogenation of lactic acid and probably of other compounds. The film formed accounts for 15% of the sucrose supplied. Aeration is the dominant factor in biological filtration. The rate of flow is the best means of controlling the time of contact and purification. The growth efficiency of film depends on the C/N and C/P_2O_5 ratios. N fixation occurs in the filter-bed, but results in the growth of film of low N content and low purification. A low C/N ratio and a high concentration of org. matter promote the rapid development of the film and attainment of high purification. Both stages of nitrification occur in the filter-bed and are subject to considerable fluctuations not correlated with the supply of N in solution. S. S. ZILVA.

Changes in blood-sugar and -phosphorus in rabbits following injection of suspensions of *B. äertrycke*. M. E. DELAFIELD (J. Path. Bact., 1931, **34**, 177—194).—Hyperglycæmia is followed by fatal hypoglycæmia. Inorg. P at first diminishes and then increases. Org. acid-sol. blood-P often tends to increase during hyperglycæmia and decreases during hypoglycæmia. Treatment of the bacterial substances with EtOH, $COMe_2$, or by steaming or autoclaving does not alter the type of chemical response, although the enzyme activity is reduced. CHEMICAL ABSTRACTS.

Possible role of micro-organisms in the precipitation of calcium carbonate in tropical seas. C. B. LIPMAN (Science, 1931, **74**, 151).—A criticism (cf. this vol., 930). L. S. THEOBALD.

Metabolism of *S* and *R* forms of pneumococcus. P. FINKLE (J. Exp. Med., 1931, **53**, 661—676).—A study of the respiration and glycolytic metabolism of various types of pneumococcus. CHEMICAL ABSTRACTS.

Specific and non-specific polysaccharides of type IV pneumococcus. M. HEIDELBERGER and F. E. KENDALL (J. Exp. Med., 1931, **53**, 625—639).—Autolysed cultures afford three N-containing polysaccharides: a type-sp. carbohydrate (I), a chemically similar carbohydrate (II) without sp. function, and the *C*-substance (III). (I) had $[\alpha]_D$ +17·0° to 35·0°, N 4·7—5·9%, acid equiv. 1250—3330; (II) had $[\alpha]_D$ +10°, N 5·9%, acid equiv. 4540; (III) had $[\alpha]_D$ +42°, N 6·1%, acid equiv. 1050; the hydrolytic products in each case are AcOH and an amino-sugar derivative, and also glucosamine from (II) and H_3PO_4 from (III). CHEMICAL ABSTRACTS.

Combination of bacterial polysaccharides and collodion particles as antigens. J. ZOZAYA (Science, 1931, **74**, 270—271).—Anthrax polysaccharide adsorbed on collodion particles is antigenic. L. S. THEOBALD.

Carbohydrates in biological processes. Fractions of the tubercle bacillus. T. B. JOHNSON and A. G. RENFREW (Amer. Rev. Tuberculosis, 1930, **22**, 655—663).—Sugars probably form one of the most important classes of bacterial cell constituents; they function in all the fractions which have been separated. CHEMICAL ABSTRACTS.

Carbohydrates produced by tubercle bacilli. M. DORSET and R. R. HENLEY (J. Amer. Vet. Assoc., 1930, **29**, 696—699).—Tuberculin prepared from cultures of human type on a sugar-free synthetic medium contains a polysaccharide which gives Molisch's test and pentose reactions, but fails to give the naphthoresorcinol test for glycuronic acid. The biuret test is usually positive. The tuberculin potency is decreased by attempts to remove protein. Hydrolysis with HCl affords arabinose and mannose. These sugars were also found in tuberculins of the bovine and avian types. CHEMICAL ABSTRACTS.

Carbohydrates associated with the ether-soluble lipins of tubercle bacilli. R. J. ANDERSON and E. G. ROBERTS (Amer. Rev. Tuberculosis, 1930, **22**, 664—668).—The carbohydrates in the phosphatide fraction from avian and bovine tubercle bacilli are described. The Et_2O-sol. constituents of the lipins consist of palmitic acid, oleic acid, and phthioic acid, liquid, saturated, and of high mol. wt. The H_2O-sol. constituents consist of glycerophosphoric acid, mannose, inositol, invert sugar, *d*-arabinose, glucosamine, and unidentified carbohydrates. CHEMICAL ABSTRACTS.

Bacterial derivatives. XII. Preparation of human tubercle bacillus polysaccharide MB-200 and some of its biological properties. P. MASUCCI, K. L. MCALPINE, and J. T. GLENN. **XIII. Occurrence of mannose and *d*-arabinose in the polysaccharide. XIV. Preparation and composition of timothy bacillus polysaccharide MB-200.** P. MASUCCI and K. L. MCALPINE (Amer. Rev. Tuberculosis, 1930, **22**, 669—677, 678—681, 682—684).—XII, XIII.—The gum, $[\alpha]$ +67°, contains 30% of pentose; the sol. sp. N-free substance appears to contain units of mannose, *d*-arabinose, and a sugar acid.

XIV. The polysaccharide, when hydrolysed, affords mannose and *d*-arabinose; it is comparable with that isolated from tubercle bacillus cultures. CHEMICAL ABSTRACTS.

Attempt to influence the growth of tubercle bacillus in the animal body by modifying the concentration of a growth-promoting substance (glycerol) in the tissues. E. R. LONG and A. J. VORWALD (Amer. Rev. Tuberculosis, 1930, **22**, 636—654).—Glycerol (fed or injected) enhanced the growth

of tubercle bacilli in lesions in rats; on administration of palmitic acid the extent of tuberculosis was in general decreased, although the fatty acid was deleterious to general health.

CHEMICAL ABSTRACTS.

Ammonium malate as source of nitrogen for tubercle bacilli in cultures. R. R. HENLEY and P. W. LE DUC (Amer. Rev. Tuberculosis, 1930, **22**, 568—570).—NH_4 malate can replace asparagine; a medium having p_H 7 is specified.

CHEMICAL ABSTRACTS.

Composition of the active principle of tuberculin. XIV. Analysis of the colloidal components of tuberculin with special reference to the relation of protein and carbohydrate. F. B. SEIBERT and B. MUNDAY (Amer. Rev. Tuberculosis, 1931, **23**, 23—40).—The tuberculin action of tuberculin protein appears to be due to a sp. portion of the protein mol. present only in the first hydrolytic cleavage product. Polysaccharide is chemically associated chiefly with these early cleavage products, and cannot be removed by washing, but is released at 4·8. A very potent H_2O-sol. tuberculin has been prepared; the N content is 16% and the polysaccharide content <2·7%. CHEMICAL ABSTRACTS.

Precipitation of diphtheria toxoid by potash alum. A. T. GLENNY and M. BARR (J. Path. Bact., 1931, **34**, 131—138).—The amount of sp. toxoid precipitated varied with the quantity of alum in relation to the vol. of a given toxoid. At certain alum concentrations the ppt. is relatively pure, but becomes associated with non-sp. material when kept. The quantity of alum required differs for different toxoids.

CHEMICAL ABSTRACTS.

Ability of aluminium hydroxide *B* to adsorb diphtheria toxin. E. MASCHMANN, E. KÜSTER, and W. FISCHER (Ber., 1931, **64**, [*B*], 2174—2178).—Diphtheria toxin is readily adsorbed by $Al(OH)_3$ *A*, *B*, and *C*, but prep. *B* has the most marked selective action. The best results are obtained from dil., faintly acid solutions. With increasing age of $Al(OH)_3$ *B* preserved under H_2O, the adsorptive power decreases greatly, sinking to less than 42% after 4 months. The phenomenon is ascribed, not only to alteration in size of the particles, but also to the conversion of the prep. into another individual of different chemical constitution. This assumption is in agreement with the gradual transformation of dialuminium hydroxide into bayerite (this vol., 1020). H. WREN.

Combined action of silver nitrate and formaldehyde on proteins and micro-organisms. M. DEGANELLO (Arch. Farm. sperim., 1931, **52**, 269—282; cf. *ibid.*, 1929, **47**, 177).—Addition of $AgNO_3$ and CH_2O to serum causes slow coagulation of the protein, but only in the light and concurrently with reduction of the Ag salt. $AgNO_3$ and CH_2O also increase the viscosity of serum and exert bactericidal action on *Staphylococcus pyogenes aureus*. In all these cases the effects produced by $AgNO_3$ and CH_2O together are greater than the sums of the effects produced by each separately. R. K. CALLOW.

Bactericidal efficiency of certain organic peroxides. B. E. PROCTOR and N. A. MILAS (J. Bact., 1931, **21**, 55).—The germicidal power of org. peroxides varied somewhat according to the chemical nature of the parent substances. A. G. POLLARD.

Bactericidal properties of monoethers of dihydric phenols. I. Monoethers of resorcinol. E. KLARMANN, L. W. GUTYAS, and V. A. SHTERNOV.—See this vol., 1289.

Preparation and bacteriological study of *sym.* organic sulphides. F. DUNNING, B. DUNNING, jun., and W. S. DRAKE.—See this vol., 1289.

Effect of adrenaline on some phosphorus compounds of muscle. S. I. VINOKUROV and S. F. EPSTEIN (Arch. exp. Path. Pharm., 1931, **161**, 669—673).—In the presence, but not in the absence, of dextrose, muscle perfused with Ringer's solution containing adrenaline shows a decrease of total inorg. P associated with a rise of $H_4P_2O_7$, the acid-sol. P remaining approx. const. W. O. KERMACK.

Origin of dextrose liberated by adrenaline in depancreatised animals. J. L. BOLLMAN, F. C. MANN, and C. M. WILHELMJ (J. Biol. Chem., 1931, **93**, 83—91).—Depancreatised dogs were maintained in good condition by large doses of insulin and an appropriate diet including pancreas. The insulin was then withdrawn and after 4 days the liver, muscle, and blood before and after continuous administration of adrenaline for 12 hr. were examined for dextrose and glycogen, whilst the D : N ratio of the urine was determined during the experimental period. Little change occurred in the liver-dextrose and -glycogen or in the blood- and muscle-dextrose, whilst the increase in glycosuria due to the adrenaline could not be accounted for by conversion of protein or fat into dextrose. A marked decrease in the muscle-glycogen corresponded with, and hence was responsible for, the extra dextrose appearing in the urine during adrenaline administration. F. O. HOWITT.

Effect of ultra-violet rays on adrenaline and related products. P. L. EWING, P. BLICKENSDORFER, and H. A. MCGUIGAN (J. Pharm. Exp. Ther., 1931, **43**, 125—129).—Adrenaline suffers a decrease in pressor activity, "synephrin" (*p*-hydroxyphenylmethylaminoethanol) an increase when irradiated as the tartrate, citrate, oxalate, or succinate, but not as the base (when it is unchanged), ephedrine a reversal to depressor activity, whilst ψ-ephedrine, its sulphate, and *l*-methylephedrine hydrochloride are unchanged. Such changes are probably due to oxidation and may be effected by H_2O_2. F. O. HOWITT.

Influence of electrolytes on the permeability of tissues to crystalline insulin. R. J. HAMBURGER (J. Pharm. Exp. Ther., 1931, **43**, 233—243).—A frog's intestinal loop was filled with salt solution containing insulin and the vessels of the mesentery and intestinal walls were perfused by a solution which was subsequently examined by its action on the blood-sugar of the rabbit. Insulin dissolved in Ringer's solution is absorbed, the absorption being decreased by an increase of KCl concentration to 0·1% and nearly inhibited by increase of Ca to 0·1% $CaCl_2,2H_2O$. Replacement of Ringer's by NaCl solution indicates that the permeability of the intestinal mucosa to insulin is increased by $K^{\cdot}$ and decreased by $Ca^{\cdot\cdot}$.

F. O. HOWITT.

Action of thyroxine. K. OBERDISSE (Arch. exp. Path. Pharm., 1931, **162**, 150—168).—In rats which have had the dorsal cord cut thyroxnie causes the same increase in CO_2 production as in normal rats. Thyroxine does not act, therefore, through the central nervous system, but directly on the cell. There is a quant. relationship between dosage of thyroxine and its effect on metabolism. A. COHEN.

Influence of intravenous injection of thyroxine on the blood-iodine level and on the urinary iodine excretion in man. J. BØE and A. W. ELMER (Biochem. Z., 1931, **240**, 187—191).—After intravenous injections of thyroxine (2 mg.) in man, the blood-I increases, the increase being limited to the EtOH-insol. components, but returns to normal in 2 hr. About of the I is excreted in the urine, the excretion being ended after 24 hr.

P. W. CLUTTERBUCK.

Detection of thyroid hormone in the blood in pregnancy. K. J. ANSELMINO and F. HOFFMANN (Arch. Gynakol., 1931, **145**, 95—103; Chem. Zentr., 1931, i, 2779).—The increase, in rats, of the blood-$COMe_2$ substances after injection of serum of pregnancy is due to the presence of thyroxine, the concentration of which is max. at the end of pregnancy and falls rapidly after parturition. Thyroxine was not detected in fœtal blood. A. A. ELDRIDGE.

Detection of thyroid hormone in the blood of pregnancy. F. HOFFMANN and K. J. ANSELMINO (Arch. Gynakol., 1931, **145**, 104—113; Chem. Zentr., 1931, i, 2779).—The residue of ultra-filtered serum of pregnancy, when injected into rats, caused a 30% increase in basal metabolism. The active substance (thyroxine) appears in the third or fourth month.

A. A. ELDRIDGE.

Detection of thyroid hormone in the blood of pregnancy, and the effect of increased thyroid activity on the metabolism, course, and nervous irritability of pregnancy. K. J. ANSELMINO and F. HOFFMANN (Arch. Gynakol., 1931, **145**, 114—131; Chem. Zentr., 1931, i, 2779).

Properties and stability of a powder prepared from anterior pituitary lobe. A. LOESER (Arch. exp. Path. Pharm., 1931, **161**, 730—731).—An active powder prepared from the anterior lobe of the pituitary showed no deterioration when kept for 18 months. W. O. KERMACK.

Action of the hormone of the anterior lobe of the pituitary on the oxygen utilisation of guinea-pigs. F. VERZÁR and V. WAHL (Biochem. Z., 1931, **240**, 37—49).—The hormone increases the metabolism of guinea-pigs (especially of male) by causing increased secretions of the thyroid. The effect is not obtained with thyroidectomised animals but is replaced by a decrease of metabolism. "Prolan" does not produce the effect. P. W. CLUTTERBUCK.

Gonad-stimulating substances of the anterior lobe of the pituitary body and of pregnancy-urine. Z. WALLEN-LAWRENCE and H. B. VAN DYKE (J. Pharm. Exp. Ther., 1931, **43**, 93—123).—The term "hebin" is proposed for the gonad-stimulating principle of the anterior pituitary lobe. A method of assay of hebin based on the increase in wt. of the seminal vesicles in the male rat or of the ovaries in the female is described. Extraction of the desiccated gland by $M/7{\cdot}5$ acetate buffer at p_H 4·5 and treatment of the extract with 90% EtOH gives an active ppt. with fresh rat, sheep, or pig pituitary glands, but not with fresh ox or rat glands frozen for 9—36 days. The active principle, which initiates follicular maturation, corpus luteum formation, uterine hypertrophy, and œstrus in the hypophysectomised rat, does not dialyse through parchment or collodion and is heat-stable. Hebin prepared from urine of pregnancy by precipitation with EtOH following acidification to p_H 4·5 by AcOH is also non-dialysable, but deteriorates on boiling in aq. solution. Its stimulating action on the testis is equal to, whereas that of pituitary hebin is less than, the effect on the ovary, indicating a extra-hypophyseal origin for the gonad-stimulating principle of urine of pregnancy.

F. O. HOWITT.

Increase of metabolism by ovarian hormone. F. VERZAR and A. VON ÁRVAY (Biochem. Z., 1931, **240**, 28—36).—The basal metabolism of female rats is increased by 10—20% on injection of either of the ovarian hormone preps. menoformon or theelin. Ovarian hormone does not increase the basal metabolism of normal or castrated male rats. The increase of metabolism is obtained after extirpation of the ovaries and the thyroid, but disappears if the genital organs are removed. P. W. CLUTTERBUCK.

Crystalline follicular hormone (ovarian or œstrus hormone). A. BUTENANDT and G. F. MARRIAN (Z. physiol. Chem., 1931, **200**, 277—278).—The new triol ("theelol") of Doisy and his co-workers (this vol., 879) has already been characterised by the authors (A., 1930, 1320). J. H. BIRKINSHAW.

Œstrus-producing hormones. G. F. MARRIAN and A. BUTENANDT (Nature, 1931, **128**, 305).—The view of Doisy and co-workers (cf. this vol., 879) that the substance previously described (A., 1930, 1320) is a mixture of both the active substances found in urine of pregnancy is untenable.

L. S. THEOBALD.

Action of ovarian hormone on plants. W. SCHOELLER and H. GOEBEL (Biochem. Z., 1931, **240**, 1—11).—Hyacinths grown in H_2O to which was added 200 mouse units of hormone per week showed development of bloom considerably earlier than the controls. Addition of 100 units per week had no effect, but of 300 units caused injury to roots and general development. This injury was due, however, to lipoidal impurities in the prep. Similar experiments with onions and maize are described.

P. W. CLUTTERBUCK.

Absorption spectrum characteristic of vitamin-*A*. J. W. WOODROW and H. L. CUNNINGHAM (Physical Rev., 1930, [ii], **35**, 125).—Fresh cod-liver oil and spinach juice give prominent absorption bands with max. at 310 and 326 mμ, and minor bands at 320, 330, and 337 mμ. Extraction with Et_2O shifts the bands by 3 mμ towards the shorter wave-lengths. Egg-yolk and butter also give these bands. Exposure of cod-liver oil to a quartz–Hg arc for 20 min. or treatment with a current of air

at 90° for 1 hr. caused the bands at 310, 320, 326, and 330 mμ to disappear. L. S. THEOBALD.

Vitamin-B_1. I. Concentration of vitamin-B_1 from rice-polishings. I. A. SIMPSON (Bull. Inst. Med. Res. Fed. Malay States, 1931, no. 2, 1—10).—Active acid clay prepared according to Jansen and Donath had a pigeon-curative day-dose of 14 mg. Further concentration by the same authors' methods yielded a Pt compound from which a semi-cryst. material was obtained with a curative day-dose of 0·01 mg. R. K. CALLOW.

Determination of vitamin-B_1. E. F. CHASE and H. C. SHERMAN (J. Amer. Chem. Soc., 1931, 53, 3506—3510).—The rate of growth of rats is determined during 4—8 weeks on a vitamin-*B*-free diet supplemented by autoclaved yeast (for vitamin-B_2) and the material under investigation. H. BURTON.

Chemical nature of vitamin-B_1 from evidence afforded by its electrical transference. T. W. BIRCH and B. C. GUHA (Biochem. J., 1931, 25, 1391—1396).—Crude and purified extracts of vitamin-B_1 behave as a base even at p_H 8·5 when electrodialysed at different [H˙]. Vitamin-B_1 can be conc. in appreciable quantities free from vitamin-B_2 at the cathode by electrolysing crude yeast extracts. S. S. ZILVA.

Physiological function of vitamin-B_1. B. C. GUHA (Biochem. J., 1931, 25, 1367—1384).—The requirement of vitamin-B_1 for young growing rats receiving a sub-optimum dose is independent of the protein/carbohydrate ratio of the diet and of the nature of the carbohydrate. With galactose and lactose as sole sources of carbohydrate in the diet the animals decline in wt. Palm-kernel oil and olive oil have little sparing action on vitamin-B_1, whilst lard has a definite effect. The ingestion of Na lactate does not hasten the appearance of symptoms of vitamin-B_1-deficiency in rats, and raises the p_H of the urine of animals on a vitamin-*B*-free diet. The lethal dose of injected Na lactate is lower for deficient than for normal animals. The cytochrome content of the liver, kidney, brain, and heart-muscle tissues of rats is not diminished in vitamin-B_1 deficiency. Lactic acid is oxidised fairly efficiently by the liver and brain tissues of deficient rats. S. S. ZILVA.

Galactose as dietary carbohydrate. B. C. GUHA (Biochem. J., 1931, 25, 1385—1390).—When galactose is the sole carbohydrate of the diet, mice and rats decline in wt. and die. The animals develop typical "beriberi" symptoms although receiving ample quantities of the vitamin-*B* complex. S. S. ZILVA.

Biochemical lesions in vitamin-*B* deficiency. N. GAVRILESCU and R. A. PETERS (Biochem. J., 1931, 25, 1397—1409).—Brain tissue from polyneuritic pigeons shows *in vitro* a lowered power of O_2 uptake in the presence of dextrose as substrate. This is the case, when symptoms are prolonged, in all parts of the brain except the cerebellum. The phenomenon is an expression of vitamin-B_1 deficiency. The symptoms of opisthotonus are associated with chemical changes in certain parts of the brain. S. S. ZILVA.

Carbohydrate metabolism in birds. III. Effects of rest and exercise on lactic acid content of the organs of normal and rice-fed pigeons. R. B. FISHER (Biochem. J., 1931, 25, 1410—1418).—There are marked differences between the normal and the polyneuritic pigeon in the responses of the lactic acid contents of the heart, liver, and muscle to exercise and rest. These are probably due to the fact that in normal birds lactic acid formed in exercise is removed much more rapidly from the tissues than in polyneuritic birds. S. S. ZILVA.

Determination of vitamin-*G* (B_2). A. BOURQUIN and H. C. SHERMAN (J. Amer. Chem. Soc., 1931, 53, 3501—3505).—The rate of growth of rats is determined during 4—8 weeks on a vitamin-*B*-free diet to which is added the residue from an 80% EtOH extract of ground whole wheat (*i.e.*, vitamin-B_1) and the material under investigation. H. BURTON.

Biological assay of water-soluble antineuritic and antipellagric vitamins. H. T. GRABER and R. A. COWLES (J. Amer. Pharm. Assoc., 1931, 20, 876—881).—A review of present methods. Autoclaved yeast and EtOH extract of whole wheat are favoured for antineuritic and antipellagric concentrates, respectively. H. DAVSON.

Vitamin-*C* content of Japan green tea. H. S. MITCHELL (J. Amer. Dietet. Assoc., 1929, 5, no. 1, 28—31).—No demonstrable amount is present. CHEMICAL ABSTRACTS.

Antiscorbutic vitamin of apples. IV. M. B. CRANE and S. S. ZILVA (J. Pomology, 1931, 9, 228—231; cf. this vol., 531).—The antiscorbutic potency of Belle de Boskoop equals that of Bramley's Seedling, whilst that of Blenheim Orange and of Lane's Prince Albert is a little lower. The first three varieties are "triploid," and a connexion between high vitamin-*C* content and high chromosome no. is possible. R. K. CALLOW.

Antiscorbutic fractions of cabbage and their biological value. N. BEZSSONOFF (Bull. Soc. Chim. biol., 1931, 13, 950—961).—Addition of neutral $Pb(OAc)_2$ to cabbage juice ppts. the impurities and leaves the vitamin-*C* content unimpaired. On making the filtrate alkaline the vitamin itself is precipitated, but its properties, after removal of Pb, are modified so that it cannot preserve the original wt. of a guinea-pig for 80 days, during which time it is free from scurvy. This is additional evidence of the existence of a C_2 factor. P. G. MARSHALL.

Standardisation of vitamin-*D* preparations. J. W. R. EVERSE and J. VAN NIEKERK (Nederl. Tijdschr. Geneeskunde, 1931, 75, I, 1101—1107; Chem. Zentr., 1931, i, 2781).—A graphic method of comparison of the absorption spectrum with the antirachitic activity is described. A. A. ELDRIDGE.

Relation of calcium and phosphorus intake to the hypercalcæmia and hyperphosphatæmia induced by irradiated ergosterol. J. H. JONES and M. RAPOPORT (J. Biol. Chem., 1931, 93, 153—166).—Normal or thyroparathyroidectomised dogs fed on Ca-poor diet experience an increase in blood-Ca on administration of irradiated ergosterol (4500 *D* units per kg. body-wt.). Administration of Ca gluconate by stomach tube results in a slight rise of serum-Ca and occasionally in serum-P. Simultaneous

administration of vitamin-*D* results in a more pronounced increase in the Ca, whilst the P level is unchanged. Similarly, administration of Na_2HPO_4 produces a slightly greater degree of hyperphosphatæmia after than before administration of irradiated ergosterol, the serum-Ca decreasing in both cases. Aq. suspensions of $CaHPO_4$ normally induce a slight fall in the blood-Ca and practically no change in the P, whereas after vitamin-*D* administration there is no change in the P, but an increase in the Ca. Vitamin-*D* appears to function by increasing absorption of Ca and possibly of P from the intestinal tract. F. O. Howitt.

Avitaminosis. XV. Basal metabolism of rats in *E*-avitaminosis with and without administration of the hormone of the anterior lobe of the pituitary. F. Verzár, A. von Árvay, and E. von Kokas (Biochem. Z., 1931, **240**, 19—27).—Changes of the texture of the hair of male rats occur when they receive a diet free from vitamin-*E*, and complete recovery is obtained either when the vitamin is administered or when the hormone of the anterior lobe of the pituitary is injected. The basal metabolism of rats on a vitamin-*E*-free diet and of castrated animals is 18% below normal and in both cases is restored to normal by injection of the pituitary hormone. Formation of the hormone normally occurs only when vitamin-*E* is present in the diet.

P. W. Clutterbuck.

Temperature characteristics for the production of carbon dioxide by germinating seeds of *Lupinus albus* and *Zea Mays*. P. Tang (J. Gen. Physiol., 1931, **15**, 87—95).—The rates of production of CO_2 by germinating seeds of *L. albus* at various temp. below 20° lie on a smooth curve corresponding with a temp. characteristic of 16,100 g.-cal.; the rates above 20° lie on another curve and give a temp. characteristic of 24,000 g.-cal. With germinating seeds of *Zea Mays* there is no point at which discontinuity occurs, the temp. characteristic in this case being 20,750 g.-cal. over the range of temp. employed (12·5—25°). W. O. Kermack.

Effect of certain hydrocarbon oils on the transpiration rate of some deciduous tree fruits. V. W. Kelley (Illinois Agric. Exp. Sta. Bull., 1930, no. 353, 581—600).—Petroleum oils, whether refined or not, reduced transpiration rates of all trees examined. The effect is confined to the under surface of the leaves and is greater in old than in young leaves. A. G. Pollard.

Lignin formation in plants during lignification. K. Sisido (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, **16**, 136—139).—Bamboo lignin is similar to lignin from wood. The OMe content of bamboo lignin increases with age. The pectin and hemicellulose show similar behaviour.

A. A. Levi.

Distribution of lignin in the cell wall of wood. H. E. Dadswell (J. Counc. Sci. Ind. Res. Australia, 1931, 4, 185—186).—Sections of jarrah wood after destruction of the cellulose with 72% H_2SO_4 showed the lignin from cell walls to be arranged in numerous fine radial lines. Chemical combination of lignin and cellulose in the cell is unlikely. A. G. Pollard.

Chemical study of cranberries. F. W. Morse (Massachusetts Agric. Exp. Sta. Bull., 1930, no. 265, 102 pp.).—During the ripening of cranberries on the vines there is an increase in total sugar content, without appreciable change in the total acid present. During cold storage there is a decrease in sugar by respiration and a smaller decrease in total acid content. A. G. Pollard.

Distribution of the nitrogenous and mineral constituents in the oat plant at different stages of growth. T. W. Fagan and J. E. Watkin (Welsh J. Agric., 1931, 7, 229—246).—With advancing growth the dry matter content of the whole oat plant rises steadily to the "under-ripe" stage and subsequently increases more rapidly. There is a progressive decrease in total ash, K, CaO, and Cl contents, whilst the PO_4''' content remains practically unchanged. The N content falls steadily to a min. at the "milky-ripe" stage, rising again to the "under-ripe" stage, and finally decreasing somewhat to maturity. In the leaf the % of total ash, P, and N decrease with growth, whilst that of Fe increases slightly. In comparison with other constituents, the proportion of the total CaO of the plant present in the leaf is high and that of PO_4 low. In the stem there is a continuous decrease in the P and N contents from the first appearance of the panicle to the ripe stage. Dry matter and K rise to a max. at the "milky" stage and subsequently decline, whilst the ash and Fe remain practically const. throughout. A high proportion of the total Cl of the plant exists in the leaf at all stages of growth. In the spikelet the % P and N remain const. throughout, but there is a decrease in K, Cl, and CaO with maturity. The migration of N and P from the straw to the spikelet is much more complete than that of the other constituents. The ratio N : P in the spikelet remains const. throughout growth, but in the straw the ratio decreases with maturity. In the spikelet the ratios N : CaO and H_3PO_4 : CaO increase during the ripening stages, but in the straw these ratios decrease from the beginning of panicle formation to the "milky-ripe" stage. A. G. Pollard.

Some carbohydrate and nitrogen constituents of alternate-bearing sugar prunes associated with fruit-bud formation. L. D. Davis (Hilgardia, 1931, 5, no. 6, 119—154).—In a comparison of bearing and disbudded trees the former were characterised by a higher content of reducing substances from about mid-season onward and a lower starch content. The roots of bearing trees had a low, and of disbudded trees a high, proportion of starch. In the aerial portions the starch and moisture contents showed an inverse relationship. The proportion of reducing substances per flower or fruit increased throughout the season, the sugar content rising very rapidly during the 3 weeks prior to maturity.

A. G. Pollard.

Influence of soil moisture on plant growth. K. Tsukunaga (Agric. Exp. Sta. S. Manchuria Rly. Co. Bull., 1930, no. 1, 31—44).—Soya bean and wheat grew best at 80% H_2O-absorbing capacity of the soil, but the seed yield was best at 70%. The H_2O

requirement for the production of 1 g. of dry matter is 1 kg. for soya beans and 0·7 kg. for wheat.

CHEMICAL ABSTRACTS.

Effect of the p_H of the reservoir on the acid–base balance of peat. I. A. SMORODINCEV and A. N. ADOVA (Bull. Soc. Chim. biol., 1931, **13**, 943—949).—If sufficient Na_2CO_3 is added to a suspension of peat (p_H 7·29) to change the p_H immediately to 10·91, a fixation of alkali rapidly occurs which reduces the p_H to 9·71. Penetration varies with the amount of alkali added. Additions of NaCl, $CaCl_2$, or HCl (0·003*N*) have scarcely any effect on the acid–base balance of peat.

P. G. MARSHALL.

Effects of Shive's three-salt nutrients on rice seedlings. S. K. MITRA and L. PHUKAN (Proc. XV Indian Sci. Cong., 1928, 167).—Max. root development was associated with a culture in which 0·5 of the total osmotic concentration was due to KH_2PO_4, 0·2 to $MgSO_4$, and 0·3 to $Ca(NO_3)_2$, and min. root development with 0·3, 0·2, and 0·5, respectively.

CHEMICAL ABSTRACTS.

Injection experiments with special reference to the production of alkaloids etc. and general metabolism in plants. S. KRISHNA and H. CHAUDHURI (Proc. XV Indian Sci. Cong., 1928, 224).—Injection of colloidal Fe into the opium poppy diminished the berberine content, but produced berberine when injected into the red poppy.

CHEMICAL ABSTRACTS.

Biochemistry and physiology of organic phosphorus compounds in plants and animals. V. Influence of light and temperature on the occurrence of water-soluble phosphatides in plants. VI. Influence of salts, acids, and alkalis on the occurrence of water-soluble phosphatide in plants. H. MAGISTRIS and P. SCHAFER (Beitr. Biol. Pflanz., 1930, **18**, 116—140, 141—160; Bied. Zentr., 1931, [ii], **1A**, 367, 368).—I. The extent of exosmosis of phosphates is a direct measure of the permeability of the outer cell-walls. The latter is increased by exposure to light, either before or during dialysis, the shorter waves being particularly effective. Changes in permeability so induced are due to chemical changes in labile mols. rather than to altered physical conditions in the cell-wall. The elimination of H_2O-sol. phosphatides and of phosphates and carbohydrates is increased by rising temp. These changes are reversible.

II. The elimination of phosphatides is increased by the presence of the alkali metal and Mg ions, is arrested by the alkaline earths, and reduced by metallic salts. Acids and alkalis increase permeability in proportion to the concentrations used. CO_2 and H_2S increase exosmosis, the effect being reversible. In their effect on P osmosis cations are arranged in the series, K (greatest), Na, NH_4, . . . Sr.

A. G. POLLARD.

Importance of sulphur and phosphorus in plant nutrition. G. BERTRAND and L. SILBERSTEIN (Ann. sci. agric. franç., 1930, **47**, 324; Bied. Zentr., 1931, [ii], **1A**, 370).—The ratio of S : P in numerous types of plants varied between 0·3 and 1·7, and was greater in leaves than in roots. During flowering the ratio ranged from 0·44 to 1·56. In numerous soils the proportion of S in an assimilable form is insufficient for the normal growth of plants.

A. G. POLLARD.

Anatomical and physiological changes in citrus produced by boron deficiency. A. R. C. HAAS and L. J. KLOTZ (Hilgardia, 1931, **5**, no. 8, 175—197).—B is essential for cell division in the meristematic tissue of the growing points of citrus. B-deficiency is marked by a gradual reduction in the size of buds, a disintegration of the cambium and portions of the phloem, gum formation, and an abnormal accumulation of carbohydrate in the leaves.

A. G. POLLARD.

Formation of chlorophyll and yellow plant pigments. K. SJOBERG (Biochem. Z., 1931, **240**, 156—186).—The formation of chlorophyll and carotenoids by *Vicia faba* and *Tropæolum majus* was investigated under natural conditions in July—Sept. The amounts of these pigments vary only within narrow limits and the variations can be correlated with changes in daylight. Electric light in addition to daylight in February and March causes an increase in the chlorophyll content of the leaves of *Phaseolus vulgaris*. Short-wave light (Hg lamp) increased the chlorophyll content of young plants in February more than did long-wave light (W lamp). The chlorophyll and carotenoid contents of *Rubus idæus* leaves decrease in autumn but may be brought back almost to the summer vals. by irradiation with electric light. With leaves of *Brassica rapa*, irradiation with light of feebler intensity for a longer time caused quicker and greater pigment formation than irradiation for a shorter time and greater intensity. Both carotene and xanthophyll, but not chlorophyll, are present in the leaves of plants grown in the dark.

P. W. CLUTTERBUCK.

Effect of chlorates on the catalase activity of the roots of bindweed. J. R. NELLER (J. Agric. Res., 1931, **43**, 183—189).—Spraying with $NaClO_3$ solution reduced the catalase activity of bindweed roots, the depth of root affected increasing with the concentration of spray used. For the eradication of the plant, the spray strength must be sufficient to lower the catalase activity of the roots to 2 ft. Apparatus for determining catalase activity is described.

A. G. POLLARD.

Chemical investigations of the tobacco plant. I. The non-volatile organic acids of tobacco leaves. II. Changes which occur during the curing of Connecticut shade-grown tobacco. H. B. VICKERY and G. W. PUCHER (Connecticut Agric. Exp. Sta. Bulls., 1931, nos. 323—324, 155—202, 207—240).—I. The org. acids of tobacco leaves are precipitated by $Ba(OH)_2$ in presence of EtOH, and subsequently esterified and fractionated. Malic acid predominates and there is a considerable proportion of citric and small quantities of fumaric, succinic, oxalic, and other acids. Citric is the principal acid of the seed, and malic and fumaric acids occur in small amounts. The $H_2C_2O_4$ content decreases but does not entirely disappear with the development of the plant. Malic acid reaches its max. concentration in the young plant and the proportion does not change appreciably in the mature leaf. Citric acid decreases

in maturing green leaf but increases again during curing.

II. During the curing of tobacco the loss in org. solids falls mainly on the protein and the originally insol. carbohydrate of the leaf. Considerable amounts of these constituents are probably transformed into a sol. condition and on subsequent decomp. yield CO_2, H_2O, NH_3, and other volatile substances. About 22% of the nicotine evaporates from the tissues and more than 80% of the sol. carbohydrates of the fresh leaf disappear as such. The crude fibre of the leaves remains unchanged. Much of the leaf protein is hydrolysed to NH_2-acids, which are subsequently involved in the production of amides and NH_3. There is a loss of 14% of the total N, of which only a small proportion is represented by nicotine evaporation. Amides less sol. than asparagine (*e.g.*, those of glutamic or hydroxyaspartic acids) probably exist in curing tobacco. The nitrate-N is not affected by curing. A. G. POLLARD.

Resistance to poisons of *Elodea* leaves of different ages. W. A. COLLINS (Protoplasma, 1931, **12**, 549—553).—The injurious effects of solutions of EtOH, $H_2C_2O_4$, $BaCl_2$, $MgSO_4$, and $AgNO_3$ of similar concentrations, acting for similar times, were greater on old leaves than on young. A. G. POLLARD.

Edible cellulose. I. Recovery of crude fibre from raw and cooked potato cellulose. S. WOODRUFF and E. F. MILLER (J. Amer. Dietet. Assoc., 1929, **5**, no. 1, 23—27).—Crude fibre was recovered in fæces of rats in greater amounts when uncooked than when cooked potato was fed.

CHEMICAL ABSTRACTS.

Occurrence of dulcitol in a red seaweed. P. HAAS and T. G. HILL (Nature, 1931, **128**, 378).—Dulcitol has been isolated from *Bostryschia scorpioides*.

L. S. THEOBALD.

Change in composition of soya-beans and iodine values of the oil during periods of maturity. K. TSUKUNAGA and T. NISHINO (Agric. Exp. Sta. S. Manchuria Railway Co., Res. Bull., 1931, no. 2, 21—48).—The N-free extract, crude fibre, and ash contents decrease, whilst the crude protein and Et_2O extract increase, as maturity is approached. The I val. of the oil is max. at 53—54 days after blooming. Oil from soya-beans grown in arid regions or kept long in storage had low I vals.

CHEMICAL ABSTRACTS.

Relation between composition of Manchurian soya-beans and colours of seed-coat and hilum. K. TSUKUNAGA, H. OHARA, and T. NISHINO (Agric. Exp. Sta. S. Manchuria Railway Co., Res. Bull., 1931, no 2, 1—20).—The relation of the colours to the crude protein, N-free extract, crude fibre, and ash contents is recorded. CHEMICAL ABSTRACTS.

Tea-seed oil. A. HEIDUSCHKA and C. SHU-SHENG (Arch. Pharm., 1931, **269**, 456—468).—Hydrolysis of the oil obtained either by expressing or extracting the air-dried seeds (containing H_2O 5·49%, saponin 2·73%, and oil 46·89%) gives 95·86% of its wt. of fatty acids. The saturated acids (5·69% of oil) are mainly palmitic and stearic, whilst the unsaturated acids (88·79% of oil) consist of oleic (96—98%) and linoleic (2—4%). Fractional crystallisation of the oil from light petroleum or Et_2O at −20° to −25° affords palmitostearo-olein, m. p. 30·5°; the liquid glycerides present are mainly triolein. The unsaponifiable matter (0·72% of oil) contains 19·7% of phytosterol. Numerous colour reactions of the oil are given. H. BURTON.

Unsaponifiable lipins of lettuce. II. Fractionation. III. Antioxidant. H. S. OLCOTT and H. A. MATTILL (J. Biol. Chem., 1931, **93**, 59—64, 65—70).—II. The unsaponifiable fraction of the EtOH extract of dried lettuce leaves was fractionated by the use of org. solvents. Alcohols of high mol. wt. ($COMe_2$-insol. fraction), resins and a substance of m. p. 240—247° (petrol-sol. fraction), carotene and a mixture of sterols (MeOH-insol. fraction), vitamin-*E* and an antioxidant concentrate (92% MeOH-sol. fraction) were isolated. Thus the antioxidant and vitamin-*E* are two distinct entities.

III. Fractional distillation of the antioxidant concentrate yields a fraction, b. p. 165—185°/0·1—0·2 mm., which contains the greatest amount of activity. From this separate active crystals, m. p. 143° (corr.), of probable formula $C_{13}H_{14}O_5$ and yielding an Ac derivative, m. p. 72°, possessing no activity. F. O. HOWITT.

Non-nitrogenous constituents of corn-silk. K. TSUKUNAGA (Agric. Exp. Sta. S. Manchuria Railway Co., Res. Bull., 1931, no. 2, 59—68).—Dry corn-silk contained 52·09% of N-free extract (Et_2O extract 2·20, total N 3·24, non-protein-N 0·66, crude fibre 20·26, ash 0·41%). The carbohydrate is chiefly dextrose, xylan, and galactan. The Et_2O extract contains phytosterol. CHEMICAL ABSTRACTS.

Constituents of the dried rind of the fruit of *Garcinia Gambogia*. K. I. KURIYAN and K. C. PANDYA (J. Indian Chem. Soc., 1931, **8**, 469—470).—The aq. extract of the dried rind ("Kadumpuli") contains tartaric acid (10—13·6% of rind), H_3PO_4 (1·52%), reducing sugars (as dextrose) (7·4%), citrate, Fe, Ca, Mg, Na, and K. H. BURTON.

Biochemistry of *Salix*. IV. Constitution of salipurposide. C. CHARAUX and J. RABATÉ (Bull. Soc. Chim. biol., 1931, **13**, 814—820).—Hydrolysis of salipurposide yields dextrose and salipurpol, which when treated with $Ba(OH)_2$ or dil. KOH gives phloroglucinol and *p*-coumaric acid. Salipurposide has a marked glycosuric action. C. C. N. VASS.

Comparison of proteins from representatives of the family *Malvaceæ*. A. N. BELOZERSKI (Bull. Univ. Asie Centr., 1929, no. 18, 1—4).—An albumin and two globulins were obtained from the seeds of *Hibiscus cannabinus*, *H. esculentus*, *Abutilon avicennæ*, and *Althæa nudiflora*. Analytical results for histidine-, arginine-, tyrosine-, lysine-N, total N, and S are recorded. CHEMICAL ABSTRACTS.

Potassium atractylate. H. WUNSCHENDORFF and P. BRANDEL (Bull. Soc. Chim. biol., 1931, **13**, 758—763, 764—770).—The aq. extract of the ground root of *Atractylis gummifera*, L., is neutralised with $CaCO_3$, kept at 60° for 20 min., filtered, and left for 24 hr., when inulin is precipitated. The inulin is dissolved in H_2O at 0° and mixed with the supernatant fluid. The solution is treated with CO_2 and

filtered. The filtrate is evaporated under reduced pressure to a brown solid which is extracted with 85% EtOH. The alcoholic extract, on evaporation under reduced pressure, yields a syrup which is freed from fats and colouring matter and crystallises on keeping under Et_2O. K atractylate, $C_{35}H_{50}O_{18}S_2K_2$, m. p. 172°, $[\alpha]_D$ −64·39°, sol. in hot EtOH and H_2O giving an acid solution, is a non-reducing glucoside which on acid hydrolysis yields 1 mol. of dextrose, 2 mols. of $KHSO_4$, 1 mol. of valeric acid, and a resin, $C_{19}H_{34}O_6$. C. C. N. Vass.

Ipomœin, a globulin from sweet potatoes, *Ipomœa batatas*. Secondary protein derived from ipomœin by enzymic action. D. B. Jones and C. E. F. Gersdorff (J. Biol. Chem., 1931, **93**, 119—126).—Sweet potatoes were extracted by 5% aq. NaCl and the extract was treated with AcOH, yielding a ppt. which was dissolved in NaOH and salted out by $(NH_4)_2SO_4$. The crude globulin was purified by re-precipitation and heat-coagulation at 82°. Storage of sweet potatoes at room temp. or the action of proteolytic enzymes on ipomœin results in formation of a secondary protein which was isolated by removal of the ipomœin by acidification and heating the filtrate to 68°. The percentage of NH_2-acids and the N-distribution of the protein and its fission product are given and compared with those of tuberin. F. O. Howitt.

Change of barley protein in storage and germination. E. Takahashi and K. Shirahama (J. Fac. Agric. Hokkaido Imp. Univ., 1931, **30**, II, 119—161).—Storage for 1 year increased the 70% EtOH-sol. and decreased the -insol. and H_2O-sol. N; storage for 2—3 years increased the 0·2% NaOH-sol. and decreased the -insol. and H_2O-sol. N. Germination for 72 hr. increased the H_2O-sol. and -insol. and decreased the NaOH- and EtOH-sol. N; that for 120 hr. increased the NaOH-sol. and decreased the -insol. and H_2O-sol. N. No change in 10% NaCl-sol. protein was observed. It appears that the EtOH-sol. and NaOH-sol. and -insol. proteins are synthesised from the H_2O-sol. and NaCl-sol. proteins. Bynin is an EtOH-sol., denatured hordein. Chemical Abstracts.

Characteristic chemical reactions of *Cannabis indica*. L. Hébert (Bull. Biol. Pharm., 1931, **2**, 189—190).—Froehde's reaction, which consists of the production of a red coloration when an amyl alcohol extract of *C. indica* is treated with a drop of 0·01% $NaWoO_4$ in H_2SO_4, whilst not sp., is given with all the preps. of the drug, whereas Beam's reaction, in which the residue of a petroleum extract is treated with 5% EtOH solution of KOH to give a violet coloration, is not sp., and is given only by fresh preps. of the drug. Tcherski's reaction is unsuitable. C. C. N. Vass.

Enzymes of *Gibberella Saubinetii*. G. Spitzer and M. M. Diehm (J. Agric. Res., 1931, **43**, 223—229).—The presence of glucosidase, invertase, catalase, lipase, trypsin, and erepsin is indicated. A. G. Pollard.

Hydrocyanic acid in sorghum. K. Tsukunaga (Agric. Exp. Sta. S. Manchuria Railway Co., Res. Bull., 1931, no. 2, 49—58).—Leaves of *Andropogon sorghum*, Broth., contain 0·0358—0·1066 (dry) % HCN. Variations associated with differences in seed colour and consistency are recorded. Kafir and Sudan grass contain much less HCN. Chemical Abstracts.

Concentration of potassium isotopes in plants. K. Heller and C. L. Wagner [with K. Langer] (Z. anorg. Chem., 1931, **200**, 105—112).—No concentration of K^{41} could be detected in the crude potash from sugar-beet vinasse or leaves. O. J. Walker.

Sap analysis. I. Carbohydrates. M. Sreenivasaya and H. N. Sastry (Proc. XV Indian Sci. Cong., 1928, 163—164).—The dextrins and the greater part of the proteins are removed by addition of 10 vols. of 95% EtOH containing a little NH_3. The alcoholic filtrate is concentrated, tannins etc. are eliminated with dialysed Fe, and the clear filtrate is used for the determination of sugar. Alternatively, the sap can be absorbed on fat-free filter-paper and extracted with alcoholic NH_3. Chemical Abstracts.

Biochemical determination of starch in plants. C. Bourdouil (Bull. Soc. Chim. biol., 1931, **13**, 809—813).—After extraction with EtOH, the finely powdered residue is hydrolysed by powdered pancreas at 40° for 4 days and the quantity of reducing sugars determined. The error does not exceed 2%. C. C. N. Vass.

Water hemlock, *Cicuta virosa*. I. Determination of cicutoxin. J. Z. Schneider (Chem. Obzor, 1931, **6**, 90—94).—Švagr's spectroscopic method is invalid. Chemical Abstracts.

Determination of calcium by alkalimetric titration. II. Precipitation of calcium. C. H. Fiske and M. A. Logan (J. Biol. Chem., 1931, **93**, 211—226).—The separation of Ca in presence of large amounts of PO_4''', SO_4'', and $Mg^{\cdot\cdot}$ is effected by precipitation by 1% $H_2C_2O_4$ at p_H 5 when the concentration of Ca is 0·001—0·003% and the solution is 0·5*N* in NH_4Cl or NH_4NO_3, which increase the solubility of MgC_2O_4. The ppt. is washed, dissolved in HNO_3, reconverted into CaC_2O_4 and ignited, the residue being dissolved in excess of 0·02*N*-HCl and titrated with 0·02*N*-NaOH. The application of the method to various types of urine is described. F. O. Howitt.

Application of the uranyl zinc acetate method for determination of sodium in biological material. A. M. Butler and E. Tuthill (J. Biol. Chem., 1931, **93**, 171—180).—The method of Barber and Kolthoff (A., 1928, 859; 1930, 52) is modified and adapted for analysis of tissue, urine, and fæces. With urine (6 c.c.) PO_4''' is removed by powdered $Ca(OH)_2$ and proteins by solid $HgCl_2$, Na then being precipitated by the U Zn acetate reagent, the ppt. washed with EtOH, dried, and weighed. Fæces and tissue are ashed and extracted with HCl whilst serum is digested with H_2SO_4–HNO_3 and H_2O_2 to remove org. matter. F. O. Howitt.

F.-p. determination of small quantities of solutions with a thermocouple. T. Minosima (Pflüger's Archiv, 1931, **226**, 794—798; Chem. Zentr., 1931, i, 2789).—The method, employing 0·5—1 c.c. of biological fluids (*e.g.*, toad's blood), is subject to an error of 2%. A. A. Eldridge.

BRITISH CHEMICAL ABSTRACTS

A—PURE CHEMISTRY

DECEMBER, 1931.

General, Physical, and Inorganic Chemistry.

Intensity distribution in continuous bands of H_2. L. GOLDSTEIN (Compt. rend., 1931, **193**, 485—488). C. A. SILBERRAD.

Intensities of Balmer emission lines in stellar spectra. O. STRUVE and H. F. SCHWEDE (Physical Rev., 1931, [ii], **38**, 1195—1204). N. M. BLIGH.

Resonance spectrum of hydrogen. K. R. RAO and J. S. BADAMI (Nature, 1931, **128**, 585).—The peculiar distribution of intensity of the Lyman series of H obtained by the Paschen hollow-cathode discharge in He and As is interpreted as a resonance effect occurring only in the presence of As. L. S. THEOBALD.

Striations and magnetic effect in electrodeless discharges. J. T. TYKOCINER and J. KUNZ (Physical Rev., 1930, [ii], **35**, 1436). L. S. THEOBALD.

Excitation of the visible spectrum of helium. II. J. S. TOWNSEND and F. L. JONES (Phil. Mag., 1931, [vii], **12**, 815—823; cf. this vol., 539).—The variation of intensity with pressure in the visible spectrum of a high-frequency discharge in He was investigated. H. J. EMELÉUS.

Zeeman effect in ortho-helium band spectrum. J. S. MILLIS (Physical Rev., 1931, [ii], **38**, 1148—1163).—Resolved and partly resolved Zeeman patterns obtained at high dispersion agree with theoretical predictions for small rotational energy vals. Departures from predictions are discussed. N. M. BLIGH.

Band spectra of negative ions. R. MECKE (Z. Physik, 1931, **72**, 155—162).—The rule that mols. with like numbers and configurations of valency electrons have similar spectra indicates that bands in the BeH and MgH spark spectra are due to negative ions. Data for many hydrides suggest that the elastic vibration const. is characteristic only of the number and configuration of electrons forming the chemical linking, and this fits the conception of single, double, and triple linkings. A. B. D. CASSIE.

Properties of the third positive carbon and associated bands. J. KAPLAN (Physical Rev., 1930, [ii], **36**, 784).—The third positive group of CO and the two systems usually associated with it have been studied under different excitation conditions. L. S. THEOBALD.

New spectra in nitrogen. J. J. HOPFIELD (Physical Rev., 1930, [ii], **36**, 789).—With He as a source of continuous light, absorption band spectra of N_2 have been found in the region 600—1100 Å. The bands below 750 Å. form approx. Rydberg series with 18·6 volts as the common limit. In a N_2–He mixture the resonance series of N I has been extended and a strong continuous spectrum has been found at the series limit; details of a new system of bands in emission are also given. L. S. THEOBALD.

Quenching of mercury resonance radiation by nitrogen and carbon monoxide. J. KAPLAN (Physical Rev., 1930, [ii], **36**, 788).—The more effective quenching power of CO is discussed. L. S. THEOBALD.

Active nitrogen glow. R. RUEDY (Physical Rev., 1930, [ii], **35**, 125).—A discussion. L. S. THEOBALD.

Third order spectrum of oxygen: quintuplets and triplets of O III. J. GILLES (Compt. rend., 1031, **193**, 584—586). C. A. SILBERRAD.

New oxygen spectra in the ultra-violet. J. J. HOPFIELD (Physical Rev., 1930, [ii], **36**, 789).—The resonance series of at. O has been extended and a strong continuous spectrum found to set in at the series limit and extend towards the ultra-violet. Many new lines, probably due mainly to O_1, have been found in O_2 and O_2–He mixtures. L. S. THEOBALD.

Rotational analysis of the first negative group of oxygen (O_2^+) bands. D. S. STEVENS (Physical Rev., 1931, [ii], **38**, 1292—1311).—Full data are tabulated. N. M. BLIGH.

New absorption band of atmospheric oxygen and the vibrational frequency of the normal molecule. H. D. BABCOCK (Physical Rev., 1930, [ii], **35**, 125).—30 lines of the absorption band (1, 1) in atm. O_2 have been identified. The most probable val. of the vibrational frequency of the normal mol. having 1 unit of vibrational energy is 1556·31 $\pm$0·05 cm.$^{-1}$ This val. is compared with the Raman displacement and discussed in connexion with isotopic displacement and heat of dissociation. L. S. THEOBALD.

Zeeman effect of neon. K. MURAKAWA and T. IWAMA (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1931, **16**, 256—259; cf. A., 1930, 1227).—Using improved methods, results previously reported are corrected and extended. N. M. BLIGH.

Intensity measurements in neon spectrum. H. N. SWENSON (Physical Rev., 1930, [ii], **35**, 126). L. S. THEOBALD.

Vectorial photo-electric effect in thin films of alkali metals. H. E. IVES (Physical Rev., 1931, [ii], **38**, 1209—1218). N. M. BLIGH.

Temperature shift of spectral lines and pole effect in vacuum arc. F. T. Holmes (Physical Rev., 1930, [ii], **35**, 652—653). L. S. Theobald.

Absorption of sodium vapour in the extreme ultra-violet. S. A. Korff and J. L. Nickerson (Physical Rev., 1930, [ii], **35**, 1433).—Na vapour is practically transparent to radiation in the region 1300—300 Å. L. S. Theobald.

Ultra-violet light reflecting properties of aluminium. A. H. Taylor and J. D. Edwards (J. Opt. Soc. Amer., 1931, **21**, 677—684).—Detailed directions are given for etching Al so as to obtain max. reflectivity. Reflexion factors range from 82 to 87% for visible light and from 81 to 82% for ultra-violet. C. W. Gibby.

New bands in the sulphur spectrum. W. E. Curtis and S. Tolansky (Proc. Durham Phil. Soc., 1931, **8**, 323—331).—The relevant data for emission bands of S_2 vapour and visual estimates of the intensity are tabulated. Two types are encountered, strong and weak; these are analysed into vibrational progressions and compared with existing data. The weak system arises from a second electron transition having the same lower level as the strong system. W. R. Angus.

Sparking potential of A–NO mixtures. F. M. Penning (Z. Physik, 1931, **72**, 338—343).—NO lowers the sparking potential of A provided the electrodes are previously saturated with NO (cf. A., 1928, 214). A. B. D. Cassie.

Intensity relations in some of the stronger multiplets of Cr I and Cr II. C. E. Hesthal (Physical Rev., 1930, [ii], **35**, 126). L. S. Theobald.

Classification of iron lines. H. D. Babcock (Physical Rev., 1930, [ii], **36**, 784—785). L. S. Theobald.

Interferometric measurements in the spectrum of the iron arc in air in the region 3100—3500 Å. C. V. Jackson (Proc. Roy. Soc., 1931, **A**, **133**, 553—564).—A set of 46 lines in the spectrum of the Fe arc in air, in the region 3100—3500 Å., has been measured by interferometric comparison with the red line of Cd or the Fe secondary standards. L. L. Bircumshaw.

Resonance spectrum of diatomic molecules of selenium and tellurium. P. Swings and J. Genard (Bull. Acad. roy. Belg., 1931, [v], **17**, 1099–1106).—A criticism of the work of Kessel (Compt. rend. Soc. polon. Phys., 1931, **5**, 409) on the resonance spectra of Se_2 and Te_2. W. R. Angus.

Vibrational quantum analysis of the visible absorption bands of bromine. W. G. Brown (Physical Rev., 1931, [ii], **38**, 1179—1186).—The absorption bands from 5100 to 7600 Å. are classified into two band systems having a common lower level; one system includes previously recorded bands, the other a group of relatively weak bands in the extreme red. Measurements of the vibrational isotope effect are given for bands in the main system, leading to a revision of quantum numbering and vibrational consts. N. M. Bligh.

Hyperfine structures in the first spectra of krypton and xenon. C. J. Humphreys (Bur. Stand. J. Res., 1931, **7**, 453—463).—The stronger arc lines of Kr and Xe have been analysed. R. Cuthill.

Spark spectrum of rhodium. A. G. Shenstone and J. J. Livingood (Physical Rev., 1930, [ii], **36**, 380).—New terms in the first spark spectrum of Rh are given. L. S. Theobald.

Effect of low temperatures on the ultra-violet transmission band of silver. J. C. McLennan, C. E. Smith, and J. O. Wilhelm (Phil. Mag., 1931, [vii], **12**, 833—840).—The position of max. intensity in the ultra-violet transmission band of a Ag film was determined at the temp. of liquid air, H_2, and He. H. J. Emeleus.

Bands of silver hydride. E. Bengtsson and E. Olsson (Z. Physik, 1931, **72**, 163—176).—New bands between 3180 and 4700 Å. give the energy of dissociation of the ground state as 19,000 $cm.^{-1}$ A. B. D. Cassie.

Voltage-intensity relations of the cadmium spectra. D. Colson (Physical Rev., 1930, [ii], **35**, 294).—Crit. potentials of the more prominent arc and spark lines are given and their behaviour as a function of the energy of the imparting electron is traced. L. S. Theobald.

Spectrum of singly-ionised indium. R. J. Lang (Physical Rev., 1930, [ii], **35**, 126).—The deepest term corresponds with an ionisation potential of 18·81 volts. L. S. Theobald.

Multiplet structure and Zeeman effect. J. B. Green and R. A. Loring (Physical Rev., 1931, [ii], **38**, 1289—1291).—The relations deduced by Houston and by Goudsmit (cf. A., 1930, 971) applied to the Zeeman effect of Sn III and Sb I give results in good agreement with observed vals. N. M. Bligh.

Spectra of trebly- and quadruply-ionised antimony, Sb IV and Sb V. J. S. Badami (Proc. Physical Soc., 1931, **43**, 538—544).—A study of the spark spectrum of Sb under various conditions of excitation. A. B. D. Cassie.

Infra-red absorption band system of iodine. W. G. Brown (Physical Rev., 1931, [ii], **38**, 1187—1189).—A vibrational analysis is given for a weak band group in the region 8300—9300 Å. of the absorption spectrum of saturated I vapour between 80° and 150°; the system is analogous to the extreme red of Br. A region of continuous absorption having a max. at 7320±50 Å. was observed. N. M. Bligh.

Iodine fluorescence in the infra-red. F. W. Loomis (Physical Rev., 1930, [ii], **35**, 662).—When the yellow lines are filtered from the Hg arc the lines in the neighbourhood of the infra-red doublets of the fluorescence spectrum of I disappear. They should therefore be attributed to higher members of the fluorescence series excited by the yellow lines. L. S. Theobald.

Arc spectrum of iodine. S. F. Evans (Proc. Roy. Soc., 1931, **A**, **133**, 417—430).—The arc spectrum of I has been photographed over the region 4763—10,481 Å. Wave-lengths are tabulated

and a term scheme is proposed which accounts for the majority of the strong arc lines. The ionisation potential, calc. from the deepest term $5p^2P_{3/2}$= 84,560 cm.$^{-1}$, is 10·44 volts. L. L. Bircumshaw.

Hyperfine structure and Zeeman effect in the resonance lines of Ba II. R. Ritschel and R. A. Sawyer (Z. Physik, 1931, 72, 36—41).—The 4934 and 4554 Å. lines of Ba II were investigated with fields up to 2600 gauss; the components observed are in agreement with the isotopes 136 and 138 having no nuclear spin, and the 137 isotope having some spin. A. B. D. Cassie.

***M*-Series absorption spectrum of tantalum.** C. A. Whitmer (Physical Rev., 1931, [ii], 38, 1164—1169).—Spectrograms were obtained for 3 absorption limits at 5·64 (M_{III}), 6·773 (M_{IV}), and 6·997 (M_V) Å. Discrepancies between experimental ν/R vals. and those calc. from L absorption and emission data are discussed. N. M. Bligh.

Magnetic resolution and nuclear moment of rhenium. P. Zeeman, J. H. Gisolf, and T. L. de Bruin (Nature, 1931, 128, 637).—Data obtained for the arc and under-water spark spectra of Re are discussed. The nuclear moment of Re is 5/2. L. S. Theobald.

High-frequency spectrum of mercury and fine structures of λ 6123 (Hg I) and λ 4797 (Hg II). S. Tolansky (Proc. Physical Soc., 1931, 43, 545—553).—Intensity modifications in the high-frequency electrodeless discharge in Hg vapour near 0·001 mm. are explained by the electron excitation curves. The 6123 and 4797 Å. lines were investigated with a Fabry–Perot interferometer. A. B. D. Cassie.

Mercury band spectrum in fluorescence. (Lord) Rayleigh (Nature, 1931, 128, 724—725).—Three bands, originally found in absorption by Wood, occur at 2345, 2338, and 2334 Å. when Hg vapour saturated at 5 mm. pressure is excited to fluorescence by a cooled Hg vac. arc. the light of which is filtered by a dil. solution of thiophen in EtOH. L. S. Theobald.

Hyperfine structure of mercury. K. Murakawa (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, 16, 243—255).—The hyperfine structure and Paschen–Back effect of the Hg line λ 4046·5 are described. The Paschen–Back effect determines uniquely the nuclear moment of all the Hg isotopes: I=0 for even isotopes, 1/2 for Hg^{199}, and 3/2 for Hg^{201}. N. M. Bligh.

Relative intensities of arc and spark lines of the electrodeless discharge in mercury vapour. O. P. Hart and O. Stuhlman, jun. (Physical Rev., 1930, [ii], 35, 1437). L. S. Theobald.

High-frequency electrodeless discharge characteristics. O. Stuhlman, jun., M. D. Whitaker, and M. L. Braun (Physical Rev., 1930, [ii], 35, 1436—1437). L. S. Theobald.

Near infra-red spectrum of mercury. H. J. Unger (Physical Rev., 1930, [ii], 36, 784).—Several lines in the region 1—2 μ have been resolved into 2 or more lines. L. S. Theobald.

Electrodeless discharge in mercury vapour. H. Smith, W. A. Lynch, and N. Hilberry (Physical Rev., 1930, [ii], 36, 374). L. S. Theobald.

Paschen–Back effect in the hyperfine structure of thallium II. J. B. Green and J. Wulff (Z. Physik, 1931, 71, 593—599).—Zeeman components in the 3092 Å. Tl II lines were measured for the fields 14,700, 32,500, and 43,350 gauss, and are in agreement with theory. A. B. D. Cassie.

Hyperfine structure in Tl II. Relative *g* (*I*) factors of Tl, Bi, and Pb (207), and nuclear structure. J. C. McLennan, A. B. McLay, and M. F. Crawford (Proc. Roy. Soc., 1931, A, 113, 652—667).—The status of the theory of hyperfine structure separation is considered. Certain conclusions regarding nuclear structure are reached by comparing the observed vals. of the interaction consts. of certain s electrons of Tl, Bi, and Pb. The fact that the g (I) factors of Bi and Pb (207) are of the same order, whereas that of Tl is about four times as great, invalidates the assumption that the resultant moments of momentum of nuclei are entirely due to spinning protons. L. L. Bircumshaw.

Appearance of continuous spectra during cathode-ray bombardment. IV. Experiments with thorium and other elements in gases. W. M. Cohn (Z. Physik, 1931, 72, 392—422).—Th, U, and Po when exposed to electron bombardment in presence of gases at low pressures exhibit a blue or violet surface luminosity which is continuous and unpolarised. A. B. D. Cassie.

Colorimetric properties of the spectrum. J. Guild (Phil. Trans., 1931, A, 230, 149—187).—The colorimetric properties of the eye have been averaged for 7 observers. A standard for a "normal" eye in colorimetry is suggested. J. W. Smith.

Coupled duplet and octet. A. F. Richter (Phil. Mag., 1931, [vii], 12, 764—768).—The ionisation potential curves and chemical properties of certain elements are explained in terms of the neutralisation of residual moments, and coupling. H. J. Emeléus.

Origin of the line absorption spectra of the rare earths. O. Laporte (Physical Rev., 1930, [ii], 35, 130).—Theoretical. L. S. Theobald.

Excitation of the green auroral line. J. Kaplan (Nature, 1931, 128, 304). L. S. Theobald.

Space-charged Townsend discharge in dense clouds. W. Deutsch (Ann. Physik, 1931, [v], 10, 847—867).—Charging of suspended particles in an ionic atm. is determined and the effect of surrounding particles taken into account. A. B. D. Cassie.

Pauli exclusion principle. W. Heisenberg (Ann. Physik, 1931, [v], 10, 888—904).—At. systems requiring n electrons to complete a closed shell can be approx. investigated by a Schrödinger equation in the co-ordinates of the n "missing" electrons. The method is used to discuss the lowest terms of at. spectra, such as Ti and Ni, and O^{++} and O; the anomalous Hall effect provides another example. A. B. D. Cassie.

Perturbation in band spectra. G. P. ITTMANN (Z. Physik, 1931, 71, 616—626).—Theoretical.
A. B. D. CASSIE.

Allowed levels for equivalent (s, p, d, f) electrons with (j j) coupling. S. D. BRYDEN, jun. (Physical Rev., 1931, [ii], 38, 1145—1147).—Allowed levels are tabulated. N. M. BLIGH.

Plasma-electron resonance, plasma resonance, and plasma shape. L. TONKS (Physical Rev., 1931, [ii], 38, 1219—1233; cf. this vol., 888).
N. M. BLIGH.

Generalisation of the Rydberg formula. R. M. LANGER (Physical Rev., 1930, [ii], 35, 649—650).
L. S. THEOBALD.

Quantitative application of the irregular doublet law to an isoelectronic sequence. R. A. SAWYER and J. E. MACK (Physical Rev., 1930, [ii], 35, 661). L. S. THEOBALD.

Energy distribution in the ultra-violet spectrum of skylight. B. O'BRIEN (Physical Rev., 1930, [ii], 36, 381). L. S. THEOBALD.

Calculation of ionic spectra. E. FERMI (Mem. R. Accad. Ital., Sci. Fis. Mat. Nat., 1930, 1, Fis., No. 2, 8 pp.; Chem. Zentr., 1931, i, 2845).—Theoretical. A. A. ELDRIDGE.

Apparatus for the evaluation of absorption [and line] spectrograms. G. W. KÜHL (Chem. Fabr., 1931, 373—374).—The distances between the lines or absorption edges on the spectrograms are amplified mechanically and read on a scale which may be calibrated in wave-lengths or wave numbers.
H. F. GILLBE.

Absolute measurement of certain X-ray wave-lengths. J. M. CORK (Physical Rev., 1930, [ii], 35, 128).—An X-ray vac. spectrograph and glass grating have been used to obtain abs. wave-lengths of the elements from Mo to Sb. L. S. THEOBALD.

Ionisation of inert gases (except helium) by X-rays. O. GAERTNER (Ann. Physik, 1931, [v], 10, 825—832).—The energy absorbed per pair of ions formed when X-rays of wave-length 1·27 X traverses Ne is 43, A 29, Kr 32, and Xe 47·5 volts. For shorter wave-lengths A gave 28—29 volts.
A. B. D. CASSIE.

Incoherent scattering of X-rays. W. HEISENBERG (Physikal. Z., 1931, 32, 737—740).—Mathematical. J. W. SMITH.

Incoherent scattering of X-rays. L. BEWILOGUA (Physikal. Z., 1931, 32, 740—744).—The theoretical curves for the incoherent scattering of X-rays, calc. according to the method of Heisenberg (cf. preceding abstract), are compared with experimental data. J. W. SMITH.

Interference of X-rays in thin layers. H. KIESSIG (Ann. Physik, 1931, [v], 10, 769—788; cf. A., 1930, 1334).—Interference of X-rays reflected at the upper and lower surfaces of a thin layer of Ni on a glass plate was observed; separation of the fringes gives vals. of the layer thickness and its refractive index. A. B. D. CASSIE.

Atomic photo-electric effect in the K shell according to Dirac's relativistic wave mechanics. F. SAUTER (Ann. Physik, 1931, [v], 11, 454—488; cf. this vol., 994).—Mathematical. J. W. SMITH.

Satellites of $K\alpha$ for the elements nickel to arsenic. F. K. RICHTMYER and E. RAMBERG (Physical Rev., 1930, [ii], 35, 661). L. S. THEOBALD.

Excitation of the $L\alpha$ satellites of silver. S. W. BARNES and F. K. RICHTMYER (Physical Rev., 1930, [ii], 35, 661). L. S. THEOBALD.

Multiple ionisation and secondary X-ray absorption edges. A. SANDSTRÖM (Nature, 1931, 128, 759).—Multiple ionisation in X-ray spectra has been confirmed by finding a secondary edge in S at 4644·0 X.
L. S. THEOBALD.

Apparatus for measuring absorption coefficients of soft X-rays in gases and the absorption in air of the $K\alpha$ line of carbon. E. DERSHEM and M. SCHEIN (Physical Rev., 1930, [ii], 36, 378).
L. S. THEOBALD.

Modified line in scattered X-rays. P. A. ROSS and J. C. CLARK (Physical Rev., 1930, [ii], 36, 378).—No step structure or breadth of line inexplicable by lack of homogeneity of scattering angle has been detected in the scattering of Sb $K\alpha_1$ and $K\alpha_2$ from Be at angles between 55° and 75°. L. S. THEOBALD.

X-Ray absorption by a Thomas–Fermi atom. L. C. ROESS and E. H. KENNARD (Physical Rev., 1931, [ii], 38, 1263—1269).—The calc. ionisation potential for a K electron of Sn shows approx. agreement with the observed energy of the K absorption edge. N. M. BLIGH.

Dependence of Compton line breadth on primary wave-length with the multi-crystal spectrograph. J. W. M. DU MOND and H. A. KIRKPATRICK (Physical Rev., 1931, [ii], 38, 1094—1108; cf. this vol., 405).—The breadth of the Compton line diminished with shorter primary wave-lengths in accordance with Du Mond's theory.
N. M. BLIGH.

Index of refraction and absorption coefficient of gold for the $K\alpha$ line of carbon. E. DERSHEM (Physical Rev., 1930, [ii], 35, 128).—The reflexion intensity–glancing angle curve for sputtered Au and the $K\alpha$ line of C (44·6 Å.) has been obtained. The extinction coeff. is 0·0086 and $1-n=0·009$.
L. S. THEOBALD.

Atmospheric ionisation at Glencree, Co. Wicklow. J. J. NOLAN and P. J. NOLAN (Proc. Roy. Irish Acad., 1931, 40, 11—59).—Data for observations extending over 14 months are tabulated. The concentration of condensation nuclei varied from 40 to 43,000 per c.c.; the average vals. for positive and negative ions were 495 and 369, respectively. The effects of rain and diurnal variations were noted. An expression for the rate of production of ions is found.
N. M. BLIGH.

Ionisation of cæsium vapour by light. F. W. COOKE (Physical Rev., 1931, [ii], 38, 1351—1356).—The photo-ionisation of Cs vapour as a function of the wave-length of the light was measured at low pressure and plotted. The abs. val. of the at. ionisation coeff. at the series limit was 6×10^{-19}.
N. M. BLIGH.

Emission of positive ions from thoriated tungsten. H. B. WAHLIN (Physical Rev., 1930, [ii], **35**, 653).—On heating, thoriated W gives W ions of mass 184, Th ions of mass 232, and an ion of mass 247±2. The last appears at approx. 2300° and may be ThO or an element. L. S. THEOBALD.

Photo-electric effect and the *J* phenomenon. T. H. OSGOOD (Physical Rev., 1930, [ii], **35**, 1407).—A discussion. L. S. THEOBALD.

Photo-electric properties of extremely thin films of alkali metals. H. E. IVES and H. B. BRIGGS (Physical Rev., 1930, [ii], **35**, 669; cf. A., 1925, ii, 344). L. S. THEOBALD.

Effect of adsorbed thorium on the thermionic emission from tungsten. W. H. BRATTAIN (Physical Rev., 1930, [ii], **35**, 1431).—Deposition of Th on a W ribbon at a given temp. increases thermionic emission to a max. and then decreases it to a stationary val. L. S. THEOBALD.

Ionisation efficiency of electrons in potassium vapour. J. KUNZ and A. HUMMEL (Physical Rev., 1930, [ii], **35**, 123). L. S. THEOBALD.

Inhibition of photo-electric emission by near infra-red light. A. R. OLPIN (Physical Rev., 1930, [ii], **36**, 376).—The response of K photo-electric cells to white light is increased when small amounts of Br or I vapour are distilled on to the cathodic surface. A marked decrease in the photo-electric current then occurs when the cell is irradiated with infra-red light. L. S. THEOBALD.

Search for critical potentials for electron recombination with Hg^+. A. M. CRAVATH (Physical Rev., 1930, [ii], **35**, 659—660).—No effect due to recombination of 10·4-volt electrons with Hg^+ could be detected. L. S. THEOBALD.

Direct measurement of the velocity of cathode rays. C. T. PERRY and E. L. CHAFFEE (Physical Rev., 1930, [ii], **35**, 1437). L. S. THEOBALD.

Mathematical equivalence of two ways of regarding the excitation of an atom by a fast-moving electron. J. W. FRAME (Proc. Camb. Phil. Soc., 1931, **27**, 511—517).

Wentzel-Brillouin approximation method in wave mechanics, particularly for the hydrogen molecule ion. (FRL.) M. WILLSTATTER (Ann. Physik, 1931, [v], **10**, 873—887).—Mathematical. A. B. D. CASSIE.

Diffraction and brake-effect of electrons. A. SOMMERFELD (Ann. Physik, 1931, [v], **11**, 257—330).—Mathematical. W. R. ANGUS.

Release of secondary electrons by means of hydrogen canal rays in metals. G. SCHNEIDER (Ann. Physik, 1931, [v], **11**, 357—384).—The apparatus and technique are discussed. The no. and velocity of secondary electrons released by the bombardment of thin plates of Al and Au by H canal rays have been measured. W. R. ANGUS.

Electronic emission from a metal target bombarded with positive ions. C. L. UTTERBACK and W. GEER (Physical Rev., 1930, [ii], **36**, 785—786). L. S. THEOBALD.

Scattering of high-velocity electrons by thin foils. H. V. NEHER (Physical Rev., 1931, [ii], **38**, 1321—1341).—Scattering by thin foils of Al, Ag, and Au was investigated as a function of primary energy, at. no., and angle. Elimination of secondary electrons was effected. N. M. BLIGH.

Capture and loss of electrons by helium ions in helium. P. RUDNICK (Physical Rev., 1931, [ii], **38**, 1342—1350).—Mean free paths for capture and loss were measured, using an ion source giving strictly homogeneous velocities. Results are compared with available data and with information on ionisation and energy loss. N. M. BLIGH.

Elastic scattering of slow electrons in gases. II. E. C. BULLARD and H. S. W. MASSEY (Proc. Roy. Soc., 1931, **A**, **133**, 637—651).—The angular distributions of slow electrons scattered elastically in He, Ne, N_2, H_2, and CH_4 have been measured over the range 20—125°, using the apparatus previously described (this vol., 542). The results are interpreted in terms of the quantum theory of electron scattering. The effects due to the field of the atom, the distortion of the incident wave by the at. field, and the exchange of electrons between the atom and the colliding beam are discussed. For heavy atoms the second factor is of chief importance, whereas for light atoms the effect of exchange predominates. L. L. BIRCUMSHAW.

Diffraction of electrons in gases. F. L. ARNOT (Proc. Roy. Soc., 1931, **A**, **133**, 615—636).—The angular distributions of the elastically scattered electrons in Xe, Kr, A, Ne, H_2, N_2, CH_4, and CO have been measured for velocities of the primary beam between 30 and 800 volts. The lower-velocity curves of the rare gases all show distinct diffraction patterns, whilst those of the mol. gases have a min. at about 90°. At the higher velocities the max. and min. have practically disappeared in the cases of Kr and Xe, and have completely disappeared in the other gases. The angular distribution curves have been used to determine the effective cross-section curves for elastic collisions; these give information concerning the variation with velocity of the proportion of elastic to inelastic collisions. The similarity of the angular scattering curves and the cross-section curves of CH_4 and H_2 may be accounted for by assuming that the electrons in CH_4 are scattered mainly by the four H_2 nuclei of the CH_4 mol. It may be possible to examine the structure of complex mols. by analysis of the diffraction patterns in the angular scattering curves. L. L. BIRCUMSHAW.

Photo-electrons and negative ions. E. M. WELLISH (Nature, 1931, **128**, 547—548).—A summary of experiments on the formation of negative ions from electrons. The majority of negative ions appear to be formed near the electrode at which the electrons originate, and electrons which do not give rise to negative ions near this electrode in general cross the interval between the electrodes in the free condition. L. S. THEOBALD.

Secondary emission from nickel by impact of metastable atoms and positive ions of helium. M. C. HARRINGTON (Physical Rev., 1931, [ii], **38**, 1312—1320; cf. A., 1930, 1336). N. M. BLIGH.

Recombination of ions in air and oxygen in relation to the nature of gaseous ions. O. LUHR (Physical Rev., 1930, [ii], **36**, 787; cf. this vol., 783). L. S. THEOBALD.

Properties of natural *H*-rays. C. PAVLOVSKI (Ann. Physique, 1931, [x], **16**, 150—195).—Natural H-rays have been obtained by the action of α-rays from Po on H_2, paraffin, cellophane, and collodion, the scintillation method, Wilson's method, and the chamber method having been used in their measurement. The max. range is 4·1 times the range of the α-particles used; thus the H-rays are produced by the elastic collision of an α-particle with an H nucleus, but the number of H-rays diminishes with diminishing speed of the α-rays, contrary to the theory of elastic collisions. The H-ray emission of a substance depends only on its H content, other atoms causing no modification of the effect. J. W. SMITH.

Action of positive ions of cæsium on a hot nickel surface. P. B. MOON (Proc. Camb. Phil. Soc., 1931, **27**, 570—577).—The emission of secondary electrons from hot Ni surfaces bombarded by Cs^+ ions at normal incidence increased with increasing energy of the primary ions and diminished with rise of target temp. W. R. ANGUS.

Recombination of electrons with cæsium ions. E. H. KURTH (Physical Rev., 1930, [ii], **36**, 374).—No positive effect was observed under the conditions employed. L. S. THEOBALD.

Excitation of spectral lines by collision of slowly moving positive ions. A. GÜNTHER-SCHULZE and F. KELLER (Z. Physik, 1931, **72**, 143—154).—Spectra due to He, Ne, A, Kr, H_2, O_2, and N_2 were excited by positive ions of 200—700 volts energy. A. B. D. CASSIE.

Scattering of atoms. S. MIZUSHIMA (Physikal. Z., 1931, **32**, 789—803).—Mathematical. Angular distributions are calc. for scattering of light atoms by heavy atoms, and of atoms by atoms of comparable mass. A. B. D. CASSIE.

Mobilities of gaseous ions in chlorine and chlorine–air mixtures. L. B. LOEB (Physical Rev., 1930, [ii], **35**, 137).—Mobilities in Cl_2 on the new abs. standard for positive and negative ions are 0·654 and 0·510 cm. per sec. per volt per cm., respectively. Traces of Cl_2 ($<0·1\%$) in dry air reduce the negative mobility below that of the positive ion, which is little affected by the presence of Cl_2. L. S. THEOBALD.

Cross-section of argon with respect to argon⁺. F. WOLF (Z. Physik, 1931, **72**, 42—53).—The cross-section of A to an A positive ion remains const., and greater than the gas kinetic cross-section, up to 520 volts, when a steady increase begins. A. B. D. CASSIE.

Specular reflexion of atoms from crystals. A. ELLETT (Physical Rev., 1930, [ii], **35**, 293; cf. this vol., 14).—Theoretical. L. S. THEOBALD.

Mean free path of potassium atoms in nitrogen. J. J. WEIGLE and M. S. PLESSET (Physical Rev., 1930, [ii], **36**, 373—374).—Preliminary measurements give an average val. of $3—5\times10^{-9}$ for the mean free path of K atoms in 10^{-2} to 10^{-5} cm. pressure of N_2. L. S. THEOBALD.

Scattering of atomic hydrogen by gases: mercury, argon, oxygen, and iodine. E. G. LUNN and F. R. BICHOWSKY (Physical Rev., 1930, [ii], **35**, 671).—The collision diameter of H atoms passing through gaseous Hg, A, O_2, or I is a property of the degree of interaction between the colliding particles. L. S. THEOBALD.

At. wt. of thallium. H. V. A. BRISCOE, S. KIKUCHI, and J. B. PEEL (Proc. Roy. Soc., 1931, A, **133**, 440—457).—Full details are given of a method, more rapid and precise than that of nephelometric titration, of titrating halides with Ag, and the method has been applied to the redetermination of the at. wt. of Tl by measurement of the ratio TlCl : Ag. The result Tl=204·34, with an average deviation of ±0·015, is in good agreement with the val. 204·39 (average deviation of ±0·012) given by Honigschmid and Striebel (this vol., 141). Crookes' ratio, Tl : $TlNO_3$, is found to be unsuitable for determining the at. wt. Crookes' val. Tl=204·04 must therefore be abandoned. In the absence of any direct evidence by the positive-ray method as to the existence of isotopes of Tl, it is concluded that the fractional val. deduced for the at. wt. indicates that the element is probably a mixture of two or more isotopes. (Cf. Aston, this vol., 1349.) L. L. BIRCUMSHAW.

Element 87. J. PAPISH and E. WAINER (J. Amer. Chem. Soc., 1931, **53**, 3818—3820).—The product obtained by working up 10 kg. of samarskite to obtain a high concentration of Cs afforded *X*-ray lines appropriate to element 87 in the Moseley diagram. J. G. A. GRIFFITHS.

Relative abundance of lithium isotopes. W. R. VAN WIJK (Naturwiss., 1931, **17**, 894—895).—Sources of error in Schuler's calculation of the ratio of the relative abundance of Li isotopes (this vol., 1207) are discussed. The ratio is $<10·5$ and the author's val. of 7·2 (*ibid.*, 992) is not precluded, although considerably less than Aston's val. of 10·2 (*ibid.*, 994). W. R. ANGUS.

Isotope effect in the band spectrum of lithium hydride. G. NAKAMURA (Nature, 1931, **128**, 759—760).—The isotope effect is clearly established for each strong line in the spectrum (A., 1930, 124) due to the less abundant Li^6H mol. With a change in conditions the relative intensity of the isotope lines varies from 2 : 1 to 8 : 1 for the ratio Li^7H : Li^6H. L. S. THEOBALD.

Origin of O^{17}. S. C. LIND (Physical Rev., 1930, [ii], **35**, 1408).—Considerations are advanced showing it to be highly improbable that any important fraction of O^{17} in the atm. has been generated in the earth's crust or atm. by α-ray bombardment. L. S. THEOBALD.

Demonstration of the existence of isotopes of sulphur by analysis of the fine structure of the resonance spectrum of diatomic sulphur molecules. P. SWINGS (Bull. Acad. roy. Belg., 1931, [v], **17**, 1095—1097).—The necessity for examining the absorption spectrum of S_2 with large dispersion in order to detect isotopic effects is advocated. W. R. ANGUS.

Chlorine isotope Cl^{39}. G. HETTNER and J. BOHME (Z. Physik, 1931, **72**, 95—101).—Vibration-rotation lines due to the HCl^{39} mol. were detected in

the first harmonic at 1·76 μ of the fundamental band, using the second-order spectrum of an echelette grating. A. B. D. CASSIE.

Vibrational isotope effect. R. T. BIRGE (Physical Rev., 1930, [ii], **35**, 133).—Results for Cl_2 and ICl are discussed. L. S. THEOBALD.

Nuclear moments of the isotopes of lead. Relative values of the g (I) factors of Pb^{207} and thallium. J. C. MCLENNAN, M. F. CRAWFORD, and L. B. LEPPARD (Nature, 1931, **128**, 301).—Optical data show that the g (I) factor of the Tl nucleus is approx. 4 times that of the Pb^{207} nucleus. The moment of at least one of the nuclei is composite and not due simply to a spinning proton. This invalidates the rule that each proton contributes $\pm\frac{1}{2}h/2\pi$ to the resultant; some of the protons in one of the nuclei must be endowed with a property additional to spin. L. S. THEOBALD.

Constitution of thallium and uranium. F. W. ASTON (Nature, 1931, **128**, 725).—Tl consists of two isotopes 203 and 205, the latter predominating to an extent in agreement with the accepted at. wt. (204·39). Mass spectra for UF_6 indicate that U is probably simple to at least 2 or 3%. The 238 line is strong, and is followed by a series 257 UF, 276 UF_2 . . . 333 UF_5, the last being the heaviest mass recorded on a mass spectrum. L. S. THEOBALD.

Periodic system of atomic nuclei and the principle of regularity and continuity of series. W. D. HARKINS (Physical Rev., 1931, [ii], **38**, 1270—1288).—New relations and rules for the existence and stability of at. nuclei, and for the abundance and isotopic nos. of isotopes are given. The regularities of the He, U, Li, and Be series are plotted. The at., mass, isotopic, and electronic nos. of all known isotopes are recorded, and related to the periodicity of at. nuclei; undiscovered isotopes are predicted. N. M. BLIGH.

Microneutrons. V. A. PLOTNIKOV (J. Gen. Chem. Russ., 1931, **1**, 446—454).—The difference between the at. wt. of He and of 4H amounts to $4\times0{\cdot}00724$, representing 4 microneutrons, each consisting of one electron and one microproton; these would be liberated as energy in the condensation of 4 H atoms to form He. R. TRUSZKOWSKI.

Periodicity of the atomic nucleus. R. SWINNE (Wiss. Veroff. Siemens-Konz., 1931, **10**, No. 4, 137—147).—Empirical relations have been derived between the degradation const. and at. wt. and no. of nuclear electrons of radioactive elements. The abundance of elements is discussed and results are extrapolated beyond U to a hypothetical trans-U, for which an especially long life period is to be expected. J. W. SMITH.

Radioactive disintegration. A. BRAMLEY (Proc. Nat. Acad. Sci., 1931, **17**, 579—583).—An equation for nuclear energy levels has been developed and the wave-lengths of γ-rays deduced from it are compared with experimental vals. This equation also affords a means of calculating the mean life of a radioactive atom. W. R. ANGUS.

Processes of ionisation by α-rays and their measurement by a Millikan condenser. G. SCHMIDT (Z. Physik, 1931, **72**, 275—292).—The Millikan oil drop forms a convenient small electrometer for determination of ionisation at different points along an α-ray track; ionisation of the K-level in air was followed along a Po α-ray track. A. B. D. CASSIE.

Analysis of α-particles emitted from thorium-C and actinium-C. (LORD) RUTHERFORD, C. E. WYNN-WILLIAMS, and W. B. LEWIS (Proc. Roy. Soc., 1931, **A**, **133**, 351—366).—Two distinct groups of long-range α-particles are emitted from Th-C, of ranges 9·781 and 11·662 cm. The question of their origin is discussed. Earlier conclusions on the complexity of the main group of α-particles (range about 5·4 cm.) from Ac-C have been confirmed (cf. A., 1930, 1338). No α-particles of range greater than 6·6 cm. have been found. L. L. BIRCUMSHAW.

β-Particle emission of radium-D. H. O. W. RICHARDSON (Proc. Roy. Soc., 1931, **A**, **133**, 367—380).—The tracks formed by the β-particles of Ra-D have been photographed in a Wilson expansion chamber, and the ranges of 377 tracks have been measured, using a stereoscopic method. An energy distribution curve has been constructed for the particles emitted; the secondary electronic groups are identified in this distribution, and the extent to which the continuous spectrum is represented is discussed. An attempt has been made to estimate the abs. no. of particles emitted per disintegration. L. L. BIRCUMSHAW.

Soft γ-rays from the active deposit of thorium. R. ARNOULT (Ann. Physique, 1931, [x], **16**, 196—207).—The results of Rutherford and Richardson (A., 1914, ii, 13) have been confirmed. In addition, a very readily absorbable radiation not reported by these authors has been detected. Disintegration of 100 atoms of Th-B produces about 80 quanta of radiation of wave-length 0·97 Å., 15 of 1·6 Å., and 260 of 4·6 Å. J. W. SMITH.

Measurement of the intensity of γ-rays of radium in r-units. O. GLASSER and V. B. SEITZ (Physical Rev., 1930, [ii], **35**, 1432). L. S. THEOBALD.

Complete dissociation of hydrogen. E. U. CONDON (Physical Rev., 1930, [ii], **35**, 658).—Theoretical. L. S. THEOBALD.

Average life for ionised helium. L. R. MAXWELL (Physical Rev., 1930, [ii], **36**, 379). L. S. THEOBALD.

Possibility of bringing mean life directly into the Schrödinger equation for the hydrogen atom. A. BRAMLEY and A. C. G. MITCHELL (Physical Rev., 1930, [ii], **35**, 1419). L. S. THEOBALD.

Life and radius of the metastable mercury atom. M. L. POOL (Physical Rev., 1930, [ii], **35**, 1419). L. S. THEOBALD.

Theory of excitation by collision with heavy particles. N. F. MOTT (Proc. Camb. Phil. Soc., 1931, **27**, 553—560).

Evaporation of glowing wires in a vacuum. I. L. PRASNIK (Z. Physik, 1931, **72**, 86—94).—Theoretical. A. B. D. CASSIE.

Matter and radiation. F. G. DONNAN (Nature, 1931, **128**, 290—292).—A lecture.
L. S. THEOBALD.

Magnetic experiments on the cosmic rays. B. ROSSI (Nature, 1931, **128**, 300—301).
L. S. THEOBALD.

Nature of cosmic radiation. L. F. CURTISS (Physical Rev., 1930, [ii], **35**, 1433).—The application of a magnetic field to two Geiger–Müller tube counters decreases the no. of coincidences by 25%, an effect attributed to cosmic radiation, which is thus a corpuscular radiation of high energy.
L. S. THEOBALD.

Similarity between cosmic rays and gamma rays. R. A. MILLIKAN and I. S. BOWEN (Nature, 1931, **128**, 583).—The cause of the similar divergence from linearity in the pressure–ionisation curves of cosmic rays and the γ-rays of Ra and Th is discussed.
L. S. THEOBALD.

Absorption and dissociative or ionising effect of monochromatic radiation in an atmopshere on a rotating earth. II. S. CHAPMAN (Proc. Physical Soc., 1931, **43**, 483—501).
A. B. D. CASSIE.

Electrical charging of suspended particles. C. TRAGE (Ann. Physik, 1931, [v], **10**, 833—845).—A Wollaston wire replaced the suspended particle in a test of the gas kinetic theory of the charging of particles; the results are in agreement with Arendt and Kallmann's theory (cf. Z. Physik, 1926, **35**, 421).
A. B. D. CASSIE.

Angular momentum of light. (SIR) C. V. RAMAN (Nature, 1931, **128**, 545).
L. S. THEOBALD.

Spin of light quanta. (SIR) C. V. RAMAN and S. BHAGAVANTAM (Nature, 1931, **128**, 727).—Spectroscopic measurements of the depolarisation of scattered light in the case of CS_2 and C_6H_6 (by Venkateswaran) confirm the results predicted by the theory that photons possess intrinsic angular momentum.
L. S. THEOBALD.

Experiments with an automatic photo-electric spectrophotometer. P. J. MULDER and J. RAZEK (Physical Rev., 1930, [ii], **35**, 1424).—The instrument can be used for testing solutions which change colour rapidly. Records for hæmatin and oxyhæmoglobin solutions have been obtained. L. S. THEOBALD.

Analysis of complicated band spectra with the aid of magnetic rotation spectra. R. W. WOOD and G. H. DIEKE (Nature, 1931, **128**, 545—546).—The absorption spectrum of NO_2 is much simplified by the application of a magnetic field. The theoretical significance of magnetic rotation structure for diat. gases is discussed. L. S. THEOBALD.

Effect of magnetic field on absorption spectrum of nitrogen peroxide. P. LAMBERT and I. AGARBICEANU (Compt. rend., 1931, **193**, 732—733; cf. preceding abstract).—These effects are being investigated by means of the great electromagnet of Bellevue, and the sensitiveness of some lines to the magnetic field has been demonstrated.
C. A. SILBERRAD.

Secondary structure of lithium fluoride. T. H. JOHNSON (J. Franklin Inst., 1931, **212**, 507—514; cf. A., 1930, 1232).—The reflexion of at. H from the cleaved (100) surface of a LiF crystal yields diffuse secondary spectra, and this phenomenon is regarded as evidence for a secondary structure on the surface, which may have the period required by Zwicky's theory (*ibid.*, 139). N. H. HARTSHORNE.

Spectrum of barium fluoride in the extreme red and near infra-red. T. E. NEVIN (Proc. Physical Soc., 1931, **43**, 554—558).—The spectrum of BaF_2 was investigated between 6700 and 8700 Å.
A. B. D. CASSIE.

Ultra-violet bands of CO in the electrodeless ring discharge. H. P. KNAUSS and J. C. COTTON (Physical Rev., 1931, [ii], **38**, 1190—1194).—The relative intensities of bands in the region 2900—2150 Å. were observed, and compared with Geissler tube spectra. The Cameron bands including the 2157 Å. band appeared at low pressures; the bands of the CO^+ ion were strong at all pressures, and the fourth positive bands at high pressures. N. M. BLIGH.

Absorption spectra of some mercury and cadmium halides in the vapour phase. K. BUTKOW (Z. Physik, 1931, **71**, 678—688).—The absorption spectra of the vapours of HgI_2, CdI_2, and $HgBr_2$ were measured in the region 7000—1950 Å.; absorption maxima in the ultra-violet are associated with different modes of dissociation of the mol. The spectra are similar to those obtained from solutions, except for additional maxima obscured by the presence of a solvent. A. B. D. CASSIE.

Spectrum of potassium permanganate. F. VLES and A. SIMCHEN (Compt. rend., 1931, **193**, 581—584).—The visible and ultra-violet spectrum of $KMnO_4$ in buffered solution of p_H 8·7 consists of 21 bands in two groups, indicating two modes of mol. vibration. Some ten successive states of the MnO_4' ion are indicated. The moment of inertia is therefore dependent on the (cf. A., 1930, 12).
C. A. SILBERRAD.

Absorption spectra of pure hydrochloric acid and of bromine in the ultra-violet. (MME.) N. DEMASSIEUX and V. HENRI (Compt. rend., 1931, **193**, 591—592).—The absorption spectrum in aq. HCl beyond λ 2500 is due to a trace of Br. Pure aq. HCl shows no absorption up to λ 2144. Br in aq. HCl shows an absorption ten times as strong as is shown by the same amount of Br in H_2O, whence it is inferred that a compound of Br and HCl is present, and that addition of aq. HCl should accelerate bromination (cf. A., 1913, ii, 690). C. A. SILBERRAD.

Absorption spectra of the alkyl halides; energies of the C–I and C–Br linkings. T. IREDALE and A. G. MILLS (Proc. Roy. Soc., 1930, **A**, **133**, 430—439).—The energies of the C–I and C–Br linkings, calc. from the heats of combustion of the alkyl iodides and bromides, are in good agreement with the spectroscopic energies calc. from the long-wave limits of the continuous absorption bands of the alkyl halides in the near ultra-violet. It is considered that the alkyl halides dissociate on absorption of light into alkyl residues and excited halogen atoms. The fact that the absorption limits shift towards the red when the alkyl halides are liquefied may be explained on

the basis of energy level changes due to mol. association. L. L. BIRCUMSHAW.

Transmission of ultra-violet radiation by lake water. C. D. HODGMAN (Physical Rev., 1930, [ii], 35, 1423).—H_2O is rendered less transparent to ultra-violet radiation by the presence of small amounts of dissolved salts and org. substances such as occur in natural river and lake waters. L. S. THEOBALD.

Mirror image correspondence of absorption and fluorescence spectra. I. V. L. LEVSCHIN (Z. Physik, 1931, 72, 368—381).—Between 20° and −70° fluorescence spectra are exact mirror images of absorption spectra; this holds for C_6H_6 as well as for coloured solutions, and is a fundamental property of luminescence. A. B. D. CASSIE.

Fluorescence spectrum of benzene. F. ALMASY and C. V. SHAPIRO (Physical Rev., 1930, [ii], 35, 1422).—The fluorescence spectrum of C_6H_6 excited by a quartz Hg arc agrees with the absorption spectrum in the range where both overlap. Most of the bands can be accounted for by assuming that the electronic origin of the system lies at 37,489 cm.$^{-1}$ The vibrational frequencies are 923 cm.$^{-1}$ for the excited state and 998 and 160 cm.$^{-1}$ for the normal state. L. S. THEOBALD.

Electronic transitions in the spectra of benzene. C. V. SHAPIRO, R. C. GIBBS, and J. R. JOHNSON (Physical Rev., 1930, [ii], 35, 1422).—Spectroscopic data for C_6H_6 show that only two electronic transitions, at 37,489 and 38,612 cm.$^{-1}$, need be assumed to provide an adequate energy level scheme. The fluorescence spectrum is confined to the first system, whilst the absorption spectrum is distributed between both. The Tesla luminescence spectrum is similar to that of fluorescence. L. S. THEOBALD.

Band spectrum of benzene: existence of a small vibrational frequency in the normal state. C. V. SHAPIRO, R. C. GIBBS, and J. R. JOHNSON (Physical Rev., 1931, [ii], 38, 1170—1178).—A postulated vibrational frequency of 160 cm.$^{-1}$ is discussed, and is shown to be in agreement with theoretical deductions. N. M. BLIGH.

Determination of the structure of absorption resonators of organic chromophores. VIII. Mechanism of the absorption of light and of shared-resonators. IX. Extinction curves of ωω′-diphenylpolyenes. X. Extinction curves of azines. XI. Structure of shared-resonators in anthracene, acridine, phenazine, phenanthrene, and pyrene. XII. Influence of mode of attachment on the frequency of a shared-resonator. XIII. Determination of the structure of the halochromic compounds of polyene hydrocarbons, quinones, and polyene ketones. XIV. Structure of the shared-resonators of polyene ketones. D. RADULESCU (Ber., 1931, 64, [B], 2223—2225, 2225—2229, 2230—2233, 2233—2240, 2240—2242, 2243—2249, 2249—2250).—VIII. A polyene resonator is compared with a vibrating string made up of several similar components in which the tension and proper vibration of the elementary components can be individually varied. The properties of shared-resonators are expressed as follows. Tension being kept const., the main frequencies of shared-resonators diminish with increase in the no. of elementary components. Powerful, polar-negative substituents cause marked diminution of the main frequencies; an even stronger effect is produced by the addition of strong positive charges to the electrons of the resonator. Mechanical strains and distortions of the mol. cause corresponding changes of the characteristic vibrations. The atoms united by these electrons undergo harmonic vibration during the vibrations of the shared-resonator, so that every frequency of a shared-resonator corresponds with a copulated, infra-red at. frequency. The light energy absorbed by the electrons in any given period is completely utilised by the at. structure and transformed into heat or potential energy.

IX. [With F. BARBULESCU.] Examination of the extinction curves of αδ-diphenylbutadiene, αζ-diphenylhexatriene, αθ-diphenyloctatetraene, and αμ-diphenyldodecahexaene shows that the wave-length of the extinction max. increases with the no. of elementary components. At least 11 copulated elementary resonators (6 continuously conjugated double linkings) are necessary for the production of a pronounced crocetene spectrum. Two double linkings exhibit only a single structureless band, whereas with three, fission into bands is first noticed, which is well developed in diphenyloctatetraene without attaining the true crocetene structure.

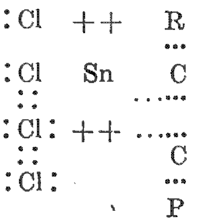
X. [With V. ALEXA.] The spectra of αδ-diphenylbutadiene, αθ-diphenyloctatetraene, αμ-diphenyldodecahexaene, benzylidene-, cinnamylidene-, and ε-phenylpentadienylidene-azine are compared. Replacement of the C atoms by 2 N atoms caused marked change in the electric tension in three of the elementary resonators, since the shared-resonator is not made up of completely similar but of three types of components, C:C, C:N, and N:N, with atom-carrying pairs of differing polarity and, consequently, of differing tension. The heterogeneity of the components of the shared-resonator finds its expression in a partial obscuring of the characteristic spectrum of the resonator. Replacement of the C by N atoms in the resonator-carrier causes the individual bands to flow together, and a somewhat scattered shading of the band system of the initially homogeneous resonator results.

XI. [With G. OSTROGOVICH.] As predicted by the author's theories, the extinction curve of anthracene shows two well-marked peaks, a band spectrum of long wave-length of the crocetene or naphthacene type with several pronounced maxima corresponding with electromeride I_A and a short wave-length peak corresponding with a diffused C_6H_6 band and due to electromeride I_B. The extinction curve of phenanthrene is not similar to that of anthracene and there is absorption much further towards the ultra-violet. The acridine and phenazine spectra consist of two well-separated peaks, a long wave-length peak corresponding with a diffused anthracene peak and a short wave-length peak due to the C_6H_6 nuclei. The extinction curve of pyrene exhibits three peaks, anthracenoid, naphthalenoid, and belonging to an otherwise unknown, highly-unstabilised, two-membered resonator.

XII. [With G. OSTROGOVICH and F. BARBULESCU.]

The expected relationship between perylene and naphthacene is exhibited in their spectra, each of which consists of a long wave-length crocetenoid peak and a short wave-length naphthalenoid peak. With the former hydrocarbon the long wave-length peak is displaced towards the region of short wave-length and somewhat blurred in comparison with the latter hydrocarbon. The difference is ascribed to the mode of angulation, since it is also shown by pyrene and anthracene, the *A* forms of which possess the same number of elementary components; the spectrum of the angularly arranged resonator is strongly displaced towards the ultra-violet.

XIII. The extinction curves of polyenes (benzylideneacetophenone etc.) in EtOH and EtOH–HCl have been measured. The complexes which cause intense coloration are exclusively substances with a positive-polar central atom which have the tendency to fill the inner sphere with negative polar groups (NR_3, OR_3, etc.). It follows, therefore, that the polyene hydrocarbons must add with their negative-polar component in the inner sphere at the positive central atom. The sole negative component in a simple polyene chain is the elementary resonator (:), *i.e.*, the electrons of the conjugated double linkings. Such a complex, *e.g.*, with $SnCl_4$, can correspond only with the general scheme (I). The immediate proximity the strongly positive metallic ion causes an unusually pronounced loosening of the electron arrangement in the resonator and explains the marked deepening of the colour. In accordance with the octet theory, the Cl atom of $HClO_4$ must be unusually strongly polar-positive, thus explaining the formation of coloured complexes with polyenes of the same spectral character as those with $SnCl_4$. The coloured compounds given by many aromatic hydrocarbons with polynitro-compounds are considered to be formed by the attachment of their resonator electrons to the NO_2-group.



XIV. [With V. ALEXA.] The long wave-length absorption max. of polyene ketones is displaced in the direction of greater wave-length in the sequence Ph styryl, distyryl, Ph δ-phenyl-$\Delta^{\alpha\gamma}$-butadienyl, di-δ-phenyl $\Delta^{\alpha\gamma}$-butadienyl, and di-ζ-phenylhexatrienyl ketone. In addition to the long wave-length-maxima, shorter wave-length maxima occur corresponding with the not continuously conjugated electromerides. These correspond with the non-conjugated CO group ($COMe_2$), the group C:C:C:C in cinnamyl derivatives, and the group C:C:C:C:C:C hexadienyl compounds.

H. WREN.

Absorption of light and complex formation with unsaturated compounds. B. ARENDS (Ber., 1931, **64**, [*B*], 1936—1951; cf. A., 1917, i, 261; 1919, ii, 40; 1923, ii, 201).—The absorption spectra of the following substances have been quantitatively examined: stilbene, *iso*stilbene, α-methyl- and αβ-dimethyl-stilbene in EtOH; tetraphenylethane, tetraphenylethylene dichloride, stilbene, tri- and tetraphenylethylene in $CHCl_3$; *cis*-dichloro-, *cis*-dibromo-, and *p*-methyl-stilbene in EtOH; cinnamic acid, styrene, αβ-dichloro-β-phenylpropionic and β-phenylpropionic acids in EtOH; cinnamic, *allo*cinnamic, *cis*- and *trans*-dibromocinnamic acid in MeOH. The results are discussed in detail. The decomp. consts. of the following complex compounds have been examined by measurement of the changes of solubility in heterogeneous system and by photometric determination of the concentrations in homogeneous system: picric acid with stilbene, *p*-methyl-, *p*-chloro-, α-methyl-, phenyl-, dichloro-, and dibromo-stilbene, tetraphenylethylene, and dibenzyl. H. WREN.

Infra-red absorption of fused and crystalline quartz from 2 μ to 8 μ. F. E. MCGINNETY (Proc. Durham Phil. Soc., 1931, **8**, 337—350).—Available data on the absorption of fused and cryst. quartz have been collected, unified, and discussed.

W. R. ANGUS.

Infra-red absorption of hydrates. A. E. VAN ARKEL and C. P. FRITZIUS (Rec. trav. chim., 1931, **50**, 1035—1045).—The distinction between hydrate and hydroxyl formation is discussed. The ability of a salt to form hydrates depends on the energy required to separate the ions sufficiently to permit a H_2O mol. to be inserted between them being greater than the energy gained by the effect of the H_2O dipole on the field of the ions, and this, in turn, depends on the ionic radii and charges. In the cases studied hydrates may be distinguished from OH-compounds by their infra-red spectra, which for the former show, like H_2O, bands at 1·5 and 2·0 μ, whilst those for the latter do not. N. H. HARTSHORNE.

Absorption of acetylene and ethylene in the near infra-red. R. M. BADGER (Physical Rev., 1930, [ii], **35**, 1433).—Absorption spectra of C_2H_2 and C_2H_4 have been photographed in the region 6800—9200 Å. C_2H_2 has a band with sharp lines, showing marked intensity alternation, with centre at approx. 7886 Å.; C_2H_4 has a complex band, centre at approx. 8706 Å., which also shows convergence.

L. S. THEOBALD.

Infra-red absorption spectrum of carbonyl sulphide. C. R. BAILEY and A. B. D. CASSIE (Nature, 1931, **128**, 637—638).—The absorption spectrum of COS, obtained by means of a monochromator method, has bands at 527 *, 859, 1051, 1718 *, 1898 *, 2079, 2904, 3095 *, 3742 *, and 4084 * $cm.^{-1}$ (* signifies relatively weak intensities). The results are discussed and a few *P*—*R* branch separations given. L. S. THEOBALD.

Technique of the Raman effect. P. GRASSMANN (Z. Physik, 1931, **72**, 240—241).—Multiple reflexions can be used to give measurable Raman scattering from 0·1 c.c. of liquid. A. B. D. CASSIE.

Kinetics of fluctuations. M. LEONTOVITSCH (Z. Physik, 1931, **72**, 247—265).—Mathematical. The results are applied to fine structure of lines due to scattering by solutions. A. B. D. CASSIE.

Raman effect in rock-salt. E. FERMI and F. RASETTI (Z. Physik, 1931, **71**, 689—695).—The Raman effect of rock-salt is a weak continuous displacement extending to a limit at 365 $cm.^{-1}$ from the original line. Vibrations in rock-salt are symmetrical and to a first approximation should show no Raman effect; quadratic terms of the elastic dis-

placements must be included in the polarisability of the crystal to account for any Raman effect; this explains a limit at twice the residual ray frequency.
A. B. D. CASSIE.

Fine structure of Raman bands. I. Structure of carbon tetrachloride Raman bands and the symmetry of quadrivalent carbon. A. LANGSETH (Z. Physik, 1931, **72**, 350—367; cf. this vol., 1111).—Normal vibrations and isotope effects in molecules of type XCl_4 are discussed. Raman spectra due to CCl_4, $SnCl_4$, CBr_4, $POCl_3$, and SO_2Cl_2 were investigated with a dispersion of 8 Å. per mm.; the 458 cm.$^{-1}$ displacement in CCl_4 is a triplet, due to isotopes, and the 218 and 314 are doublets, probably due to C having C_3^v symmetry. A. B. D. CASSIE.

Structure of Raman band of water. G. BOLLA (Nature, 1931, **128**, 546—547).—Nine weak, diffuse components (wave-lengths given) have been observed in the Raman band of H_2O excited by the Hg line 2536 Å. at 17°. The average distance between two components is 50 cm.$^{-1}$ L. S. THEOBALD.

Structure of the Raman band of water. S. RAFALOWSKI (Nature, 1931, **128**, 546).—The Raman bands of H_2O become sharper with an increase in concentration of HNO_3 in its aq. solution; the central component divides into two, whilst the intensity of the short wave-length component increases rapidly. With HCl, the intensity of both outer components decreases with an increase in concentration, whilst the inner component apparently enlarges.
L. S. THEOBALD.

Raman lines due to co-ordination linking. D. M. BOSE and S. DATTA (Nature, 1931, **128**, 725—726; cf. this vol., 25).—A co-ordination linking is a weak valency linking between the central atom and one of the co-ordinated group and should manifest itself in the Raman spectra. The spectra of the Hg radiation scattered by solutions of $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_6]Cl_2$ give evidence of the presence of modified lines in the case of the cobaltic compound only. The former is a true co-ordination compound and the latter an associated compound.
L. S. THEOBALD.

Raman spectra of chloroform and silicochloroform. M. DE HEMPTINNE and (MLLE.) A. PEETERS (Bull. Acad. roy. Belg., 1931, [v], **17**, 1107—1118).—Raman displacements for $CHCl_3$ and $SiHCl_3$ are given and compared with existing data. Frequencies evaluated from force-const. formulæ are in good agreement with observed displacements. The displacement of 587 cm.$^{-1}$ is characteristic of the Si·Cl linking. W. R. ANGUS.

Raman effect in some acid derivatives and esters. V. N. THATTE and A. S. GANESAN (Phil. Mag., 1931, [vii], **12**, 823—832).—The Raman spectra of Ac_2O, mono-, di-, and tri-chloroacetic acids, *iso*amyl nitrate, allylthiocarbimide, $Et_2C_2O_4$, AcCl, and BzCl were measured and discussed. H. J. EMELÉUS.

Dispersion of polarisation of light scattering. K. S. KRISHNAN and A. SARCAR (Indian J. Physics, 1931, **6**, 193—205).—The dispersion of the polarisation of the light scattered by C_6H_6 has been measured by a method which is independent of the polarisation of the instrument. Measurements with liquid C_6H_6 extending to 3100 Å. give a const. val. for the depolarisation factor suggesting, presumably, const. optical anisotropy. W. R. ANGUS.

Intensity and polarisation of lines scattered by ring-shaped hydrocarbons. J. WEILER (Z. Physik, 1931, **72**, 206—214).—The 992, 803, 826, 886, and 905 cm.$^{-1}$ Raman lines of C_6H_6, C_6H_{12}, C_6H_{10}, C_5H_{10}, and of C_5H_8, respectively, are ascribed to radial vibrations, and the absence of the 1030 cm.$^{-1}$ line from C_6H_6 scattering indicates that this frequency is due to tangential vibration. A. B. D. CASSIE.

Angular distribution of intensity of Raman lines. D. P. RAY-CHAUDHURI (Z. Physik, 1931, **72**, 242—246).—The angular distribution of intensity of the Raman lines 4215, 4555, and 4617 Å. due to C_6H_6, using a Hg vapour lamp, obeyed the $(1+\cos^2\theta)$ law between 15° and 145°. A. B. D. CASSIE.

Raman effect. XIV. Raman spectrum of organic substances (nitro-compounds, nitrates, nitrites). A. DADIEU, F. JELE, and K. W. F. KOHLRAUSCH (Monatsh., 1931, **58**, 428—455).—Data are given for 34 different compounds, including aromatic and aliphatic NO_2-compounds, aliphatic nitrates and nitrites, inorg. nitrates and nitrites, and HNO_3. The lines 1340 and 1529 cm.$^{-1}$ appear to be characteristic of the NO_2-group in aromatic compounds, with the possible exception of *o*- and *p*-$BrC_6H_4{\cdot}NO_2$. In the aliphatic compounds the frequencies are a little higher and vary with the position of the NO_2-group. The org. nitrates have lines in the neighbourhood of 1274, 1627, 860, and 580. The org. nitrites have only one strong high frequency, 1635, and also one at 600. Several show exceptional features. The results are discussed with reference to the large dipole moment of the NO_2-group. The question of the presence of the ψ-acid form, $HO{\cdot}NO_2$, in HNO_3 is considered. M. S. BURR.

Raman spectra of liquid mixtures. P. KRISHNAMURTI (Nature, 1931, **128**, 639).—Dilution of AcOH to 95% introduces at 1712 cm.$^{-1}$ a new faint component to the line at 1667 cm.$^{-1}$ Further dilution increases intensity until at 75% acid only one broad line at 1712 cm.$^{-1}$ is present. The results indicate that $AcOH,H_2O$ is formed. L. S. THEOBALD.

Effect of temperature on fluorescence of dye solutions and some consequences of the law of mirror image correspondence. II. V. L. LEVSCHIN (Z. Physik, 1931, **72**, 382—391).—The effect of temp. for changes in intensity, width of spectral region, and the position of max. fluorescence relative to the max. of absorption was investigated. Quenching of fluorescence of solutions was also investigated.
A. B. D. CASSIE.

Energy transformations at surfaces. II. Photoluminescence of fluorescent dyes at surfaces. H. KAUTSKY, A. HIRSCH, and W. BAUMEISTER (Ber., 1931, **64**, [*B*], 2053—2059; cf. this vol., 1033).—According to their nature, the dyes are adsorbed on SiO_2 gel *E* or $Al(OH)_3$ gel. The adsorbates are washed with H_2O, heated for about 2 hr. at about 150°/high vac., and sealed in evacuated glass tubes. Fluorescence, similar to that of their solutions, occurs with all the adsorbates in daylight, particularly

with brightly fluorescing dyes (fluorescein, rhodamines, *iso*quinoline-red, acridines). Trypaflavine–SiO_2 gel adsorbates exhibit very marked phosphorescence initially very little weaker than the emission during irradiation, but declining rapidly. The property is shared by many other acridine dyes. The colour of the phosphorescence is similar to that of the fluorescence of corresponding adsorbates. (For the detection of very short phosphorescence a simple phosphoroscope is described.) Brightness and duration of phosphorescence are not connected with intensity of fluorescence. Duration is diminished greatly by rise in temp., but prolonged by powerful cooling and then accompanied by alteration in the nature of the emitted light in the direction of longer wave-length. A similar but less pronounced effect is observed with the fluorescence. With small concentration of dye the gel particles glow throughout their whole mass, whereas with greater concentrations the glow is restricted to the outer surface and displaced towards longer wave-length. Fluorescence is not markedly diminished in brightness, but the phosphorescence is greatly curtailed. Gel particles are much more highly fluorescent than equiv. droplets of aq. or EtOH solution. H. WREN.

Chemiluminescence in oxidation of dyes and phenols by hydrogen peroxide and ferrous sulphate, or by ozone. N. N. BISWAS and N. R. DHAR (Z. anorg. Chem., 1931, **199**, 400—405).—The luminescence of various dyes and phenols is more marked in non-aq. solution than in aq. solution, and increases with rise in temp. With the dyes the luminescence diminishes as the concentration increases, whereas the reverse is true of the phenols.

R. CUTHILL.

Chemiluminescence of solid sodium. R. M. BOWIE (J. Physical Chem., 1931, **35**, 2964—2967).—Moist air, O_2, H_2, or CO_2, but not the dried gases, produce light when in contact with solid Na. H_2O vapour, H_2S, dry HNO_3 vapour, and dry AcOH vapour also produce luminescence, but not SO_2 or the halogens. Liberation of H_2 always accompanied luminescence, which appears to be associated with the rupture of a H–O linking of a vaporised, polar mol. The spectrum consists of a narrow band with a max. at approx. 5100 Å. L. S. THEOBALD.

Selective maxima in the spectral response curves of light-sensitive compounds as a function of valency. A. R. OLPIN (Physical Rev., 1930, [ii], **35**, 671).—Spectral response curves for photoelectric Na_2O_2, Na_2O, Na_3O, and Na_4O cells show all the selective maxima demanded by the Lindemann formula when n is chosen to agree with the valency of the metal. This condition is general for the other alkali metals, a max. response to red or infra-red light being dependent on the formation of a subvalent compound. L. S. THEOBALD.

Temperature variation of the dielectric polarisation of benzene derivatives. E. BRETSCHER (Physikal. Z., 1931, **32**, 765—773).—The polarisations of $CH_2Ph{\cdot}OBz$ and of Et phthalate follow closely the $P=A+B/T$ law, their dipole moments being 2·69 and $2{\cdot}08\times10^{-18}$, respectively. Pyrocatechol Et_2 ether follows the same law, but the val. of A varies widely with the method of measurement adopted, differences being observed according to the solvent used and these differing from the val. of the mol. refraction. This is explained by assuming different states of the mol., with different electric moments.

J. W. SMITH.

Dielectric constant of liquids under high pressure. W. E. DANFORTH, jun. (Physical Rev., 1931, [ii], **38**, 1224—1235).—Dielectric consts. were determined at two temp. and at pressures up to 12,000 atm. for PhCl, PhBr, eugenol, hexyl, *iso*butyl, and ethyl alcohol, glycerol, CS_2, C_5H_{12}, and Et_2O. Density is plotted against reciprocals of the Clausius-Mosotti function. N. M. BLIGH.

Change of the dielectric constant of carbon disulphide with temperature. J. MAZUR (Nature, 1931, **128**, 761).—The dielectric const. of CS_2 increases from 2·630 at 20° to 2·936 at −90°, decreases to a min. of 2·810 at approx. −109°, and rises again to a max. of 2·819 at −112°. L. S. THEOBALD.

Change of dielectric polarisation of nitrobenzene with temperature. M. WOLFKE and J. MAZUR (Nature, 1931, **128**, 584).—Computed vals. of the dielectric polarisation, P, of $PhNO_2$ fall linearly with temp. from 30° to 9·6°, where a sudden drop in the val. of P occurs, indicating that at 9·6° the mol. of $PhNO_2$ undergoes a change (cf. this vol., 899).

L. S. THEOBALD.

Differences between the dipole moments of saturated and unsaturated substances. L. E. SUTTON (Proc. Roy. Soc., 1931, **A**, **133**, 668—695).—The dielectric const., refractive index, and density of C_6H_6 solutions of *o*- and *m*-nitrobenzonitrile, $CHPhCl_2$, $CPhCl_3$, and $CMeCl_3$ have been measured at 25°, from which the electric dipole moments have been calc. The available data supplemented by the above and a comparison of corresponding aliphatic and aromatic compounds show that there is an electron shift towards the C_6H_6 ring (+) when the group substituted is *o*-*p*-directing, and away from the ring (−) when it is *m*-directing. These effects occur independently of the polarisation caused by the group dipole and are in agreement with Lapworth's and with Robinson's theories of activation in conjugated systems. The mean effect is small, and probably there is a small effect in each mol., not a large effect in only a fraction of the mols. Similar effects occur in unsaturated open-chain compounds, and if the double linkings are conjugated these are greater than those in aromatic compounds. L. L. BIRCUMSHAW.

Complex compounds of aluminium halides. H. ULICH and W. NESPITAL (Z. angew. Chem., 1931, **44**, 750—753).—Determinations of the mol. wt. and measurements of the dipole moment of additive compounds of the type $MHal_3,X$ and $MHal_2,2X$ lead to the assumption that these compounds have a tetrahedral configuration with the metal atom as centre. The compounds have large dipole moments which are approx. equal to the sum of the moments of the halide and the ligand. A. R. POWELL.

Effect of thermal treatment on the electrical conductivity of cuprous oxide. F. WAIBEL (Wiss. Veroff. Siemens-Konz., 1931, **10**, No. 4, 65—69).—The

effect of thermal treatment on the conductivity of Cu_2O has been investigated from 0° to 1050° and at O_2 pressures of 0—1 atm. Prolonged tempering at 450—550° and rapid cooling lead to max. conductivity.

J. W. SMITH.

Rectifying action of cuprous oxide. F. WAIBEL (Wiss. Veröff. Siemens-Konz., 1931, **10**, No. 4, 70—72).—The rectifying action of pure Cu_2O in contact with foreign conductors is identical with that shown by the material formed on a Cu base.

J. W. SMITH.

Rectifying effect and photo-phenomena in carborundum crystals. B. CLAUS (Ann. Physik, 1931, [v], **11**, 331—356).—The rectifying influence of SiC crystals was studied in relation to the pressure of the contact metal. A yellow light and a blue light are emitted depending on the potential. The spectra of these emissions have been observed.

W. R. ANGUS.

Contact rectification. II. Cupric sulphide–magnesium junction. M. BERGSTEIN, J. F. RINKE, and C. M. GUTHEIL (Physical Rev., 1930, [ii], **35**, 1425). L. S. THEOBALD.

Bismuth-black and its applications. A. H. PFUND (Physical Rev., 1930, [ii], **35**, 1434).—The optical properties and applications of black Bi films obtained by evaporating Bi from W wire in a vac. are described. L. S. THEOBALD.

Optical rotation and atomic dimensions. Halogeno-tetra-acetyl derivatives of mannose, and their configurative peculiarities. D. H. BRAUNS (Bur. Stand. J. Res., 1931, **7**, 573—583; cf. A., 1929, 913).—The prep. of *α-iodomannose tetra-acetate*, m. p. 95°, $[\alpha]_D^{20}$ +190·5° in $CHCl_3$, is described. The vals. of $[\alpha]^{20}$ for the corresponding Cl and Br compounds are +90·13° and +131·57° (in $CHCl_3$). These vals. for [α] do not agree with the at. dimension relation established for the halogen derivatives of other monosaccharides (A., 1928, 157). This is due to the fact that in the derivatives of mannose, but not in the other halogen derivatives, the H of the first asymmetric C atom, to which the halogen is also attached, is influenced by atoms of the Ac group attached to the second C atom.

R. CUTHILL.

Refraction and dispersion of gaseous pentane and chloroform. H. LOWERY and T. S. HARTLEY (Proc. Physical Soc., 1931, **43**, 559—561).—*n*-Pentane has n_{Hg5461}, 1·001683, and $CHCl_3$ 1·001448 at n.t.p. conditions; Sellmeier formulæ are given for the range 4358—6708 Å. A. B. D. CASSIE.

Refraction and dispersion of gaseous ethyl bromide. H. LOWERY and J. K. ELLIOT (Proc. Physical Soc., 1931, **43**, 562—563).—Gaseous EtBr has n_{Hg5461}, 1·001261 at n.t.p. conditions; a Sellmeier formula is given for the dispersion in the range 4358—6708 Å. A. B. D. CASSIE.

Refractometric value of fluorine in organic compounds. G. SCHIEMANN [with R. PILLARSKY, S. KÜHNE, W. ROSELIUS, and W. WINKELMÜLLER] (Z. physikal. Chem., 1931, **156**, 397—418).—A detailed account of work already published (this vol., 1113). H. F. GILLBE.

Optical properties of some aromatic organic crystals. K. L. NARASIMHAM (Indian J. Physics, 1931, **6**, 233—240).—The optical properties of Ph_2, phenanthrene, and fluorene have been studied. The birefringence for each is less than for $C_{10}H_8$. The results are discussed with respect to chemical constitution and *X*-ray crystal structure.

W. R. ANGUS.

Magnetic spectra produced by magnetic after-effects. V. ARKADIEV (Z. Physik, 1931, **72**, 116—124).—Theoretical, indicating the relationship for the fall in permeability of ferromagnetics in alternating fields found by various observers.

J. FARQUHARSON.

Magnetic and electric spectroscopy. V. ARKADIEV (Z. Physik, 1931, **72**, 125—129; cf. preceding abstract).—Theoretical. J. FARQUHARSON.

Magnetic double refraction in aliphatic liquids. S. W. CHINCHALKAR (Indian J. Physics, 1931, **6**, 165—179).—The magnetic birefringence of many aliphatic liquids has been measured relative to $COMe_2$ as standard. A gradual diminution is found for ketones with higher alkyl groups. The val. for H_2O is smaller than for EtOH. Vals. for esters are of the same order as those for acids. The magnetic anisotropy is estimated for those mols. of which light-scattering data are available and is strongly positive for the CO group and negative for Me and OH. The negative birefringence of CS_2 is due to its strong optical anisotropy. J. FARQUHARSON.

New type of magnetic birefringence. (SIR) C. V. RAMAN and S. W. CHINCHALKAR (Nature, 1931, **128**, 758—759).—Magnetic birefringence of the kind indicated by the orientation theory is shown by aq. solutions of Ce, Pr, Er, and Yt when observed in strong magnetic fields. With light in the visible region the birefringence is negative (same sign as shown by CS_2) and apparently proportional to concentration. Solutions of La and Gd show no such effect.

L. S. THEOBALD.

Electric double refraction in gases. J. W. BEAMS and E. C. STEVENSON (Physical Rev., 1930, [ii], **35**, 1440).—A new method for studying the Kerr effect in gases at high pressures and with intense electric fields indicates that the Kerr const. for CO_2 remains unchanged to within 2% between 15 and 45 atm. at 21°. A Kerr effect has been observed in O_2 and N_2 at 100 atm. L. S. THEOBALD.

Physics of the nitrobenzene Kerr cell. II. Validity of Kerr's law for nitrobenzene in fields up to 1·5×10⁵ volts per cm. F. HEHLGANS (Physikal. Z., 1931, **32**, 803—808; cf. this vol., 1220).—Kerr's law is valid within the range quoted.

A. B. D. CASSIE.

Objections to a proof of molecular asymmetry of optically active phenylaminoacetic acid. L. PAULING and R. G. DICKINSON (J. Amer. Chem. Soc., 1931, **53**, 3820—3823).—Polemical. The evidence presented by Clark and Yohe (A., 1929, 1294) is insufficient to prove mol. asymmetry or to fix the space-group. J. G. A. GRIFFITHS.

Theory of space-groups in crystal structure determinations. M. L. HUGGINS (J. Amer. Chem.

Soc., 1931, **53**, 3823—3826).—Polemical. The space-groups assigned to several compounds (this vol., 290) are open to doubt. J. G. A. GRIFFITHS.

Space-groups and molecular symmetry of optically active compounds: a reply. G. L. CLARK (J. Amer. Chem. Soc., 1931, **53**, 3826—3831; cf. preceding abstracts).—Further data are submitted, and the author, in general, maintains his position. J. G. A. GRIFFITHS.

Why does molecular hydrogen reach equilibrium so slowly? H. HALL and J. R. OPPENHEIMER (Physical Rev., 1930, [ii], **35**, 132—133).—A mol. of para-H_2 may be converted by collision with any other mol. into ortho-H_2, or two mols. may be converted into ortho-H_2 by the interchange of nuclei between the mols. The probabilities of both processes are small. At n.t.p., para-H_2 should be half converted into ortho-H_2 in a period of the order of 10^8 sec. L. S. THEOBALD.

Affinity. VIII. T. DE DONDER (Bull. Acad. roy. Belg., 1931, [v], **17**, 1001—1007).—Mathematical. W. R. ANGUS.

Geometrical relations in the structures of the modifications of a substance. H. SHÔJI (Bull. Inst. Phys. Chem. Res. Tokyo, 1931, **10**, 909—930).—Structural changes in the space lattices of Fe, Co, Tl, Ce, Sn, C, NH_4Cl, NH_4Br, ZnS, CdS, AgI, TiO_2, $CaCO_3$, SiC, HgS, and SiO_2 as a result of their transformations have been studied, particularly in relation to at. and mol. cohesion. The following pairs of elements and compounds have similar structural relations between their individual modifications: Fe and NH_4Cl, Co and ZnS, Sn and TiO_2, C and $CaCO_3$. E. S. HEDGES.

Internal structure of inorganic compounds at high temperatures. W. JANDER (Z. angew. Chem., 1931, **44**, 870—872).—The types of interchange of lattice positions which can occur in crystals are described. Methods available for the differentiation of these types include conductivity and diffusion measurements, and observations of reactivity between solids. Diffusion measurements with pairs of compounds of the type $M'_2M''X_4$, where M' is an alkali metal, M'' an alkaline-earth metal, and X a halogen, at 200—500°, show that the depth of penetration of the halogen of one compound into the other compound amounts often to about 0·6 mm., compared with 0·2 mm. or less for the metal. Complexes such as $(M''X_4)''$ can therefore exist only in very small concentration. Various spinels have been studied. The results show that $MgAl_2O_4$ and $ZnAl_2O_4$ are ionic conductors and that the mobility of the tervalent metals (Al, Cr) is greater than that of Mg or Zn. H. F. GILLBE.

Three different effects of conjugation. A. F. RICHTER (Phil. Mag., 1931, [vii], **12**, 768—770).—Three types of conjugation are distinguished, according to the nature of the unsaturated group. H. J. EMELÉUS.

Valency and symmetry. P. VINASSA (Atti R. Accad. Lincei, 1931, [vi], **13**, 642—645).—Theoretical. H. F. GILLBE.

Valency electrons in the diamond. M. L. HUGGINS and R. PARRISH (Physical Rev., 1930, [ii], **35**, 136).—Small peaks midway between each two neighbouring C atoms on the density of scattering power curves may be due to electron pairs forming the valency linkings. L. S. THEOBALD.

Nature of the chemical linking. II. The one-electron linking and three-electron linking. L. PAULING (J. Amer. Chem. Soc., 1931, **53**, 3225—3237; cf. this vol., 670).—Theoretical. A stable one-electron linking can be formed only when there are two conceivable electronic states of the system with essentially the same energy, the states differing in that for one there is an unpaired electron attached to one atom, and for the other the same unpaired electron is attached to the second atom. This criterion is satisfied in H_2^+, H_3^+, Li_2^+, and the boron hydrides. A three-electron linking, involving one eigen-function for each of 2 atoms and 3 electrons, can be formed when the two configurations A:·B and A·.B correspond with essentially the same energy, *i.e.*, the energies of the two unperturbed configurations differ by less than the possible resonance energy. This criterion is satisfied in He_2, He_2^+, NO, N_2O, and O_2 which contains 2 3-electron linkings. The electronic configuration of metallic nitroso-complexes is discussed in relation to the magnetic moments. J. G. A. GRIFFITHS.

Electron distribution in the chlorine ion. G. G. HARVEY and G. E. M. JAUNCEY (Physical Rev., 1930, [ii], **35**, 1427). L. S. THEOBALD.

Aromatic electronics. H. H. HODGSON (Proc. Durham Phil. Soc., 1931, **8**, 313—322).—The electronic theory is applied to chromophores and auxochromes and to the decomp. of diazo-salts by aliphatic alcohols. W. R. ANGUS.

Molecular energy levels and valency linkings. J. C. SLATER (Physical Rev., 1931, [ii], **38**, 1109—1144; cf. A., 1930, 126; this vol., 548).—The method of discussing the structure of atoms according to wave mechanics is extended to a consideration of electronic levels in mols. N. M. BLIGH.

Molecular dissymmetry. R. DE MALLEMANN (Compt. rend., 1931, **193**, 651—654, 729—732).—Mathematical. An extension of the author's theories on optical rotatory power (cf. A., 1930, 981; this vol., 1215). The rotatory power of a fluid formed of the simplest possible mols. would in general be expressed by the sum of 576 ternary products. C. A. SILBERRAD.

Inner molecular potential of substituents and its influence on the stability of *cis*- and *trans*-isomerides (dichloro-ethylene and -ethane). Stability of valency angles. H. A. STUART (Physikal. Z., 1931, **32**, 793—798).—Theoretical. Transverse vibration frequencies of simple linear mols. indicate great stability of the valency angle in $C_2H_2Cl_2$, temp. motions giving at most only a 10° deformation. The sphere of influence of the Cl atom is determined from the electrostatic energy of the dipole moment, polarisation, and dispersion effect, and explains the greater stability of the *cis*-form in $C_2H_2Cl_2$, and of the *trans*-form in $C_2H_4Cl_2$. A. B. D. CASSIE.

Quantum theoretical analysis of the benzene problem. II. Quantum theory of induced polarity. E. HÜCKEL (Z. Physik, 1931, **72**, 310—337; cf. this vol., 1000).—The change in distribution of the mean electric density about the quasi-at. core of

the C_6H_6 ring is determined for mono-derivatives. The results are applied to substitution reactions of the mono-derivatives, and explain the difference in heat of activation of *o*- and *p*-mols., and its approx. equality for *m*- and the undisturbed ring. No simple vector addition of dipole moments is likely for di-substituted C_6H_6 rings. A. B. D. CASSIE.

X-Ray analysis of the structure of hexachlorobenzene, using the Fourier method. (MRS.) K. LONSDALE (Proc. Roy. Soc., 1931, A, **133**, 536—552; cf. A., 1929, 750).—The unit cell is simple, monoclinic prismatic, with *a* 8·07, *b* 3·84, *c* 16·61 Å., 116° 52′; *d* 2·044; 2 mols. per unit cell; space-group probably C_{2h}^5 ($P2_1/c$). From the {*h*0*l*} planes 80 reflexions have been observed and measured on the ionisation spectrometer. A Fourier analysis of the {*h*0*l*} zone indicates that each C atom is roughly triangular, appearing to be definitely polarised in the direction of its appropriate Cl atom and of the two neighbouring C atoms. There is a kind of buffer region of low electron density outside each Cl atom. It is not possible to state whether the C_6H_6 ring in this compound is plane or not, but if it is plane, then the C–C distance must be 1·42 Å., the distance found in graphite and C_6Me_6. L. L. BIRCUMSHAW.

Empirical crystal radii for ions with inert gas configuration. W. H. ZACHARIASEN (Z. Krist., 1931, **80**, 137—153).—The radii are determined for co-ordination no. 6, and a standard Coulomb force (that between a univalent cation and a univalent anion). They are deduced from the most trustworthy existing observations, cases of crystals containing anion contacts being avoided, K^+ (1·33 Å.) and Cl^- (1·81 Å.) being the bases. Corrections for different co-ordination nos., Coulomb forces (valency), and radius ratio are discussed and tabulated, and results compared with those of Goldschmidt and Pauling (cf. A., 1927, 399; 1929, 122, 747). C. A. SILBERRAD.

Polar valency of phosphorus. T. MIŁOBĘDZKI (Rocz. Chem., 1931, **11**, 600—606).—Polemical. R. TRUSZKOWSKI.

Natural classification of chemical compounds. I. F. M. SCHEMJAKIN (J. Gen. Chem. Russ., 1931, **1**, 359—366).—A certain parallelism exists between the curves obtained for various physical properties of compounds, arranged in series according to a classification based on their structure and on the at. nos. of their constituent atoms. R. TRUSZKOWSKI.

Temperature variation of intrinsic magnetisation and associated properties of ferromagnetics. E. C. STONER (Phil. Mag., 1931, [vii], **12**, 737—763).—The observed characteristics of Ni are compared with those calc. for an idealised ferromagnetic. H. J. EMELEUS.

Magnetic properties of platinum: different varieties: influence of field: passage of one state to another. P. COLLET and G. FOEX (J. Phys. Radium, 1931, [vii], **2**, 290—308).—Four different specimens of Pt, at low temp. and under the same field conditions, gave moments of 8, 9·5, 11, and 13 magnetons, whereas at high temps. all give 8 magnetons. By increasing the field at low temp. the magneton val. is lowered. With fields below 3000 gauss Pt shows steps of const. paramagnetism with change in temp. J. FARQUHARSON.

Dependence of the magnetic properties of nickel on elastic strain. M. KERSTEN (Z. Physik, 1931, **71**, 553—592).—The experimental initial permeability, magnetisation curves, and remanence of strained Ni wires are compared with theory. J. FARQUHARSON.

Anomalous diamagnetism of bismuth. R. N. MATHUR and M. R. VARMA (Indian J. Physics, 1931, **6**, 181—182).—Bi sol and finely-powdered Bi are found to be much less diamagnetic than Bi metal crystals. J. FARQUHARSON.

Diamagnetism and the colloidal state. S. R. RAO (Indian J. Physics, 1931, **6**, 241—254; cf. this vol., 1000).—With Bi and Sb free from oxides (cf. preceding abstract), χ decreases with particle size until it tends to a const. with diameters $<0·5$ μ. The val. for graphite falls rapidly with particle size. For Bi and C the fall in χ is proportional to the surface area of the particle. The decrease in χ with diameter is discussed by means of Richardson's electron theory (A., 1930, 1081). J. FARQUHARSON.

Ferromagnetism and electrical properties. III. Relation between increase of resistance and magnetisation. K. SCHNEIDERHAN (Ann. Physik, 1931, [v], **11**, 385—405).—The increased resistance observed with a ferromagnetic material in a magnetic field is examined in relation to the magnetisation. J. W. SMITH.

Influence of temperature on the diamagnetism of liquids. R. N. MATHUR (Indian J. Physics, 1931, **6**, 207—224).—The sp. susceptibility of H_2O increases with rise of temp. Aliphatic compounds show practically no change. Aromatic compounds, especially $PhNO_2$, show a definite decrease with rise in temp., which may be due to different degrees of mol. orientation at different temps. J. FARQUHARSON.

Molecular aggregation. A. M. TAYLOR (Physical Rev., 1930, [ii], **35**, 668).—Van 't Hoff's equilibrium equation provides a method for determining mol. aggregation, and for I gives I_2 as the mol. size in the solid state in agreement with X-ray measurements. L. S. THEOBALD.

Mol. size of crystalline carbon tetrabromide, determined by the partition coefficient method. J. P. SOHIER (Bull. Soc. chim. Belg., 1931, **40**, 403—426).—The m.-p. curve and the transition intervals for the system CCl_4–CBr_4 have been determined; the m.-p. and transition curves are continuous and are approx. parallel throughout the whole concentration range. The partition of CCl_4 between the saturated solution and the mixed crystals of CCl_4–CBr_4 has been investigated, and the mol. wts. of the components have been found to be the same in the two phases. Owing to the instability of CBr_4 at high temp., Barger's method was employed for the mol. wt. of the compound in solution; the mol. is $(CBr_4)_2$, in agreement with X-ray measurements with the form stable at low temp. The catalytic hydrogenation method of Ter Meulen and Heislinga is suitable for the analysis of mixtures of CCl_4 and CBr_4. H. F. GILLBE.

Cohesion. J. E. LENNARD-JONES (Proc. Physical Soc., 1931, **43**, 461—482).—A lecture. Contributions of the new quantum mechanics to cohesion include density pictures of atoms permitting calculation of electrostatic interaction of atoms, exchange energies accounting for homopolar linking, pictures of asymmetrical atoms and their electron affinity, and finally an explanation of van der Waals forces as due to dynamic polarisation induced in atoms or mols. by mutual sympathetic motion of their charge densities.
A. B. D. CASSIE.

Energy of dissociation of normal Cd_2. J. G. WINANS and R. ROLLEFSON (Physical Rev., 1930, [ii], **35**, 1436).—The val. 1 volt for the dissociation energy of normal Cd_2 (A., 1929, 1352) is probably too high.
L. S. THEOBALD.

Decrease of the fundamental frequency as a preliminary stage in chemical decomposition. E. CREMER and M. PÓLANYI (Z. physikal. Chem., Bodenstein Festband, 1931, 770—774).—Theoretical. It is shown from the magnitude of the heat of activation of the dissociation of HI that a loosening of the intramol. forces plays a definite part in chemical change. This conclusion is supported by the decrease of the fundamental frequency observed in the Raman spectra of liquefying HCl and HBr. It is suggested that the effect results from homopolar influences in the sense of London's theory; agreement between observed and calc. data is unconvincing.
H. F. GILLBE.

Density and surface tension of isomerides of Δ^β-pentene and β-methyl-Δ^β-butene. W. F. SEYER (J. Amer. Chem. Soc., 1931, **53**, 2588—3596; cf. this vol., 579).—The data refer to temp. between −70° and 80°. The density and surface tension of the metastable pentene are between those of the other compounds. The surface energy of β-methyl-Δ^β-butene is approx. const., but that of the stable and especially that of the metastable pentene decrease with rise of temp. The parachor of the last two is 0·55 unit $>$ the calc. val., and decreases with rise of temp. The Eotvos const. is slightly higher than the normal val.
J. G. A. GRIFFITHS.

Hilger *X*-ray crystallograph and the cubic-crystal analyser. S. ZEIDENFELD (Proc. Physical Soc., 1931, **43**, 512—523).—Difficulties of ordinary powder crystal methods are enumerated, and the method of using slit, specimen, and photographic plate on the circumference of one circle is described; lines on the plate are cusps, and the time of exposure can be considerably reduced, increasing the val. of *X*-rays for commercial analysis. A. B. D. CASSIE.

***X*-Ray examination of electroplated chromium coatings.** W. A. WOOD (Phil. Mag., 1931, [vii], **12**, 853—864).—The existence of hexagonal Cr, in addition to the normal body-centred cubic form, was confirmed, and conditions for obtaining it were determined. The broad diffuse *X*-ray diffraction lines from electrically deposited Cr were attributed to very finely-divided deposits, the grain size being estimated and correlated with the conditions of electro-deposition.
H. J. EMELEUS.

Crystal hydrate as a closed atomic and ionic microcosmos. M. A. RAKUSIN (Zentr. Min., Geol., 1931, **A**, 43—56; Chem. Zentr., 1931, i, 2577).
A. A. ELDRIDGE.

Disappearance of the crystal in an isotropic active medium. L. ROYER (Bull. Soc. Franç. Min., 1930, **53**, 350—374; Chem. Zentr., 1931, i, 2839).—The effect of conc. aq. org. acids on calcite, dolomite, calamine, *d*- and *l*-tartaric acid, and S is discussed from the crystallographic point of view.
A. A. ELDRIDGE.

***X*-Ray determination of crystal orientation in silver sheet produced by cold rolling.** C. B. HOLLABAUGH (Physical Rev., 1930, [ii], **35**, 1426).—The two symmetrical orientations produced in 99·9% sheet Ag by cold rolling are described.
L. S. THEOBALD.

Arrangement of the microcrystals in compressed single-crystal plates of aluminium. III. Y. FUKAMI (Mem. Coll. Sci. Kyoto, 1931, **A**, **14**, 97—113; cf. A., 1930, 139, 1098).—When a rectangular single-crystal plate of Al is compressed to 3—10% of its initial thickness the axis of the resulting fibrous arrangement of microcrystals is always parallel to the direction of flow of the metal on compression. The fibrous structure can be of four types. M. S. BURR.

Mechanical twins in white tin and zinc. K. TANAKA and K. KAMIO (Mem. Coll. Sci. Kyoto, 1931, **A**, **14**, 79—83).—The orientation of twin bands with reference to the mother crystal may be determined from the Laue photographs in the case of mechanical twins obtained by stretching the single crystal.
M. S. BURR.

***X*-Ray study of very pure iron.** O. L. ROBERTS (Physical Rev., 1930, [ii], **35**, 1426).—Diffraction patterns of Fe, prepared from $Fe(NO_3)_3$ and spectroscopically free from C, show that the face-centred cubic structure exists at 921°. L. S. THEOBALD.

Radial asterism in multi-crystalline materials. C. NUSBAUM (Physical Rev., 1930, [ii], **35**, 1426).
L. S. THEOBALD.

Alkali hydrides. E. ZINTL, A. HARDER, and (in part) E. HUSEMANN (Z. physikal. Chem., 1931, **B**, **14**, 265—284).—Apparatus is described for preparing and analysing the alkali metal hydrides, and for introducing them into capillary tubes for crystal analysis by the powder method without exposure to the air. All have the NaCl structure and the following lattice consts.: LiH 4·084, NaH 4·880, KH 5·700, RbH 6·037, CsH 6·376 Å.; *d* calc., 0·77, 1·36, 1·43, 2·59, and 3·41, respectively. The effective hydride ion radii in these compounds are 1·26, 1·46, 1·52, 1·53, and 1·54 Å., respectively, in close agreement with previous work (A., 1929, 697). Intensity measurements do not support the view (A., 1925, ii, 296) that the hydride ions have free mobility in the lattice. The internuclear distances in LiH and NaH are about 30% greater than when these compounds are in the gaseous state, this result being in harmony with other work (A., 1929, 747). The similarity between the hydrides and the fluorides is discussed, and is shown by the fact that the lattice consts. of LiH and LiF differ by only 1·5%. These compounds do not, however, form an unbroken isomorphous series.
N. H. HARTSHORNE.

Asterisms in Laue photographs of rock-salt and internal tensions. V. Laschkarev and A. Alichanian (Z. Krist., 1931, **80**, 353).—The asterisms are no evidence of the existence of internal strains; they indicate only deformations of the crystal lattice.
C. A. Silberrad.

Structure of the azides from their electric dipole moments. L. E. Sutton (Nature, 1931, **128**, 639).—The electric dipole moments of Ph, *p*-chlorophenyl, and *p*-tolyl azides are 1·55, 0·35, and $1·96 \times 10^{-18}$ e.s.u., respectively, and strongly support the ring structure.
L. S. Theobald.

Crystal structure of potassium nitrate. D. A. Edwards (Z. Krist., 1931, **60**, 154—163).—KNO_3 is orthorhombic holohedral; the unit cell has *a* 5·43, *b* 9·17, *c* 6·45 Å., with 4 mols.; space-group V_h^{16}. K has the co-ordination no. 9.
C. A. Silberrad.

Gradual transition in sodium nitrate. II. Structure at various temperatures and its bearing on molecular rotation. F. C. Kracek, E. Posnjak, and S. B. Hendricks (J. Amer. Chem. Soc., 1931, **53**, 3339—3348; cf. this vol., 549).—*X*-Ray diffraction data for the powder between 25° and 290° show that at temp. >200° reflexions from planes in which O atoms alone contribute are progressively weakened until at 280°, where the gradual transition is complete, only uncertain traces remain. Otherwise, there is no major change in the structure within the transition interval. The phenomena are attributed to the initiation of rotation of the NO_3 ion about the trigonal axes of the crystal. The lattice consts. are: α 45° 35′, *a* 6·56 Å. at 280°; α 47° 14′, *a* 6·32 Å. at 25°.
J. G. A. Griffiths.

Crystal structure of potassium chromate. W. H. Zachariasen and G. E. Ziegler (Z. Krist., 1931, **80**, 164—173).—The unit cell has *a* 5·92, *b* 10·40, *c* 7·61 Å.; otherwise previous results are confirmed (cf. this vol., 1218). The structure is the same as that of the alkali sulphates (cf. A., 1929, 243; 1930, 671).
C. A. Silberrad.

Crystal structures of silver and cuprous mercuri-iodides. J. A. A. Ketelaar (Z. Krist., 1931, **80**, 190—203).—Ag_2HgI_4 at room temp. (cf. A., 1903, ii, 482) is pseudocubic tetragonal; *a* 6·340 Å., *c/a* 1·000±0·005. Cu_2HgI_4 is isomorphous; *a* 6·08, *c* 6·135. In both cases the unit cell contains 1 mol., and the space-group is V_d^1. The I atoms form an almost cubic close packing.
C. A. Silberrad.

Habit-variation in crystals of potassium permanganate. H. E. Buckley (Z. Krist., 1931, **80**, 238—254; cf. this vol., 1115).—The effects of the following ions are considered (those of ions grouped together are similar): (*a*) NO_3' (resembles ClO_3', Cr_2O_7'', and S_2O_6''); (*b*) PO_4''', AsO_4''', H_2AsO_4'; (*c*) H_2PO_4', CO_3''; (*d*) HPO_4'', $HAsO_4''$, MnO_4''; (*e*) B_4O_7'', BrO_3' (no effect).
C. A. Silberrad.

Crystal structure of methyl orthosilicate. W. Eulitz (Z. Krist., 1931, **80**, 204—237).—Me_4SiO_4 crystallises at −4° (approx.) in cubes, which pass into less stable anisotropic needles at a lower temp., although no definite transition point could be determined; formation of the needles is favoured by rapid cooling. The isotropic form has a unit cell with *a* 9·85 Å., and contains 4 mols. In each mol. the four C atoms are arranged tetrahedrally around the Si with the OMe groups directed away from the Si, an arrangement explaining the condensation to polymeric silicic esters (cf. A., 1930, 461). The 4 mols. are also arranged tetrahedrally *inter se*. The structure and interat. distances are closely similar to those of the inorg. silicates (cf. A., 1929, 749).
C. A. Silberrad.

Isomorphous relations and double salt formation between gypsum and brushite [ardealite]. F. Halla (Z. Krist., 1931, **80**, 349—352).—PO_3F'' and SO_4'' are isomorphous (cf. A., 1929, 662), as also F′ and OH′, hence PO_3OH'' and SO_4'' should be so. Powder diagrams of gypsum, brushite ($CaHPO_4,2H_2O$), and ardealite (the natural compound of the two) are closely similar, although that of the last named shows sufficient difference from that of an artificial mixture of its components to prove it to be a definite chemical individual (cf. dolomite). Its unit cell has *a* 10·47, *b* 14·64, *c* 6·28, and an analysis of a sample from the Cioclovina cavern (Siebenbürgen) gives CaO 31·61, P_2O_5 21·85, SO_3 21·25, H_2O 25·19, insol. in HCl 0·39, or approx. $CaSO_4,CaHPO_4,4H_2O$. As, however, $MgSO_4,7H_2O$ and $MgHPO_4,7H_2O$ are not isomorphous it is concluded that the isomorphous ions are $HPO_4'',2H_2O$ and $SO_4'',2H_2O$.
C. A. Silberrad.

[Crystal] structure of the trifluorides of aluminium, iron, cobalt, rhodium, and palladium. J. A. A. Ketelaar (Nature, 1931, **128**, 303).—These trifluorides are all isomorphous and the hexagonal unit cell contains 3 mols.; AlF_3 *a* 4·93, *c* 6·25, FeF_3 *a* 5·20, *c* 6·66; CoF_3 *a* 5·06, *c* 6·63, RhF_3 *a* 4·88, *c* 6·81, and PdF_3 *a* 5·05, *c* 7·08 Å. These structures are not purely rhombohedral (cf. this vol., 549); they consist of alternating planes of metal and F ions, with the latter close-packed round the former. The distance between two F′ is slightly less than that calc. with a radius of 1·33; AlF_3 2·46, FeF_3 2·60, CoF_3 2·53, RhF_3 2·44, and PdF_3 2·52 Å. Other details are given.
L. S. Theobald.

Structure of cementite. S. Shigetaka (J. Fac. Eng. Tokyo, 1931, **20**, 1—53).—Both Fe_3C and spiegeleisen have the simple orthorhombic lattice Γ_0 and the space-group V_h^{16}, the lattice consts. in each case being *a* 4·51, *b* 5·04, *c* 6·73 Å. In spiegeleisen the Fe atoms at the c_1 equiv. positions are replaced by Mn atoms. The C in austenite is present as free atoms, but when the transformation to martensite occurs the C atoms associate with neighbouring Fe atoms to form Fe_3C groups, ultimately segregating as Fe_3C crystals. C in metastable solution in α-Fe is present as Fe_3C groups.
R. Cuthill.

Gallium-zinc spinel. F. Buschendorf (Z. physikal. Chem., 1931, **B**, **14**, 297—302).—Ga_2ZnO_4, prepared by heating a mixture of Ga_2O_3 and ZnO at 1000°, is face-centred cubic, *a* 8·323 Å., *n* 1·74, $d_{calc.}$ 6·1544. The results show that Ga can replace Al in a Zn spinel without important alterations to the lattice.
N. H. Hartshorne.

Crystal structure of eulytine. G. Menzer (Fortschr. Min. Kryst. Petr., 1931, **15**, 67; Chem. Zentr., 1931, i, 2983).—The unit cell, *a* 10·272±0·003 Å.,

contains 4 mols. of $Bi_4Si_3O_{12}$. The lattice is body-centred cubic; space-group T_d^6. A. A. ELDRIDGE.

Crystal cell of chlorites. C. MAUGUIN (Bull. Soc. Franç. Min., 1930, **53**, 279—300; Chem. Zentr., 1931, i, 2736).—The true chlorites have a rhombohedral unit cell, *a* 5·32, *b* 9·21, *c* 14 Å.

A. A. ELDRIDGE.

Extent of noticeable cybotactic condition in a liquid as exhibited by triphenylmethane. G. W. STEWART (Physical Rev., 1930, [ii], **35**, 291).—*X*-Ray diffraction peaks for solid and liquid $CHPh_3$ indicate that the effective groupings of the mols. are of approx. the same extent in the finely-powdered crystal as in the liquid. L. S. THEOBALD.

Diffraction of *X*-rays in organic mixtures. A. W. MEYER (Physical Rev., 1931, [ii], **38**, 1083—1093).—Diffraction curves are given for varying concentrations of the mixtures: EtOH–methyl*cyclo*hexane, BuOH–1 : 2-dimethyl*cyclo*hexane, quinoline–PhOH, paraldehyde–*cyclo*hexane, $C(NO_2)_4$–*cyclo*hexane, and PhOH–H_2O. Results indicate the existence in solution of a single type of cybotactic group, and in emulsions two types of cybotactic groups. N. M. BLIGH.

Effect of impurities on the physical and crystallographic properties of hemimellitic acid. V. AGAFONOFF (Bull. Soc. Franç. Min., 1930, **53**, 25—34; Chem. Zentr., 1931, i, 2752).

A. A. ELDRIDGE.

Crystal structure of wood. (FRL.) B. SCHMIDT (Z. Physik, 1931, **71**, 696—702).—An *X*-ray investigation of the alinement of cellulose crystals in different woods; in general, alinement is greater the more compact is the wood in an annual layer, and the greater is the alinement the greater is the tensile strength. A. B. D. CASSIE.

***X*-Ray diffraction pattern of native cellulose.** U. YOSHIDA and N. MATSUMOTO (Mem. Coll. Sci. Kyoto, 1931, **A**, **14**, 115—121).—The lattice form of native cellulose is tetragonal. $a=b=7{\cdot}79$, c 10·26 Å.; there are 4 $C_6H_{10}O_5$ groups per unit cell.

M. S. BURR.

Spontaneous crystallisation of supercooled melts and of supersaturated solutions. G. TAMMANN and H. E. VON GRONOW (Z. anorg. Chem., 1931, **200**, 57—73).—The theoretical relationship between the rate of formation of crystal nuclei in a liquid and the degree of supercooling (cf. A., 1929, 986) has been verified in the case of piperonal and of piperine. Measurements with saturated solutions of $K_2Cr_2O_7$ at various temps. show that with increasing supersaturation the time required for the formation of the first nucleus decreases. In general, with increasing supersaturation or supercooling the no. of nuclei formed in equal time intervals increases. Crystallisation centres cannot exist in a melt at temp. above the m. p. O. J. WALKER.

Magnetostriction and hysteresis. W. N. BOND (Proc. Physical Soc., 1931, **43**, 569—571).—The longitudinal extension and intensity of magnetisation of unannealed wrought Fe both show hysteresis.

A. B. D. CASSIE.

Magnetostriction in single crystals of iron and nickel. F. C. POWELL (Proc. Camb. Phil. Soc., 1931, **27**, 561—569).—A theoretical note.

Theory of magnetostriction. T. HAYASI (Z. Physik, 1931, **72**, 177—190).—Mathematical.

A. B. D. CASSIE.

Cohesion. II. Effect of pressure and of percussion on rock-salt. H. TERTSCH (Z. Krist., 1931, **78**, 53—75).

Electric and mechanical effects in metal wires of heat, magnetic, and acoustic disturbance of structure. A. VON HIPPEL, O. STIERSTADT, and O. VON AUWERS (Z. Physik, 1931, **72**, 266—274; cf. this vol., 790).—Displacements of electric charge during magnetic and acoustic disturbances were investigated in relation to induced currents and the Barkhausen effect. A. B. D. CASSIE.

Diminution of fissure hardness by adsorption of surface-active substances. Sclerometry and physics of dispersed systems. P. REHBINDER (Z. Physik, 1931, **72**, 191—205).—Diminution in hardness of a crystal surface on adsorption of polar substances from solution follows the adsorption isotherm, reaches a max. on saturation of the adsorption layer, and increases with the ease of orientation of adsorbed mols. The thermodynamics of the processes is discussed. A. B. D. CASSIE.

Young's modulus determined with small stresses. D. K. FROMAN (Physical Rev., 1930, [ii], **35**, 120—121). L. S. THEOBALD.

Superconductivity a polarisation phenomenon. J. C. MCLENNAN (Nature, 1931, **128**, 373).—No superconductivity discontinuity occurs in the resistance of Pb wires down to 2° abs. with frequencies as low as 12×10^6 per sec. L. S. THEOBALD.

Electrical conductivity and structure of thin metal layers. II. Functional relations between specific resistance and layer thickness (refracting metal sublimates etc. at low temperatures). L. HAMBURGER (Ann. Physik, 1931, [v], **10**, 789—824).—The relation of electrical resistance of W and Ag to layer thickness is discussed, taking into account possible size of the elementary crystals, and the porous nature of the layer; noticeable conductivity first appears on formation of the disordered monat. layer.

A. B. D. CASSIE.

Electrical resistance of carbon. Z. NISHIYAMA (Z. Physik, 1931, **71**, 600—615).—Pure graphite is a metallic conductor, and as a granular structure increases the electrical resistance increases and its temp. coeff. becomes negative. A. B. D. CASSIE.

Electrical properties of spectroscopically pure zinc crystals. A. G. HOYEM (Physical Rev., 1931, [ii], **38**, 1357—1371).—The Voigt–Thomson symmetry relation was confirmed by measurement of the Thomson coeff. at 49·5° as a function of orientation. The thermal e.m.f. against Cu was determined as a function of orientation for the range −180° to 200°. The dependence of resistivity on temp. was investigated for the range −170° to 25°, and gave $4{\cdot}058\times10^{-3}$ for the average temp. coeff. of resistivity. Corresponding data for Kahlbaum Zn were determined for comparison. N. M. BLIGH.

Changes in the specific resistance of aluminium. G. E. DAVIS and G. GREENWOOD (Physical Rev., 1930, [ii], **35**, 1429). L. S. THEOBALD.

Theory of the resistance of alloys. L. W. NORDHEIM (Physical Rev., 1930, [ii], **35**, 1430). L. S. THEOBALD.

Thermocouples with elements of longitudinally and transversely magnetised ferromagnetic substances. S. SEASS (Physical Rev., 1931, [ii], **38**, 1254—1257; cf. Ross, this vol., 1117).—The e.m.f. due to longitudinal and transverse magnetisation of the sections of a U-shaped conductor is investigated for different magnetic fields. Its relation to the Thomson and Ettingshausen–Nernst effect is discussed. N. M. BLIGH.

Transformation phenomena in so-called semiconductors [group IV elements]. A. SCHULZE (Z. Metallk., 1931, **23**, 261—264).—Measurements of the thermal expansion and electrical conductivity of pure single and polycryst. Si, Ge, and Ti failed to reveal evidence of allotropic modifications below 1000°, but Zr appears to undergo such a transformation at about 800—850°. A. R. POWELL.

Determination of thermal conductivity and its temperature-variation for medium conductors. C. R. ENSOR (Proc. Physical Soc., 1931, **43**, 581—591) —A plate method for determination of thermal conductivity and its variation between 0° and 100° is described. A. B. D. CASSIE.

Measurement of the total heat of a liquid by the continuous mixture method. H. R. LANG (Proc. Physical Soc., 1931, **43**, 572—580).—A development of Callendar's continuous mixture method (Phil. Trans., 1912, **A**, **212**, 1) is discussed. A. B. D. CASSIE.

F. p. of organic compounds. XIII. Compounds containing from 7 to 10 carbon atoms. L. DEFFET (Bull. Soc. chim. Belg., 1931, **40**, 385—402).—Data are given for the f. p., b. p., rate of change of b. p. with pressure, d_4^0, d_4^{15}, d_4^{30}, n at 7 wavelengths, and viscosity at 15° and 30° of a number of n-aliphatic halogen derivatives, alcohols, aldehydes, acids, nitriles, esters, acid chlorides and anhydrides, and amides of C_7, C_8, C_9, and C_{10} series. The regularity of the alternation of the f. p. in the various series is discussed. H. F. GILLBE.

M. p. of nitrobenzene and of benzene. I. MASSON (Nature, 1931, **128**, 726).—Further determinations indicate that Richards' val. of 5·493° for the m. p. of C_6H_6 is approx. 0·1° too low and that the m. p. of dry $PhNO_2$ is near 5·83°. Mazur's val. of 5·5° (this vol., 899) is decidedly low. L. S. THEOBALD.

Inter-comparison of the high-temperature scale. W. E. FORSYTHE (Physical Rev., 1931, [ii], **38**, 1247—1253).—Results for the scales in use at 9 leading laboratories in Europe and America are recorded, and show close agreement over the range 1400—2700° abs. N. M. BLIGH.

Method of measuring the temperature of gases. Application to the determination of their specific heats at high temperatures. M. CHOPIN (Ann. Physique, 1931, [x], **16**, 101—149).—By measuring the fall in pressure produced on passing a gas through a narrow aperture the temp. of the gas can be calc. This method is applied to the measurement of the sp. heat of N_2 and CO_2 between 300° and 1000° for which the empirical equations $C_p=6·82+0·00058t$ and $C_p=8·9+0·62(t/100)^{0·63}$ are deduced, respectively. These are in good agreement with previous vals. J. W. SMITH.

[Thermal] emission from metals. W. DEL REGNO (Rend. Accad. Sci. Fis. Mat. Napoli, 1931, [iv], **1**, 53—62).—The thermal emission of a number of metals has been studied at temp. between 50° and 500°. H. F. GILLBE.

Thermal expansion of lead. P. HIDNERT and W. T. SWEENEY (Physical Rev., 1930, [ii], **35**, 296).—For 3 samples of cast Pb, the coeff. of linear expansion $\times 10^{-6}$ between 20° and 60°, 20° and 100°, 20° and 200°, and 20° and 300° varies from 28·3 to 29·2, 28·6 to 29·6, 29·4 to 31·2, and 30·9 to 32·5, respectively. L. S. THEOBALD.

Heats of fusion and molecular heats of aluminium halides. W. FISCHER (Z. anorg. Chem., 1931, **200**, 332—342).—The heat capacities of $AlCl_3$, $AlBr_3$, and AlI_3 have been determined between −183° and 40° above the m. p. $AlCl_3$ has an abnormally small mol. heat just below its m. p., which latter is regarded as corresponding with a transformation into a form with lower m. p. The mol. heats of fusion are: $AlCl_3$ 8·5, $AlBr_3$ 2·7, AlI_3 3·8 kg.-cal. F. L. USHER.

Latent heat of fusion. K. HONDA and H. MASUMOTO (J. Study Met., Japan, 1930, **7**, 65—71).—The increase in internal potential energy during melting was calc. For elements having a cubic lattice (1) the internal pressure at the m. p. is proportional to the square of the m. p. abs., (2) the increase in vol. of 1 g.-atom due to a rise of temp. of 1° at the m. p. is inversely proportional to the square of the m. p. abs., (3) the at. heat of fusion is proportional to the product of the vol. change of 1 g.-atom during melting and the square of the m. p. abs. CHEMICAL ABSTRACTS.

Calculation of the specific heats of solid organic compounds from Raman spectra. D. H. ANDREWS and J. C. SOUTHARD (Physical Rev., 1930, [ii], **35**, 670—671).—Sp. heats calc. from Raman frequencies for MeOH, EtOH, C_6H_6, PhMe, PhCl, and PhBr over the range 15—260° abs. agree to within approx. 5% with the experimental vals. L. S. THEOBALD.

Cryoscopic constant, heat of fusion, and heat capacity of camphor. M. FRANDSEN (Bur. Stand. J. Res., 1931, **7**, 477—483).—The latent heat of fusion of camphor at the m. p., 178·4°, is 10·74±0·40 cal.$_{15}$ per g., from which the mol. lowering of the f. p. is calc. to be 37·7±1·4° mol.$^{-1}$ kg. The heat capacity of solid cryst. camphor over the range 20—178·4° is $0·4208+0·000215t\pm0·0035$ cal.$_{15}$ g.$^{-10}$ C.$^{-1}$, and that of liquid camphor over the range 178·4—210° is 0·571±0·045 cal.$_{15}$ g.$^{-10}$ C.$^{-1}$ R. CUTHILL.

Specific heats of air, oxygen, and nitrogen from 20° to 370°. P. S. H. HENRY (Proc. Roy. Soc., 1931, **A**, **133**, 492—506).—Improvements in the new flow method for comparing the sp. heats of gases (A., 1930, 282) are described; the method is accurate to

$\pm 0.5\%$ at room temp. and 1.0% at higher temp. The vals. of C_v for air, O_2, and N_2 at 15° are in good agreement with the I.C.T. vals., but the rise in the temp. is much more rapid than that found by previous investigators (A., 1929, 128, 1372). The disadvantages of the sound-velocity method are discussed. L. L. BIRCUMSHAW.

Specific heat of saturated vapours at the b. p. II. N. A. KOLOSOVSKI and V. V. UDOVENKO (J. Gen. Chem. Russ., 1931, 1, 255—262).—The mol. latent heat of vaporisation of liquids (L) and their sp. heat are given by $C_p-A-L_0/T+BT$, where A and B are consts. and T is temp. abs. The sp. heat of saturated vapour is given by $C_g=C_{pg}-L/T$, where C_{pg} is the sp. heat at const. pressure. The val. of C_g at the b. p. is negative for liquids the mols. of which contain < 10 atoms, and positive where > 10 atoms are present in the mol. The inversion temp., T_i, at which $C_g=0$, is given by $T_i=-C_0/2\alpha\pm\sqrt{[(C_0/2\alpha)^2+L/\alpha]}$. R. TRUSZKOWSKI.

Deviations from the law of Neumann, Joule, and Kopp. III. Specific heat of mullite. N. A. KOLOSOVSKI (J. Gen. Chem. Russ., 1931, 1, 253—254).—Greater deviations from the above law are found for mullite than for cyanite, kaolinite, china clay, and bauxite. R. TRUSZKOWSKI.

Thermal energy. I. Phenyl derivatives of methane, ethane, and related compounds. II. Phenyl derivatives of metals. R. H. SMITH and D. H. ANDREWS. **III. The octanols.** J. K. CLINE and D. H. ANDREWS. **IV. Comparison of continuous and discontinuous methods of measuring heat capacities. Heat capacities of aliphatic bromides.** R. F. DEESE, jun. **V. Heat capacity of nitrogen pentoxide at low temperatures.** J. MCGRAW, jun. (J. Amer. Chem. Soc., 1931, 53, 3644—3660, 3661—3667, 3668—3673, 3673—3683, 3683—3693).—I. The technique has been improved (cf. A., 1930, 533) and heat capacities between 101° and 346° abs. are recorded for 25 Ph derivatives of CH_4, C_2H_6, C_2H_4, C_2H_2, MeOH, and MeCl. The heat capacity increment, at const. temp. in the hydrocarbon series, for the addition of a Ph group is almost const. Thus, the heat capacity of the Ph groups is independent of environment in these groups, the force const. of the C·C linking in C_2H_6 is not greatly affected by phenylation, and this linking is to be regarded as a structural unit relatively independent of environment.

II. Heat capacity data in the temp. range 101—346° abs. are recorded for $HgPh_2$, Hg di-*p*-tolyl, CPh_4, $SiPh_4$, $SnPh_4$, XPh_3, where X=N, P, As, Sb, Bi, and for Ph_2O, Ph_2S, Ph_2SO, and Ph_2SO_2. The heat capacity of the compounds XPh_3 generally increases with at. wt. of X, and substitution of C by Si produces a large increase. The results indicate a weakening of the force of linking between the Ph groups and the central atom as the wt. of the latter increases.

III. Data in the temp. range 101—311° abs. are recorded for 4 *n*- and 11 *iso*-octanols. Marked differences of heat capacity occur between 120° and 240° abs.; at other temp. the capacities are more nearly equal. The results are related to the internal energy and the tendency of the compounds to form glasses. The heat capacity increases from straight-chain compounds which readily crystallise to unsymmetrical mols. which form glasses only.

IV. By means of a special calorimeter it is found that the continuous method, with a const. correction, affords accurate vals. of heat capacity. Data for Bu^aBr, m. p. 160·4° abs., *n*-amyl bromide, m. p. 185·1° abs., and *n*-hexyl bromide, m. p. 188° abs., between 93° and 248° abs. are recorded. *n*-Amyl bromide probably has a transition point at about 160° abs. The heats of fusion and the entropies at 298·1° are: Bu^aBr, 2208·6 g.-cal. per mol., 78·22 g.-cal. per 1°, *n*-amyl bromide 3435·3, 97·29, *n*-hexyl bromide 4318·2, 108·33.

V. The sp. heats of pyrex glass, NaCl, and N_2O_5 have been determined between 90° and 250° abs. by measuring the vol. of O_2 evolved when the heated sample is lowered into liquid O_2. The entropy of N_2O_5 between 0° and 250° abs. has been evaluated. J. G. A. GRIFFITHS.

Heat capacity and entropy of silver iodate from 16° to 300° abs. Entropy of iodate ion. B. S. GREENSFELDER and W. M. LATIMER (J. Amer. Chem. Soc., 1931, 53, 3813—3817; cf. A., 1929, 142).—The heat capacities of $AgIO_3$ were determined between 16·16° and 297·6° abs., and the entropy at 298·1° abs. is computed to be 36·0 g.-cal. per 1°. The mol. heat and free energy of solution are 14,478 and 10,233 g.-cal. at 25°, from which the entropy of solution is 14·2 and that of the IO_3' ion in a 1*M* aq. solution is 34·3 g.-cal. per 1°. J. G. A. GRIFFITHS.

Equations of state and thermodynamic functions for a substance with variable specific heat. W. P. BOYNTON (Physical Rev., 1930, [ii], 36, 787).—Theoretical. L. S. THEOBALD.

New equation of state. H. J. BRENNEN (Physical Rev., 1930, [ii], 35, 129—130; cf. A., 1929, 252).—Dieterici's equation is criticised. The proposed new equation, $P(V-b)=RTe^{[-A(V-b)/RTV^n]}$, where n is the missing, third parameter, predicts that the law of corresponding states is true only for substances having the same val. of RT_c/P_cV_c. L. S. THEOBALD.

Huang's general equations of energy and entropy of gases: the general adiabatic equation of gases. T. C. HUANG (Physical Rev., 1931, [ii], 38, 1385—1386; cf. this vol., 793).—Mathematical. N. M. BLIGH.

Fusion and transition data for hydrocarbons. G. S. PARKS and H. M. HUFFMAN (Ind. Eng. Chem., 1931, 23, 1138—1139).—Heats of fusion, many of which have not hitherto been published, are tabulated for 59 hydrocarbons, including normal and branched paraffins, aliphatic olefines, aromatics, hydroaromatics, and naphthenes. Heats of transition are given for 8 cryst. hydrocarbons. There appears to be no quant. relation between heat of fusion and chemical constitution, but the following qual. tendencies are recognised: (*a*) in normal paraffins the mol. heats of fusion increase with increasing mol. wt., at first rapidly and later slowly; (*b*) the heat of fusion decreases markedly with increasing branching of a paraffin (with const. no. of C atoms); (*c*) cyclic hydrocarbons have lower heats of fusion than the corresponding normal paraffins; (*d*) withdrawal of H has no regular effect;

(e) when there are two cryst. forms of a given hydrocarbon at low temp., the sum of the heat of transition and the heat of fusion is comparable in magnitude with the heat of fusion of a compound existing in only one cryst. form. Thus, for *cyclo*hexane this sum is 2230 g.-cal. per mol., as against 2350 g.-cal. per mol. for the heat of fusion of C_6H_6.

E. S. HEDGES.

Thermal data for organic compounds. X. Heat capacities, entropies, and free energies of hydrocarbons. H. M. HUFFMAN, G. S. PARKS, and M. BARMORE (J. Amer. Chem. Soc., 1931, **53**, 3876—3888).—The following heats of fusion (g.-cal./g.) are recorded: propylene, 16·67; butane (I), 17·98; *n*-hexane, 36·14; *n*-octane, 43·21; *n*-nonane (II), 41·22; *n*-decane, 48·34; *n*-undecane (III), 34·12; *n*-dodecane, 51·33; methyl*cyclo*pentane, 19·55; 1 : 2-dimethyl*cyclo*pentane, 15·66; ψ-cumene, 25·15; *iso*durene (IV), 23·04; prehnitene, 20·0; *p*-cymene, 17·2; *n*-butylbenzene, 19·55; 2-methylnaphthalene, 20·11. The sp. heats of the above hydrocarbons and durene, pentamethylbenzene (V), anthracene, and phenanthrene have been measured over a wide range of temp. by the method previously described (A., 1925, ii, 491). (I), (III), and (V) exhibit solid transitions at 107°, 236·1°, and 296·8° abs.; the heats of transition are 8·7, 9·69, and 3·19 g.-cal./g., respectively. (II) and (IV) also exhibit solid transitions. The entropies of the hydrocarbons agree fairly well with those calc. (where possible) from the equation $S_{298}=25{\cdot}0+7{\cdot}7n-4{\cdot}5r+19{\cdot}5p$ (cf. A., 1930, 677; this vol., 42). The free energies of 14 of the above hydrocarbons show that the order of decreasing thermodynamic stability at 298° abs. is paraffin, *cyclo*paraffin, olefine, aromatic hydrocarbons. H. BURTON.

Adiabatic expansion of water and viscous liquids. G. TAMMANN and A. ELBRACHTER (Z. anorg. Chem., 1931, **200**, 153—167).—When H_2O expands adiabatically under pressures of 1600 kg. per sq. cm. and upwards at 0° or at 30° the observed fall in temp. is less, and below 600 kg. and at 0° it is greater, than is calc. on the assumption that internal equilibrium is established instantaneously. At 70° there is no divergence at any part of the pressure range. The work of expansion of glycerol, aq. sucrose, and aq. $ZnCl_2$ is equal to the heat effect if the abs. viscosity is less than about 0·6, whereas at higher viscosities an increasing proportion of the work remains in the liquid as potential energy.

R. CUTHILL.

Definition and evaluation of the fugacity of an element or compound in the gaseous state. G. TUNELL (J. Physical Chem., 1931, **35**, 2885—2913).—Mathematical. The definition of fugacity adopted is based on the physical hypothesis stated by Lewis and Randall that $\lim_{P=0}(RT'/P-v)=K(T')$, where $K(T')$ denotes at a given temp. a const. difference from zero except at the Boyle temp. The equation of definition leads directly to the equations given by Lewis and Randall as their definition of fugacity. The α function of gaseous N_2, calc. from the Beattie–Bridgeman equation, is represented graphically, and the calc. vals. of α are compared with experimental vals. obtained by other investigators. The fugacity equation for gaseous N_2, with numerical coeffs. based on the consts. of Beattie and Bridgeman, is given.

L. S. THEOBALD.

Cubic compressibility of certain substances. L. H. ADAMS and R. E. GIBSON (J. Wash. Acad. Sci., 1931, **21**, 381—390).—The compressibilities of pyrex glass, vitreous SiO_2, obsidian, duralumin, NH_4NO_3, K_2SO_4, Na_2SO_4, and $Bu^{\alpha}{}_2O$ have been measured.

N. H. HARTSHORNE.

Isothermal and adiabatic compressibilities, specific heat, and heat conductivity of liquids. H. SHIBA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, **16**, 205—241).—Complete data, together with those of previous investigators, and calc. vals. are tabulated for the following liquids: CS_2, $CHCl_3$, CCl_4, $MeNO_2$, C_6H_6, PhCl, PhBr, $PhNO_2$, PhMe, *m*-xylene, *n*-hexane, $COMe_2$, MeOH, EtOH, PrOH, BuOH, amyl alcohol, allyl alcohol, ethylene glycol, Me, Et, Pr, Bu, amyl, and octyl acetates, Et propionate and butyrate.

N. M. BLIGH.

Dependence of viscosity in liquids on the molecular space arrangement as shown by *X*-ray diffraction. R. L. EDWARDS and G. W. STEWART (Physical Rev., 1930, [ii], **35**, 291).—A comparison of *X*-ray and viscosity measurements for 21 octyl alcohols shows that when the OH group is in a fixed position and the Me group is placed in possible positions in the mol. the change in viscosity coeff. varies in a manner similar to that of the magnitude of the secondary diffraction peaks. L. S. THEOBALD.

Viscosity of liquids. G. W. STEWART (Nature, 1931, **128**, 727).—Andrade's theory of viscosity is, in a limited way, in harmony with the cybotactic condition of liquids revealed by *X*-ray diffraction.

L. S. THEOBALD.

Azeotropism. New equations of indifferent states. I. R. DEFAY (Bull. Acad. roy. Belg., 1931, [v], **17**, 940—955).—The theory of indifferent states is developed in a simpler manner than previously and the equations of these states are presented in a simpler form. The theory is applicable also to systems not in equilibrium. J. W. SMITH.

Azeotropism. New equations of indifferent states. II. R. DEFAY (Bull. Acad. roy. Belg., 1931, [v], **17**, 1066—1094; cf. preceding abstract).—The idea of indifferent states is extended to systems not in equilibrium and new equations are given.

W. R. ANGUS.

Dynamic azeotropism. VII. (MLLE.) G. SCHOULS (Bull. Acad. roy. Belg., 1931, [v], **17**, 927—939).—Mathematical. J. W. SMITH.

Isomorphous replaceability of atoms and atom groups bound by non-polar linkings. H. G. GRIMM, M. GÜNTHER, and N. TITTUS (Z. physikal. Chem., 1931, **B**, **14**, 169—218).—Atoms and groups which are similar according to the hydride displacement principle (A., 1925, ii, 1123) may be expected to replace one another in solid compounds without causing much alteration in the cryst. structure. Examination of 89 such org. binary systems, many of which have not been previously investigated, shows, however, that mixed crystals are formed in about half of them only. N. H. HARTSHORNE.

Influence of temperature on the diffusion coefficient of solid metals. O. MATANO (Mem. Coll. Sci. Kyoto, 1931, A, **14**, 123—130; cf. A., 1930, 1509; this vol., 1118).—By the electrical resistance method for determining the coeff. of diffusion D at different temp. it has been confirmed that the relations $D=Ae^{-\alpha/\theta}$ and $D=A\theta e^{-\alpha/\theta}$, where A and α are consts. and θ is the abs. temp., represent the experimental results for the Ag–Au and Ni–Cu systems between 300° (or 330°) and 500°.

M. S. BURR.

Zinc–manganese alloys. N. PARRAVANO and V. MONTORO (Mem. R. Accad. Ital., Sci. Fis. Mat. Nat., 1930, **1**, Chim., No. 4, 15 pp.; Chem. Zentr., 1931, i, 2801).—X-Ray examination shows the presence of three phases: η (hexagonal Zn lattice, up to 0·98% Mn), ε (hexagonal Zn lattice; 2 $MnZn_7$ in the unit cell), and γ (space-centred cubic lattice; 12 $MnZn_3$ in the unit cell).

A. A. ELDRIDGE.

X-Ray investigation of some copper–aluminium alloys. G. D. PRESTON (Phil. Mag., 1931, [vii], **12**, 980—993).—The cubic γ phase exists from 31 to 35·5 at.-% Al. It is followed by a hexagonal phase with approx. 43 at.-% Al, and then by an orthorhombic phase, CuAl (a 4·087±0·005, b 12·00±0·02, c 8·635±0·01 Å., 16 mols. CuAl in unit cell). The hexagonal phase is probably stable down to room temp.: the orthorhombic phase exists at 600°, but probably undergoes transformation on cooling.

H. J. EMELEUS.

X-Ray fibre structure of alloys containing precipitated crystals. C. S. BARRETT (Physical Rev., 1930, [ii], **35**, 1425).—A discussion.

L. S. THEOBALD.

Diagram of state of copper–gold alloys. G. GRUBE, G. SCHONMANN, F. VAUPEL, and W. WEBER (Z. anorg. Chem., 1931, **201**, 41—74).—Previous work is supplemented by micrographic examination and by measurements of electrical conductivity and thermal expansion. Between 17 and 85 at.-% Au the primarily formed α mixed crystals are transformed below 460° into three new series of mixed crystals, viz., β with Cu_3Au as principal constituent, γ with CuAu, and δ (> 65 at.-% Au) which is free from Cu_3Au. These series are separated by narrow regions (34—38, 62—64·5%) of heterogeneity. The mode of transformation of the cubic mixed crystals into the tetragonal CuAu is discussed.

F. L. USHER.

Equilibrium diagram of the tin–antimony system and the crystal structure of the β-solid solution. K. IWASE, N. AOKI, and A. ÔSAWA (Sci. Rep. Tohoku, 1931, **20**, 353—368).—The equilibrium diagram has been determined by thermal and X-ray analyses, by resistivity measurements, and by micrographic examination. The results in general confirm the work of earlier workers. The change which occurs at 320° with 30—70% Sb is, however, attributed to an allotropic transformation in the β solid solution; below 320° this phase has a simple cubic structure.

A. R. POWELL.

System silver–copper–manganese. M. KEINERT (Z. physikal. Chem., 1931, **156**, 291—303).—The behaviour of this system has been investigated microscopically, and a triangular diagram is constructed on the basis of 18 points. Alloys with < 30% Mn yield a homogeneous liquid phase; those with between 30 and 90% may give rise to 2 liquid phases, the saturation curve of which has been approx. determined. The solid phases consist of Ag crystals containing small amounts of the other metals, and of Cu–Mn mixed crystals containing < 7% Ag. The hardness of alloys with > 80% Ag is greatly influenced by suitable thermal treatment.

F. L. USHER.

Crystal structures of certain chromium–nickel alloys. F. C. BLAKE and J. O. LORD (Physical Rev., 1930, [ii], **35**, 660).—Ni–Cr alloys containing 63—85% Cr show the following phases: (i) body-centred Cr, d 6·93, (ii) Cr_2Ni, with 96 atoms per unit cell which consists of 4 interpenetrating lattices of Cr, and body-centred tetragonal lattice with a 10·64 Å. and axial ratio 1·040; (iii) Cr nitride, close-packed hexagonal with a 2·751 Å. and axial ratio 1·605; unit cell, 2 atoms of Cr and 2 of Ni; $d_{calc.}$ 7·75; space-group D_3^5.

L. S. THEOBALD.

Magnetic structural analysis. I. N. S. AKULOV (Z. Physik, 1931, **71**, 764—777).—It is shown that the position of the points of max. curvature on the magnetisation curve of a pseudo-isotropic alloy depends chiefly on the lattice structure of the elementary crystal. By deformation of the alloy, the anisotropic point can be moved. These points make it possible to study the crystal structure by magnetic methods.

A. J. MEE.

Microstructure of some magnetic alloys of high platinum concentration. F. W. CONSTANT (Physical Rev., 1930, [ii], **35**, 116).—Alloys containing 5 and 10% Co are solid solutions; no evidence of eutectic structure is obtained. Cubic formations are shown by many of the crystals.

L. S. THEOBALD.

Micro-optical investigation of non-ferrous alloys by polarised light. M. VON SCHWARZ (Metallurgia, 1931, **4**, 180—186).—The microstructure of a number of materials, notably Cu–Si alloys, has been investigated. Photomicrographs resulting from the use of crossed Nicols appear sharp in colour contrast, but are sometimes indefinite in outline as compared with those obtained under ordinary methods of lighting or with parallel Nicols. The method serves to differentiate between constituents similar in colour under ordinary methods of illumination, but differing in mode of crystallisation and optical behaviour. Thus Cu_2O, being anisotropic, appears blue under parallel Nicols and red under crossed Nicols, whereas the isotropic silicon-copper appears blue in all positions of the prisms.

E. H. BUCKNALL.

Physical properties of concentrated aqueous salt solutions. J. N. PEARCE and M. A. HOOPER (Proc. Iowa Acad. Sci., 1930, **37**, 225).—Vals. of d^{25} and n^{25} and dielectric const. for alkali halides were determined from 0·1M nearly to saturation.

CHEMICAL ABSTRACTS.

Diffusion of liquids. E. MUNTER (Ann. Physik, 1931, [v], **11**, 558—578).—A photographic method is used for the determination of concentration gradients.

Diffusion measurements with three pairs of substances agree with those obtained by other methods. The optical method has the advantage that observations can be made over the complete concentration range, and over short time intervals. A. J. MEE.

Changes of state in viscous systems. I—VI. E. BERL and collaborators (Kolloidchem. Beih., 1931, **34**, 1—79).—Partly a summary of work published during the last 10 years (cf. A., 1930, 1114; this vol., 301, 302) on the dependence of the viscosity of complex systems on concentration and temp. The viscosity and dielectric const. of "voltol" oils have been measured. The slight deviation of these liquids (also H_2O and HCO_2H) from the linear relation between n and $1/T$ is correlated with a high dipole moment. The results suggest that the "voltol" oils consist of associated radicals, which are dissociable in solution, and mol. wt. determinations support this view. An electrodynamic theory of viscosity, applicable to systems in all states of aggregation, is developed and shown to be consistent with the results.

E. S. HEDGES.

Ternary systems: water, *iso*propyl alcohol, and salts at 25°. P. M. GINNINGS and Z. T. CHEN (J. Amer. Chem. Soc., 1931, **53**, 3765—3769; cf. A., 1930, 989).—The miscibility of $Pr^{\beta}OH$ and H_2O has been examined in the presence of inorg. salts. $Pr^{\beta}OH$ is salted out more easily than EtOH or MeOH, but less easily than $Pr^{\alpha}OH$ or *tert.*-butyl alcohol. K_2CO_3 and KF have the greatest salting-out effects.

J. G. A. GRIFFITHS.

Ebullioscopic method applied to ternary heteroazeotropic mixtures: ternary heteroazeotropic mixture of carbon disulphide, acetone, and water. W. SWIENTOSLAWSKI and (MLLE.) L. WAJCENBLIT (Compt. rend., 1931, **193**, 488—489, 664—666).—The author's method (cf. this vol., 704) is applied to a mixture of CS_2, $COMe_2$, and H_2O, for which the heteroazeotropic b. p. is 38·042°, and composition (by wt.) CS_2 75·21, $COMe_2$ 23·98, H_2O 0·81%.

C. A. SILBERRAD.

Solubility of gases. I. Solubility of argon at high pressures. B. SISSKIND and I. KASARNOVSKI (Z. anorg. Chem., 1931, **200**, 279—286).—The solubility of A in H_2O (0·2°, 25—125 atm.), MeOH and EtOH (0·2°, 25—100 atm.), and in n-pentane, Et_2O, $COMe_2$, and PhCHO (0·2°, 25 atm.) has been determined. It diminishes in the order EtOH, MeOH, H_2O, and exhibits large deviations from Henry's law, which are negative for H_2O and positive for the alcohols. The significance of the results is discussed.

H. F. GILLBE.

Solubility of salts in liquid ammonia. P. C. SCHERER, jun. (J. Amer. Chem. Soc., 1931, **53**, 3694—3697).—The data refer to NH_4Cl, NH_4Br, NH_4I, and NH_4NO_3, and the corresponding Na salts between −31° and −51°. The solubility increases with rise of temp. except in the case of $NaNO_3$, for which compound formation with the solvent is indicated.

J. G. A. GRIFFITHS.

Solubility of copper iodate in aqueous salt solutions. B. H. PETERSON and E. L. MEYERS (Proc. Iowa Acad. Sci., 1930, **37**, 223—224).—The solubility of $Cu(IO_3)_2$ in H_2O and in solutions of KCl, K_2SO_4, $MgCl_2$, and $MgSO_4$ has been measured. Below 0·007M the observed activity coeffs. agree with those calc. from the Bronsted and Le Mer form of the Debye–Hückel equation. CHEMICAL ABSTRACTS.

Solubility of sodium chloride in acetic acid. O. WILLE (Fischwirt., 1931, **7**, 37—39; Chem. Zentr., 1931, i, 3444—3445).—The saturated solutions contain 27·6, 28·2, 28·5, 29·0, 29·3, 29·7, 30·1, 30·6, 31·2, 31·9, 32·0% NaCl when the AcOH is present to the extent of 8·4, 7·6, 6·9, 6·1, 5·4, 4·4, 3·5, 2·6, 1·9, 0·9, and 0%, respectively. A. A. ELDRIDGE.

Comparison of solubilities of calcium and strontium *p*-bromobenzoates in acetone–water mixtures. J. C. BAILAR (Ind. Eng. Chem. [Anal.], 1931, **3**, 362—363).—The solubilities of the p-chloro-, p-bromo-, and p-iodo-benzoates of Ca, Sr, and Ba in 94% $COMe_2$ have been determined. Ca p-bromobenzoate has a solubility about 45 times as great as that of the Sr salt. Attempts to effect a quant. separation of Ca and Sr, using these salts, failed.

E. S. HEDGES.

Equilibrium in the system phthalic acid–potassium phthalate–water. S. B. SMITH (J. Amer. Chem. Soc., 1931, **53**, 3711—3718).—Solubility data have been determined at 0°, 25°, 35°, and 60°; the double *salt* $K_2C_8H_4O_4,4C_8H_6O_4,4H_2O$ is stable in contact with saturated solutions below 36·67°, $KHC_8H_4O_4$ should be recrystallised from aq. solution above 35° (cf. A., 1920, ii, 628).

J. G. A. GRIFFITHS.

Adsorption of certain vapours by activated charcoal. J. N. PEARCE and P. E. PETERS (Proc. Iowa Acad. Sci., 1930, **37**, 223).—Isotherms (almost rectilinear for the hydrocarbons) for the adsorption of C_2H_6, C_3H_8, Me_2O, and Et_2O by activated charcoal have been obtained at 0—183° and 1—760 mm. At low temp. the isotherms for the hydrocarbons show a peculiar inflexion. The amount of vapour adsorbed decreases with increase in the complexity of the adsorbed mols. CHEMICAL ABSTRACTS.

Sorption of hydrogen on copper. I. Adsorption and the heat of adsorption. II. Rate of dissolution. A. F. H. WARD (Proc. Roy. Soc., 1931, **A**, **133**, 506—522, 522—535).—I. The sorption and heats of adsorption of H_2 on activated Cu have been measured for successive additions of gas at 25° and 0·001—3·0 cm. Differences in the velocity of surface adsorption and solid solution formation permit the separation of these processes and the determination of the true adsorption isotherms. These are reversible. The heats of adsorption (corr. for gas dissolved and the heat of compression of the gas) are independent of the amount of gas adsorbed, but decrease after each baking of the metal until a val. of 9000 g.-cal. per mol. is reached. The isotherms are unaffected by heating below 150°, the temp. of prep. of the metal, but above this temp. the adsorption decreases.

II. The adsorption of H_2 on Cu and rates of diffusion into the metal have been measured between 25° and 200° for various pressures of gas. As the rate of diffusion at any temp. is proportional to the amount of gas adsorbed on the surface, this rate is related to the gas pressure by the same form of equation as the adsorption isotherm. From the variation of rate of

diffusion with temp. the energy of activation of the process is calc. to be 14,100 g.-cal. per mol. It is considered that grain-boundary diffusion occurs rather than lattice diffusion, and the previously accepted theory that the diffusing mols. are dissociated into atoms is criticised. L. L. BIRCUMSHAW.

Adsorption and activation of carbon monoxide at palladium surfaces. [Hydrogenations.] H. S. TAYLOR and P. V. MCKINNEY (J. Amer. Chem. Soc., 1931, **53**, 3604—3624).—$PhNO_2$ is reduced quantitatively to NH_2Ph at room temp. by H_2 and Pd-black freshly reduced from PdO. Alcohols and rise of temp. accelerate the reaction, which is retarded by H_2O and NH_2Ph and almost completely inhibited by C_6H_6. The temp. of dehydrogenation of PhEt vapour is lowered by Pd-black and Pd–asbestos and the yield of styrene is increased by adding air. A $1CO : 5H_2$ mixture affords a 90% yield of CH_4 in contact with Pd-black at 300°. CO strongly inhibits the reduction of PdO by H_2. Pd does not catalyse the reaction $2CO=C+CO_2$.

Adsorption isotherms for CO on Pd at temp. between 86° and 553° abs. are given. More gas is adsorbed at 86° abs. than at 195° abs.; the gas is more easily desorbed at 86°. The adsorption at 273° abs. is greater but slower than at 86° abs. The isobars for pressures >10 mm. have high vals. at 86°, decreasing to min. at 195°, rising to max. at 273°, followed by decreases with further rise of temp. These data and the effect of change of temp. on the rate and magnitude of adsorption support the view that chiefly " physical " or " low-temp." adsorption occurs at 86° and 195°, whilst adsorption requiring energy of activation has a max. at 273° on unsintered and at 383° on sintered Pd. The heat of activated adsorption is approx. 15,000 g.-cal. per mol. on the less active parts of the surface. J. G. A. GRIFFITHS.

Adsorption of aliphatic acids on evacuated charcoal. L. K. LEPIN (J. Gen. Chem. Russ., 1931, **1**, 388—392).—The adsorptive power of degassed charcoal for aliphatic acids from C_1 to C_4 is less than that of ordinary charcoal, whilst for acids above C_4 no difference is observed. These effects are explained on the assumption that the surface of degassed and ordinary charcoal is covered with a layer of a less and a more basic oxide, respectively. For the acids C_1—C_4 adsorption corresponds with the displacement of oxide by the CO_2H group, which is oriented towards the charcoal surface, but with the higher acids the orientation is reversed, the terminal Me group being in contact with the adsorbent surface. R. TRUSZKOWSKI.

Influence of surface layers of adsorbed gas on the optical constants of mercury. (FRL.) E. HERSCHKOVITSCH (Ann. Physik, 1931, [v], **10**, 993—1016).—The influence on the optical consts. of Hg of adsorbed layers of air, H_2, O_2, CO_2, Ne, N_2 and C_2H_2 has been examined. The mol. thickness of the layers cannot be estimated. W. R. ANGUS.

Adsorption at the surface of a solution W. F. K. WYNNE-JONES (Phil. Mag., 1931, [vii], **12**, 907—912; cf. A., 1925, [ii], 960).—The total amount of EtOH adsorbed at the surface of aq. EtOH suggests the formation of a unimol. surface layer of EtOH mols. at concentrations >30% EtOH. Similar results are obtained for aq. solutions of MeOH and $COMe_2$. H. J. EMELÉUS.

Aminolysis of alanine. E. BAUR (Z. physikal. Chem., Bodenstein Festband, 1931, 162—171).—The decomp. of alanine solutions in presence of animal C at 100° is incomplete, but a condition of true equilibrium is not attained. The concentration of NH_4 lactate formed is proportional to the wt. of C per litre, and it appears that the primary decomp. is that of an adsorption compound of alanine and C and that the lactate formed is present initially as a second adsorption compound. The reaction ceases when the active points capable of adsorbing the lactate are fully occupied. Other reaction products are $(NH_4)_2CO_3$, HCO_2NH_4, EtOH, and EtCHO, and the mechanism of their formation is discussed. The heat effect of the aminolysis is −7·8 kg.-cal. H. F. GILLBE.

Starch–iodine reaction. J. FIELD (J. Biol. Chem., 1931, **92**, 413—419).—Radiomicrometric titration shows that aq. solutions of maize and wheat starches have, at the same concentration, approx. the same I capacity. This capacity is not proportional to the starch concentration, but is influenced by a dilution factor in a way which supports the view that " starch iodide " is an adsorption compound. A. COHEN.

Surface-tension determination by the ring method, and the surface tension of dilute solutions of salts. G. SCHWENKER (Ann. Physik, 1931, [v], **11**, 525—557).—The ring method has been considerably improved so that it is now possible to carry out a determination with an accuracy of 0·022%. Relative measurements can be made with an even greater accuracy. The surface tension of H_2O is 75·59 dynes per cm. at 0° and 72·86 at 18°. The surface tensions of aq. solutions of LiCl, KCl, and NaCl in the concentration range 0—0·15N have the same val. A. J. MEE.

Surface tension of different dilutions of Boys' soap solution. L. D. MAHAJAN (Phil. Mag., 1931, [vii], **12**, 954—959).—The surface tension of H_2O, measured by the drop-wt. method or surface-tension balance, falls rapidly on adding up to 5% of soap solution, passes through a min. at approx. 30 dynes per cm. (15% soap solution), and rises very slowly with further additions. H. J. EMELÉUS.

Method for study of the unimolecular film. E. GORTER and W. A. SEEDER (Naturwiss., 1931, **19**, 738).—Stationary waves are generated on a H_2O surface by an electrically-driven tuning fork, and the reflected light is brought by means of a lens to a focus. As the result of the wave movement the point of light moves in a straight line. A film of the compound under investigation is produced on the surface of the liquid, *e.g.*, by allowing a solution in light petroleum to evaporate, and the damping which this causes results in a shortening of the straight line. This effect affords a new method for the study of surface films. W. O. KERMACK.

Membrane behaviour. I. Equilibrium conditions with gelatin membranes in acetate buffer solutions. W. L. FRANCIS (Proc. Roy. Soc., 1931,

A, **133**, 587—604).—Equilibrium potentials across membranes of unglazed Berlin porcelain (with and without gelatin) have been measured for buffer concentration gradients of 10 : 1, using $N/40$—$N/400$ and N—$0{\cdot}1N$ solutions. The results for the p_H range 2·35—7·3 support the modified diffusion theory which attributes the potential to altered ionic mobilities within the membrane, but more direct evidence, obtained from determinations of the transport nos. of the $Na^{\cdot}$ and OAc' ions across the membrane in $0{\cdot}5N$ solution, is not in agreement with this theory. The transport no. of the OAc ion remains steady over the p_H range 0·29—0·37. A theory offered to explain the results is based on the known behaviour of gelatin in electrolyte solutions.

L. L. Bircumshaw.

Determination of osmotic pressure by isothermal distillation. I. M. Ulmann (Z. physikal. Chem., 1931, **156**, 419—434).—Various modifications of the high-vac. apparatus of Frazer and Patrick are described. The apparatus may be freed from air within 5—6 hr. Troublesome distillation of the solvent has been obviated, and the observations have been rendered independent of temp. fluctuations. Typical measurements with $0{\cdot}01M$ solutions of dextrose, sucrose, and raffinose are described.

H. F. Gillbe.

Striations in chemical processes. IV. *D*-Striations and related phenomena. E. Schally (Monatsh., 1931, **58**, 399—427).—By examining the shadow distribution of the *D*-striations (cf. A., 1930, 149) when one solution is allowed to flow into another of the same refractive index a comparison of the diffusion velocities of the two solutes can be made, if the vol. change on mixing is not too great and if there is no chemical action. The presence of such disturbances is detected by interchanging the solutions. The particular shadow distribution caused by the disturbance is not reversed. *D*-Striations thus afford a method for the determination of approx. mol. wts. Equally diffusible substances give no *D*-striations. Slight differences in n result in a much more complicated shadow distribution. Data are given for the shadow distribution of the *D*-striations for a no. of pairs of solutions of alcohols and carbohydrates.

M. S. Burr.

Dielectric constants of aqueous potassium chloride solutions. A. Astin (Physical Rev., 1930, [ii], **35**, 1428—1429).—Corr. results for the dielectric consts. of 0·00025—$0{\cdot}01N$-KCl do not differ from that of H_2O within the experimental limits of error (2 in 1000 at $0{\cdot}001N$ and 6 in 100 at $0{\cdot}01N$). Uncorrected results show the apparent decrease of dielectric const. reported by other observers. This decrease, which is much larger than that predicted by Hückel, varies with frequency, size of condenser, or dimensions of the leads.

L. S. Theobald.

Constitution of solutions deduced from absorption measurements. P. Vaillant (Compt. rend., 1931, **193**, 654—656).—Absorption measurements are given for λ 4800—5700 on solutions of $CoCl_2$ in presence of EtOH and other chlorides.

C. A. Silberrad.

Electrolytic dissociation as revealed by the Raman effect. L. A. Woodward (Physikal. Z., 1931, **32**, 777—792).—Raman displacements are absent in solutions of KCl, indicating almost complete dissociation, whilst $HgCl_2$ and $Hg(CN)_2$ show displacements due to the undissociated mol. HNO_3, H_2SO_4, and the HSO_4' ions in solutions of $KHSO_4$ appear to be partly dissociated. For HCl, HIO_3, $CCl_3{\cdot}CO_2H$, $CHCl_2{\cdot}CO_2H$, NaOH, and KOH the results are inconclusive. A spectrograph of large aperture is described.

A. B. D. Cassie.

Viscosity of suspensions. J. Duclaux and (Mlle.) D. Sachs (J. Chim. phys., 1931, **28**, 511—516).—The val. of K in the viscosity formula $\eta=\eta_0(1+K\phi)$ is 36 for a Bredig Au hydrosol (cf. $K=2{\cdot}5$ for spherical particles). Large vals. of K are not necessarily due to solvation, but are probably related to the shape of the particles, since $K=19{\cdot}2$ for particles (0·2—0·3 μ) of SiC, which is not solvated by H_2O, and $K=4{\cdot}6$—5·9 for PbI_2 in BuOH, the particles of which approximate less closely to spheres than those of SiC.

J. G. A. Griffiths.

Effect of hydrogen-ion concentration on the measurement of the mean particle size of emulsions. I. C. Weeks (Physical Rev., 1930, [ii], **35**, 668; A., 1927, 108).—At p_H 7·0 the area of a H_2O-spread emulsion stabilised with Na myristate, palmitate, or stearate is const. for a given pressure and quickly reaches equilibrium; at $p_H < 7{\cdot}0$ the area increases with time without reaching equilibrium, whilst at $p_H > 7{\cdot}0$ the area ultimately becomes const., but the equilibrium vals. are large and depend on p_H.

L. S. Theobald.

Shape of particles in hydrosols of sodium oleate. P. A. Thiessen and E. Triebel (Z. physikal. Chem., 1931, **156**, 309—316).—Measurements of the fluxional birefringence of Na oleate hydrosols show that the particles are rod-shaped. The amount of the double refraction increases with concentration or with lowering of temp. The particles also possess a sp. double refraction and are therefore cryst.

F. L. Usher.

Molecular arrangement in soap micelles. P. A. Thiessen and R. Spychalski (Z. physikal. Chem., 1931, **156**, 435—456).—*X*-Ray examination shows the particles in Na soap hydrogels to be cryst. and to consist of neutral, anhyd. salts of fatty acids. The structure is independent of the H_2O content of the system and is identical with that of the corresponding salts when cryst. from org. solvents. H_2O contained in the gel is entirely intermicellary. Observations with threads of Na soaps indicate that the salt mols. are oriented perpendicularly to the long axes of the micelles. The distribution of electric charges on the surface of the micelles is discussed.

H. F. Gillbe.

Formation of a lattice during the sol–gel transition of a colloidal system containing elongated particles. P. A. Thiessen [with (Frl.) E. Triebel] (Z. physikal. Chem., 1931, **156**, 457—468).—The changes of double refraction and electrical conductivity which occur during the transition of supercooled Na oleate hydrosol to the gel form indicate that tho formation of a lattice structure

depends essentially on the size and form of the particles, the mol. orientation, and the distribution of the charges on the surface of the particles.

H. F. GILLBE.

Coagulation of strongly solvated sols by organic substances and salts. IV. B. JIRGENSONS (Biochem. Z., 1931, **240**, 218—231).—In the coagulation of albumin and caseinogen with $FeCl_3$ or $AlCl_3$ and alcohols, the salts in small concentrations (0·0001—0·001*M*) sensitise, in mean concentrations (0·001—0·1*M*) stabilise, and in high concentrations (0·1—0·4*M*) either sensitise ($FeCl_3$) or stabilise ($AlCl_3$). With $CuCl_2$ and $Cu(NO_3)_2$, small concentrations sensitise and mean concentrations stabilise. The stabilisation is dependent on the alcohol concentration and also varies inversely with the dielectric const. With $MnCl_2$ and $CoCl_2$ small and mean concentrations sensitise and high concentrations stabilise. NaOAc sensitises, whilst Na_2HPO_4 and $K_4Fe(CN)_6$ feebly stabilise the alcohol coagulation of albumin. Glycine, alanine, and carbamide stabilise the coagulation of albumin by $HgCl_2$, $CuCl_2$, and $AlCl_3$. Lower temp. (—10°) have no decided influence on the alcohol coagulation in presence of salts. When dil. albumin and starch sols are coagulated in presence of salts with varying amounts of alcohol, the degree of coagulation is not a linear function of the alcohol concentration, each alcohol having a max.; *e.g.*, PrOH with albumin has a sharp max. at 1·6*M* (cf. A., 1929, 507).

P. W. CLUTTERBUCK.

Rapid coagulation of sols. I and II. H. J. C. TENDELOV (Chem. Weekblad, 1931, 28, 634—637, 637—640).—I. An account of the mathematical treatment of the kinetics of sol coagulation developed by Smoluchovski and by Müller, and of the experimental investigation of the equations obtained.

II. A *résumé* of the work of Tuorila and Müller.

H. F. GILLBE.

Coagulation of egg-albumin by supersonic waves. H. WU and S. C. LIU (Proc. Soc. Exp. Biol. Med., 1931, 28, 782—784).—Coagulation results only in solutions containing dissolved air, H_2, or O_2; it does not occur when CO_2 or H_2S is used and no gas bubbles are formed.

CHEMICAL ABSTRACTS.

Anisotropy due to flow in cellulose sols. J. M. PRESTON (Nature, 1931, **128**, 796—797).—Flowing cellulose sols in Cu-aq. NH_3 show double refraction, indicating the presence of non-spherical particles. The ageing of cellulose sols in air gives rise to lower double refraction, suggesting a diminution in particle size.

L. S. THEOBALD.

Theory of jelly formation. S. PRAKASH (J.S.C.I., 1931, **50**, 387—388T).—A brief summary of the author's results (cf. A., 1929, 1008, 1235; 1930, 1114, 1117, 1369).

Electrical method of determining gelation temperature of starch. E. C. McCRACKEN (Physical Rev., 1930, [ii], **35**, 1423).—A sudden decrease in resistance occurs at 87—88° when an electric current is passed through a potato. This effect is attributed to a disruption of starch grains.

L. S. THEOBALD.

Dependence of osmotic pressure and micellar weight of gelatin solutions on the temperature, *i.e.*, on the previous history of the solution. M. FRANKEL (Biochem. Z., 1931, **240**, 149—155).—A solution of pure gelatin gave at 6° a micellar wt. of 53,800 and at 30° of 19,800. The same solution after 500 hr. at 37° gave a wt. of 16,500, whereas the control was 24,000.

P. W. CLUTTERBUCK.

Diffusion and cataphoresis of methylene-blue in gelatin. (MLLE.) S. VEIL (Compt. rend., 1931, **193**, 768—771).—The spectrophotometric method was used. Diffusion extends gradually (cf. A., 1929, 28), with no discontinuities (cf. A., 1928, 238). Cataphoresis produces marked singularities—a thick accumulation at the anode which moves steadily away, leaving a clear space; then comes a series of thinner bands with finally a thick one at the cathode.

C. A. SILBERRAD.

Contraction caused by hydration of proteins. C. MARIE and N. MARINESCO (Compt. rend., 1931, **193**, 736—738).—The contraction on adding 1 c.c. of H_2O of varying p_H to 1 g. of gelatin (Merck's "isoelectric") decreases sharply from p_H 3·5 to the isoelectric point, and then rises more slowly to p_H 8·5, with an arrest around the neutral point. With const. p_H and varying amounts of H_2O the contraction per g. of gelatin diminishes rapidly with increased quantity of H_2O.

C. A. SILBERRAD.

Morphology of chemical reactions in gels. V. Theory of periodic reactions. F. M. SCHEMJAKIN (J. Gen. Chem. Russ., 1931, 1, 455—459).—A drop of liquid is a definite unit of the same order as micelles and crystals; in most cases it is analogous in structure to radial or zonal mono- or poly-crystals. The gel reactions previously described (cf. this vol., 428) can be explained from this point of view, and the nature and dimensions of the figures obtained when a drop of $FeCl_3$ is placed on gelatin containing K_2CrO_4 are predicted.

R. TRUSZKOWSKI.

Numerical evaluation of infinite series and integrals which arise in certain problems of linear heat flow, electrochemical diffusion, etc. W. L. MILLER and A. R. GORDON (J. Physical Chem., 1931, **35**, 2785—2884).—Mathematical.

L. S. THEOBALD.

Equations of motion in thermodynamics. Y. MIMURA (J. Sci. Hiroshima Univ., 1931, **A**, 1, No. 2, 117—123).—An attempt to evolve the thermodynamics of systems of varying state by analogy with Hamilton's principle.

CHEMICAL ABSTRACTS.

Molecular association. G. G. LONGINESCU (Bul. Chim. pura appl., Bukarest, 1930, **31**, No. 4—6, 21—76; Chem Zentr., 1931, i, 2837).—A discussion.

A. A. ELDRIDGE.

Two-component systems involving compound formation. J. RUSSELL and O. MAASS (Canad. J. Res., 1931, 5, 436—441).—The *p*, *v*, *T* relations suggest that compound formation takes place between gaseous HCl and Et_2O, and between HCl and MeOH; the heats of reaction (const. between 50° and 200°) are 5400 and 9200 g.-cal. per mol., respectively.

R. S. CAHN.

Electrolytic dissociation of acids in salt solutions. I. Dissociation constant and activity relationships of the ions of acetic acid in solu-

tions of certain alkali and alkaline-earth chlorides. II. Dissociation constants and the activity relationships of the ions of some fatty acids in sodium and potassium chloride solutions. E. LARSSON and B. ADELL (Z. physikal. Chem., 1931, **156**, 352—380, 381—396).—I. Quinhydrone electrode measurements of the activity coeff. at 18° of the H˙ in 0·01*N*-HCl solutions containing Na, K, Sr, and Ba chlorides at various concentrations agree closely with those obtained by Bjerrum and Unmack with the H electrode. The activity relations in solutions of AcOH and NaOAc containing chlorides have been determined by quinhydrone electrode measurements, and the variations of the classical ionisation const. α and of the activity coeffs. of the acid mols. and ions with the salt concentration have been examined. With increase of the chloride concentration to about 0·5*M* α and $-\log\phi$ increase, but thereafter they fall; $-\log\phi$ diminishes in the series $SrCl_2$, $BaCl_2$, NaCl, KCl. The activity coeff. of OAc′ in the salt solutions has been calc. from that of the acid as obtained by partition measurements.

II. Determinations have been made of the ionisation const. and activity functions in chloride-containing solutions of the *n*-fatty acids to C_7, and of $Bu^{\beta}CO_2H$, $CMe_3{\cdot}CO_2H$, and *iso*hexoic acid. The influence of the constitution of the acids is appreciable only at high salt concentrations. If the CO_2H group is attached to a CH_2 or Me group the val. of $-\log\phi$ in a given salt solution is independent of the no. of C atoms in the chain, but in other cases it assumes higher vals. For all the acids $-\log\phi$ is a max. in 0·5*M* salt solutions, and it is always greater in NaCl solutions than in solutions of KCl. The activity coeffs. of the acid ions have not been determined, as those of the acids are not known.

H. F. GILLBE.

Dissociation constants of bile acids. O. M. HENRIQUES (Acta Path. Microbiol. Scand. Suppl., 1930, 3, 141—149; Chem. Zentr., 1931, i, 3130).—Vals. for aq. solutions were extrapolated from those for aq.-alcoholic solutions of taurocholic, taurocholeic, glycocholic, and glycocholeic acids.

A. A. ELDRIDGE.

Hydrolysis constant of iodine. E. ANGELESCU and V. D. POPESCU (Z. physikal. Chem., 1931, **156**, 304—308).—The val. of K $(=[HOI][H^{\cdot}][I']/[I_2])$ has been derived from the error in the titration of I with $Na_2S_2O_3$ in presence of $NaHCO_3$. K varies with the I concentration from 10^{-10} (large [I′]) to $1{\cdot}5\times10^{-13}$ (small [I′]) at 20°. The thermal equiv. of the hydrolysis is calc. to be −11,700 g.-cal. at 25°.

F. L. USHER.

Composition of complex cyanide radicals. IV. Nickel cyanide. K. MASAKI (Bull. Chem. Soc. Japan, 1931, 6, 233—236).—Despite the variations of colour of solutions containing $Na_2Ni(CN)_4$, the complex ion at all concentrations is $Ni(CN)_4''$. The equilibrium const. for the dissociation of the complex into Ni˙˙ and CN′ is $1{\cdot}8\times10^{-14}$ according to e.m.f. measurements.

H. F. GILLBE.

F. p. of mixtures of sulphuric and nitric acids. W. C. HOLMES, G. F. HUTCHISON, and B. ZIEBER (Ind. Eng. Chem., 1931, **23**, 1102—1104).—Further measurements have been made, in which the concentration of H_2SO_4 in the solvent extends from 100 to 109%; the results are plotted with other available data on triangular co-ordinates and the isothermal lines are indicated. The most effective concentrations of HNO_3 for preventing freezing of H_2SO_4 are 1% for 104·5% H_2SO_4, 4% for 107% H_2SO_4, and 6% for 109% H_2SO_4. Low f. p. occur in all these systems at 10% HNO_3.

E. S. HEDGES.

Amphoteric oxide hydrates, their aqueous solutions and crystalline compounds. XII. Systems undergoing hydrolysis and their aggregation products, with special reference to aqueous aluminium salt solutions. G. JANDER and A. WINKEL (Z. anorg. Chem., 1931, **200**, 257—278).—The properties of solutions of easily hydrolysable salts are discussed, with special reference to the aggregation which occurs in molybdate solutions. The diffusion coeff. of $Al(NO_3)_3$ solutions has been determined as a factor of the p_H. It does not vary with the age of the solution, and equilibrium is therefore established rapidly; with rise of p_H to about 3 it remains almost const., but thereafter falls rapidly and continuously, indicating progressive aggregation. Evidence has been obtained of the formation of the complexes $[Al(OH)(NO_3)_2,aq.]_x$ and $(AlO{\cdot}NO_3)_y$. The course of the aggregation process is probably $Al(H_2O)_6(NO_3)_3\rightarrow(AlO{\cdot}NO_3)_8\longrightarrow AlO{\cdot}OH$, in analogy with the process in Fe˙˙˙ salt solutions. The complexes probably result from chain formation. The occurrence of aggregation has been confirmed by extinction coeff. measurements.

H. F. GILLBE.

System iron–oxygen. H. SCHENCK and E. HENGLER (Arch. Eisenhüttenw., 1931—1932, 5, 209—214).—The solubility of O_2 in γ-Fe is about 0·2% and in α-Fe about 0·035%. The A3 point is slightly raised and the A4 point slightly lowered by the presence of O_2 in solid solution. There is a gap of miscibility in the liquid phase between 0·22 and 21·5% O at 1519°. In the system FeO–Fe_3O_4 a homogeneous liquid phase is obtained with mixtures containing 23—26% O, but the presence of a eutectic m. p. 1200° in the system has not been confirmed. FeO melts incongruently at 1370° and, after cooling from above 1385°, the presence of well-formed Fe crystals in the mass has been detected micrographically. Wüstite and Fe_3O_4 form a eutectic, m. p. 1300°, with 25·3% O, but the eutectic horizontal extends only over a short range of composition. Pure FeO cannot be produced by prolonged heating in vac. of a stoicheiometric mixture of Fe_3O_4 and Fe. A tentative diagram of the stable and metastable equilibria in the system Fe–O based on the above results together with those of other investigators has been constructed.

A. R. POWELL.

Equilibrium pressure of calcium cyanamide formation. N. KAMEYAMA and S. OKA (J. Soc. Chem. Ind. Japan, 1931, **34**, 325—327B).—A mixture of $CaCN_2$, graphite, and CaC_2 heated at 900° evolved CO and N_2 owing to the presence of $Ca(OH)_2$ as impurity. The equilibrium pressures were 5 mm. Hg at 956°, 183·5 mm. at 1200°. According to these data the heat of reaction is 54,800 g.-cal.

Higher vals. found experimentally may perhaps be due to the heat of dissolution of CaC_2 in $CaCN_2$.

C. IRWIN.

Ternary system CO–N–H and the component binary systems between $-185°$ and $-215°$ and 0 and 225 atm. T. T. H. VERSCHOYLE (Phil. Trans., 1931, A, **230**, 189—220).—For liquid CO log $p = -691{\cdot}91/T + 6{\cdot}9059 - 0{\cdot}006044T$, and for solid CO log $p = -520{\cdot}85/T + 10{\cdot}7005 - 0{\cdot}02923T$ (p in cm.); b. p. $-191{\cdot}47°$, triple point $-205{\cdot}03°$, m. p. $-205{\cdot}03° + 0{\cdot}0225p$. The triple point of N_2 is $-209{\cdot}95°$, and the m. p. $-209{\cdot}95° + 0{\cdot}0216p$. Isotherms and the f.-p. curves are given for the CO–N_2 and CO–H_2 systems, and data are given for the ternary system at 30, 90, and 150 atm. and $-185°$, $-195°$, and $-205°$.

H. F. GILLBE.

Equilibrium in binary systems under pressure. I. Experimental and thermodynamic investigation of the system NaCl–H_2O, at 25°. L. H. ADAMS (J. Amer. Chem. Soc., 1931, **53**, 3769—3813; cf. this vol., 40).—The compressibility of aq. NaCl solutions (0—25%) has been determined at pressures between 500 and 12,000 bars at 25°. The "compression," k $[=(V_0-V)/V]$, for H_2O is given by $k = 16{\cdot}362\times10^{-6}P - 3{\cdot}42\times10^{-10}P^2 + 0{\cdot}068(1-e^{-0{\cdot}00042P})$, and k decreases with increasing concentration of the solutions. The calc. vals. of the "fictive" or partial vols. of NaCl in solution increase with pressure except at the highest pressures and concentrations; the vals. for H_2O decrease with increase of pressure. The pressure–concentration equilibrium diagram resembles an inverted temp.–concentration diagram. The solubility of NaCl at 25° rises to a max. (27·6 wt.-%) at 4000 bars and then decreases. Between 8000 and 11,800 bars, $NaCl,2H_2O$ is the stable solid phase, and at higher pressure the solubility of NaCl decreases to 25·4 wt.-% at 16,700 bars, where the curve intersects the freezing pressure curve for ice VI, thus affording a "pressure eutectic." Direct determinations confirm the results of the indirect (thermodynamic) method.

J. G. A. GRIFFITHS.

Calcium aluminates. I. Crystallisation of calcium aluminate solutions at 20°. G. ASSARSSON (Z. anorg. Chem., 1931, **200**, 385—408).—The solid phases in equilibrium at 20° with solutions containing varying proportions of CaO and Al_2O_3 have been investigated. CaO,H_2O is not found, although present in cements. $Al_2O_3,3$—$4H_2O$ is deposited in isotropic grains, in flakes adhering to the walls, or as an amorphous gel. The aluminates identified were: $4CaO,Al_2O_3,13{\cdot}5H_2O$ (not $12H_2O$ as stated by previous workers); $3CaO,Al_2O_3,12{\cdot}5H_2O$; $3CaO,Al_2O_3,6H_2O$; and $2CaO,Al_2O_3,8(?)H_2O$. Optical and chemical characters are given. In solutions containing < 50 mg. CaO per 100 c.c. the solubility decreases with increasing proportion of CaO. The results are shown in a triangular diagram.

F. L. USHER.

Reciprocal salt pair $MgCl_2$–$NaNO_3$–H_2O. II. A. SIEVERTS and E. L. MÜLLER (Z. anorg. Chem., 1931, **200**, 305—320).—The 75° and 110° isotherms have been determined. The solid phases at these temp. are NaCl, $NaNO_3$, $MgCl_2,6H_2O$, $MgCl_2,4H_2O$, $MgCl_2,2H_2O$ (110° only), $Mg(NO_3)_2,6H_2O$ (75° only), and $Mg(NO_3)_2,2H_2O$. No double salts exist. The transition temp. of $MgCl_2,4H_2O \rightleftharpoons MgCl_2,2H_2O$ (181·5°) is reduced to below 110° by the presence of $Mg(NO_3)_2$, and that of $MgCl_2,6H_2O \rightleftharpoons MgCl_2,4H_2O$ (116·7°) to below 75°. Attempts to isolate the lower hydrates of $MgCl_2$ and $Mg(NO_3)_2$ are described.

H. F. GILLBE.

Heat of dissociation of oxygen. J. KAPLAN (Physical Rev., 1930, [ii], **35**, 436).—The heat of dissociation is $5{\cdot}7\pm0{\cdot}1$ volts.

L. S. THEOBALD.

Atomic number and heat of formation. W. A. ROTHBRAUNSCHWEIG (Naturwiss., 1931, **42**, 860).—The heats of formation of the oxides of C, Si, Ti, Zr, Hf, and Th are plotted against the at. nos.

A. B. D. CASSIE.

Thermodynamics of the synthesis of methyl alcohol from water-gas. A. V. FROST (J. Gen. Chem. Russ., 1931, **1**, 367—376).—The free energy of the reaction $CO+2H_2$ MeOH is $-\Delta F/4{\cdot}573T = \log K(RT)^2 = 3925/T - 9{\cdot}840 \log T + 0{\cdot}00347T + 14{\cdot}8$. The val. calc. on the basis of Nernst's heat theorem differs from the experimental val. by $+1{\cdot}04\pm0{\cdot}4$, whilst for other reactions the discrepancy is, according to Eucken and Fried's figures, $+0{\cdot}9$.

R. TRUSZKOWSKI.

Conductivity and dielectric constant of electrolyte solution at high frequency. M. WIEN (Ann. Physik, 1931, [v], **11**, 429—453).—Using the Barett method (cf. this vol., 801) the conductivities and dielectric consts. of $MgSO_4$ and $Ba_3[Fe(CN)_6]_2$ solutions have been measured at wave-lengths of 10, 20, and 40 m., and those of $Ba_3[Fe(CN)_6]_2$ and Li_2SO_4 at 10 and 20 m., respectively, for equiv. concentrations up to 5×10^{-2}. The results are in agreement with the Debye–Falkenhagen theory.

J. W. SMITH.

Mobility of some ions containing iron. IV. Nitroprusside ion. F. HÖLZL and W. STOCKMAIR (Monatsh., 1929, **52**, 289—294; cf. A., 1930, 1253, 1524).—Conductivity and transport measurements of solutions of Na, K, NH_4, Rb, and Ba nitroprussides give 69·45 for the mobility of the ion $[Fe(CN)_5NO]''$.

M. S. BURR.

Temperature coefficient of the antimony electrode. II. G. P. AVSEJEVITSCH and I. I. SHUKOV (Z. Elektrochem., 1931, **37**, 771—775).—The stability of the electrode (cf. A., 1929, 899) is largely dependent on the condition of the electrodeposited Sb, and experiments have therefore been made with various org. solvents for the $SbCl_3$. A steady potential is obtained only if the deposit is of the greyish, matte type. Solutions in HCO_2H, MeCN, and $PhNO_2$ yield a smooth deposit for which the potential is unstable, whilst MeOH solutions yield a deposit of suitable structure but of less satisfactory behaviour than that obtained with $COMe_2$ solutions. By final anodic polarisation of the electrode in dil. H_2SO_4 a reproducible, stable electrode is obtained. The p_H of a solution for which the electrode potential (N-calomel electrode) is E at $T°$ is given by $p_H = \{E - 0{\cdot}1 - (T-18)0{\cdot}00025\}/\{0{\cdot}0542 + (T-18)0{\cdot}000275\}$.

H. F. GILLBE.

Use of saturated ammonium chloride in the elimination of contact potentials. C. N. MURRAY and S. F. ACREE (Bur. Stand. J. Res., 1931, **7**, 713—

721).—Liquid junction potentials may be reduced to ± 1.0 mv. by the use of saturated solutions of NH_4Cl, which is considered superior to KCl by reason of its greater mol. solubility. The p_H of the solution must be sufficiently low to avoid errors due to liberation of NH_3. Preliminary experiments on the use of RbBr, $LiIO_3$, and NH_4ClO_4 for the purpose have been carried out. E. S. HEDGES.

Isothermal metallic cells. O. SCARPA (Mem. R. Accad. Ital., Sci. Fis. Mat. Nat., 1930, **1**, Chim., No. 5, 26 pp.; Chem. Zentr., 1931, i, 2848).—Metallic cells can produce a current when two metals in contact form a solution or compound. The e.m. f. of the cells: Cu|Hg|Zn|Cu (0.7×10^{-6} volt at 15°); Cu|Hg|Cd|Cu (1.10×10^{-6} volt at 15°); Cu|Hg|Zn–Hg|Cu; and Cu|Hg|Cd–Hg|Cu have been measured. Vals. of the last two depend on the concentration of the amalgam. The theoretical aspect of the phenomenon is discussed. A. A. ELDRIDGE.

Electrochemical investigation of solid silver-gold alloys. A. OLANDER (J. Amer. Chem. Soc., 1931, **53**, 3577—3588).—The e.m.f. of the cell Ag|AgCl,KCl|Ag, 0·015—0·75 mol. fraction Au has been determined between 707° and 1207° abs. With mol. fractions of Au >0.75, large drifts of e.m.f. are observed. Activity coeffs. of Ag, as well as partial molal heats and entropies of mixing are calc. Phases of low entropy exist below 800° with 0—18 at.-% of Au and with >50 at.-% of Au. A phase diagram is suggested. J. G. A. GRIFFITHS.

Oxidation–reduction of pyocyanine. II. Redox potentials of pyocyanine. B. ELEMA (Rec. trav. chim., 1931, **50**, 1004).—The equation previously given for E_h (cf. this vol., 1013) is incorrect; an improved method for showing the marked drop of potential at 50% reduction for high vals. of the equilibrium const. is given. N. H. HARTSHORNE.

Anodal polarisation of smooth and platinised platinum. V. V. PITSCHETA (J. Gen. Chem. Russ., 1931, **1**, 377—387).—The potential at Pt anodes during the passage of a current depends on the formation of a film of O_2 or suboxide. When the current is broken the potential depends on the accumulation of at. O. The behaviour of a given anode is profoundly affected by its previous history, and reproducible results are obtained only under strictly uniform conditions. The depolarisation potentials are inversely proportional to the current density for both smooth and platinised Pt. R. TRUSZKOWSKI.

Relations between galvanic and voltaic potential and ionic adsorption as determining potential. M. ANDAUER and E. LANGE (Z. physikal. Chem., 1931, **156**, 241—257).—A thermodynamic treatment of the relation of the three types of potential to the concentration of ions in an electrolyte in the case of conducting electrodes. F. L. USHER.

Temperature measurements at working electrodes. VI. B. BRUZS (Z. physikal. Chem., 1931, **156**, 279—290; cf. this vol., 435).—The partial molal entropies of $Cu^{••}$ in solutions of $CuSO_4$, viz., 27·8, 25·1, and 20·7 g.-cal. per 1°, for mol fractions 0·018, 0·004, and 0·0004, respectively, have been calc. from the Peltier effect at Cu electrodes measured by means of a calorimeter which is described in detail. F. L. USHER.

Copper depositing potentials in complex solutions of cuprous halides. N. THON and J. PINILLA (Compt. rend., 1931, **193**, 661—664).—Current density–cathode potential curves for the deposition of Cu from solutions of CuX (X=Cl, Br, I, or CNS) in aq. MX+nHX (M=alkali metal) are all similar. Those for X=Br are discussed. For low current density the potential is relatively positive, then follows an arrest, after which it increases rapidly, whilst the potential decreases but slightly. The arrest is due to the reaction $Cu^{++}+\ominus\longrightarrow Cu^{+}$; this with increased current density is overbalanced by $Cu^{+}+\ominus\longrightarrow Cu$, which requires a lower potential. C. A. SILBERRAD.

Anode phenomena in the electrolysis of potassium acetate solutions. II. Discharge potential of the acetate ion. S. N. SHULK and O. J. WALKER (Trans. Faraday Soc., 1931, **27**, 722—730).—At a smooth Pt anode C_2H_6 and CH_4 are produced only above a crit. anode potential; this is 2·14 volts up to $2N$, but decreases in more conc. solutions. The ratio CH_4/C_2H_6 increases with concentration but decreases rapidly with increasing current density. C. W. DAVIES.

Application of theory of similarity to chemical phenomena. I. Y. HORI (J. Soc. Chem. Ind. Japan, 1931, **34**, 388—391B).—Theoretical. E. S. HEDGES.

Effective (molecular) cross-sections in gas reactions. J. SCHAY (Z. physikal. Chem., 1931, **B**, **14**, 237—240).—Theoretical. In gas reactions which are bimol. in both directions the effective mol. collision cross-sections for the forward and reverse changes are of the same order of magnitude. Their ratio appears not to depend on the heat tone of the reaction. N. H. HARTSHORNE.

Rationale of movement of flame through explosive mixtures of gases. I. Explosions in closed containers. O. C. DE C. ELLIS (J.S.C.I., 1931, **50**, 403—409T).—It is shown with the aid of timed snapshot photographs that all flame movement may be reduced to a simple meteorological basis. The flame surface is an isobaric boundary between two winds of opposite direction. The outward wind, taken with the lie of the gas space, controls the shape and displacement of the flame. In multiple ignitions, it forms nodal calms. The inward wind is the mode of compression of the ignited gases, which continue their combustion, often with luminance, as "after-burning." Tracts of wall where the flame surface touches act as anchors, since they not only stop the production of pressure, but also act as pressure drains. Wind movements that increase the area of the flame surface, thereby increasing the rate of combustion and of energy release, and this is the role of motion and turbulence in increasing the speed of the flame by distorting it.

Oxidation of fuel vapours in air. I. Carbon disulphide and carbon monoxide. II. Hydrogen, methane, and coal gas. III. Comparative studies of (*a*) ethane and ethylene, (*b*) pent-

anes and amylenes, (*c*) ethyl and amyl alcohols, (*d*) acetaldehyde and valeraldehyde. IV. Aromatic hydrocarbons, *cyclo*hexane and *cyclo*hexene. V. Acetylene. E. W. J. MARDLES (Trans. Faraday Soc., 1931, 27, 681—721; cf. A., 1928, 597).—Results are recorded for the pressure changes accompanying the slow reaction in fuel–air mixtures at various concentrations, the min. temp. at which oxidation is appreciable after 20 sec., the available O_2 consumed in this time at various temp., the composition of the products, and the effect of solid and gaseous inhibitors. The pressure changes are complex; usually there is an initial decrease, not detectable at the higher temp., followed by a rise. The temp. of initial combustion normally shows a min. for approx. 50% mixtures, but for CS_2 rises throughout with increasing mixture strength. The temp. coeff. is markedly greater for the paraffins than for the other compounds. Metal surfaces may raise or lower the temp. of initial combustion, but "anti-knock" properties are always associated with a reduced temp. coeff. and a reduced yield of aldehyde in the products. Theories of combustion are discussed; it is held that the primary stage is the formation of a peroxide. C. W. DAVIES.

Flow method for measuring the velocities of gas reactions. E. W. R. STEACIE and H. A. REEVE (Canad. J. Res., 1931, 5, 448—454).—A method for measuring the velocities of gas reactions by pressure changes is found, when tested by the decomp. of NH_3 on a SiO_2 surface, not to be very sensitive. R. S. CAHN.

Kinetics of thermal chlorination of methane. R. N. PEASE and G. F. WALZ (J. Amer. Chem. Soc., 1931, 53, 3728—3737).—The reaction has been investigated dynamically between 225° and 285°. The rate of chlorination is proportional to the product $[Cl_2][CH_4]$ in the absence of O_2. O_2 strongly retards the reaction and the velocity is approx. proportional to $[Cl_2]^2/[O_2]$ and independent of $[CH_4]$. "Packing" the reaction vessel with glass tubing or altering the nature of the surface has relatively small effects. Thus, the reaction is predominantly homogeneous and of the "chain" type. The temp. coeffs. indicate an energy of activation 77,300 g. cal. with 1% O_2 and 31,600 g.-cal. without O_2. A difficulty in assigning a mechanism similar to that of the photo-chemical H_2–Cl_2 reaction is indicated. J. G. A. GRIFFITHS.

Reaction between oxygen and ethylene. I. II. S. LENHER (J. Amer. Chem. Soc., 1931, 53, 3737—3751, 3752—3765; cf. A., 1929, 1243; this vol., 1031).—I. A $C_2H_4+O_2$ mixture was passed through a cylindrical pyrex vessel (vol. 65 c.c.) at temp. between 360° and 410°; some CO_2 and H_2 were produced, but the main products were CO and material condensed in solid CO_2. The condensate contained ethylene oxide, glycol, glyoxal, CH_2O, HCO_2H, and H_2O. The yield of all products decreases to different extents with increasing rate of flow. The reaction is stopped at temp. <500° by "packing" the vessel, and at 500° the oxidation is at the surface and affords mainly CO, CO_2, and H_2O. 3—5% HNO_3 vapour does not catalyse the homogeneous reaction, but C_2H_4 reduces NO at 295° (cf. this vol., 1133). In dynamic experiments with large vessels (vol. 960 c.c.) no glyoxal was detected, but dihydroxymethyl peroxide was a principal product, probably formed by oxidation of CH_2O with H_2O_2 produced in the reaction. The yield of $C_2H_6O_4$ and formic acid is decreased and that of CH_2O is increased in SiO_2 vessels, and $C_2H_6O_4$ is absent from the products from vessels of Al, Fe, or pyrex coated with KCl or K_2SiO_3. The results indicate that although the reaction is mainly homogeneous, the surface has an important effect on its course.

The oxidation of propylene at 280—315° affords products similar to those from C_2H_4.

II. With a re-circulating system at temp. between 410° and 600°, and short times of contact with C_2H_4–10% O_2 mixtures, the principal products are ethylene oxide and CH_2O, but the yields decrease at the higher temp. and some MeCHO is formed probably by thermal rearrangement of C_2H_4O. At 450°, the polymerisation of C_2H_4, mainly to propylene and a little butylene, becomes prominent and increases with rise of temp.; O_2 catalyses the reaction. The primary process of the oxidation probably consists of the activation of C_2H_4 with the formation of a peroxide leading to the production of C_2H_4O, and also the direct oxidation of C_2H_4 to CH_2O. The other products appear in subsequent steps. J. G. A. GRIFFITHS.

New series of homogeneous unimolecular gas reactions. C. C. COFFIN (J. Amer. Chem. Soc., 1931, 53, 3905—3906).—Preliminary. Gaseous decomps. represented by the equation $R'''CO_2\cdot CHR'\cdot CO_2R'' \longrightarrow R'CHO + R'''CO\cdot O\cdot COR''$ are homogeneous and unimol. J. G. A. GRIFFITHS.

Hydration of metaphosphates in neutral and acid solution. S. S. DRAGUNOV and A. N. ROSSNOVSKAJA (Z. anorg. Chem., 1931, 200, 321—331).—Both in neutral and in acid solution $NaPO_3$ combines with H_2O to give orthophosphate only. The reaction appears unimol., but the velocity coeff. decreases with time owing to the inhibiting influence of the orthophosphate formed. $(NaPO_3)_6$ in neutral solution also gives rise to orthophosphate only, but in acid solution pyrophosphate is also formed. F. L. USHER.

Kinetics of the iodometric oxidation of thiocyanate. E. ANGELESCU and V. D. POPESCU (Z. physikal. Chem., 1931, 156, 258—278).—In presence of $NaHCO_3$ the reaction determining the observed velocity is bimol. between CNS′ and OI′, but in practice it appears unimol. on account of the extremely small concentration of OI′ compared with that of CNS′. The I′ produced in the reaction acts as a negative catalyst. In presence of NaOH the slowest of the single reactions is the hydrolysis of ICN. The oxidation is practically instantaneous when NH_3 or NH_4 borate is used as the alkali, because under these conditions the concentration of OI′ is greatly increased and the ICN is not hydrolysed. F. L. USHER.

Oxidation velocity of sodium sulphite and velocity of dissolution of oxygen in water. S. MIYAMOTO, T. KAYA, and A. NAKATA (J. Sci. Hiroshima Univ., 1931, A, 1, No. 2, 125—145).—Measurement of the velocity of oxidation of Na_2SO_3 provides a method for determining the initial rate of dissolution of O_2 in H_2O. The velocity coeffs., calc. as zero order

reactions, were a linear function of the air velocity. The oxidation velocity was also proportional to the partial pressure of O_2. The threshold val. of the velocity components vertical to the surface, above which mols. of O_2 can enter the liquid phase, is calc. to be $1{\cdot}65 \times 10^5$ cm. per sec., independently of temp. between 15° and 35°. CHEMICAL ABSTRACTS.

Period of induction of chemical reactions. II. Action of hypophosphorous acid on sodium iodate. P. NEOGI and B. SEN (J. Indian Chem. Soc., 1931, 8, 725—737).—When H_3PO_2 and $NaIO_3$ are mixed the time which elapses before the appearance of I is unaffected by light, but depends on the concentration of the reactants. $K{-}T \times C_h \times C_i$, where K is a sp. const., T the period of induction, and C_h and C_i are the concentrations of the two salts, respectively. Rise in temp. causes a decrease in T, as also does the addition of the following substances: MeOH, CCl_4, C_6H_6, CS_2, *o*-, *m*-, and *p*-xylene, $CHCl_3$, dil. mineral acids, S sol, reducing agents, finely-divided metals, Pt-black, and animal charcoal. $Na_2S_2O_3$ causes a marked diminution of T and even complete disappearance if sufficiently conc.; NH_4CNS, $Na_2S_4O_6$, and KI act similarly. T increases in presence of EtOH, $Pr^{\beta}OH$, *n*- and *iso*-BuOH, $C_3H_5(OH)_3$, Cl′, SO_4'', NO_3', citrates, tartrates, dextrose, lævulose, mannose, *d*- and *l*-tartaric acids, and maleic and fumaric acids, *l*-tartaric and fumaric acids having more influence than their optical isomerides. $Pr^{\alpha}OH$ totally inhibits the reaction, whilst sucrose has no action and oxidising agents have very little. The crit. val. of C_i at which T disappears, for a fixed val. of C_h of $0{\cdot}0172M$, is $0{\cdot}9130M$. M. S. BURR.

Velocity of hydrolysis of acyl derivatives of glyoximes. M. MILONE (Atti R. Accad. Sci. Torino, 1931, 66, 59—66; Chem. Zentr., 1931, i, 3113).—The Ac_2 and Bz_2 derivatives of α-benzildioxime were hydrolysed 6 times as rapidly as those of the β- and 3 times as rapidly as those of the γ-form. The Ac_2 derivatives have m. p. 148°, 125°, and 115°, and the Bz_2 derivatives m. p. 220°, 159°, and 135°, respectively. A. A. ELDRIDGE.

Thermal constant and temperature coefficient of fermentation by expressed yeast juice and yeast maceration juice. S. KOSTYTSCHEV and G. MEDVEDEV.—See this vol., 1457.

Dependence of reaction velocity on surface and agitation. III. Experimental study of agitation. A. W. HIXSON and J. H. CROWELL (Ind. Eng. Chem., 1931, 23, 1160—1169).—The consts. obtained by application of the cube-root law to dissolving systems form criteria of the intensity of the agitation accompanying the process. The idea of a standard agitation has been developed and applied to the investigation of the dissolution of salts in H_2O; the effects of all the known variables have been studied. E. S. HEDGES.

Rate of dissolution of a granular solid. K. M. WATSON (Ind. Eng. Chem., 1931, 23, 1146—1151).—Fick's law of diffusion is developed to express the rate of dissolution of a granular solid as a function of temp., concentration, particle size, and rate of movement. An apparatus for the quant. study of rates of dissolution, in which a thin layer of the solid charge is contained in a short chamber through which the solvent may be passed at a const. rate, is described. The coeffs. and functions of the proposed equations have been evaluated for the dissolution of $Na_2CO_3,10H_2O$ in H_2O. E. S. HEDGES.

Dissolution of metals in acids. J. N. BRONSTED and N. L. R. KANE (J. Amer. Chem. Soc., 1931, 53, 3624—3644; cf. A., 1928, 717; 1930, 1530).—The rate of dissolution of approx. $0{\cdot}024M$-Na amalgam in aq. solutions of $p_H > 7{\cdot}5$ has been investigated at 18° by the pressure of H_2 produced. The rate of reaction is directly proportional to the square root of Na concentration, and hence the reaction is completed in a finite time. The rate of reaction with aq. NaOH is slow and not reproducible. With phosphate, glycine, and PhOH buffers of const. $[H^{\cdot}]$, the velocity increases linearly with buffer concentration. Conductivity effects are absent. The results support the view that the dissolution of a pure metal (*e.g.*, Na) is due to reaction between an electron in the metal and a mol. of the acid. This idea conforms with the extended theory of acids and bases. The reactivity const. of the acids tend to increase with the strength of the acid, but other effects intervene. The presence of $0{\cdot}0001M$-$[Co(NH_3)_5H_2O]^{\cdots}$ in the glycine buffers greatly accelerates the reaction; higher concentrations lead to violent reaction and a deficiency of evolved H_2. The result is explained as an effect of the high positive charge and the resultant strong attraction for electrons. The great strength of the H_3O^+ ion is correlated with its extreme speed of reaction, and the dissolution of Na in strong acids is governed chiefly by the velocity of the diffusion process. The rate of reaction of Na with PhOH in C_6H_6 is proportional to the concentration of PhOH and the reaction const. of the latter is much higher than in H_2O. J. G. A. GRIFFITHS.

Compounds of the system CaO–FeO and their role in Portland cement. II. J. KONARZEWSKI (Rocz. Chem., 1931, 11, 607—635; cf. this vol., 1010).—Ca ferrites are formed from $CaCO_3$ and Fe_2O_3 at temp. >500°. The reaction takes place in the solid phase, its velocity being given by $y^2{-}2kt$, where y is % transformation and t is time, and the effect of temp. on k is given by $k{-}e^{B-Q_A/RT}$. The curve connecting log y with t consists of two intersecting straight lines; this is due to the fact that at lower temp. $CaCO_3$ reacts directly with Fe_2O_3, whilst at above 900° CaO is formed, which also reacts with Fe_2O_3. The velocity of reaction also depends on the degree of comminution of the substrates. H_2O has little action on $2CaO,Fe_2O_3$. The reduction of $2CaO,Fe_2O_3$ in H_2 commences at about 500°, the ratio Fe : FeO in the product increasing with rise in temp. $2CaO,Fe_2O_3$ does not decompose below 1400°. CaO forms a compound with FeO, probably 2CaO,FeO. $2CaO,Fe_2O_3$ is the only ferrite possessing cementing properties, and it is probable that this compound exerts a favourable effect on the binding of cement. The addition of Fe_2O_3 to Portland cement facilitates the grinding and burning of the raw material and enhances the strength of the product.

R. TRUSZKOWSKI.

Determination of speed of combustion of colloidal powder. H. Muraour (Technique mod., 1931, 23, 177—185; Chem. Zentr., 1931, i, 2712).—Calculation by the usual method, from $(\delta p/\delta t)_{max.}$, may lead to substantial errors. The surface $fp\delta t$ corresponding with the pressure–time curve is therefore determined by evaluation of $P_{max.}/x$; $x=\Delta \log p/\Delta t - tg\alpha$. By the use of a Krupp bomb (700 g. charge) the speed of combustion of uniform powders may be readily determined. A. A. Eldridge.

Topochemistry of corrosion and passivity. I. E. Pietsch and E. Josephy (Z. Elektrochem., 1931, 37, 823—838).—The electrochemical theory of corrosion is considered to be inadequate. A theory is evolved, according to which the primary process of corrosion consists in adsorption at active discontinuities in the surface of the metal, and is developed on the lines of quantum mechanics, with application to heterogeneous catalysis, the catalytic influence of ions on corrosion, and the phenomena of passivity and overpotential. E. S. Hedges.

Surface reaction between ethylene and the halogens. R. B. Mooney and H. G. Reid (J.C.S., 1931, 2597—2605).—The reaction between C_2H_4 and I to form $C_2H_4I_2$ occurs at 30° at the surface of I crystals, the rate (measured manometrically) being proportional to the C_2H_4 pressure. A glass surface covered with EtOH has an activity comparable with that of I, but glass and paraffin are inactive. The heat of activation (from temp. coeff.) is 19·8±3 kg.-cal. C_2H_4 and $(CN)_2$ do not react on glass at 150°, or on SiO_2 gel at 110°. CNCl and CNBr do not react with C_2H_4 at 37°, but CNI and C_2H_4 give $C_2H_4I_2$ and $(CN)_2$. H. J. Emeleus.

Kinetics of the catalytic hydrogenation of ethylene. C. Schuster (Z. physikal. Chem., 1931, B, 14, 249—264).—The rate of the reaction $C_2H_4+H_2=C_2H_6$ at the surface of activated charcoal, containing about 3% of Fe and a trace of Cu, between −84° and 50° at low pressures depends only on the H_2 pressure (to which the H_2 surface concentration is almost directly proportional) unless the surface concentration of the C_2H_4 is below 0·4—0·5 c.c. per g., in which case it depends also on this. It is concluded that the reaction occurs only at active centres, which are saturated with C_2H_4 so long as the surface concentration of this gas is not below the above crit. val. They may be the metallic atoms present, since the number of these is of the same order as the number of centres calc. from this crit. val. At 75° and, towards the end of the reaction, at 50° the rate is best represented by the equation $dx/dt=K(a-x)^{1 \cdot 5}$, the symbols a and x referring to H_2, and this is attributed to the altered form of the H_2 adsorption isotherm at higher temp. The heat of activation between −84° and 50° is 2000±500 g.-cal., and this low val. may be explained either by the reaction rate being governed by the rate of diffusion of H_2 on the charcoal towards the active centres, or, if it be assumed that the reactants can remain in contact for a long time, by the theory of Born and Weisskopf (this vol., 576, 918). N. H. Hartshorne.

Synthesis of carbamide from ammonium carbamate. B. Neumann and A. Sonntag (Z. Elektrochem., 1931, 37, 805—812).—The formation of $CO(NH_2)_2$ from $NH_3{\cdot}CO_2NH_4$ by heating in a steel bomb lined with Sn–Pb alloy increases rapidly and the yield is higher as the temp. is raised from 135° to 155°. Addition of Al_2O_3 or FeO for the purpose of removing the H_2O produced in the reaction does not improve the yield, but has the reverse effect. Since the equilibrium is altered, these substances cannot be considered as catalysts, although the velocity of reaction is increased, and they appear to act by lowering the m. p. of the mixture, thus favouring reactions in the liquid phase. Other addenda used technically probably act in the same way. E. S. Hedges.

Energy transformations at surfaces. III. Influence of polar adsorption on the rate of hydrogenation of dyes. H. Kautsky and W. Baumeister (Ber., 1931, 64, [B], 2446—2457; cf. this vol., 1353).—Silicic acid gel is combined with $[Pt(NH_3)_4]^{++}$ ions by polar adsorption and the adsorbate after desiccation in vac. is reduced by H_2 at 360°. A Th hydroxide–Pt catalyst, obtained by adsorption of $[Pt(OH)_6]$ ions and reduction at 120—150°, is also used. The rate of hydrogenation of methylene-blue in presence of these catalysts, the former of which adsorbs whereas the latter does not adsorb methylene-blue from aq. solution, is determined. The velocity is extraordinarily restricted by polar adsorption, the effect being more marked with diminution of the concentration of the solution which is in equilibrium with the amount of methylene-blue on the surface. Only that portion is hydrogenated which is dissolved in H_2O and reaches the Pt of the catalyst to be thereby adsorbed. With insol. polar adsorbed dyes the rate of hydrogenation is immeasurably small. Within the surface there is no marked diffusion of the polar adsorbed dye mols. among themselves or with the catalytically active regions and hence no direct interaction. The interchange of mols. occurs through the solution. H. Wren.

Acid and salt effects in catalysed reactions. XXV. Catalytic effects in the intramolecular transformation of phorone. H. M. Dawson and E. Spivey (J.C.S., 1931, 2658—2665).—The catalytic effect of HCl, AcOH, and acetate buffers on the change of phorone preceding its reaction with I was measured at 25° in 50% EtOH solution. The dissociation const. of AcOH in 50% EtOH is $2{\cdot}7\times10^{-6}$. The autocatalytic reaction was studied. The catalytic effect of the solvent medium was large in the early stages. H. J. Emeléus.

Action of sodium hypophosphite on aqueous solutions of cobalt salts. C. Paal and L. Friederici (Ber., 1931, 64, [B], 2561—2569).—In contrast to the behaviour of Ni solutions (this vol., 1019), aq. solutions of $CoCl_2$ are not reduced by NaH_2PO_2 even in presence of small amounts of Pd. In aq. NH_3 in presence or absence of catalyst reduction occurs with production of Co and a little Co phosphide. Addition of Pd accelerates the change, and with relatively large amounts of catalyst Co free from

phosphide is obtained. $CoCl_2$ in presence of alkaline Na K tartrate, even without Pd, yields mainly Co with a little Co phosphide. Reduction does not occur when $CoCl_2$ in presence of an excess of NaOAc is warmed with NaH_2PO_2, and addition of Pd affords salt-like materials containing Co, P, and O. Treatment of mixtures of Co and Co phosphides with HCl leaves a residue richer in P than the original material, but the phosphide is simultaneously attacked to a marked extent. H. Wren.

Influence of solvents on chemical reactions. I. Reaction between trichloroacetic acid and ethyl diazoacetate in hydrocarbon solvents, and the influence of additions. A. Weissberger and J. Högen (Z. physikal. Chem., 1931, **156**, 321—351).—The predominant reaction between $CCl_3{\cdot}CO_2H$ and Et diazoacetate in non-hydroxylic solvents at 0—10° is bimol. and yields N_2 and an ester of glycollic acid. The temp. coeff. in C_6H_{14} and C_7H_8 is 1·7. Although satisfactory vals. of the velocity coeff. k are obtained with an equimol. solution of the reactants or with an excess of acid, if an excess of ester is present k falls rapidly with decrease of the acid concentration. The effect is caused by the formation of a mol. complex between the reactants The influence of various additions to the solution has been studied. k is depressed by Et_2O, $COMe_2$, alcohols, menthone, and $NHPh_2$, and, to a smaller extent, by acetophenone and benzophenone. Anisole, Ph_2O, C_6H_6, NPh_3, and tribromoaniline are without influence. The retarding influence is due to combination of the added compound with the acid, and its extent may be regarded as a measure of the affinity between the acid and the compound. H. F. Gillbe.

Temperature coefficient of reactions catalysed by acids and bases. M. Kilpatrick, jun., and M. L. Kilpatrick (J. Amer. Chem. Soc., 1931, **53**, 3698—3710; cf. A., 1928, 848; 1930, 300).—The catalysis of the mutarotation of α-glucose has been investigated dilatometrically in 0—0·25M-HCl, acetate–AcOH, and pyridine–pyridinium chloride buffers. Catalytic consts. for H˙, AcO′, and pyridine have been evaluated, and the following heats of activation have been calc. from the temp. coeff.: H˙ 19,300 g.-cal., AcO′ 19,100, pyridine 18,000, and H_2O 17,000. Generalising from the results, little change in the relation between catalytic strength and relative acid strength is to be expected with change of temp. in the mutarotation of glucose.

J. G. A. Griffiths.

Transformation of green into violet modifications of chromium sulphate. S. I. Orlova and N. N. Petin (J. Gen. Chem. Russ., 1931, **1**, 345—358).—The spontaneous transformation of green into violet solutions of $Cr_2(SO_4)_3$ is accelerated by H˙ or SO_4'', and is represented by $[Cr_4O_4(SO_4)_4]SO_4 + H_2SO_4 \rightleftharpoons 2Cr_2(SO_4)_3 + H_2O$. This equation also explains the accelerative effect on the velocity of crystallisation of the addition of acids to Cr alum solutions.

R. Truszkowski.

Thiol compounds as anti-catalysts in oxidations with molecular oxygen. II. Oxidation of thiol compounds with hydrogen peroxide. A. Schöberl (Z. physiol. Chem., 1931, **201**, 167—190; cf. this vol., 691).—Previous work is confirmed. The anti-catalytic action of SH-compounds holds also with $SH{\cdot}CH_2{\cdot}CO_2H$. The disulphide compounds of SH-glutathione (SS-glutathione, $[\alpha]_{5461}^{22}$ −115·6°) and of $SH{\cdot}CH_2{\cdot}CO_2H$ are readily obtained by oxidation with H_2O_2; they are inactive. This confirms the slow inactivation of the anti-catalyst as being due to oxidation by H_2O_2 produced in the reaction.

J. H. Birkinshaw.

Autoxidation of benzaldehyde. Action of anti-oxygenic compounds and applications. Oxidation of ethylenic compounds. E. Raymond (J. Chim. phys., 1931, **28**, 480—510; cf. A., 1930, 1582).—Bertram's purification of oleic acid is modified (A., 1927, 750). Traces of H_2O, H_2SO_4, NaOH, and NH_3 are anticatalysts in the autoxidation of PhCHO. The velocity of autoxidation of PhCHO in the presence of oleic acid, esters of ethylenic acids, ethylenic hydrocarbons and alcohols, and cyclic compounds is given by $v{=}e^{-Kc}$, where c is the concentration of and K is characteristic of the anticatalyst. K is greatly influenced by the nature and position of the various groups relative to the ethylenic linking. Proximity and multiplicity of C_6H_6 nuclei and multiplicity of ethylenic linkings greatly increase K, which is largely diminished by CO_2H and OH. *trans*-Compounds are more active than *cis*.

BzO_2H formed in the oxidation of PhCHO oxidises dissolved substances, and good yields of the ethylenic oxides of oleic acid, stilbene, styrene, and squalene have been obtained. J. G. A. Griffiths.

Catalytic action of surfaces. J. E. Nyrop (Chem. and Ind., 1931, 752—755).—Starting from Sommerfeld's theory of the state of free electrons in conductors, the conditions for the existence of an atm. of rapidly-moving electrons in the immediate vicinity of a metallic surface are worked out and catalytic phenomena are explained by assuming chemical reactions to be promoted by these electrons. If various mols. are brought in between the surface electrons, electronic impact may ionise or activate the mols., forming ions which are able to produce new mols. by collision with other ions or mols. Such new mols. may also be ionised and thereby adsorbed, but some of them will leave the surface zone. A catalytic process is thereby produced. If new mols. are not formed, ordinary adsorption takes place. If mols. having a low energy of ionisation are also present they will preferentially occupy the zone and thereby hinder the catalytic process, thus having a "poisoning" action. The following laws governing catalytic processes are deduced: (1) The catalytic effect of a surface depends on the max. kinetic energy of the "free" electrons of the catalyst. (2) If the ionisation energy of a mol. is lower or becomes lower close to the surface than the kinetic energy of some of the surface electrons, ionisation occurs and the mol. will be adsorbed. (3) Adsorbed mols. will react as in the gaseous phase, but the energy of activation is lowered by ionisation or activation caused by the surface electrons and/or the number of active collisions between the mols. is increased. (4) New mols. having the highest ionisation energy and/or the lowest mol. wt. tend to be produced. (5) Rise of temp. increases

the number of collisions, but lowers the flow through the adsorption zone. (6) Pressure increases the flow through the adsorption zone. (7) The catalytic effect is proportional to the accessible area of the catalyst. The operation of these laws is demonstrated for the synthesis of NH_3, the decomp. of EtOH vapour, and the production of MeOH. The theory offers a simple explanation of many phenomena in which selective effects have hitherto been supposed. The theory is extended to enzymes, by assuming that an enzyme consists of mols. having electron-active groups (double linkings, C_6H_6 rings, etc.) adsorbed side by side on colloid surfaces, whereby mols. penetrating between the enzymic mols. are exposed to electronic impact.

E. S. HEDGES.

Catalytic decomposition of carbon monoxide. IV. Behaviour of nickel carbides. H. TUTIYA (Bull. Inst. Phys. Chem. Res. Tokyo, 1931, **10**, 951—973).—An *X*-ray investigation of the catalytic decomp. of CO by Ni or NiO has confirmed the formation of Ni_3C and a percarbide, Ni_xC. The percarbide is formed from NiO at 270° and rapidly decomposes into Ni_3C and C at 284°; it is also decomposed by atm. H_2O vapour. Ni_3C is quite stable at 285° and catalyses the decomp. of CO. In the temp. range of stability of Ni_3C the reaction $3Ni+2CO \rightleftharpoons Ni_3C+CO_2$ is possible, but not the reaction $2CO=C+CO_2$. Free Ni is found in the earlier stages of reduction of NiO, but later changes completely to carbides.

E. S. HEDGES.

Pressure hydrogenation with iodine as catalyst. J. VARGA and L. ALMASI.—See B., 1931, 1003.

Catalytic formation of methane from carbon monoxide and hydrogen. Simultaneous catalytic acceleration of the water-gas reaction and the Armstrong–Hilditch reaction. J. C. GHOSH, K. M. CHAKRABARTY, and J. B. BAKSHI (Z. Elektrochem., 1931, **37**, 775—779).—The reaction between CO and H_2 at 471° on a Ni–Th–Ce catalyst proceeds according to the equations $2mCO+2mH_2 \rightleftharpoons mCO_2+mCH_4$ and $nCO+nH_2+nH_2O \rightleftharpoons nCO_2+2nH_2$; no C separates. The ratio m/n diminishes with time, even with const. composition of the gas mixture, owing to the Ni losing its activity as regards CH_4 formation without, however, becoming less active as regards the water-gas reaction. The mixture of reaction products has a higher heat of combustion than blue water-gas, viz., 426·5 B.Th.U. per cu. ft., and after removal of CO_2 and H_2O a higher val. than CO or carburetted water-gas, viz., 722 B.Th.U. per cu. ft. With one catalyst, at a gas velocity of 6500 c.c. per hr. per c.c. of catalyst, the equilibrium conditions of both the water-gas and the Armstrong–Hilditch reactions are attained at 471°.

H. F. GILLBE.

Catalytic decomposition of carbon disulphide by hydrogen. B. NEUMANN and E. ALTMANN (Z. Elektrochem., 1931, **37**, 766—771).—The reaction on a number of catalysts at 180—885° has been investigated. In all cases there is a max. in the temp.–% decomp. curve. The activity of the catalysts as regards the production of H_2S falls in the order Pt (90% decomp. at 500°), Cu, Pb, Cr oxide mixture, Ag, MgO+ThO (54% at 700°). The order is quite different if determined in terms of the total CS_2 decomposed, owing to the formation of other S compounds. Fractionation of the reaction products shows that the quantity of H_2S formed is very small at temp. below 600°, but rises rapidly thereafter to a max. at 850°; the amount of C_2H_4 produced falls to zero at about 700°, its place being taken by CH_4, of which the yield is a max. at 850°. The greater part of the H_2S produced results from the decomp. of org. compounds, and the usual simple formulation of the reaction is therefore incorrect. Although the equation $CS_2+4H_2=2H_2S+CH_4$ represents approx. the total reaction at 870°, the sequence of products at lower temp. is probably $CS_2 \rightarrow HCS_2H \rightarrow CH_2S \rightarrow MeSH \rightarrow CH_4$.

H. F. GILLBE.

Velocity of catalysed hydrogenation. I. A. KAILAN and (FRL.) H. C. HARDT (Monatsh., 1931, **58**, 307—368).—The hydrogenation velocities of cinnamic acid, its Me, Et, Pr$^{\alpha}$, Bu$^{\alpha}$, Ph, and CH_2Ph esters, oleic acid, and olive oil have been measured at 180—200° using Ni deposited by reduction on kieselguhr, or in some cases without carrier, as catalyst. In general, the unimol. velocity coeff. diminishes as the reaction proceeds, especially at the beginning, and experiments under apparently comparable conditions give very different results. The coeff. is least for the Et ester and greatest for the CH_2Ph ester. For the latter and for the Pr$^{\alpha}$ and Ph esters it is greater than for cinnamic acid itself. The coeff. for oleic acid is about the same as for cinnamic acid, but less for olive oil. The coeff. for olive oil increases rapidly as the reduction temp. of the catalyst rises from 250° to 320°, but much more slowly for higher reduction temp., especially above 460° (to 550°). Increase of the wt. of catalyst from 0·025 to 0·1 g. increases the velocity of hydrogenation of 20 g. of olive oil, but a further increase of the amount of catalyst to 2 g. produces no effect. If, instead of using 2 g. of kieselguhr containing 20% Ni, 0·4 g. of Ni alone is the catalyst, the coeff. is reduced 10—15 times, and it is always 0·2—0·25 as great if a Ni–kieselguhr prepared with Na_2CO_3 instead of NaOH is used, and 0·33—0·5 as great for a Ni–silicic acid catalyst. In the total hydrogenation of oleic acid more than 2H per mol. of acid is used. Experiments with stearic acid seem to indicate that this may be due to reaction with the CO_2H group.

M. S. BURR.

Catalytic reduction of carbon monoxide at the ordinary pressure. X. Influence of certain substances on the catalytic effect of Co–Cu–MgO. K. FUJIMURA (J. Soc. Chem. Ind., Japan, 1931, **34**, 384—386B, and Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, **17**, 16—21).—The reduction of CO by H_2 in presence of Co–Cu–MgO is promoted considerably by the oxides of Th and U, and less by those of W, Mo, and Cr.

E. S. HEDGES.

Specificity of difficultly reducible oxide catalysts for hydrogenation. J. V. VAUGHEN and W. A. LAZIER (J. Amer. Chem. Soc., 1931, **53**, 3719—3728).—C_2H_4, C_3H_6, and C_4H_8, when mixed with H_2, are not hydrogenated by contact with Mo_2O_3, V_2O_3, MnO, MgO, TiO_2, ZnO alone or with Cr_2O_3, Al_2O_3, or Fe at 400°. Cu, Zn, and Zn on ZnO are effective. Hydrogenation of $COMe_2$ at 150 atm. with a ZnO–Cr_2O_3 catalyst affords 16% of Pr$^{\beta}$OH with large recovery

of $COMe_2$. Na_2CO_3 on the catalyst prevents dehydration of $Pr^{\beta}OH$. It is suggested that in the oxide surface the valency forces of the metal atom are so strongly directed to the interior of the crystal lattice that weak negative groups (*e.g.*, C⁚C) are not able to form a suitable complex with the surface to react with activated H_2. With such an oxide surface only $COMe_2$, $PhNO_2$, etc. can form an active complex.

J. G. A. GRIFFITHS.

Effect of phosphorus vapour on reaction between incandescent tungsten, water vapour, and oxygen, in presence of an inert gas. J. T. RANDALL and J. H. SHAYLOR (Trans. Faraday Soc., 1931, **27**, 730—735).—Reactions in a gas-filled lamp are studied by the changing resistance of the filament. In absence of P, small quantities of H_2O give WO, whereas traces of O_2 give higher oxides; with P present, traces of H_2O do not attack the filament, but appear to give P_3O.

C. W. DAVIES.

[Catalytic] conversion of methane. I, II. N. A. KLYUKVIN and S. S. KLYUKVINA (J. Chem. Ind., Russia, 1930, **7**, 743—752, 877—885).—CH_4 was passed alone, and with CO_2 or H_2O, in presence of a catalyst, through heated porcelain or Fe tubes. With reduced NiO at 850° only 1·6% CH_4 remained unchanged; the gas contained H 94·3, N 4·1%, and the increase in vol. was 99·6%. The thermal decomp. of CH_4 may be complicated by formation of CO and CO_2 and (in absence of Ni) of unsaturated compounds. Equal vols. of CH_4 and CO_2 at 1000° with Ni gave 97·6% conversion: $CH_4+CO_2=2CO+2H_2$ (CO 47, H_2 48·6, N_2 2·6%); formation of CO begins at 700°. Addition of Al_2O_3 to Ni retards conversion. At 1000°, without a catalyst, 43% conversion occurred in a porcelain tube and 58% in a Fe tube. Under similar conditions the conversion of CH_4 is in direct proportion to the speed of the gas; the yield at 9 litres per hr. is 90% of that at 3 litres per hr. For the conversion $CH_4+H_2O=CO+3H_2$ (at low temp. $CH_4+2H_2O=CO_2+4H_2$; $CH_4+CO_2=2CO+2H_2$; $H_2O+CO=CO_2+H_2$) the mixture of CH_4 with 4 vols. of steam was passed at a velocity of 6 litres per hr.; the best result gave 98·4% conversion of CH_4, with 218% increase in vol. (CO_2 5·8, CO 12·6, H_2 80, O_2 0·4, N_2 0·7, CH_4 0·5%). Substitution of Al_2O_3 or reduced Fe for Ni was unsatisfactory. Activated vegetable C gives 100% conversion (cf. Ni, 33·3%) at 800°; the conversion is accompanied by the reaction $C+2H_2O=CO_2+2H_2$. Conversion of CH_4 with C in absence of H_2O gives 100% conversion at 900—950° (CO_2 0·2, CO 0·8, H_2 93·1, N_2 5·9%). With Ni the reaction of CH_4 alone starts at 300° and reaches complete conversion at 850°; with C it starts at 500—600°, and at 1000° 62·4% conversion takes place. Inactivated birch C gave 47·1% conversion of CH_4 at 1000° in a porcelain tube or 100% at 900° in a Fe tube. From 27 g. of C, 26·8 g. were recovered.

CHEMICAL ABSTRACTS.

Crystallised boron. L. HACKSPILL, A. STIEBER, and R. HOCART (Compt. rend., 1931, **193**, 776—778).—A very condensed high-frequency spark is passed between electrodes of Mo or W in a mixture of H_2 and BCl_3 vapour. With 300 watts 0·5 g. of B is obtained in 3 hr. as a product of metallic appearance, resembling As, hardness 9 (Mohs), d^{20} 3·33. It is attacked by aqua regia at 120—130°, and is at least 99% pure. *X*-Rays show it to be cryst., probably hexagonal. The product of the action of incandescent W on BBr_3 vapour is similar in structure, but not $B_{48}C_2Al_3$.

C. A. SILBERRAD.

Separation of sulphide films on metals. E. BEUTEL and A. KUTZELNIGG (Monatsh., 1931, **58**, 295—306).—Anodic separation of sulphide films of Au, Pt, and Pd from complex thiosulphate solutions and cathodic separation of the sulphides of Pb, Sb, Bi, Mn, Fe, Ni, and Co may be observed. When sol., the simple thiosulphate may be used. Cu_2S cannot be obtained electrolytically, but is formed by metallic contact. The anodic film usually contains free S and the cathodic film free metal. A covering layer of S is obtained on decomposing a Cu_2S or CoS film. The films were examined by micro-analytical methods. No sulphides were obtained with Ag, Zn, Cd, Hg, Sn, As, Mo, and U.

M. S. BURR.

Preparation and some properties of amalgams of titanium, uranium, and vanadium. R. GROVES and A. S. RUSSELL (J.C.S., 1931, 2805—2814).—Conditions for depositing Ti, U, and V from aq. solution on a Hg cathode are given. The resulting amalgams have strong reducing properties, and the order of removal of the metals from Hg by oxidising solutions was determined (cf. A., 1929, 1402). The metals catalyse the production of H_2 at a Zn amalgam–dil. H_2SO_4 interface in the order (diminishing) Ti, U, V. Traces of each metal are deposited on Zn amalgam (also Ti and U on Sn and Cu amalgams and on Hg) on shaking solutions of the metal salts with the amalgams or Hg.

H. J. EMELÉUS.

Electro-deposited metal foils. H. KERSTEN (Rev. Sci. Instr., 1931, [ii], **2**, 649—653).—Electrolytic solutions are described for the deposition of Co, Ni, Cu, Ag, Cd, Sn, Au, and brass on polished stainless steel cathodes from which removal of the foil is easy.

N. M. BLIGH.

Electrolytic preparation of β-tungsten. W. G. BURGERS and J. A. M. VAN LIEMPT (Rev. trav. chim., 1931, **50**, 1050—1051).—Previous work (A., 1925, ii, 694) is incorrectly cited by other workers (this vol., 805). β-W (together with α-W) is formed when a mixture of K, Na, and Li tungstates is electrolysed at 500°.

N. H. HARTSHORNE.

Anodic precipitation of lead peroxide. M. L. NICHOLS (Ind. Eng. Chem. [Anal.], 1931, **3**, 384—385).—Experiments on the effect of rotation of the anode on the electrolysis of $Pb(NO_3)_2$ solutions indicate that the Pb is not carried to the anode in an ionic form, but is oxidised to negatively-charged PbO_2, which is then pressed against the anode by cataphoresis. This mechanism of formation of PbO_2 explains the difficulty of removing the last traces of H_2O in drying the deposit.

E. S. HEDGES.

Electrolytic production of potassium ferricyanide. V. P. ILINSKI and N. P. LAPIN.—See B., 1931, 1047.

Behaviour of solutions of chlorine dioxide in carbon tetrachloride in the dark and in the light. R. LUTHER and R. HOFFMANN (Z. physikal. Chem.,

Bodenstein Festband, 1931, 755—769).—The partition coeff. at 17° of ClO_2 between CCl_4 and the gas phase is $50{\cdot}7 \pm 0{\cdot}4$, and between H_2O and the gas phase $34{\cdot}3 \pm 0{\cdot}1$. When ClO_2 is dissolved in CCl_4, Cl_2O is formed at a const. concentration of about $0{\cdot}001M$, and causes in the dark further catalytic decomp. of the ClO_2. The active catalyst is probably ClO, and the kinetics of the reaction are represented fairly accurately by the equation $d[ClO_2]/dt = k[ClO_2]^{4/3}\,.\,[Cl_2O]^{1/3}$. By addition of alkali, preferably $Ba(OH)_2,8H_2O$, the decomp. is inhibited, but after several hr. have elapsed spontaneous decomp. commences. H. F. GILLBE.

Effect of light on formation of banded precipitates of mercuric iodide. R. TAFT and J. W. HILL (Trans. Kansas Acad. Sci., 1931, 33, 57—63).—Light favoured the formation of the red form. The yellow form was transformed into the red (slowly in the dark) in silicic acid, but not in agar or gelatin. CHEMICAL ABSTRACTS.

Blackening of photographic plates by positive ions of the alkali metals. K. T. BAINBRIDGE (J. Franklin Inst., 1931, **212**, 489—506).—The energies, expressed in electron-volts, of the singly positively charged ions of the alkali metals required to produce a threshold opacity of 1·1 on Eastman X-ray plates (the opacity being defined as the ratio of the light transmitted through the unexposed portion of the plate to that transmitted through the exposed portion) varied from 920 (Cs) to 460 (Li) for 1 min. exposure at a current density of $1{\cdot}32 \times 10^{-8}$ amp. per sq. cm. For an opacity of 2 under the same conditions they varied from 1420 (Cs) to 860 (Li). The blackening at such low energies is only to a minor extent due to the penetration of the ions into the emulsion; impact radiation and the effect of electrons derived from the material of the apparatus play the larger part. The opacity is not proportional to the current density, and it is concluded that, regardless of the current density, only a limited no. of ions are effective in unit time. Eastman X-ray plates are about three times as sensitive to low-energy ions as Eastman process plates, but Schumann plates are more sensitive than either and will record K ions at 137 electron-volts under the above conditions. N. H. HARTSHORNE.

Significance of the redox [oxidation–reduction] potential of vat dyes for photographic and photochemical systems. A. STEIGMANN (Z. wiss. Phot., 1931, **30**, 69—76).—A discussion. Dyes which cause fogging of photographic emulsions act catalytically. In a given alkaline developer, the fogging is dependent on the potential of the dye, or the difference between that of the dye and of the reducing agent. In systems analogous to glutin–methylene-blue, exposure tends to increase such difference. As the difference increases, light-sensitivity increases, until the case of reduction in the dark is reached. J. LEWKOWITSCH.

Isolation of nuclei by developing agents. LUPPO-CRAMER (Z. wiss. Phot., 1931, **30**, 65—68).—Metol, quinol, etc., in acidified KBr solution, partly remove the latent image; the more effective developers have the greater action. Development is considered as the isolation of the latent image nuclei from adsorption on AgBr before chemical action occurs. J. LEWKOWITSCH.

Photochemical studies. II. C. WINTHER (Z. wiss. Phot., 1931, **30**, 113—120).—Actinometry using a solution of $(NH_4)_2C_2O_4$ and $HgCl_2$ is described. A brief review of photographic methods is given. J. LEWKOWITSCH.

Density surface of [a solid diagram representing] the Villard effect. H. ARENS and J. EGGERT (Z. wiss. Phot., 1931, **30**, 121—126).—After a const. exposure of a film to X-rays, the densities of the images produced by exposure to various light intensities for varying times have been measured. The results, showing the solarisation and fluctuation of density with const. val. of log it, are illustrated by a solid model, and also by density contour lines on a log i–log t graph. J. LEWKOWITSCH.

Solarisation. V. The latent image in the region of solarisation with physical development. H. ARENS (Z. wiss. Phot., 1931, **30**, 127—140; cf. B., 1931, 417).—The (a) grain wt., (b) grain no., and (c) amount of the latent image Ag have been determined using a special emulsion which shows solarisation with physical development. (a) and (c) increase steadily, from a low val., in the region of solarisation and second reversal; (b) decreases, following the developed Ag curve. The latent image becomes less sol. in Farmer's reducer in the solarisation region, probably owing to the smaller solubility of larger grains. If nitrite is added to the emulsion, all the characteristics increase steadily, (c) being exceptionally large, and solarisation is absent. Solarisation can be attributed to coagulation of Ag nuclei only if these are assumed to wander, since their mean separation is greater than their diameter. J. LEWKOWITSCH.

Photodichroism and photoanisotropy. IX. Photographic experiments with polarised light. I. F. WEIGERT and F. STIEBEL (Z. wiss. Phot., 1931, **30**, 95—107; cf. A., 1930, 519, 1238; this vol., 1250).—A chemical developer containing p-phenylenediamine is best for the production of photodichroism. Exposure of the plate to red polarised light with previous or subsequent exposure to red, or blue, ordinary light increases the dichroism greatly. The blue light can produce high vals. even when the exposure to polarised light is very small; in this case the effect is greater when the exposure to the blue light follows that to polarised light. J. LEWKOWITSCH.

Desensitisation [retardation of photolysis] in uranyl formate and potassium ferrioxalate. E. BAUR [with C. OUELLET and E. WÄCKERLIN] (Z. wiss. Phot., 1931, **30**, 88—94).—The rate of photolysis of uranyl formate in the presence of foreign substances has been measured and compared with the calc. figures (cf. A., 1929, 892). Experiments with $K_3Fe(C_2O_4)_3$, when the results are corrected to const. intensity of activating light, show a const. reaction velocity up to 30% decomp., in agreement with Allmand and Webb (*ibid.*, 1023). J. LEWKOWITSCH.

Photo-reduction of alcoholic solutions of ferric chloride. M. PRASAD and N. V. SOHONI (J. Indian

Chem. Soc., 1931, **8**, 489—497).—The influence of the intensity of light, small amounts of H_2O, temp., and salts on the photo-reduction of solutions of $FeCl_3$ in anhyd. EtOH and *n*-amyl alcohol, and moist PrOH and BuOH has been studied. In conc. solutions the reaction is of almost zero order, but in dil. solution it becomes unimol., especially in presence of traces of H_2O; the order is partly governed by the light intensity. In anhyd. solutions a stationary state is attained, but addition of H_2O accelerates at first the reduction and then the back reaction. The temp. coeff. (30—40°) is 1·00—1·15. Traces of salts inhibit the reaction, and the effect increases with increase of the salt concentration. H. F. GILLBE.

Products of photochemical oxidation of acetylene. R. LIVINGSTON (J. Amer. Chem. Soc., 1931, **53**, 3909—3910).—$H_2C_2O_4$ and a trace of an aldehyde are formed when a mixture of C_2H_2 and O_2 saturated with H_2O vapour at room temp. is exposed in a flow system to the full radiation of the "hot" quartz Hg arc. The result is discussed in relation to the mechanism predicted by Mecke (this vol., 1136).

J. G. A. GRIFFITHS.

Photolysis of diazo-compounds. I, II, III. I. FUKUSHIMA and M. HORIO (J. Soc. Chem. Ind., Japan, 1931, **34**, 367—377B).—The decomp. of diazobenzenesulphonic acid (I) and of 1-diazo-β-naphthol-4-sulphonic acid (II) is influenced by light of wave-length shorter than 450 mμ and 380 mμ, respectively. The reactions proceed with const. velocity, independently of the concentration. The addition of quinine sulphate to a solution of the latter compound reduces the velocity of photolysis in proportion to the amount added. Rise of temp. has no influence on the photolysis of (II), but with (I) a thermal decomp. of the first order begins between 22° and 45°. E. S. HEDGES.

Photosynthetic activity of different catalysts. N. A. YAJNIK and F. C. TREHANA (J. Chim. phys., 1931, **28**, 517—524).—Preliminary experiments confirm the results of Baly and co-workers (A., 1927, 1040). Blank experiments afford negligible org. residue. Several coloured solids suspended in H_2O were used as catalysts. With light from a 300-watt lamp, Cu arsenate afforded 0·129—0·174 g. of org. residue containing 20 mg. of reducing substance (determined as dextrose); basic carbonates of Co and Ni, Cr phosphate, $CuCO_3$, and Cr_2O_3 afforded decreasing yields. $BaCrO_4$, Pb_3O_4, Fe_2O_3, and Ni phosphate afforded traces of org. residue but no reducing substances. Of $MgCO_3$, $BaSO_4$, $CaCO_3$, and MgO, alone, only $MgCO_3$ afforded a trace of org. substance, but when the first two were coloured with insol. dyes, org. reducing substances were obtained, the yields decreasing with change of colour from blue to red. J. G. A. GRIFFITHS.

Action of high-speed cathode rays on simple alcohols, aldehydes, and ketones, and ethylene. J. C. MCLENNAN and W. L. PATRICK (Canad. J. Res., 1931, **5**, 470—481).—Bombardment of the gaseous substances with high-speed cathode rays causes the following reactions. CH_2O gives paraformaldehyde, which decomposes into H_2, CH_4, and oxides of C. MeCHO and $COMe_2$ give gases and polymerides; with MeCHO the reaction takes place on the wall of the vessel and the gases are formed by decomp. of the polymeride. MeOH and EtOH are primarily dehydrogenated to aldehydes, which then decompose. C_2H_4 yields a liquid, which gives H_2, C_2H_2, and saturated hydrocarbons on further bombardment. It is considered that clusters of mols. are first formed, which either (*a*) form solid or liquid condensates, or (*b*) decompose into simple gases. R. S. CAHN.

Action of nitric oxide on alkaline hydroxides. E. BARNES (J.C.S., 1931, 2605—2620).—The reaction of the solid hydroxides of Li, Na, K, Rb, Cs, Ca, Sr, Ba with NO at 16—350° yields nitrites, N_2O, H_2O, and a small % of N_2, which increases with rise of temp. The reactivity of the alkali hydroxides increases with their mol. wts. The reaction of NO with 50% aq. KOH at 29·7° was approx. unimol., indicating a surface reaction or solution effect.

H. J. EMELÉUS.

Stability of potassium ferrocyanide solutions. I. M. KOLTHOFF and E. A. PEARSON (Ind. Eng. Chem. [Anal.], 1931, **3**, 381—382).—$K_4Fe(CN)_6$ solutions should be kept in bottles of brown glass. The method of recrystallisation has no appreciable effect on the stability, but the presence of $K_3Fe(CN)_6$ tends to promote decomp.; dil. solutions are less stable than conc. solutions and the stability decreases with increasing acidity. Solutions containing 0·2% Na_2CO_3 are stable for long periods. E. S. HEDGES.

Solid anhydrous copper hydride. E. PIETSCH and E. JOSEPHY (Naturwiss., 1931, **19**, 737—738).—By the passage of at. H over Cu foil, a hydride is formed, appearing as a bluish-white film which gives reactions for $Cu^{\cdot\cdot}$ and is very unstable in air.

W. O. KERMACK.

Influence of substituents in the base and the anion on the co-ordination number of a metal. N. COSTACHESCU and A. ABLOV (Ann. Sci. Univ. Jassy, 1931, **16**, 515—525).—The following *compounds* are described: $[Cu(C_5H_5N)_4](NH_2SO_3)_2$;
$Cu(NH_3)_4{:}(SO_3)_2N{\cdot}NH_4,0{\cdot}5H_2O$;
$[Cu(NH_3)_4]_3[N(SO_3)_3]_2,3H_2O$;
$Cu[{\cdot}O{\cdot}N(SO_3)_2{:}Cu(NH_3)_4]_2,6H_2O$; and
$[Cu\ en_2](SO_3)_2N(OH),2H_2O$. H. F. GILLBE.

Reduction of silver chloride by sucrose and other reducing agents. E. V. ALEXEEVSKI and M. B. GOLDBERG (J. Gen. Chem. Russ., 1931, **1**, 475—481).—AgCl is converted in alkaline solution into Ag_2O, which is reduced to Ag by sucrose, which is itself oxidised to CO_2, lævulic and formic acids. A similar reaction takes place using cellulose solutions in place of sucrose, but the velocity of reaction is considerably smaller. A suspension of AgCl in H_2O is only very slowly reduced by Zn dust; if, however, H_2O is added to an equimol. mixture of AgCl and Zn, reaction takes place with explosive violence, with the production of a hard, porous conglomerate; this reaction does not take place if the mixture is added to H_2O. Mg, Al, and Fe do not react in the same way as Zn with AgCl, and Zn has no action on $Ag_4Fe(CN)_6$ or $Ag_3Fe(CN)_6$, whilst only a feeble reaction is observed with AgBr, AgI, and AgCNS.

R. TRUSZKOWSKI.

Compounds of bi- and ter-valent silver. G. A. Barbieri (Atti R. Accad. Lincei, 1931, [vi], 13, 882—887).—Cd pyridine persulphate (A., 1911, ii, 889) forms mixed crystals with Ag pyridine persulphate and di-*o*-phenanthroline Cd persulphate with the corresponding Ag compound (A., 1928, 1381). The oxide Ag_2O_3, with the ratio active O : Ag=1·5 : 1, is obtained by hydrolysing either Ag peroxido-nitrate, $AgNO_{11}$, or a HNO_3 solution of AgO.

T. H. Pope.

Ammines of complex thiocyanates. G. Spacu and G. Grecu (Bul. Soc. Stiinte Cluj, 1931, 5, 422—440; Chem. Zentr., 1931, i, 3342).—The following compounds have been prepared : $[Ag(SCN)_3][Cu\ en_2]$, $[Ag(SCN)_3][Ni\ en_2]$, $[Zn(SCN)_4][Cu\ en_2]$, $[Zn(SCN)_4][Zn\ en_2]$, $[Cd(SCN)_4][Cd\ en_2]$, $[Hg(SCN)_4][Cu\ en_2]$, $[Hg(SCN)_4][Ni\ en_2]$, $[Hg(SCN)_4][Zn\ en]$, $[Hg(SCN)_4][Zn\ en_2]$, $[Hg(SCN)_4][Hg\ en_2]$, $[Hg(SCN)_4]_3[CO\ en_3]_2$, $[Ni(SCN)_6][Ni\ en_3]_2$, $[Cr(SCN)_6][Cu\ en_2]_3$, $[Cr(SCN)_6]_2[Cd\ en_3]_3$. SCN has a greater tendency than I to form complexes. The stability of complexes diminishes in the order CN, F, SCN.

A. A. Eldridge.

Solid gold hydride. E. Pietsch and E. Josephy (Naturwiss., 1931, 19, 737).—By the passage of at. H over pure Au foil, a Au hydride is formed which appears as a whitish film on the surface of the foil. The hydride is stable only for a short time in the air or in H_2, and is decomposed at 100°. It gives reactions indicating the presence of Au ions.

W. O. Kermack.

Hydrothermal synthesis of calcium silicates with pressure. II. S. Nagai (J. Soc. Chem. Ind., Japan, 1931, 34, 317—319B).—At 153° and 5 kg. per sq. cm. combination is very slow, the product being a hydrate of $3CaO,2SiO_2$. At 181° and 10 kg. per sq. cm. the above compound is the first product, but longer heating or an excess of SiO_2 yields CaO,SiO_2. If SiO_2 is present in great excess CaO,SiO_2 is formed first, but heating at 211°/20 kg. per sq. cm. produces a hydrate of $3CaO,2SiO_2$, which, however, differs from that produced at lower temp. in its combined H_2O.

C. Irwin.

Preparation of pure magnesium by sublimation. J. Hérenguel and G. Chaudron (Compt. rend., 1931, 193, 771—773).—The apparatus is made of steel calorised on its inner surface, with water-cooled joints made staunch with rubber, and means for filling it with A. A vac. of 0·01 mm. is maintained. Mg then sublimes without melting at 600° at the rate of 1 kg. per hr. Si remains as $SiMg_2$; Cl, Na, and C appear in the upper part of the condenser as $MgCl_2$, Na and its carbide. The sublimed Mg contains 0·001% Cl, <0·001% Si, and <0·01% Fe; resublimed, only <0·001% Cl. It forms large dendrites, which must be melted in A.

C. A. Silberrad.

Alumino-oxalates. G. J. Burrows and K. H. Lauder (J. Amer. Chem. Soc., 1931, 53, 3600—3603). —*Aluminium trioxalic acid*, $H_3Al[(C_2O_4)_3],9EtOH$, is prepared by warming $Al(OEt)_3$ with $H_2C_2O_4$ in abs. EtOH. The Na_3 (+2EtOH), trianiline, *dl*-, *d*-, and *l*-strychnine, and *d*- and *l*-K_3 salts have been prepared and described (cf. A., 1927, 339). Fractional crystallisation of the *dl*-strychnine salt from a EtOH–$CHCl_3$ mixture affords the *l*-salt. The isomerides racemise rapidly. $H_3Al[(C_2O_4)_3],9EtOH$ kept over H_2SO_4 in vac. for many weeks affords $H[Al(C_2O_4)_2],4EtOH$ when recryst. from abs. EtOH. In this *acid* and the Na *salt* (+EtOH), Al has a co-ordination valency 4. $Na_2[Al(C_2O_4)_2OHOH_2],H_2O$ and the Ba salt (+H_2O) have been prepared.

J. G. A. Griffiths

Affinity. LIV. Constitution of compounds of aluminium halides with ammonia. I. W. Klemm and E. Tanke. **LV. II. Monoammines as molecular additive compounds.** W. Klemm, E. Clausen, and H. Jacobi (Z. anorg. Chem., 1931, 200, 343—366, 367—384; cf. Haraldsen and Biltz, this vol., 1128).—LIV. Tensimetric and thermal measurements have shown the existence of the following *compounds* in addition to those previously established : $AlCl_3$ with 1, 7, 14; $AlBr_3$ with 1, 3 (probably), 5, 7, 9, 14; AlI_3 with 1, 3 and 5 probably, 7, 9, 13 mols. NH_3. Densities, heats of formation, and m. p. of the lower members have been determined. The three monoammines have the same m. p. (125°±3°), and, unlike the parent salts, probably possess the same structure. The ammines of the Al halides and of the In halides are analogous. The properties of the Al ammine halides are compared with those of some closely related compounds.

LV. Electrical conductivities and mol. vols. of the monoammines have been determined. The chloride and bromide compounds are unimol. in the state of vapour. All the experimental evidence indicates that the character of the mol. is represented by the formula $[AlX_3,NH_3]$. A model is given.

F. L. Usher.

Structure of ultramarine. K. Leschewski and H. Möller (Naturwiss., 1931, 19, 771—772).—Molten HCO_2Na and blue ultramarine, when heated at 350—400°, give a colourless compound, which turns green when washed with H_2O. The green colour disappears with further washing, and the resulting white substance is a true ultramarine, which can be converted by dry heat into blue ultramarine. The white ultramarine is a reduction product of the blue variety. Blue ultramarine yields, on prolonged boiling with ethylene chloride, a rose-coloured ultramarine, which on dry heating is converted into blue with the emission of mercaptan-like odours. White ultramarine can be prepared by the decomp. of blue ultramarine by dry gaseous HCl in high-boiling alcohols (*e.g.*, glycol, glycerol). When heated, this substance turns olive-brown, assuming a grey colour on cooling. On sulphurisation this substance reverts to the original blue colour.

W. R. Angus.

Amphoteric nature of aluminium hydroxide. R. A. Robinson and H. T. S. Britton (J.C.S., 1931, 2817—2820).—The conductometric titration of 0·003125*M*-$Al_2(SO_4)_3$ with 0·2*N*-NaOH and the back-titration with 0·2*N*-HCl indicated the following reactions : $Al_2O_3,3SO_3 \longrightarrow Al_2O_3,2{\cdot}68SO_3$ (sol.)$\longrightarrow$ $Al_2O_3,0{\cdot}6SO_3$ (insol.)$\longrightarrow Al_2O_3,0{\cdot}12SO_3$ (max. insol.) $\longrightarrow NaAlO_2$. The equiv. conductivity of $NaAlO_2$ was approx. 60.

H. J. Emeléus.

Sulphides of rare-earth metals. Picon and Cogné (Compt. rend., 1931, 193, 595—597).—By the

method used in preparing Ce_2S_3 (cf. this vol., 582) pure Y_2S_3, La_2S_3, Nd_2S_3, and Sm_2S_3 have been obtained as vitreous masses, transparent in thin sections, coloured (in the above order) citron-yellow, yellowish-white, greenish-yellow, and rose-yellow; *d* 3·910, 4·997, 5·387, and 5·729; m. p. (vac.) 1900—1950°, 2100—2150°, 2200°, and 1900°. Volatilisation begins at 1900°, 1900°, 2100°, and 1800°. Although H_2, N_2, and CO are without action at fairly high temp , by heating in H_2 for 30 min. at 2700° the losses of Y_2S_3, La_2S_3, Ce_2S_3, Nd_2S_3, and Sm_2S_3 are respectively 35, 30, 28, 30, and 82%, the residues of Y_2S_3 and Sm_2S_3 being carburised and containing 3% S; of La_2S_3, Ce_2S_3, and Nd_2S_3 slightly carburised and containing 16, 12, and 12% S, respectively. Losses in N_2 at 2800° are recorded. Stability, save in the case of Sm, increases with at. wt. C. A. SILBERRAD.

Separation of rare earths by fractional crystallisation. S. FREED (J. Amer. Chem. Soc., 1931, **53**, 3906—3907).—Utilisation of the differences of ionic radii in the separation of rare earths should be possible with unsolvated ions and crystallisation at low temp. J. G. A. GRIFFITHS.

Praseodymium and thallous sulphates. F. ZAMBONINI and S. RESTAINO (Atti R. Accad. Lincei, 1931, [vi], **13**, 650—654).—The system $Pr_2(SO_4)_3$–Tl_2SO_4–H_2O has been studied at 25°. Four compounds are formed, viz., $Pr_2(SO_3)_4,5Tl_2SO_4$, $Pr_2(SO_4)_3,4{\cdot}5Tl_2SO_4$, $Pr_2(SO_4)_3,3Tl_2SO_4,H_2O$, and $Pr_2(SO_4)_3,Tl_2SO_4,4H_2O$. Slow evaporation at a temp. not higher than 12—13° of a solution containing the two sulphates in any proportions yields $Pr_2(SO_4)_3,Tl_2SO_4,8H_2O$. The crystallography of the octo- and tetra-hydrates is discussed. H. F. GILLBE.

Permutoid reactions of graphite. U. HOFMANN and A. FRENZEL (Z. Elektrochem., 1931, **37**, 613—618).—Graphite is transformed by H_2SO_4–HNO_3 mixtures into a bluish form, which slowly reverts to the initial form. *X*-Ray spectrograms indicate an increase in the distance between the planes of the C atoms. The swelling of graphitic acid in H_2O can be followed in the same way. By gently heating graphite acid in vac., oxides of C are lost and the residue consists of graphite. *X*-Ray spectrographic examination of this change indicates that graphitic acid is a surface compound in the Langmuir sense. E. S. HEDGES.

Pneumatolytic synthesis of silicates. II. C. J. VAN NIEUWENBURG and H. B. BLUMENDAL (Rec. trav. chim., 1931, **50**, 989—996; cf. this vol., 322).—SiO_2 volatilised in supercrit. steam reacts with CdO to give Cd_2SiO_4, with kaliophilite to give leucite and orthoclase, and with nephelite to give analcite and albite, this difference in the behaviour of the K and Na compounds being in accord with the results of many hydrothermal syntheses and with geological evidence. Preliminary experiments indicate that the presence of CO_2 in such reactions markedly inhibits the formation of silicates. TiO_2 and SnO_2 do not volatilise in supercrit. steam, but MoO_3 and WO_3 do so, and in this condition react with CaO to give $CaMoO_4$ and $CaWO_4$. Cu may also be so volatilised. N. H. HARTSHORNE.

Copper, cobalt, nickel, zinc, and cadmium tetrapyridine fluosilicates. W. T. L. TEN BROECK, jun. [with P. A. VAN DER MEULEN] (J. Amer. Chem. Soc., 1931, **53**, 3596—3600).—The addition of pyridine to aq. solutions of metallic fluosilicates affords the following complex *salts*: $Cu(C_5H_5N)_4SiF_4,H_2O$ and $X(C_5H_5N)_4SiF_6$, where X=Co, Ni, Zn, and Cd. The dissociation pressures when the Co salt loses 1 and 2 mols. of pyridine have been determined between 35° and 83°; at higher temp. SiF_4 is evolved. At sufficiently high temp. the other salts yield pyridine together with SiF_4. J. G. A. GRIFFITHS.

Cerium, lanthanum, praseodymium, and neodymium mercurides. P. T. DANILTSCHENKO (J. Gen. Chem. Russ., 1931, **1**, 467—474).—The alloy obtained by fusing together CeO_2, Mg, and Hg contains up to 5% Mg, which can be removed by repeated extraction with hot, very dil. HCl. The product, on distillation under reduced pressure in the absence of O_2, loses Hg, to yield a cryst. residue of $CeHg_4$, which above 470° is converted into $CeHg_3$. $LaHg_4$, $NdHg_4$, and $PrHg_4$ are prepared in the same way as $CeHg_4$, and possess similar properties. R. TRUSZKOWSKI.

Arsenic tri-iodide. W. H. MADSON and C. KRAUSKOPF (Rec. trav. chim., 1931, **50**, 1005—1010).—AsI_3 (99·81% pure), m. p. 138·6°, was prepared by a modification of Oddo and Giachery's method (A., 1923, ii, 316), the product being extracted with mustard oil and recryst. from CS_2. In air it decomposes very slowly below 100°, slowly at 137°, and rapidly at 200°, giving I, As_2O_3, and As. In N_2 it decomposes above 100°. Solutions in a large number of common org. solvents all showed decomp. which was accelerated by H_2O and O_2, but not by light. N. H. HARTSHORNE.

Form of separation of sulphur. H. TOMINAGA (J. Fac. Sci. Hokkaido, 1931, **1**, 181—183).—The reaction between NO and H_2S was investigated between 12° and 50°. The S produced was brown and transparent in the initial stages (labile liquid form) until the point of min. pressure was reached, when it became pale yellow and turbid (stable cryst. form). P. G. MARSHALL.

Thermal behaviour of sulphur compounds in hydrocarbon solvents. I. Aliphatic mercaptans. W. M. MALISOFF and E. M. MARKS.—See this vol., 1393.

Process of decomposing chromite. II. Compounds of chromic sulphate with sulphuric acid alone and with sulphates of bivalent metals. Y. KATO and R. IKENO (J. Soc. Chem. Ind., Japan, 1931, **34**, 311—312B; cf. B., 1930, 903).—If $Cr_2(SO_4)_3$ is boiled with H_2SO_4 there is formed at 250° $Cr_2(SO_4)_3,H_2SO_4$, and this salt is decomposed at 280°. Both the acid salt and the anhyd. sulphate are almost insol. in H_2O. A series of compounds or solid solutions, also almost insol., is formed by boiling $Cr_2(SO_4)_3$ and H_2SO_4 with sulphates of Cu, Zn, Co, Cd, Mg, $Fe^{\cdot\cdot}$, and $Mn^{\cdot\cdot}$. C. IRWIN.

Amminochromic carbonates. J. BANCELIN (Compt. rend., 1931, **193**, 597—598).—By the action of ammoniacal $(NH_4)_2CO_3$ on anhyd. $CrCl_2$ a yellow insol. ppt. is formed of $[Cr(NH_3)_2(H_2O)_4]_2(CO_3)_3$, stable

in presence of NH_3, but in air soon turning greyish-violet; if washed and dried in H_2 it can be preserved in a sealed tube. Cold dil. HCl affords a green solution yielding on evaporation green $[Cr(NH_3)_2(H_2O)_4]Cl_3$ (cf. A., 1902, ii, 210). The change to the greyish-violet compound, although rapid at first, takes long to complete. The formula $[Cr_3(NH_3)_2(H_2O)_9(OH)_3(CO_3)_2](OH)_2$ is proposed.

C. A. Silberrad.

Fourth degree of oxidation of molybdenum. W. F. Jakób and E. Turkiewicz (Rocz. Chem., 1931, **11**, 569—576).—In the prep. of $K_4Mo(OH)_4(CN)_4$ from KCN and $MoO(OH)_3$ Mo^V is converted into Mo^{IV} and Mo^{VI}, which alone combines with KCN. The reaction proceeds according to the equations:

$$(OH)_4Mo\cdot O\cdot MoO(OH)_2+2OH' \rightleftharpoons [(OH)_4Mo\cdot O\cdot MoO_3]''+2H_2O, \text{ and}$$

$$[(OH)_4Mo\cdot O\cdot MoO_3]'' \rightleftharpoons [(OH)_4Mo^{IV}{-}{-}{-}{-}O{:}Mo^{VI}O_3]'' \overset{+4CN'}{\rightleftharpoons} [Mo^{IV}(CN)_4(OH)_4]''''+MoO_4''.$$

$K_4[Mo(CN)_4(OH)_4]$ is converted into octocyanide on keeping in solution with excess of CN and H ions.

R. Truszkowski.

Tungsten oxytetrachloride. W. Reinders and J. A. M. van Liempt (Rec. trav. chim., 1931, **50**, 997—1003).—$WOCl_4$ is best prepared by passing Cl_2 over an equimol. mixture of W and WO_2, followed by distillation in vac., or in a stream of CO_2 at 200—210°. The product has m. p. 209°, b. p. 233°, heat of sublimation 18,284, heat of vaporisation 16,840 g.-cal. per mol.

N. H. Hartshorne.

Heteropolycyclic compounds. I. Sodium salts of phosphotungstic acid. II. Sodium phosphomolybdate. A. V. Rakovski and E. A. Nikitina (J. Gen. Chem. Russ., 1931, **1**, 240—246, 247—252).—I. The optimum method for the prep. of Na phosphotungstate is the condensation of Na_2HPO_4 and Na_2WO_4 by the action of HCl. Recrystallisation from alkaline solution gives $Na_3H_4[P(W_2O_7)_6],nH_2O$, or from acid solution $Na_2H_5[P(W_2O_7)_6],nH_2O$. Quinoline acetate is recommended as a precipitant of tungstic and phosphotungstic acids.

II. The action of H_3PO_4 on Na paramolybdate gives yellow compounds, but on evaporation only Na phosphate and molybdate are obtained. The action of MoO_3 on Na_2HPO_4 gives $Na_4H_8[P_2O_2(Mo_2O_7)_9],nH_2O$. A method is described for the prep. of the trisubstituted salt $Na_3H_7[P(Mo_2O_7)_2],nH_2O$, which also gives the disubstituted salts in strongly acid solutions. The salt decomposes readily.

E. B. Uvarov.

Ammines of uranium. R. Răscanu (Ann. Sci. Univ. Jassy, 1930, **16**, 32—56, 459—496).—The prep. and properties of the following compounds with pyridine, quinoline, 2-methylquinoline, antipyrine (*Ap*), pyramidon (*Pm*), and phenacetin (*Pn*) are described: $[UO_2,C_5H_5N](NO_3)_2$; $[UO_2,C_5H_5N,H_2O](NO_3)_2$; $[UO_2,C_9H_7N,H_2O](NO_3)_2$; $[UO_2,C_{10}H_9N,H_2O](NO_3)_2$; $[UO_2,Ap_2](NO_3)_2$; $[UO_2,Ap_2]Cl_2$; $[UO_2,Ap_2]Br_2$; $[UO_2,Ap_2]SO_4,4H_2O$; $[UO_2,Pm_2](NO_3)_2$; $[UO_2(C_5H_5N)_2]Cl_2$; $[UO_2,Pm_2](NO_3)_2$ (dark red and light red forms); $[UO_2,Pm_2]Cl_2$; $[UO_2,Pm_2,H_2O]Cl_2,H_2O$; $[UO_2,Pm,H_2O]Cl_2$; $[UO_2,Pm,H_2O]Cl_2,2H_2O$; $[UO_2,Pm]Cl_2$; $[UO_2,Ap_2](OAc)_2$; $[UO_2,Ap,H_2O]C_2O_4$; $[UO_2,Pn_2](NO_3)_2$; $[UO_2,Pn_2]Cl_2$; $[UO_2,Pn_2(H_2O)_2]Cl_2$; $[UO_2,Pn_2(H_2O)_3]Cl_2$; $[UO_2,Pn_2(H_2O)_2]Cl_2,2H_2O$; $[UO_2,Pn_3]Cl_2$; $[UO_2,Pn,2H_2O]C_2O_4$; $[UO_2,Pn_4]Br_2$; $[UO_2,Pn_4(H_2O)_7]Br_2$.

H. F. Gillbe.

Rhenium. III. Compounds of ter- and quadri-valent rhenium. F. Krauss and H. Steinfeld (Ber., 1931, **64**, [*B*], 2552—2556; cf. this vol., 53).—Treatment of a mixture of $KReO_4$ and KI with HCl (*d* 1·18) and immediate boiling until evolution of I ceases affords the *salt* $K_3[ReCl_6]$, decomposed by a large excess of H_2O at room temp. (corresponding Tl_3 *salt*). Under somewhat different conditions the *compound* $K_4Re_2Cl_{11}$ (?$K_2[ReCl_5]+K_2[ReCl_6]$) is produced (corresponding Tl_4 *salt*). $KReO_4$, KBr, and conc. HBr give the *compound* $K_2[ReBr_6]$, whilst the *salt* $Tl_2[ReBr_6]$ is obtained from $TlReO_4$ and HBr (*d* 1·75).

H. Wren.

Nitrosothio-salts of iron: nitrosodithiocarbamates. L. Cambi and A. Cagnasso [with A. Tanara] (Atti R. Accad. Lincei, 1931, [vi], **13**, 254—257; cf. this vol., 934).—The prep. of the *dithiocarbamates* $[Me_2N\cdot CS_2]_3Fe$ and $[C_5H_{10}N\cdot CS_2]_3Fe$ is described. They are very similar to the ferric xanthates, but are stable towards atm. O_2 and towards NO. The ferrous salts, however, react with NO and form the *nitrosodithiocarbamates* $[Me_2N\cdot CS_2]_2Fe\cdot NO$ and $[C_5H_{10}N\cdot CS_2]_2Fe\cdot NO$.

O. J. Walker.

Role of hydrogen in the dissolution of iron. H. Cassel and T. Erdey-Gruz (Z. physikal. Chem., 1931, **156**, 317—318).—An explanation alternative to that proposed by Liebreich (cf. this vol., 1016) is put forward.

F. L. Usher.

[Role of hydrogen in the dissolution of iron.] E. Liebreich (Z. physikal. Chem., 1931, **156**, 319—320).—A reply (see preceding abstract).

F. L. Usher.

Hexacyanocobaltic acid and ethyl alcohol. F. Holzl [with G. Schinko] (Monatsh., 1931, **58**, 249—267; cf. this vol., 944).—By passing gaseous HCl into a solution of $H_3[Co(CN)_6]$ in abs. EtOH, a cryst. ppt. of $H_3[Co(CN)_6],3EtOH$, or more probably the oxonium compound $[Co(CN)_6](EtOH\cdot H)_3$, is formed. This compound is also in stable equilibrium with a saturated solution of $H_3[Co(CN)_6]$ in abs. EtOH between 0° and 75°. Tensimetric measurements indicate that, under diminishing pressure, EtOH is removed in successive stages, with the formation of intermediate additive compounds until the free acid is left. The process is facilitated by rise in temp. On keeping the EtOH solution at higher temp. (78° and 98°) the acidity to phenolphthalein diminishes. In the absence of H_2O an amount of EtNC, equiv. to the change in acidity, is formed. The presence of H_2O results in side reactions with the formation of HCN. According to the conditions of temp. and H_2O content a number of different *compounds* may be formed: with abs. EtOH, $[(CN)_2(H_2O)_2Co{:}(CN)_2{:}Co(CN)_2(EtNC)(H_2O)]$ and

$[(CN)(H_2O)_2Co{:}(CN)_3{:}Co(CN)_2(EtNC)]$; with 96% EtOH $[(H_2O)_3(CN)_2Co\cdot(CN)\cdot\{Co(CN)_4\}\cdot(CN)\cdot Co(CN)_2(EtNC)]H$ and $(OH)_2[(H_2O)_2(CN)_2Co{:}(CN)_2\cdot\{Co(CN)_4\}{:}(CN)_2{:}Co(CN)_2(H_2O)(EtNC)]H$; with 90% EtOH, $[(H_2O)_3(CN)_2Co\cdot CN\cdot\{Co(CN)_4\}\cdot CN\cdot\{Co(CN)_4\}\cdot(CN)\cdot Co(CN)_2(H_2O)_3]H_3$; and with 80% EtOH, $[(CN)_2(H_2O)_2Co{:}(CN)_2{:}\{Co(CN)_2\}{:}(CN)_2{:}Co(CN)_2(H_2O)_2]$ and $[(CN)_3(H_2O)Co{:}(CN)_2{:}\{Co(CN)(H_2O)\}{:}(CN)_2{:}\{Co(CN)(H_2O)\}{:}(CN)_2{:}Co(CN)_2(H_2O)_2]H$. M. S. BURR.

Complex nickel salts. J. DALIETOS (Praktika, 1931, 3, 754—760; Chem. Zentr., 1931, i, 3445—3446).—The salts $[Ni\ en]SO_4,2H_2O$, $[Ni\ en]Cl_2$, $[Ni\ en]Br_2$, $[Ni\ en](NO_3)_2$, and $[Ni(C_5H_5N)]SO_4$ were prepared. A. A. ELDRIDGE.

Complex ruthenium compounds. R. CHARONNAT (Ann. Chim., 1931, [x], 16, 123—250; cf. this vol., 1256).—*K Ru^{III} oxalate*, $2K_3Ru(C_2O_4)_3,9H_2O$, and the corresponding NH_4 and Na *salts*, $(NH_4)_3Ru(C_2O_4)_3,3H_2O$ and $Na_3Ru(C_2O_4)_3,5H_2O$, have been prepared by interaction of the alkali oxalates with the corresponding chlororuthenates or $RuCl_4$. The mixed *compounds* $Na_{19}K_5[Ru(C_2O_4)_3]_8,32H_2O$, $(Ag,K)_3Ru(C_2O_4)_3,3H_2O$, and $BaKRu(C_2O_4)_3,3H_2O$ have been obtained similarly. The double *salts* $2K_3Ru(C_2O_4)_3,KCl,8H_2O$ and $2K_3Ir(C_2O_4)_3,Hg(CN)_2,8H_2O$ have been prepared. *Compounds* with strychnine, $KH_2Ru(C_2O_4)_3,2C_{21}H_{22}O_2N_2,4H_2O$ and $H_3Ru(C_2O_4)_3,3C_{21}H_{22}O_2N_2,12H_2O$, have been obtained. The *compound* $K_3RuCl_2(C_2O_4)_2,H_2O$ is an intermediate product in the formation of $K_3Ru(C_2O_4)_3$. On oxidation in aq. solution the latter compound passes into $K_2Ru(C_2O_4)_3$; from which the strychnine *compound* $H_2Ru(C_2O_4)_3,2C_{21}H_{22}O_2N_2,8H_2O$ may be obtained, and forms with pyridine the *compounds* $K(C_5H_5N)_2Ru(C_2O_4)_2,6H_2O$ and $K(C_5H_5N)_2Ru(C_2O_4)_2,2H_2O$. *K Ru^{IV} nitrosochlorodioxalate*, $K_2Ru(NO)Cl(C_2O_4)_2,H_2O$, is formed by the action of $K_2C_2O_4$ on $K_2Ru(NO)Cl_5$, whereas with $K_2Ru(NO)I_5$ a similar I *compound*, $K_2Ru(NO)I_3(C_2O_4),H_2O$, results. The following monopyridinenitrosodioxalate *derivatives* of Ru^{IV} have been obtained: $2KRu(NO)(C_5H_5N)(C_2O_4)_2,9H_2O$, $AgRu(NO)(C_5H_5N)(C_2O_4)_2$, and $Ba[Ru(NO)(C_5H_5N)(C_2O_4)_2]_2$. The corresponding *compounds* with *l*-quinine, *d*-quinidine, NH_4, and C_5H_5N, $HRu(NO)(C_5H_5N)(C_2O_4)_2,C_{20}H_{24}O_2N_2,H_2O$, $HRu(NO)(C_5H_5N)(C_2O_4)_2,C_{20}H_{24}O_2N_2,H_2O$, $NH_4Ru(NO)(C_5H_5N)(C_2O_4)_2,H_2O$, and $HRu(NO)(C_5H_5N)(C_2O_4)_2,C_5H_5N$, respectively, each have been isolated in two forms, corresponding with the *d*- and *l*-forms of the $Ru(NO)(C_5H_5N)(C_2O_4)_2$ ion, the mol. rotation of which is about 2400°. By the action of HCl on $KRu(NO)(C_5H_5N)(C_2O_4)_2$ there is formed *K Ru^{IV} nitrosopyridine tetrachloride*, $KRu(NO)(C_5H_5N)Cl_4$. Interaction of pyridine with $K_2Ru(NO)Cl(C_2O_4)_2$ gives *dipyridine Ru^{IV} nitrosochloro-oxalate*, $(C_5H_5N)_2Ru(NO)Cl(C_2O_4)$, which yields *dipyridine Ru^{IV} nitrosotrichloride*, $(C_5H_5N)_2Ru(NO)Cl_3,3H_2O$, on addition of HCl, and by hydrolysis of this compound *dipyridine Ru^{IV} nitrosohydroxydichloride*, $(C_5H_5N)_2Ru(NO)(OH)Cl_2$, results. By interaction of $K_2Ru(NO)Cl_5$ with $C_2H_4(NH_2)_2$ and NaI there is formed the *compound* $Ru(NO)I_3,en$, then the *compound* $[Ru(NO)(OH)\ en_2]I_2$. The *compounds* $[Ru(NO)(OH)\ en\ (NH_3)_2]I_2$ and $[Ru(NO)(OH)\ en\ (C_5H_5N)_2I_2$ are obtained from $Ru(NO)I_3,en$. By the action of HCl, HBr, and HI on $[Ru(NO)(OH)\ en_2]I_2$ the *compounds* $[Ru(NO)(Cl,H_2O)\ en_2]I_2$, $[Ru(NO)Br\ en_2]I_2$, and $[Ru(NO)I\ en_2]I_2$, respectively, are obtained. The *compounds* $[Ru(NO)Br\ en_2]Br_2$, $[Ru(NO)I\ en_2]Br_2$, and $[Ru(NO)(Cl,H_2O)\ en_2]Cl_2$ have also been prepared. The *compound* $[Ru(NO)I\ en_2]I_2$ exists in two isomeric forms. It appears probable that in some of the above compounds the co-ordination no. of Ru is 8. R. CUTHILL.

Promoters of crystallisation in microchemistry. F. AMELINK (Pharm. Weekblad, 1931, 68, 1086—1088).—A review of methods suitable for micro-reactions. Various examples are given of the method in which a trace of the anticipated ppt. is added to one of the reactants. H. F. GILLBE.

Heyrovsky's electroanalytical polarographic methods and their applications in theoretical and practical chemistry. W. KEMULA (Z. Elektrochem., 1931, 37, 779—795).—A full account of the theory and practice of the method, with an extensive bibliography. H. F. GILLBE.

Tetramethyldiaminodiphenylmethane [as analytical reagent]. J. B. FICKLEN (Chem. and Ind., 1931, 869).—It is suggested that $CH_2(CH_4\cdot NMe_2)_2$ could be used to detect small quantities of many elements which have at least two relatively stable valency forms and have a higher oxide or hydroxide which are insol. in the oxidising solution. In using the reagent (cf. Harry, this vol., 1385) it is necessary to eliminate or correct for other reacting materials. E. S. HEDGES.

Indicators. XVIII. "Hydrogen effect" and salt error of indicators. A. THIEL and G. COCH (Z. anorg. Chem., 1931, 200, 419—428; cf. A., 1929, 1410).—Potentiometric determination of the p_H of phosphate buffer solutions in presence of NaCl or KCl, and colorimetric examination of the same solutions when containing various indicators, point to the non-existence of a "H effect" as defined by Wolf (A., 1930, 1391). The effect observed in weakly buffered solutions is due to contamination with traces of CO_2. The potentiometric method is free from objection when proper precautions are observed. F. L. USHER.

Continuous measurement of p_H with quinhydrone electrodes. C. C. COONS (Ind. Eng. Chem. [Anal.], 1931, 3, 402—407).—The concentration of quinhydrone necessary for measurements with an accuracy of $\pm 0{\cdot}05\ p_H$ is 7 mg. per 100 c.c. of solution. A method for determining the concentration of quinhydrone dissolved in H_2O is outlined and the solubility curve for quinhydrone is given from 0° to 50°. The practicability of various methods of adding quinhydrone to a flowing solution for the purpose of obtaining continuous p_H measurements is discussed, and the continuous addition of a solution of quinhydrone from an external source is considered to be best. Pt electrodes are better than Au electrodes

for continuous p_H measurement; they should be cleaned by washing in boiling 5—10% $NaHSO_3$ solution. E. S. HEDGES.

Modified absorption tube for determination of hydrogen in organic substances by the micro-analytical method of Pregl. W. J. BOYD and W. ROBSON (J.S.C.I., 1931, **50**, 400—402T).—The adoption of P_2O_5 as absorbent for H_2O in the Pregl process permits the use of an absorption tube which weighs 1·5 g. or $\frac{1}{4}$ the weight of the Pregl tube, and has an internal vol. $<0·5$ c.c. The modified tube has advantages over the Pregl tube in that it may be weighed much sooner after being polished, the weighing is more accurate, sweeping-out of O_2 and CO_2 is less likely to be incomplete, and transference to and from the balance-pan is much easier. The permanent rate of increase in wt. due to diffusion of moist air into the tube is only half that of the Pregl tube when the latter is charged with P_2O_5 on glass-wool. 12 tubes can be made and filled in 1 hr., the ends being kept sealed until the tube is required. A tube is used for three determinations and then discarded. W. J. BOYD.

Volumetric determination of hydrogen peroxide in presence of potassium persulphate. V. M. NAYAK (J. Indian Chem. Soc., 1931, **8**, 535—536).—Titrations of H_2O_2 with $KMnO_4$ are inaccurate if $K_2S_2O_8$ is present. The error may be corrected by determining in one sample the total available O by $FeSO_4$ and $KMnO_4$, and in another the $KMnO_4$ titre; residual $K_2S_2O_8$ in the second sample is then determined by $FeSO_4$ and $KMnO_4$. H. F. GILLBE.

Electrometric analysis of solutions of hypochlorites. M. ABRIBAT.—See B., 1931, 1047.

Determination of iodine in iodised common salt. A. GRONOVER and E. WOHNLICH.—See B., 1931, 1048.

Determination of fluorine in insecticides. C. M. SMITH, E. H. HAMILTON, and J. J. T. GRAHAM.—See B., 1931, 1048.

Determination of fluorine as calcium fluoride. E. CARRIÈRE and JANSSENS (Compt. rend., 1931, **193**, 490—491; cf. this vol., 1023).—The amount of $CaCO_3$ formed by exposure to the air, or the presence of $(NH_4)_2CO_3$ in the aq. NH_3 used, in precipitating $CaCl_2$ with aq. NH_3 in the ordinary course does not exceed the experimental error, *e.g.*, 2 mg. in dealing with 10 c.c. of 0·5*M*-$CaCl_2$. To wash gelatinous CaF_2 thoroughly the ppt. must be boiled with H_2O 15 times. C. A. SILBERRAD.

Effect of certain forms of silica on determination of fluorine by volatilisation method. D. S. REYNOLDS and K. D. JACOB (Ind. Eng. Chem. [Anal.], 1931, **3**, 371—373).—SiO_2 gel, which has not been ignited above 1000°, and silicates which are decomposable by H_2SO_4 affect adversely the determination of F by the volatilisation method. A non-volatile compound, probably $SiOF_2$, is formed. SiO_2 gel which has been ignited at or above 1100° is as effective as quartz. The volatilisation method does not give trustworthy results for F in slags and certain natural phosphates containing acid-decomposable silicates. E. S. HEDGES.

Volumetric determination of soluble sulphates. N. A. TANANAEV (J. Chem. Ind. Russ., 1931, **8**, 939—949).—Excess of *N*-$Pb(NO_3)_2$ is added to the solution, the vol. is made up to 100 c.c., the solution is filtered after 5 min., and excess of Pb is determined in an aliquot part of the filtrate by titration with 0·5*N*-Na_2CO_3 in the presence of phenolphthalein. R. TRUSZKOWSKI.

Volumetric barium chromate method for [determination of] sulphates. T. R. ANDREWS (Ind. Eng. Chem. [Anal.], 1931, **3**, 361—362).—The addition of $BaCrO_4$ to a sulphate solution, followed by titration of the liberated CrO_4'' with $FeSO_4$ and $KMnO_4$, is satisfactory for determining 2—200 mg. of SO_4''. Smaller quantities (0·5—2·0 mg.) may be determined by adding 2 mg. of Na_2SO_4 to the sample and deducting this from the amount recovered. H_2S and other reducing substances in the sample are oxidised by $KMnO_4$ before adding the $BaCrO_4$. E. S. HEDGES.

Rapid determination of [ammonia and chlorine in] ammonium chlorostannate. J. HAEGE (Chem.-Ztg., 1931, **55**, 791).—The solution is treated with 2% $Ba(OH)_2$ solution until neutral (phenolphthalein), whereby $Sn(OH)_4$ is precipitated, the Ba in solution is then removed by addition of an excess of neutral, Cl′-free Na_2SO_4, and a portion of the filtrate is titrated with $AgNO_3$ (K_2CrO_4) for Cl′. A second portion is treated with 40% CH_2O solution and titrated with 0·1*N*-NaOH (phenolphthalein) to obtain the $NH_4^{\cdot}$ content. Sn is determined by reduction to $SnCl_2$ and titration with I. A. R. POWELL.

Precipitation of mercury in the Kjeldahl method. C. F. DAVIES and M. WISE (Cereal Chem., 1931, **8**, 349—360).—In the precipitation of Hg in the Kjeldahl–Gunning procedure by means of alkali sulphides, a black ppt. indicates the use of sufficient precipitant. When $Na_2S_2O_3$ is employed, a brownish-black ppt. should be obtained, and excess of the reagent is not detrimental. E. B. HUGHES.

Selenium as catalyst in determination of nitrogen by Kjeldahl method. M. F. LAURO (Ind. Eng. Chem. [Anal.], 1931, **3**, 401—402).—Hg and $CuSO_4$ used as catalysts in the Kjeldahl process may with advantage be replaced by Se. E. S. HEDGES.

Determination of nitrate in water. W. MULDER.—See B., 1931, 1076.

Colorimetric determination of phosphorus. L. URBANEK (Mezog. Kutat., 1931, **4**, 39—57; Chem. Zentr., 1931, i, 2643—2644).—The intensity of the blue colour obtained on reduction of phosphomolybdic acid is not exactly proportional to the P content of the solution, but a correction can be applied. The effect of [H˙], acids, salts, and nature of reducing substance was studied. A. E ELDRIDGE.

Determination of carbon dioxide in air. K. SARLÓ (Chem. Fabr., 1931, 397—398).—In the new apparatus described, a known vol. of air is drawn rapidly through aq. $Ca(OH)_2$ by an aspirator (2·2

litres in 12—13 min.). The solution is titrated with HCl and phenolphthalein. The apparatus is simple and may readily be constructed in portable form.

H. F. GILLBE.

Determination of carbon dioxide in the atmosphere. F. P. LEUSDEN (Z. Hyg., 1931, **112**, 606—612).—The sample is shaken in apparatus described with aq. $Ba(OH)_2$, which is subsequently titrated with HCl using thymolphthalein. The limit of error is 2%.

A. G. POLLARD.

Semi-microchemical determination of alkali metals in natural waters (bore waters) and silicates. K. L. MALAROV (Neft. Choz., 1930, 223—225).—The halides and org. substances are removed by evaporating 2—10 c.c. of the H_2O with 0·5—2 c.c. H_2SO_4; if SiO_2 is present the H_2O is first evaporated with HF. The residue, which is not heated above 350°, is treated with $Ba(OH)_2$; the alkaline earths are precipitated from the filtrate with $(NH_4)_2CO_3$ and aq. NH_3 in the cold, NH_4 salts are removed, and the residue is titrated with HCl (Me-orange). For silicates the material ($\equiv$0·03—0·04 g. Na_2O) is decomposed in Pt with HF and H_2SO_4, and the residue treated as above. CHEMICAL ABSTRACTS.

Determination of traces of sodium in potassium salts. M. FŒRSTER.—See B., 1931, 1009.

Determination of silver in gold bars. F. MICHEL.—See B., 1931, 1056.

Gravimetric determination of calcium and magnesium using high temperatures, and the decomposition curves of carbonates and nitrates in an atmosphere of carbon dioxide. T. SOMIYA and S. HIRANO (J. Soc. Chem. Ind., Japan, 1931, **34**, 381—383B).—The following decomp. temp. in a current of CO_2 have been determined: (1) $CaCO_3$ (915—925°)$\longrightarrow$CaO; $MgCO_3,(NH_4)_2CO_3,4H_2O$ (below 200°) $\longrightarrow MgCO_3$ (240—850°)$\longrightarrow$MgO; Ca and Mg may therefore be determined simultaneously by weighing at 240°, 850°, and 925°. (2) $Ca(NO_3)_2$ (450—560°)$\longrightarrow$ $CaCO_3$ (915—925°)$\longrightarrow$CaO; $Mg(NO_3)_2,H_2O$ (210—430°)$\longrightarrow$MgO; Ca and Mg may be determined by weighing at 210°, 430°, 550°, and 925°. (3) $CaC_2O_4,4H_2O$ (50°)$\longrightarrow CaC_2O_4,H_2O$ (150°)$\longrightarrow$ CaC_2O_4 (440°)$\longrightarrow CaCO_3$ (920°)$\longrightarrow$CaO.

E. S. HEDGES.

Influence of potassium, ammonium, and hydrogen ions on Galeotti's reaction. B. KAMIEŃSKI and K. KARCZEWSKI (Rocz. Chem., 1931, **11**, 577—599).—Two breaks are observed on the potentiometric titration curve in the reaction between $ZnSO_4$ and $H_2Fe(CN)_6$ in presence of $K_2SO_4,(NH_4)_2SO_4$, or H_2SO_4; these are due, respectively, to the formation of $Zn_2Fe(CN)_6$ and $Zn_3X_2[Fe(CN)_6]_2$. As [K$^·$], [NH$_4^·$], or [H$^·$] increases, the second break becomes more, and the first break less, distinct. K$^·$, NH$_4^·$, and H$^·$ may be present in variable amount in the ppt., as a result of which the reaction is not universally applicable to the determination of K; in the determination of Zn in foundry practice by means of this method it is advantageous to ppt. Zn as $Zn_3(NH_4)_2[Fe(CN)_6]_2$, keeping the concentration of NH$_4^·$ below 0·4N.

R. TRUSZKOWSKI.

Quantitative optical spectral analysis of lead alloys. A. GUENTHER (Z. anorg. Chem., 1931, **200**, 409—418).—The systems examined were Li, Cu, Zn, Au, Tl, and Bi in Pb, and Ag in Sn. Tables are given showing pairs of lines in the emission spectra of the alloys suitable for the characterisation of alloys containing up to 10% of the other metal.

F. L. USHER.

Analysis of basic lead acetate solutions. N. SCHOORL (Chem. Weekblad, 1931, **28**, 586—589).—The refractive index and density may be employed to determine the composition of normal and basic Pb acetate solutions. The percentage of PbO in the solution is given by $K(d-1)/d$, where K is 101 for $3PbO,2Ac_2O$, 103 for $2PbO,2Ac_2O$, and 105 for $3PbO,Ac_2O$. If the composition of the solution is unknown it may be determined from the equations $(d-1)10^4 = 87x + 40y$ and $(n_D^{20} - 1{\cdot}3330)10^5 = 80x + 160y$, where x and y are the percentages of PbO and Ac_2O, respectively, in the solution. The composition may be found also by the use of suitable indicators, since a solution of $3PbO,Ac_2O$ has p_H 7·4, one of $2PbO,Ac_2O$ p_H 7·8, and one of $3PbO,Ac_2O$ p_H 9; these vals. are almost independent of the concentration. H. F. GILLBE.

Rapid determination of small quantities of lead in calcium phosphate. J. R. NICHOLLS.—See B., 1931, 1009.

Volumetric and gravimetric determination of mercury as periodate. H. W. WILLARD and J. J. THOMPSON (Ind. Eng. Chem. [Anal.], 1931, **3**, 398—399).—Hg may be precipitated quantitatively as $Hg_5(IO_6)_2$ from 0·15N-HNO_3 or 0·1N-H_2SO_4. It may be weighed in this form or determined volumetrically with KI and $Na_2S_2O_3$. Moderate amounts of Al, Cd, Zn, Cu, Ni, Ca, and Mg do not interfere.

E. S. HEDGES.

Colorimetric determination of manganese. R. G. HARRY (Chem. and Ind., 1931, 796).—The blue coloration produced by adding $CH_2(C_6H_4{\cdot}NMe_2)_2$ to a solution containing $Mn(OH)_2$ in AcOH provides a satisfactory method for determining Mn. The colour standard is reasonably stable, but slowly fades. It may be replaced by a set of colour standards, which keep for a long time and match the colours produced (ranging from pale blue to purple), prepared by mixing solutions of crystal-violet and methylene-blue.

E. S. HEDGES.

Volumetric determination of manganese after oxidation by periodate. H. W. WILLARD and J. J. THOMPSON (Ind. Eng. Chem. [Anal.], 1931, **3**, 399—401).—Mn is oxidised to $NaMnO_4$ by means of $NaIO_4$ in H_3PO_4 or H_2SO_4 solution, the excess of $NaIO_4$ is removed by precipitation as $Hg_5(IO_6)_2$, and the $NaMnO_4$ is determined by titration with standard $FeSO_4$. Co, Ce, and Cl′ must be absent and the amount of Cr must be <1 mg. Directions are given for the application of the method to the determination of Mn in Fe or steel, Fe ore, and bronze.

E. S. HEDGES.

Determination of manganese in cobalt steels. F. SPINDECK.—See B., 1931, 1054.

Reversible oxidation indicator of high potential especially adapted to oxidimetric titrations. G. H. WALDEN, jun., L. P. HAMMETT, and R. P. CHAPMAN (J. Amer. Chem. Soc., 1931, **53**, 3908; cf.

A., 1899, i, 387).—The intensely red $Fe^{\cdot\cdot}$ *o*-phenanthroline complex ion is oxidised reversibly by $Ce(SO_4)_2$, or $K_2Cr_2O_7$ in H_2SO_4 or HCl, to the less intensely blue $Fe^{\cdot\cdot\cdot}$ complex ion. The mol. potential of the indicator system is 1·14 volts. The indicator is stable in acid solution and a quantity equiv. to 0·01 c.c. of 0·1*N* solution is satisfactory in the titration of $Ce^{\cdot\cdot\cdot\cdot}$ or Cr_2O_7'' with $Fe^{\cdot\cdot}$. Common metallic ions, including $Hg^{\cdot\cdot}$, do not interfere. The $Fe^{\cdot\cdot}$ dipyridyl complex is a less satisfactory indicator owing to rapid reaction with acids.

J. G. A. GRIFFITHS.

Electrolytic determination of cobalt. D. H. BROPHY (Ind. Eng. Chem. [Anal.], 1931, 3, 363—365).—The solution recommended contains 50 c.c. of aq. NH_3, 5 g. of NH_4Cl, and 0·3—0·4 g. of $NaHSO_3$ in 80—100 c.c. With a rotating anode (800—1000 r.p.m.) and a gauze cathode, using a current density of 4—7 amp. per sq. dm., it is possible in 30 min. to deposit 15—160 mg. of Co in a bright, adherent form. The amount of S in the deposit is negligible. The use of org. acids, N_2H_4,H_2SO_4(or HCl), or NH_2OH,HCl in place of $NaHSO_3$ is unsatisfactory.

E. S. HEDGES.

Ultra-violet absorption of mixtures of chromate and dichromate solutions. N. R. TAWDE (J. Indian Chem. Soc., 1931, 8, 499—501).—Ultra-violet spectrophotometric determinations (A., 1930, 992) of CrO_4'' and Cr_2O_7'' in dil. solution agree fairly satisfactorily with the analytical vals.

H. F. GILLBE.

Determination of titanium as phosphate. J. C. GHOSH (J. Indian Chem. Soc., 1931, 8, 695—698).—0·5—1·0 g. of the dried and powdered Ti ore is fused with Na_2CO_3 or treated with HF and H_2SO_4 and the resulting Na_2TiO_3 is treated with boiling H_2O, filtered, and washed, and an insol. acid titanate, $2Na_2O,9TiO_2,5H_2O$, formed. This is dissolved in 30 c.c of boiling dil. H_2SO_4 (1 : 5) and the solution diluted to 200 c.c., cooled, nearly neutralised with aq. NH_3, and treated with 20 c.c. of 20% aq. $(NH_4)_2HPO_4$. Any ppt. formed on further dilution to about 400 c.c. is redissolved in a slight excess of H_2SO_4, 10 g. of $Na_2S_2O_3$ and 10 c.c. of AcOH are added to reduce the Fe, and the solution is boiled for about ½ hr. The ppt. of TiO_2,HPO_3 is filtered, washed with H_2O, ignited, and weighed as a pyrophosphate, $2TiO_2,P_2O_5$. HCl may be used in place of H_2SO_4, but long boiling with HCl may ppt. metatitanic acid. The results compare favourably with those obtained by the oxide method, and the phosphate method should be used when P_2O_5 is already present.

M. S. BURR.

Determination of vanadium in high-speed steel. E. FARBER.—See B., 1931, 1054.

Reaction of vanadates. Determination of tungsten with tetramethyldiaminodiphenylmethane. M. PAPAFIL and R. CERNATESCO (Ann. Soc. Univ. Jassy, 1931, 16, 526—528).—Addition of a solution of $CH_2(C_6H_4{\cdot}NMe_2)_2$ in AcOH, of p_H 3·5, to a neutral solution containing vanadate yields an immediate yellow ppt. which gradually turns green; the *compound* formed is $(VO_3)_4C_{17}H_{22}N_2$. The limiting concentration of vanadate is about 0·05 g. per litre. For determination of W with this reagent any excess of NH_4 salts should be removed; the ppt. is dried at 110° and ignited to oxide.

H. F. GILLBE.

Determination of a small amount of antimony in presence of a large amount of copper. S. MAKISHIMA (J. Soc. Chem. Ind., Japan, 1931, 34, 322—323B).—A quantity of solution containing a few mg. of Sb is neutralised, 5 c.c. of 5% $MnSO_4$ solution are added, the mixture is boiled, and *N*-$KMnO_4$ solution added. The ppt. of MnO_2 collects the Sb by adsorption. It is washed, dissolved in dil. H_2SO_4 containing a little H_2O_2, Na_2SO_3 is added, and the SO_2 boiled off. The solution is brought to 0·02—0·1*N* acidity, and the coloration developed on addition of Folin's reagent (Na_2MoO_4+Na_2HPO_4) is compared with that given by a known Sb solution.

C. IRWIN.

Indirect determination of bismuth. C. V. BORDEIANU (Ann. Sci. Univ. Jassy, 1931, 16, 546—550).—Chlorides are removed by precipitation with $AgNO_3$, the Bi is precipitated by $(NH_4)_2HPO_4$, and the excess of phosphate is determined colorimetrically.

H. F. GILLBE.

Adiabatic calorimetry. S. W. PARR and W. D. STALEY (Ind. Eng. Chem. [Anal], 1931, 3, 396—397).—Tests of the efficiency of a vac. jacket for heat-insulation are recorded.

E. S. HEDGES.

Application of electric thermometers with crossed resistances to ebullioscopic and tonometric measurements. T. BYLEWSKI (Rocz. Chem., 1931, 11, 552—568).—A modification of Jaeger and Steinwehr's resistance thermometer, giving an accuracy of 0·001° over the range 0—250°, is described. A resistance box and commutator for use with the above thermometer are also described.

R. TRUSZKOWSKI.

Photo-electric cell thermoregulator. F. G. BRICKWEDDE and R. B. SCOTT (Physical Rev., 1930, [ii], 35, 670).—A photo-electric regulator which automatically maintains temp. const. to 0·001° between 0° and the temp. of liquid air has been constructed.

L. S. THEOBALD.

Low-temperature thermostat. H. W. FOOTE and G. AKERLOF (Ind. Eng. Chem. [Anal.], 1931, 3, 389—390).—By means of a small electrical refrigerating unit and a Hg–PhMe regulator the temp. of the bath can be maintained within ±0·015° at any desired val. between 0° and min. room temp.

E. S. HEDGES.

Thermostats. V. Measurements of stirrer performance. S. KAMBARA, S. OYAMADA, and M. MATSUI (J. Soc. Chem. Ind., Japan, 1931, 34, 361—367B).—A photo-electric colorimetric procedure for measuring stirring efficiency is described. An examination of 13 types of stirrers has shown that the propeller type, used with a proper vessel, is the most effective.

E. S. HEDGES.

Balanced thermo-couple and filter method of ultra-violet radiometry, with practical applications. W. W. COBLENTZ, R. STAIR, and J. M. HOGUE (Bur. Stand. J. Res., 1931, 7, 723—749).—One receiver of a thermocouple is covered with a filter excluding ultra-violet light, and the other with

a window transparent to ultra-violet light, which exactly balances the transmission losses of the exclusion filter throughout the remaining part of the spectrum. On exposing both receivers simultaneously to radiation the deflexion of the galvanometer gives a measure of the ultra-violet light intensity. Applications of the method are discussed.

E. S. HEDGES.

Multiple spark stand for quantitative spectrum analysis. L. J. SPENCER (J. Sci. Instr., 1931, **8**, 229—232).—The intensities of the lines produced by the "unknown" sample are compared with those of a series of standard samples. The latter are mounted on a disc which can be rotated so that each sample in turn is connected in series with the one under test. C. W. GIBBY.

Direct-reading two-crystal spectrometer for *X*-rays. F. K. RICHTMYER, S. W. BARNES, and E. RAMBERG (Physical Rev., 1930, [ii], **35**, 1428).—Abs. measurements of wave-lengths can be obtained with high precision. L. S. THEOBALD.

Instrument for high-voltage *X*-ray spectrography and radiography. F. SILLERS, jun. (Physical Rev., 1930, [ii], **35**, 1428).—*X*-Ray spectrograms of coarse-grained, polycryst. material, *e.g.*, high-Si sheet steel 0·02 in. thick, can be obtained in less than 1 hr. by direct transmission using a voltage of 200 kv.

L. S. THEOBALD.

Self-recording spectrometer. H. M. RANDALL and J. STRONG (Rev. Sci. Instr., 1931, [ii], **2**, 585—599).—An instrument for emission and absorption spectra over the entire prism or grating spectral region, and capable of enclosure in an evacuated chamber, is described. Absorption band curves are given for NH_3 and MeI at various pressures.

N. M. BLIGH.

Twenty-one foot vacuum spectrograph for the extreme ultra-violet. G. R. HARRISON (Rev. Sci. Instr., 1931, [ii], **2**, 600—610).—The spectrograph body and camera box can be evacuated separately. 1 hr. exposures give spectrograms of 2·7 Å. dispersion per mm., the 2000—1000 Å. range being recorded on a 16-in. plate. High resolving power has been obtained in hot spark spectra of the elements of the first long period. The design is primarily for intensity measurements in the Schumann region.

N. M. BLIGH.

***X*-Ray powder diffraction apparatus.** T. M. HAHN (Rev. Sci. Instr., 1931, [ii], **2**, 626—631).—The time required to produce a readable diffraction pattern is minimised by utilising a larger vol. of the sample, and the formation of weaker spots nearer the sample. N. M. BLIGH.

Simple improved method for reducing Fabry–Perot observations. S. TOLANSKY (J. Sci. Instr., 1931, **8**, 223—225).—An accuracy of 0·001 of a wave no. can be obtained using 4- or 5-figure log. tables.

C. W. GIBBY.

Photomicrographs with [light of] wave-length 312 mμ. A. P. H. TRIVELLI and E. LINCKE (Z. wiss. Phot., 1931, **30**, 85—87).—Photomicrographs are given of sections of calf skin and of a leaf of *Nerium oleander*, taken at 312 and 546 mμ.

J. LEWKOWITSCH.

Ultra-violet microscopy. B. K. JOHNSON (J. Roy. Micros. Soc., 1931, [iii], **51**, 268—271).—Photographs illustrating the improved results obtainable with ultra-violet light are reproduced.

C. W. GIBBY.

Photographic method of examining crystals. A. SCHUBNIKOV (Z. Krist., 1931, **78**, 111—135).

Photo-electric determination of the turbidity of liquids. P. JAKUSCHOFF (Z. Ver. Deut. Ing., 1931, **75**, 426—428; Chem. Zentr., 1931, i, 3147).—A K cell, with Ag anodes, in H_2 (4 mm.) is employed. The turbidity, concentration, or colour of liquids is easily and rapidly determined. A. A. ELDRIDGE.

Mixed-colour colorimeter. A. THIEL (Sitzungsber. Ges. Nat. Marburg, 1930, **65**, 159—167; Chem. Zentr., 1931, i, 3147).—The advantages of the method, which depends on the achievement of equality of tint and not of intensity of colour, are discussed. It is specially suitable for p_H determinations.

A. A. ELDRIDGE.

Measurement of the brightness of radioactive luminous compounds. H. F. MEACOCK and G. E. V. LAMBERT (J. Sci. Instr., 1931, **8**, 214—220).—Two instruments are described, for use respectively with surfaces of diameter larger or smaller than 6 mm. The reproducibility is 2% with the former and 10% with the latter. C. W. GIBBY.

Applications of thermionic valves in the technique of physico-chemical measurements. W. HILTNER (Chem. Fabr., 1931, 389—392, 398—400).—The theory of the thermionic valve is given, together with details, including circuit diagrams, of the operation of such valves for the production of oscillatory currents for dielectric const. determinations with electrolytic conductors and of a.c. for measurement of the conductivity of electrolytes, as relays for the control of thermostats and for the measurement of small pressures, as rectifiers and amplifiers of a.c., as amplifiers for, *e.g.*, ionisation currents, as potentiometers for p_H measurements and potentiometric titrations, and as null instruments for e.m.f. measurements by a compensation method.

H. F. GILLBE.

Capillary glass electrode. W. J. YOUDEN and I. D. DOBROSCKY (Contr. Boyce Thompson Inst., 1931, **3**, 347—362).—The construction and use of thin-walled glass electrodes are described.

A. G. POLLARD.

Development of Kohlrausch's conductivity apparatus with the aid of electron-tubes. E. GOTTE and W. SCHRAMEK (Z. Elektrochem., 1931, **37**, 820—823).—An improved apparatus is described.

E. S. HEDGES.

Galvanometer for measurement of conductivity of solutions. G. GOLLNOW (Chem.-Ztg., 1931, **55**, 827—828).—The instrument resembles the D'Arsonval galvanometer, but the moving coil has no core and the field magnet is of laminated Fe provided with a field coil which is energised (at 110 volts) from a transformer connected to the mains. The e.m.f. for the bridge circuit is obtained by shunt connexion across an adjustable resistance placed in series with the field coil. The moving coil of the

galvanometer is connected in place of telephones in the bridge circuit. Zero corrections may be made for errors of the pointer and for errors due to the magnet. The instrument may also be used for d.c.
H. E. BLAYDEN.

Sensitive direct-reading mercury manometer. H. W. MELVILLE (J.C.S., 1931, 2509—2511).—The vertical displacement of an inverted glass cup floating on Hg is used to measure pressure differences down to 0·001 mm. Hg. H. J. EMELEUS.

Simple pressure regulator. J. D. A. JOHNSON (J.C.S., 1931, 2523—2524).—A diagram is given of a simple apparatus for controlling the pressure to a few mm. of Hg in distillations at reduced pressures.
H. J. EMELÉUS.

Gas-pressure regulator. A. C. ROBERTSON (Ind. Eng. Chem. [Anal.], 1931, **3**, 383—384).—The apparatus permits const. pressure regulation for small loads and, by the use of two such regulators, gases may be mixed in any proportion.
E. S. HEDGES.

Simple apparatus for analytical control. R. FEIBELMANN (Chem. Fabr., 1931, 405—407, 414—416).—By the use of suitably calibrated measuring cylinders the approx. active contents of solutions of, *e.g.*, $NaOCl$, H_2O_2, $NaBO_3$, and $Na_2S_2O_4$ may be determined titrimetrically. A simple apparatus is described in which the reduction val. of a vat dye is determined by measuring the vol. of air necessary for complete oxidation of 10 c.c. of the solution. The fatty acid content of such materials as soaps and Turkey-red oil may be determined by hydrolysis in a 200-c.c. flask having a long graduated neck; when hydrolysis is complete warm H_2O is added and the length of the oily layer in the neck is measured. H. F. GILLBE.

High-vacuum pressure control apparatus. T. L. HO (Proc. Nat. Acad. Sci., 1931, **17**, 548—550).—The pressure is indicated by an ionisation gauge, which operates a galvanometer. A contact attached to the latter controls a thermionic amplifier, which in turn operates a relay, opening a leak. C. W. GIBBY.

Elementary apparatus for static determination of the partial pressures of gases in solution. U. M. NAYAK and S. LAKHMINARAYANAN (J. Indian Chem. Soc., 1931, **8**, 531).—A burette and a side tube are fitted to a large empty bottle. A known vol. of, *e.g.*, SO_2 solution is placed in the bottle, the whole is shaken, and a known vol. of the solution is then withdrawn and titrated. From the fall of concentration and the vol. of the apparatus the partial pressure may be calc. H. F. GILLBE.

Apparatus for absorption of hydrogen by silver permanganate according to the method of Hein and Daniel. B. RASSOW and L. WOLF (Chem. Fabr., 1931, 407).—The advantage of a mechanical shaking device is noted. The evolution of O_2 observed during the absorption of H_2 is ascribed to insufficient washing of the Ag catalyst; the quantity of O_2 evolved may be reduced by shaking the freshly filled pipette with air or N_2 before introducing the mixture to be analysed. The method is recommended for illuminating gas, cracked gas, and N_2–H_2 mixtures.
H. F. GILLBE.

Gas absorption pipette. A. C. EGERTON and L. M. PIDGEON (J. Sci. Instr., 1931, **8**, 234).—The pipette consists of two bulbs joined by a narrow neck. The reagent is drawn down into the lower one by lowering a Hg reservoir, and can be forced up again in the form of a fountain. Samples and reagents can be admitted through a side-tube which can be sealed with Hg. Honey has been found satisfactory as a greaseless lubricant. C. W. GIBBY.

Water distillation apparatus. A. SCHLEEDE and E. KÖRNER (Chem.-Ztg., 1931, **55**, 808).—The apparatus previously described (A., 1930, 884) is modified by replacing the Cu distillation flask with a flask of "R" glass having an inlet at the bottom through which the overflow cooling H_2O from the condenser enters the flask which is heated with a ring burner. A. R. POWELL.

Reflux condensers for extraction and distillation apparatus. C. ZINZADZE (Bull. Soc. chim., 1931, [iv], **49**, 1204—1205).—(1) The condensed vapours flow over the tube from which the vapour issues to the condenser and are returned to the material under extraction through a three-way cock which allows the solvent to be eliminated when the extraction is complete. (2) The condensate falls into a receiver, round which the vapours ascend to the condenser, and is similarly returned to the material under extraction through a three-way cock.
R. BRIGHTMAN.

Methods of using the Liebig condenser. Asbestos shields for distilling flasks. I. ENDLER (Chem. Ztg., 1931, **55**, 799).—Common errors in the use of glass condensers are noted and the correct method is described. A disc of asbestos, with a central circular depression conforming to the shape of the bottom of the flask, is recommended as a shield for distilling flasks; it may readily be formed from wet 2—3-mm. asbestos sheet. The flat portion should be wide enough to prevent direct heat from the burner reaching the flask. H. F. GILLBE.

Differential ebullioscope fitted with a rectifying column, and its application. W. SWIENTOSŁAWSKI (Rocz. Chem., 1931, **11**, 545—551).—The above apparatus serves for the determination of the difference between the temp. of ebullition of a liquid and of condensation of its vapours after passage through the column. The technique of making comparative measurements, whereby the b. p. of a liquid before and after purification is compared with that of H_2O at the same pressure, is described. R. TRUSZKOWSKI.

Still-head for laboratory columns. E. B. KESTER and R. ANDREWS (Ind. Eng. Chem. [Anal.], 1931, **3**, 373). E. S. HEDGES.

Gauze-plate laboratory rectifying column. S. PALKIN (Ind. Eng. Chem. [Anal.], 1931, **3**, 377—378).—The construction of a column containing plates of Ni wire-gauze is described. Data are given in illustration of its efficiency. E. S. HEDGES.

Economy of time in laboratory distillation. D. F. STEDMAN (Canad. J. Res., 1931, **5**, 455—465).—A mathematical consideration of fractional distillation is approx. verified with MeOH–EtOH mixtures.
R. S. CAHN.

Pump for water vapour at low pressure. P. SCHLUMBOHM (Chem. Fabr., 1931, 429—430).—A detailed account of a combined pump and continuously operating H_2SO_4 absorber for H_2O vapour, which is especially suitable for the evaporation at low temp. of biochemical and other temp.-sensitive solutions; it may be employed also as a refrigerating machine.
H. F. GILLBE.

Transparent cellulose covers for Nessler comparison tubes. E. ZIMBON (Ind. Eng. Chem. [Anal.], 1931, **3**, 356).—Cellophane covers are recommended for the tubes containing the colour standards, thus obviating errors due to the removal of stoppers.
E. S. HEDGES.

Solid carbon dioxide in laboratory technique. D. H. KILLEFFER (Ind. Eng. Chem. [Anal.], 1931, **3**, 386—387).—Applications of solid CO_2 to laboratory practice are suggested. E. S. HEDGES.

Large-capacity Soxhlet extractor. V. H. MORRIS (Chemist-Analyst, 1931, **20**, No. 4, 18—19).—The outer container (32×17 cm.) is of Cu, Sn, or Al; the inner vessel is $13{\cdot}5\times11$ cm. A 3-litre flask filled with H_2O and placed on top serves as a condenser.
CHEMICAL ABSTRACTS.

Microgravimetric analyses. P. L. KIRK and R. CRAIG (Ind. Eng. Chem. [Anal.], 1931, **3**, 345—347).—An apparatus which permits precipitation and filtration to be carried out in the same vessel is described. No loss of ppt. occurs in the determination of SO_4'', halide, or PO_4''' in very small samples. E. S. HEDGES.

Alloys for vacuum-tight glass–metal joints. D. E. OLSHEVSKY (Physical Rev., 1930, [ii], **35**, 1424).—Alloys containing 50% Pb, 37·5% Bi, 12·5% Sn, and 31·1% Pb, 12·5% Sn, 47% Bi, 9·4% Cd have little or no tendency to crack glass, and when backed by cement form strong, rigid, and replaceable vac.-tight joints. L. S. THEOBALD.

Electromagnet for investigation of the magnetic properties of atoms and molecules. E. J. SHAW (Rev. Sci. Instr., 1931, [ii], **2**, 611—617).—A design to prevent overheating, to allow an increased region of field, to minimise stray field, and to allow easy assembly is described. N. M. BLIGH.

Representation of the results of investigations of mixtures. G. BRUHNS (Chem.-Ztg., 1931, **55**, 798—799).—Partly an account of a method described previously, and applicable to, *e.g.*, natural waters, with details of its use in the case of potash mother-liquors.
H. F. GILLBE.

Geochemistry.

Analysis of the springs at Raducaneni [Rumania]. R. CERNATESCO and A. MAYER (Ann. Sci. Univ. Jassy, 1931, **16**, 529—532).—Detailed analyses are given. H. F. GILLBE.

Thermal waters of the north-east spring at Termini Imerese. G. MASSARA and S. CAPUANO (Annali Chim. Appl., 1931, **21**, 403—418).—The composition of this spring is substantially that found by Oliveri (1894), except that Li, Rb, and Cs are now detectable. Physical and physico-chemical data are also given. T. H. POPE.

Buffer capacity of sea-water. T. G. THOMPSON and R. U. BONNAR (Ind. Eng. Chem. [Anal.], 1931, **3**, 393—395).—The buffer capacity of sea-water is defined as the no. of millimol. of $H^{\cdot}$ which a unit vol. of sea-water will neutralise when an excess of standard acid is added. Normal sea-waters have a fairly const. buffer capacity, but the val. varies with land drainage, effects of biological phenomena, and industrial pollution. Buffer capacity may be only partly dependent on the concentration of CO_3'' and HCO_3', and the total CO_2 cannot be determined by direct acidimetry. E. S. HEDGES.

Bacteriological precipitation of lime in tropical sea. H. FISCHER (Ber. deut. Bot. Ges., 1931, **49**, 357—359).—Sedimentation of $CaCO_3$ and $MgCO_3$ in sea-water may result from decay of various organisms, from the action of CO_2 and NH_3, produced by decay, on Ca salts, and from bacteriological denitrification and desulphurisation. The cyclic processes which take place are outlined. H. F. GILLBE.

Tidal flat and salt marsh studies in Nelson Haven. II. Soil chemistry of the Nelson mud flat. B. W. DOAK (N.Z. J. Sci. Tech., 1931, **13**, 1—11).—Analyses of sol. matter, exchangeable bases, and p_H vals. at varying soil depths are recorded. The flora of these soils is controlled mainly by their salinity; the Mg content is closely related. The salts are characterised by a low exchangeable Ca and high exchangeable Mg content. A. G. POLLARD.

Analysis of the powder deposited at Jassy in February 1929. M. PONI and R. CERNATESCO (Ann. Sci. Univ. Jassy, 1931, **16**, 533—535).—Approx. 5 g. of dust per sq. m. were deposited in 2 days during a dust storm; the material consisted largely of SiO_2 (72·6%), Al_2O_3 (7·76%), Fe_2O_3 (4·95%), alkalis and alkaline earths, and P_2O_5 (1·71%).
H. F. GILLBE.

Mean composition of meteorites. I. I. ZASLAVSKI (J. Gen. Chem. Russ., 1931, **1**, 406—410).—The mean ratio in meteorites of silicate : metal : troilite=1 : 0·25 : 0·07; this result is in good agreement with Fersman's, but not with Farrington's, figures. R. TRUSZKOWSKI.

Tilden meteorites. A. R. CROOK and O. C. FARRINGTON (Trans. Ill. Acad. Sci., 1930, **22**, 442—449).—The meteorite (July 13, 1927) contained Fe 6·38, N 0·31, Co 0·02, S 2·31, P 0·15, SiO_2 41·22, Al_2O_3 3·69, FeO 22·28, NiO 0·99, CoO 0·04, MgO 22·30, CaO 0·91, Na_2O 0·53, K_2O 0, H_2O 0·03, less O for S and P 1·38; total 99·78%. CHEMICAL ABSTRACTS.

Mean composition of the earth. I. I. ZASLAVSKI (J. Gen. Chem. Russ., 1931, **1**, 401—405).—The % composition of the earth, computed on the basis of the mean composition of meteorites, agrees well with

Washington's figures, arrived at by a different method. R. TRUSZKOWSKI.

Crystal type of barytes in relation to minerogenetic succession. G. KALB and L. KOCH (Z. Krist., 1931, 78, 169—170).

Dehydration of natural ferric hydroxides. S. GOLDSZTAUB (Compt. rend., 1931, 193, 533—535).—Goethite and lepidocrocite have respectively *a* 4·64, 3·87; *b* 10·0, 12·4; *c* 3·03, 3·06 Å.; space-groups $V_h^{16}bnm$, $V_h^{17}mmm$ (cf. A., 1929, 988). On dehydration goethite passes into a mass of small crystals of hæmatite oriented in parallel. When slowly heated to 460° fibrous lepidocrocite of Chizeul acquires the structure of magnetite, and the coeff. of magnetisation increases 100 times; when heated rapidly to 440° it acquires that of hæmatite, and the coeff. increases only 50-fold. A crystal from Siegen when heated rapidly did not disintegrate, and became magnetic (cf. A., 1925, ii, 845; 1928, 503). C. A. SILBERRAD.

Vanadiferous nodules in the Permian beds of South Devon. G. E. L. CARTER (Min. Mag., 1931, 22, 609—613).—Greenish-black nodules surrounded by a bleached pale green aureole occur in certain beds of red clay near Budleigh Salterton and Exmouth. Analyses show the material to be a siliceous clay with V_2O_5 13·96% in the dark portion and 1·91% in the pale green aureole. The adjacent red clay contains 0·17% V_2O_5. L. J. SPENCER.

Chemical, optical, and *X*-ray study of nepheline and kaliophilite. F. A. BANNISTER [with M. H. HEY] (Min. Mag., 1931, 22, 569—608).—Detailed determinations of the optical, density, and *X*-ray data were made for a number of selected specimens of nepheline from Vesuvius and of elæolite and "pseudonepheline," and chemical analyses were made on the same samples of material. A strict correlation of the various properties was thus possible. The hexagonal unit cell of dimensions *a* 9·94—9·99, *c* 8·31—8·38 Å. contains a const. no. (32) of O atoms, whilst the no. of other atoms varies, the contents of the unit cell being $Si_{16-n}Al_n(Na,K,\frac{1}{2}Ca)_nO_{32}$, where *n* ranges from 6·6 to 8·2. The cell dimensions increase slightly with the content of K, the higher vals. quoted above being for "pseudonepheline," which is richest in K. In kaliophilite the unit cell is much larger, *a* 26·7—27·0, *c* 8·49—8·51 Å., and contains 54 $KAlSiO_4$. A kaliophilite structure built up from nepheline cells is suggested. L. J. SPENCER.

Brown hornblende and biotite from Shabō-zan, Taiwan. T. ICHIMURA (Min. Mag., 1931, 22, 561—568).—Chemical analyses and optical data are given for brown hornblende and basaltic hornblende, the former occurring in brown andesite and the latter in grey andesite, of the Shabō-zan volcano in Taiwan (Formosa). The brown hornblende and biotite have arisen by the heating and oxidation of the basaltic varieties. L. J. SPENCER.

Residual liquids of crystallising magmas. C. N. FENNER (Min. Mag., 1931, 22, 539—560).—A general discussion of the process of crystallisation-differentiation in basaltic magmas, with criticism of the views of other authors. L. J. SPENCER.

Wearing of rocks in water. F. W. FREISE (Tsch. Min. Petr. Mitt., 1931, 42, 48—58).—Experiments on the wearing hardness of various Brazilian rocks in H_2O are continued on the same lines as previously used for minerals (A., 1931, 459). L. J. SPENCER.

Iron ores of the Sulin district in the Donetz coal-basin. D. SERDJUTSCHENKO (Tsch. Min. Petr. Mitt., 1931, 42, 27—47).—Analyses are given of the limonitic ores, which were formed by metasomatic replacement of limestone. L. J. SPENCER.

Determination of acid plagioclases by the zonal method. H. EBERT (Tsch. Min. Petr. Mitt., 1931, 42, 8—26).—Measurement on the universal microscope-stage of the extinction angles in the zone perpendicular to the face (010) affords a means of determining the twin law and the percentage of the anorthite mol. in the plagioclase felspars. L. J. SPENCER.

Proposed change in calculation of norms of rocks. T. F. W. BARTH (Tsch. Min. Petr. Mitt., 1931, 42, 1—7).—In the system of Cross, Iddings, Pirsson, and Washington (1902) chemical analyses of rocks are calc. in amounts of arbitrarily selected "normative" minerals (not necessarily actually present in the rock). Better results are obtained for the "norm" if the "normative" pyroxenes are expressed as $CaSiO_3$, $MgSiO_3$, and $FeSiO_3$, and the olivine mols. in terms of Mg_2SiO_4 and Fe_2SiO_4. L. J. SPENCER.

Forms and places of occurrence of pyrites. L. TOKODY (Z. Krist., 1931, 80, 255—348).—A list of 238 definite and 221 uncertain or vicinal forms of pyrites with place of origin; of 272 places of occurrence with the forms found at each, with discussion thereon, and a bibliography of 706 references. C. A. SILBERRAD.

Rosickyite: natural nacreous sulphur. J. SEKANINA (Z. Krist., 1931, 80, 174—189).—On the clay-covered inner walls of concretions, consisting of a limonite crust interspersed with radiating aggregates of pyrite, occurring in clay deposits in chalk at Kunstadt and Lettowitz (Czechoslovakia), are found small ($\not>$0·5 mm.), slightly yellow crystals of adamantine lustre, easily sol. in C_6H_6, CH_2I_2, and CS_2. They are monoclinic, $a:b:c=1·0606:1$ 0·7094, β 91° 48′, agreeing with Muthmann's results (cf. Z. Krist., 1890, 17, 336; A., 1927, 216) for nacreous S, or S III. The crystals readily pass into the rhombic modification, but as found are free therefrom, and are clearly the result of slow decomp. of pyrites. Results are confirmed by comparison with artificial nacreous S, and Muthmann's different result for the extinction angle is shown to be due to change to rhombic S, the course of which is traced. The name rosickyite is proposed. It is probably identical with the variety of S found in the crater of Stromboli by Panichi in 1911 (cf. Zambonini, Z. Krist., 54, 393). C. A. SILBERRAD.

Optical study of tarbuttite. H. BUTTGENBACH and J. MELON (Bull. Acad. roy. Belg., 1931, [v], 17, 892—901).—The orientation of the principal axes and the coeff. of refraction and birefringence of tarbuttite have been measured. J. W. SMITH.

Kolm. R. C. Wells and R. E. Stevens (J. Wash. Acad. Sci., 1931, **21**, 409—414).—The Pb : U ratio is 0·061, whence the age is calc. to be $4·58 \times 10^8$ years. The kolm (from Sweden) is only slightly permeable to gases. C. W. Gibby.

Diopside and tremolite of Monte Spinoza, Campiglia. F. Rodolico (Atti R. Accad. Lincei, 1931, [vi], **13**, 705—710).—The analysis of a sample of tremolite conformed to the formula $CaMg_3(SiO_3)_4$, but to the formula $H_2Ca_2Mg_5(SiO_3)_8$ if the possibility of the substitution of SiO_2 by Al_2O_3 is admitted. If the substitutions postulated by Warren (A., 1930, 844) are recognised, the second formula appears to be correct. The analysis and crystallographic data of a specimen of diopside are described. H. F. Gillbe.

Dolomite problem. H. Udluft (Z. Deut. Geol. Ges., 1931, **83**, 1—13; Chem. Zentr., 1931, i, 2599—2600).—The solubility curves of $CaCO_3$ and $MgCO_3$ in relation to the CO_2 partial pressure of the solvent intersect at a point below which $CaCO_3$ is less sol. than $MgCO_3$. In sea-water vals. usually below this point are obtained; when the val. corresponds with the point of intersection dolomite separates. Dolomitisation of $CaCO_3$ therefore takes place when the CO_2 partial pressure rises above the intersection point. A. A. Eldridge.

Classification of magmatic rocks. E. Tröger (Neues Jahrb. Min., 1931, A, **62**, 249—330; Chem. Zentr., 1931, i, 2599).—The classification depends on a projection system relating to the composition. A. A. Eldridge.

Strontium content of magmatic rocks. W. Noll (Naturwiss., 1931, **19**, 773—774).—The Sr contents of magmatic minerals and rocks containing Ca have been determined. Ca and Sr are isolated chemically and the relative wts. of CaO and SrO are determined by means of *X*-ray spectroscopy. The SrO content of pyroxene is 0·10%, of labradorite 0·12%, of larvikite felspar 0·36%, and of sanidine 0·48%. W. R. Angus.

Evidence of the presence of element 87 in pollucite and lepidolite ores. F. Allison and E. J. Murphy (Physical Rev., 1930, [ii], **35**, 285).—Application of the magneto-optic method of analysis (A., 1930, 1541) to these ores shows min. corresponding with eka-Cs; several isotopes are indicated. L. S. Theobald.

Organic Chemistry.

Determination of small quantities of methane. H. R. Ambler (Analyst, 1931, **56**, 635—637).—H_2 and CO are oxidised by powdered CuO in an electric furnace at about 300° and the H_2O and CO_2 formed are removed by absorption with $CaCl_2$ and ascarite, or measured, as desired. The CH_4 is determined by burning with O_2 in presence of Pt wire at a bright yellow heat. The apparatus is described. T. McLachlan.

Catalytic oxidation of paraffins. M. Goswami and S. K. Chatterjee (J. Indian Chem. Soc., 1931, **7**, 533).—Passage of the vapour of paraffin (m. p. 49°) in a current of air over reduced Ni gives mixed aldehydes, probably of the C_8 to C_{11} series. R. S. Cahn.

F. p. of organic compounds. XIII. L. Deffet.—See this vol., 1361.

Reactions of addition to unsaturated organic compounds. P. Pratesi (Atti R. Accad. Lincei, 1931, [vi], **13**, 779—784).—The regularities in the mode of formation of additive compounds by org. compounds of different types pointed out by Markovnikov and by Ipatiev are explained on the basis of the electronic theory of valency. T. H. Pope.

Orientation in the addition of halogens and hydrogen halides to simple ethylene derivatives. I. Additions with iodine monochloride. C. K. Ingold and H. G. Smith. **II. Addition of hydrogen halides to propylene and Δ^a-pentene.** C. K. Ingold and (Miss) E. Ramsden (J.C.S., 1931, 2742—2746, 2746—2752).—I. Propylene reacts with ICl in dil. HCl, giving a mixture (*A*) of 69% of β-chloro-α-iodopropane (I) and 31% of α-chloro-β-iodopropane (II); the amounts of (I) and (II) are determined by treatment of *A* with EtOH–KOH at 0° and subsequent refractometric analysis of the resultant mixture of α- and β-chloro-Δ^a-propenes. Styrene and ICl in presence of conc. HCl and CH_2Cl_2 afford a product containing at least 95% of α-chloro-β-iodo-α-phenylethane; crotonic acid and ICl in $CHCl_3$ give at least 92% of β-*chloro*-α-*iodobutyric acid*, m. p. 64° (converted by boiling pyridine into crotonic and α-*iodocrotonic acid*, m. p. 113°), whilst ethylenesulphonic acid and ICl in aq. HCl furnish at least 90% of $CH_2Cl·CHI·SO_3H$ (converted by neutralisation with K_2CO_3 and evaporation into *K* α-*iodoethylenesulphonate*). These results and others (lit.) confirm the theory that reaction (addition) is initiated by I.

II. Addition of HI to propylene in presence of propane, $PhNO_2$, AcOH, and H_2O gives in all cases mainly $Pr^{\beta}I$; the amount of $Pr^{a}I$ produced decreases for the solvents in the order quoted (when the mol.-fraction of HI present is 0·1). The amount of $Pr^{a}I$ formed varies (especially in H_2O) with the concentration of HI; curves are given showing the variations. Addition of HBr and HI to Δ^a-pentene in presence of H_2O gives the *sec.*-amyl halides exclusively. In the addition of HX to $CHR{:}CH_2$, orientation is considered to be determined by the electron-repelling effect of R acting both inside and outside the mol., the external effect being affected by the medium. Orientation can be correlated better with the internal pressures than with the dielectric consts. of the media; neither of these factors is, however, accurate. H. Burton.

Modes of addition to conjugated unsaturated systems. III. Mechanism of addition of halogens and hydrogen halides. C. K. Ingold and H. G. Smith. **IV. Additions of ψ-acids.** J. Bloom and C. K. Ingold (J.C.S., 1931, 2752—2765, 2765—2774).—III. Butadiene and ICl in CH_2Cl_2 at

—35° give a mixture (*A*) of (mainly) α-chloro-δ-iodo-Δ^{β}-butene (I) and 22% of γ-chloro-δ-iodo-Δ^{α}-butene (II); the constitutions of (I) and (II) are established by treatment of *A* with powdered NaOH, addition of 1 mol. of Br to the resultant chlorobutadiene mixture, and ozonolysis of the resulting chlorodibromobutenes. The production of (I) and (II) indicates that the C_{α}-atom is the point of incidence of reaction. β-Methylbutadiene and Br in aq. EtOH give a product which, after treatment with 3% Na–Hg in dil. AcOH, acetylation of the resultant unsaturated alcohols, and oxidation of these with O_3 (whereby CH_2O, MeCHO, $COMe_2$, α-hydroxy*iso*butaldehyde, and glycollaldehyde are obtained), is calc. to contain at least 47% of $CH_2Br\cdot CMe\colon CH\cdot CH_2\cdot OH$ (III), at least 16% of $CH_2Br\cdot CMe(OH)\cdot CH\colon CH_2$ (IV), and a little $OH\cdot CH_2\cdot CMe\colon CH\cdot CH_2Br$ (V); the production of (III) and (IV) involves initial reaction at C_{α}, whilst (V) probably results from initial attack at C_{δ}. Addition of Br to α-phenylbutadiene under similar conditions is initiated at C_{δ}, since $CHPh\colon CH\cdot CH(OH)\cdot CH_2Br$ (reduced mainly to -phenyl-α-methylallyl alcohol) is formed. *αγδ-Tri-romo-Δ^{α}-butene*, b. p. 114—115°/18 mm. (ozonolysis products, CO, HBr, and α-bromoacraldehyde), is produced from α-bromobutadiene and Br (1 mol.) in hexane at —35°, $CHCl_3$ at ±35°, and AcOH at 20°, whilst addition of HBr affords *αγ-dibromo-Δ^{α}-butene*, b. p. 59—61°/15 mm. (oxidised by $KMnO_4$ in aq. $COMe_2$ to $CHMeBr\cdot CO_2H$). These and other (lit. 1929—1930) results are discussed in relation to the theory previously proposed (A., 1928, 634).

IV. Me malonate and Me β-vinylacrylate give an additive product (cf. Kohler and Butler, A., 1926, 713) (containing less than 2% of the αβ-additive compound) reduced catalytically (Pt-black) in aq. AcOH to *Me pentane-αεε-tricarboxylate*, b. p. 172—176°/19—20 mm., hydrolysed by 20% HCl to pimelic acid. Et cyanoacetate and Et sorbate afford a mixture of Et α-cyano-β-methyl-Δ^{γ}-pentene-αε-dicarboxylate (VI) and Et α-cyano-β-propenylglutarate (VII) (10±2%). The amount of (VII) is determined by complete hydrolysis of the mixture, subsequent reduction with red P and HI and then with Zn dust and AcOH, dehydration of the mixed acids with Ac_2O, and conversion of the resulting β-*n*-propylglutaric anhydride into its anilic acid; multimol. β-methylpimelic anhydride is formed from (VI). Me crotonylidenemalonate and $CN\cdot CH_2\cdot CO_2Me$ yield a mixture of Me α-cyano-β-methyl-Δ^{γ}-pentene-αεε-tricarboxylate and Me α-cyano-β-propenylpropane-αγγ-tricarboxylate (16±2%), whilst *Et β-methylsorbate*, b. p. 102—104°/17—18 mm. (cf. A., 1930, 64), and $CN\cdot CH_2\cdot CO_2Et$ give essentially *Et α-cyano-βγ-dimethyl-Δ^{γ}-pentene-αε-dicarboxylate*, b. p. 195—200°/15—16 mm., and Et α-methylsorbate and $CN\cdot CH_2\cdot CO_2Et$ afford mainly *Et α-cyano-αε-dimethyl-Δ^{γ}-pentene-αε-dicarboxylate*, b. p. 196—200°/17—18 mm.; the amount of αβ-addition in the last two cases is not more than 2%. The additive product from Me malonate and Me cinnamylideneacetate is wholly αβ, since successive hydrolysis, decarboxylation, and ozonolysis give BzOH and tricarballylic acid. The reaction between Me cinnamylidenemalonate and $CN\cdot CH_2\cdot CO_2Me$ is initiated by αβ-addition, since *Me α-cyanocinnamylideneacetate*, m. p. 143—145° (from cinnamaldehyde and $CN\cdot CH_2\cdot CO_2Me$), and Me malonate are produced. These results and others (lit. 1930—1931) are discussed with reference theory previously proposed (*loc. cit.*), which is amplified.

Ph styryl ketone, $CH_2Br\cdot CO_2Et$, and Zn in C_6 give *Et β-hydroxy-β-phenyl-β-styrylpropionate*, m. p. 93°, dehydrated to *Et β-styrylcinnamate*, b. p. 237°/10 mm. (free *acid*, m. p. 145°, converted by Br in $CHCl_3$ into a *Br*-derivative, m. p. 170°), which could not be combined with $CN\cdot CH_2\cdot CO_2Et$ in presence of NaOEt. *p-Bromobenzyl cyanoacetate*, m. p. 84—85° (from p-$Br\cdot C_6H_4\cdot CH_2Br$ and $CN\cdot CH_2\cdot CO_2Ag$), and *Me γ-benzoyl-β-phenylpropane-αα-dicarboxylate*, m. p. 104° (from Ph styryl ketone and Me malonate in presence of piperidine), are described.

H. BURTON.

Pentene derivatives. R. PAUL (Compt. rend., 1931, **193**, 598—600).—Δ^{δ}-Pentenol with $NPhMe_2$ and $SOCl_2$ gives *Δ^{δ}-pentenyl chloride* (I), b. p. 105°/745 mm., with PBr_3 and a little pyridine *Δ^{δ}-pentenyl bromide* (II), b. p. 126—127°/765 mm., and with Ac_2O yields Δ^{α}-pentenyl acetate, b. p. 150—151° (*αβ-dibromoamyl acetate*, b. p. 156—157°/23 mm.). δε-Dibromo-*n*-amyl alcohol with solid KOH gives 2-bromomethyltetrahydrofuran and *δ-bromo-Δ^{δ}-pentenyl alcohol*, b. p. 97°/15 mm.; this with PBr_3 and dry pyridine yields *αδ-dibromo-Δ^{δ}-pentene*, b. p. 83—86°/15 mm., and with KOAc *δ-bromo-Δ^{δ}-pentenyl acetate*, b. p. 102—105°/18 mm. The difference in the physical consts. of succeeding members of the series $CH_2\colon CH\cdot[CH_2]_n\cdot CH_2X$ decreases as *n* increases. (I) and (II) react normally with Mg. R. S. CAHN.

Photochemical oxidation of acetylene. R. LIVINGSTON.—See this vol., 1379.

Stability of hexa*tert*.-alkylethinylethanes. Effect of increasing the weight of the alkyl groups. D. W. DAVIS and C. S. MARVEL (J. Amer. Chem. Soc., 1931, **53**, 3840—3851).—γδ-Dimethylhexane-γδ-diol is converted by Nybergh's method (A., 1922, i, 802) into Me α-methyl-α-ethylpropyl ketone (admixed with a little Et *tert*.-amyl ketone), which with PCl_5 gives impure β-chloro-γ-methyl-γ-ethyl-Δ^{α}-pentene. Treatment of this with $NaNH_2$ in high-boiling mineral oil at 160—175° (whereby some δδ-dimethyl-Δ^{β}-hexinene is evolved) and subsequent hydrolysis affords *γ-methyl-γ-ethyl-Δ^{α}-pentinene*, b. p. 98—100°/745 mm. [*Ag* salt, m. p. 191·5° (darkens at 167°)], converted by the method previously described (A., 1928, 988) into *tri-(γ-methyl-γ-ethyl-Δ^{α}-pentinyl)carbinol*, b. p. 130—133°/0·5 mm. The corresponding bromide (from the carbinol and AcBr in light petroleum) and "mol." Ag in Et_2O and N_2 give *hexa-(γ-methyl-γ-ethyl-Δ^{α}-pentinyl)ethane* (I), m. p. 122—127° according to rate of heating, m. p. (Maquenne block) 195°. (I) in EtOH absorbs O_2 readily, but a peroxide could not be isolated; CO_2 and α-methyl-α-ethylbutyric acid (p-*toluidide*, m. p. 113·5—114°) are formed. (I) is cleaved readily by liquid Na–K alloy or 40% Na–Hg in Et_2O; the resultant products with CO_2 give *tri-(γ-methyl-γ-ethyl-Δ^{α}-pentinyl)acetic acid*, m. p. 171—174° (corr.). (I) is cleaved more readily with 1% Na–Hg than is hexa*tert*.-butylethinylethane (*loc. cit.*);

the decreased stability of the central C·C linking is attributed to the increase in wt. of the alkyl groups. When (I) is heated in EtOH and N_2 an *isomeride*, m. p. 82·3—83° (corr.), is produced. H. BURTON.

Determination of organic halogen by liquid ammonia–sodium process. T. H. VAUGHN and J. A. NIEUWLAND (Ind. Eng. Chem. [Anal.], 1931, **3**, 274—275).—A simple modification of the method of Chablay (A., 1914, i, 918), which is also applicable to the determination of F in org. compounds.

H. BURTON.

Addition of hydrogen bromide to vinyl bromide. J. P. WIBAUT (Rec. trav. chim., 1931, **50**, 1021—1022; cf. this vol., 598).—A reply to Burkhardt and Cocker (this vol., 1031). J. W. BAKER.

Resolution of unsaturated asymmetric alcohols into optically active isomerides. G. KAMAI (J. Gen. Chem. Russ., 1931, **1**, 460—466).—Ethylvinylcarbinol can be resolved through its *H phthalate*, m. p. 121—124° (*benzylamine* salt, m. p. 102°; *brucine* salt, m. p. 143—144°). *Brucine* β-*methylenebutyl phthalate*, m. p. 85—86°, was synthesised in order to show that during the formation of the former brucine salt no rearrangement had taken place. Phenylvinylcarbinol is not resolvable by this method, as the action of phthalic anhydride gives *cinnamyl H phthalate*, m. p. 88—89°. The following new compounds are described: d-*ethylvinylcarbinyl H phthalate* (*benzylamine* salt, m. p. 89—90°), d-*ethylvinylcarbinol*, b. p. 110—112°, l-*phenylethylammonium ethylvinylcarbinyl phthalate*, m. p. 142—142·5°, l-*ethylvinylcarbinol*, b. p. 111—112°. E. B. UVAROV.

Determination of acetylenic alcohols and the composition of their silver compounds. W. KRESTINSKI and M. KELBOVSKAJA (Ber., 1931, **64**, [B], 2371—2375).—Treatment of γ-ethyl-Δ^{α}-pentinen-γ-ol, γ-methyl-Δ^{α}-pentinen-γ-ol, and δ-methyl-Δ^{α}-pentinen-γ-ol with AgOAc ppts. *Ag* salts 2XAg,AgOAc, reaction being of the type $2OH\cdot CEt_2\cdot C{:}CH+3AgOAc=2OH\cdot CEt_2\cdot C{:}CAg,AgOAc+2AcOH$. After removal of the ppt. the alcohol is determined by titration of the acid with NaOH in presence of phenolphthalein. γ-Methyl-Δ^{α}-butinen-γ-ol and Δ^{α}-butinen-γ-ol do not give ppts. with AgOAc or Ag propionate. With saturated Ag *iso*butyrate, the *ppts.* have the compositions $OH\cdot CMe_2\cdot C{:}CAg,C_4H_7O_2Ag$ and $OH\cdot CHMe\cdot C{:}CAg,C_4H_7O_2Ag$; titration of the *iso*butyric acid in the filtrates from these ppts. is not a satisfactory method for determining the alcohols.

H. WREN.

Reaction of pentaerythritol with aldehydes under the influence of zinc chloride. H. J. BACKER and H. B. J. SCHURINK (Rec. trav. chim., 1931, **50**, 1066—1068).—*spiro*Cyclic acetals of the type $C\left(<^{CH_2\cdot O}_{CH_2\cdot O}>CR^1R^2\right)_2$ are readily prepared by warming $C(CH_2\cdot OH)_4$ with 20—25% excess of the appropriate aldehyde in presence of a little anhyd. $ZnCl_2$, and thus are obtained: *di*-(β-*tribromoethylidene*)- (R^1=H; R^2=CBr_3), m. p. 248—249° (decomp.), and *difurfurylidene*- (R^1=H; R^2=C_4H_3O), m. p. 164·5—165°, *-pentaerythritol*. With *cyclo*pentanone and *cyclo*hexanone the tetracyclic trispirans *di*(cyclo*pentylidene*)- [R^1R^2=$(CH_2)_4$>], m. p. 153·5°, and *di*(cyclo*hexylidene*)- [R^1R^2=$(CH_2)_5$>], m. p. 115·5°, *-pentaerythritol*, are obtained. With α-hydrindone the $C(CH_2\cdot OH)_4$ plays no part in the reaction, the products being α-anhydrobishydrindone and truxene.

J. W. BAKER.

Action of chloroformic esters on alkylsulphuric acids. M. Y. KRAFT and F. V. LIUTINA (J. Gen. Chem. Russ., 1931, **1**, 190—192).—The reaction $RHSO_4+ClCO_2R'=RR'SO_4+CO_2+HCl$ proceeds smoothly when R and R′ are Et or Me. The reaction is recommended for the prep. of Me_2SO_4.

E. B. UVAROV.

α- and β-Glycerophosphates. P. KARRER and H. SALOMON (J. Biol. Chem., 1931, **93**, 407).—Polemical (cf. Kay and Lee, this vol., 766). H. BURTON.

α- and β-Glycerophosphates. H. D. KAY (J. Biol. Chem., 1931, **93**, 409).—A reply to Karrer and Salomon (preceding abstract) H. BURTON.

Synthesis of galactose 6-phosphate. B. HVISTENDAHL (Svensk Kem. Tidskr., 1931, **43**, 202—205; cf. A., 1930, 1166).—*Ba diiso*propylidenegalactose 6-*phosphate*, $C_{12}H_{19}O_9PBa$, $[\alpha]^{20}_{\mathrm{Hg\ yellow}}$ −27·8° in H_2O, has been prepared from di*iso*propylidenegalactose and $POCl_3$ in pyridine solution. This compound is hydrolysed to *Ba galactosephosphate*, $C_6H_{11}O_9PBa$, $[\alpha]^{20}_{\mathrm{Hg\ yellow}}$ +21° in H_2O. The ester obtained by treatment of the Ba compound with the calc. amount of H_2SO_4 has $[\alpha]^{20}_{\mathrm{Hg\ yellow}}$ +31°.

H. F. HARWOOD.

Thermal behaviour of sulphur compounds in hydrocarbon solvents. I. Aliphatic mercaptans. W. M. MALISOFF and E. M. MARKS (Ind. Eng. Chem., 1931, **23**, 1114—1120).—Experiments on the thermal decomp. of mercaptans in org. solvents are reproducible in calibrated furnaces. Below 475°, C_6H_6, *n*-heptane, ββδ-trimethylpentane, and straight-run naphthas are sufficiently stable to serve as solvents which do not react with mercaptans or their decomp. products. The $AgNO_3$ method has been adapted for the determination of mercaptans in mixtures containing the thermal decomp. products, giving an accuracy of ±5 to ±2%. Decomp. of the aliphatic mercaptans is homogeneous in the gaseous phase up to 475°. The decomp. of amyl mercaptan is depressed by mixing with CO_2 or H_2, but is promoted by C_6H_6, in relation to naphtha as solvent, but the contrary is true for aromatic types. The data suggest a first-order reaction, although a final decision is not possible. The decomp. of the aliphatic types is apparently to H_2S and an olefine. The higher homologues in the aliphatic series appear to be more unstable than the lower, although there is no marked difference. Benzyl mercaptan is less stable than the lower members of the aliphatic series. Branched-chain isomerides are less stable than the straight-chain compounds, markedly so only at 475°. Some activation of decomp. may be attributed to a solvent such as C_6H_6 compared with naphtha as standard, but naphtha itself may be a promoter. The temp. coeff. for a rise of 10° is calc. to be 1·38 for *n*-amyl mercaptan, with a heat of activation of 33,500 g.-cal. The val. of E/RT is 24·7, of the same order of magnitude as those calc. for the decomp. of NH_2Et, O_3, N_2O_5, $COMe_2$, and Et_2O. E. S. HEDGES.

Reaction of silver nitrate with organic sulphides. P. C. RAY, N. ADHIKARI, and H. RAY (J. Indian Chem. Soc., 1931, **8**, 689—693).—Unstable additive (1 : 1) *compounds* (m. p. given in parentheses) are obtained from a conc. solution of $AgNO_3$ and the following sulphides: Me_2S (126°), Et_2S (112°), Pr_2S (109°), Bu_2S (98°), MeEtS, $(CH_2Ph)_2S$ (93—95°), Me_2S_2, Et_2S_2, and $(CH_2Ph)_2S_2$ (103°); allyl sulphide gives the *compound* $3AgNO_3,2(C_3H_5)_2S$, m. p. 152°. These compounds are binary electrolytes and are decomposed by pyridine and NH_3 to $AgNO_3,2C_5H_5N$ and $AgNO_3,2NH_3$, respectively. The *complexes* $Hg(NO_3)_2,2Me_2S$, $HgClNO_3,Et_2S$, m. p. 110°, $HgClNO_3,Pr_2S$ m. p. 100—102°, and $HgClNO_3,Bu_2S$, m. p. 132°, are obtained when the $AgNO_3,R_2S$ compounds are treated with $HgCl_2$ in EtOH.

H. BURTON.

Complexes of antimony trichloride with organic sulphides. P. C. RAY, N. ADHIKARI, and A. N. ROY (J. Indian Chem. Soc., 1931, **8**, 711—716).—The following *complexes* are obtained when the components are heated at 120—190°: $SbCl_3,Et_2S$ (I), m. p. 143°; $SbCl_3,Me_2S$; $SbCl_3,Pr_2S$, m. p. 124°; $4SbCl_3,3Bu_2S$ (II), m. p. 105°. (I) and (II) are converted by warm EtOH into the *complexes* $2SbCl_3,HCl,3Et_2S$, m. p. 75°, and $2SbCl_3,HCl,3Bu_2S$, m. p. 125°, respectively; (I) and $HgCl_2$ in $COMe_2$ give the *compound* Hg_2Cl_2,Et_2S. (I) is decomposed by $AgNO_3$ and NH_3 to Sb_2S_3. The conductivity of (I) in $COMe_2$ is greater than that of $SbCl_3$ under the same conditions.

H. BURTON.

Reactions of divinyl sulphide, sulphoxide, and sulphone. J. R. ALEXANDER and H. MCCOMBIE (J.C.S., 1931, 1913—1918).—Divinyl sulphide and Cl_2 (1 mol.) in CCl_4 affords *αβ-dichloroethyl vinyl sulphide*, b. p. 84—85°/20 mm. (converted by KOH in EtOH into *β-chlorodivinyl sulphide*, b. p. 123—124°/760 mm.), whilst with 2 mols. of Cl_2 *αβα′β′-tetrachlorodiethyl sulphide*, b. p. 132—133°/15 mm., converted by NEt_3 (1 mol.) in C_6H_6 into *αβ-dichloroethyl-chlorovinyl sulphide*, b. p. 103—104°/20 mm., is obtained. Similar addition of PhSH gives di-β-phenylthioldiethyl sulphide. Divinyl sulphoxide (by NEt_3 on ββ′-di-iododiethyl sulphoxide in dry C_6H_6) forms no additive compounds with hydrogen halides, but by addition of the appropriate halogen are obtained: *αβα′β′-tetrachloro-*, m. p. 121°, and *-tetrabromo-*, m. p. 119°, *-diethyl sulphoxide*, whilst 5% NaOH converts it into 1 : 4-thioxan oxide, and NaOR in ROH gives the corresponding ββ′-dialkoxydiethyl sulphoxide. *β-Chlorodivinyl sulphoxide*, b. p. 73—74°/15 mm., is obtained by the action of NEt_3 on trichlorodiethyl sulphoxide. Divinyl sulphone (by NEt_3 on ββ′-dichlorodiethyl sulphone in dry C_6H_6) is very reactive, suitable addition of halogens or hydrogen halides giving *β′-tetrabromodiethyl sulphone*, m. p. 138°, ββ′-dibromodiethyl sulphone (no reaction with Cl_2 or HCl), and β-chloroethyl vinyl sulphone (NEt_3 on the dichloro-sulphone), converted by aq. HI into *β-chloro-β′-iododiethyl sulphone*, m. p. 125—126° (decomp.); *ββ′-dicyanodiethyl sulphone* has m. p. 84°. With 5% NaOH divinyl sulphone gives 1 : 4-thioxan dioxide, whilst NaOMe in boiling MeOH affords *ββ′-dimethoxydiethyl sulphone*, b. p. 170—171°/17 mm., the diethoxy- and di*iso*amyloxy-compounds being obtained similarly; NH_2Ph at 100° affords *ββ′-dianilinodiethyl sulphone*, m. p. 94—95°, glycine ester in EtOH gives Et 1 : 4-sulphonazan-4-acetate, whilst with $NHPh{\cdot}NH_2$, 4-anilino-1 : 4-sulphonazan, $NHPh{\cdot}N{<}(CH_2{\cdot}CH_2)_2{>}SO_2$, m. p. 192°, is obtained. Divinyl sulphone with H_2S gives mainly polymerisation products and a small yield of 1 : *4-dithian dioxide*, $SO_2{<}(CH_2{\cdot}CH_2)_2{>}S$, m. p. 206°.

J. W. BAKER.

Salts of methanetrisulphonic acid. H. J. BACKER and P. TERPSTRA (Rec. trav. chim., 1931, **50**, 1069—1077).—Crystallographic data are given for the following salts of $CH(SO_3H)_3+3H_2O$, m. p. 162—162·5° (cf. this vol., 64): $NH_4+0{\cdot}5H_2O$; *Li*+$4H_2O$; *Na*+$3H_2O$; *Rb*+H_2O (mixed crystals with K salt); *Cs*+H_2O, and +$2H_2O$; Ag+H_2O; *Ca*+$12H_2O$; *Ba*+$9H_2O$; La+$6H_2O$; *cinchonine* $8H_2O$; and *K dibrucine* +$9H_2O$.

J. W. BAKER.

Trisulphonylmethanes. D. T. GIBSON (J.C.S., 1931, 2637—2644).—Disulphonylmethanes are prepared either by Posner's method (A., 1903, i, 242) or by successive hydrolysis and oxidation of sulphonylthiolacetones (I), $SR'{\cdot}CHAc{\cdot}SO_2R$, obtained by condensation of sulphonylacetones and alkyl thiosulphonates (cf. Brooker and Smiles, A., 1926, 947): $CH_2Ac{\cdot}SO_2R+R{\cdot}SO_2{\cdot}SR' \longrightarrow$ (I). Condensation of the disulphonylmethanes with disulphoxides in presence of NaOEt or Na_2CO_3 gives disulphonylthiolmethanes, oxidised further to trisulphonylmethanes, $CH(SO_2R)(SO_2R')(SO_2R'')$, which could not be resolved. The following are prepared: $CH_2(SO_2Me)_2$, m. p. 142° (Cl_2-derivative, m. p. 152°); *αα-dimethylthiolethane*, b. p. 156—158°; *αα-di(methanesulphonyl)ethane*, m. p. 122° (*I*-derivative, m. p. 225°); *methylthiolethylthiolmethane*, b. p. 163—167°; *methanesulphonylethanesulphonylmethane*, m. p. 94—95°; *phenylthiolethylthiolmethane*, b. p. 147—151°; $CH_2(SO_2Ph)(SO_2Et)$ [also formed by oxidising the reaction product from Et *p*-toluenethiosulphonate and Et benzenesulphonylacetate (*Na* salt)]; *α-phenylthiol-α-methylthiolethane*, b. p. 140—145°/10 mm.; *α-benzenesulphonyl-α-methanesulphonylethane*, m. p. 104°; *phenylthiolmethylthiolmethane*, b. p. 148—152°/11 mm.; *benzenesulphonylmethanesulphonylmethane*, m. p. 147°; *α-benzenesulphonyl-α-*p*-tolylthiolacetone*, m. p. 99°; *benzenesulphonyl-*p*-tolylthiolmethane*, m. p. 85°; *benzenesulphonyl-*p*-toluenesulphonylmethane*, m. p. 115°; *methanesulphonylethanesulphonylphenylthiolmethane*, m. p. 126°; *benzenesulphonylethanesulphonylmethylthiolmethane*, m. p. 98°; *benzenesulphonylmethanesulphonylethanesulphonylmethane*, m. p. 216—219° [*Br*-derivative, m. p. 141°; *brucine*, m. p. 140—150° (decomp.), and d-*hydroxyhydrindamine*, m. p. 159°, salts]; *benzenesulphonyl-*p*-toluenesulphonyl-*3 : 5-*dichlorophenylthiolmethane*, m. p. 145° (sinters at 123°); *benzenesulphonyl-*p*-toluenesulphonylmethylthiolmethane*, m. p. 105°; *benzenesulphonylmethanesulphonyl-*p*-tolylthiolmethane*, m. p. 169°; *benzenesulphonyl-*p*-toluenesulphonylmethanesulphonylmethane*, m. p. 174°; *benzenesulphonylmethanesulphonyl - 3 : 5 - dichloro - phenylthiolmethane*, m. p. 147°, and *benzenesulphonyl-3 : 5-dichlorobenzenesulphonylmethanesulphonylmethane*, m. p. 208° (becoming blue). $CH_2(SO_2Et)_2$ and

Ph·SO_2Cl give *chlorodi(ethanesulphonyl)methane*, m. p. 96°. *Me* p-*toluenethiosulphonate*, m. p. 58°, and benzenesulphonylacetone afford a *compound*, $C_{11}H_{14}O_3S_2$, m. p. 77°, hydrolysed to a *substance*, $C_9H_{12}O_2S_2$, m. p. 80°, which is oxidised to p-*toluenesulphonylmethanesulphonylmethane*, m. p. 158°.

Halogen (X) in compounds containing the ·SO_2·CX_2·SO_2· group is readily determined by dissolving the compound in warm alkaline sulphite solution and subsequent precipitation as AgX. The method works well with 2 : 2-*dichloro*-, m. p. 233°, and 2-*bromo*-2-*methyl*-, m. p. 248°, -1 : 3-*dithiolan dioxides* and with the *Br_4* derivative, m. p. 205°, of *methyl*-1 : 3 : 5-*trithian* 1 : 3-*dioxide* (from the trithian dioxide and Me_2SO_4 in the cold). H. Burton.

Sodium ethane-αβ-disulphonate. H. J. Backer and P. Terpstra (Rec. trav. chim., 1931, **50**, 1078—1081).—Contrary to various data in the literature this salt exists in only two forms, $+2H_2O$ (prisms or pseudo-octahedra) and $+3H_2O$ (thin plates), crystallographic data for which are given. J. W. Baker.

Determination of organic acids. V. Application of partition method to determination of acetic, propionic, and butyric acids in mixture. O. L. Osburn and C. H. Werkman (Ind. Eng. Chem. [Anal.], 1931, **3**, 264—265).—The amount of each acid in an aq. solution of the mixture is determined from the percentage partition coeffs. (A., 1930, 1161) of the mixture (adjusted to 0·08—0·12*N*) with two different amounts of Pr^{β}_2O. H. Burton.

Ring-chain tautomerism of partly acetylated, polyhydric alcohols. H. Meerwein and H. Sonke (Ber., 1931, **64**, [*B*], 2375—2381; cf. this vol., 206). —The resistance towards alkali and ready hydrolysis by dil. acid of the compound obtained by the action of diazomethane on β-hydroxyethyl trichloroacetate is explained by assuming it to be *Me ethylene trichloro-orthoacetate*, $CCl_3{\cdot}C(OMe)<^{O{\cdot}CH_2}_{O{\cdot}CH_2}$. This view is supported by its non-identity with β-*methoxyethyl trichloroacetate*, b. p. 92—93°/10 mm., m. p. 14·6—14·8°, prepared from CCl_3·COCl and β-methoxyethyl alcohol and readily converted by cold H_2O into CCl_3·CO_2H and glycol Me ether; further, treatment of Me ethylene trichloro-orthoacetate with $Pr^{\alpha}OH$ and HCl affords *Pr^{α} ethylene trichloro-orthoacetate*, b. p. 128—130°/12 mm. The possible tautomerism of β-hydroxyethyl trichloroacetate is thus established, whilst its ready hydrolysis by cold H_2O or dil. NaOH and its conversion by NH_3 into CCl_3·CO·NH_2 and ethylene glycol are evidence of acyclic structure. Similarly, with AcCl it gives smoothly β-*acetoxyethyl trichloroacetate*, b. p. 122°/11 mm., quantitatively converted by cold H_2O or dil. alkali into CCl_3·CO_2H and β-hydroxyethyl acetate and prepared also from CCl_3·COCl and β-hydroxyethyl acetate. With $SOCl_2$ it affords exclusively β-*chloroethyl trichloroacetate*, b. p. 97°/10 mm., prepared also from CCl_3·COCl and ethylene chlorohydrin.

The work of Hibbert and Greig (this vol., 820) is criticised. H. Wren.

Preparation of *n*-decoic acid. C. H. Kao and S. Ma (J.C.S., 1931, 2046—2047).—Bromination of lauryl chloride (by $SOCl_2$ on the acid) and subsequent treatment with the appropriate alcohol afford the following esters of α-bromolauric acid: *Me*, b. p. 135—137°/3 mm.; *Et*, b. p. 144—146°/3 mm.; *Pr^{β}*, b. p. 146—148°/3 mm.; *Pr^{α}*, b. p. 149—151°/3 mm.; *Bu^{β}*, b. p. 152—154°/3 mm.; *Bu^{α}*, b. p. 154—156°/3 mm.; and iso*amyl*, b. p. 158—160°/3 mm. Hydrolysis of these with KOH in EtOH affords Δ^{α}-dodecenoic acid (*amide*, m. p. 112·5—113·5°; p-*toluidide*, m. p. 85—86°), which, when heated with moist KOH at 300°, readily affords *n*-decoic acid in good yield. J. W. Baker.

Oxidation of unsaturated fatty acids. I. Oxidation of highly purified oleic acid by gaseous oxygen with and without catalysts. J. H. Skellon (J.S.C.I., 1931, **50**, 382—386T).—When oleic acid was oxidised at 100° by O_2 without catalyst a tenfold increase in the percentage of "oxidised acids" recorded by earlier workers was obtained. The following were also produced: ικ-dihydroxystearic acid, m. p. 132°, crude nonoic acid, a mixture containing hydroxylated acids and *iso*oleic acid, and traces of HCO_2H and AcOH.

Oxidation of oleic acid at 120° in presence of a trace of "blown" whale oil as catalyst yielded ικ-dihydroxystearic acids of m. p. 132° and 95°, small percentages of azelaic acid and κ-hydroxystearic acid, m. p. 84°, crude hydroxylated acids (equiv. 313—319), a mixture containing *iso*oleic acid, traces of formic, acetic, and oxalic acids, and MeCHO. Rupture of the carbon chain had not occurred in 15 hr.; quant. yields of scission products were not obtained.

Isomerism of linoleic acid. I. G. V. Pigulevski and A. Y. Vasiliev (J. Gen. Chem. Russ., 1931, **1**, 235—239).—Oxidation of Me linoleate gives two isomeric *Me dihydroxylinoleates* in equal quantities: solid, m. p. 32°, and a liquid. These give the corresponding *dihydroxylinoleic acids*, solid, m. p. 78°, and a liquid. Hydrolysis of the solid gives tetrahydroxystearic acid, not given by the liquid isomeride. E. B. Uvarov.

Composition of linseed oil. H. van der Veen (Chem. Umschau, 1931, **38**, 277—279).—A reply to Kaufmann and Keller (cf. this vol., 1034). Purification of the linoleic–linolenic acid mixture through the Li salts is questioned: this method might conceivably separate existing stereoisomerides. E. Lewkowitsch.

Composition of linseed oil. J. van Loon (Chem. Umschau, 1931, **38**, 279—281).—A reply to Kaufmann and Keller (this vol., 1035). The reaction time in the determination of CNS val. may safely be prolonged to 3 days: the linseed oil in question had an abnormally high CNS val. The CNS val. of Et linolenate indicates the probable presence of isomerides of different reactivity. The CNS val. of *Picramnia* fat (containing ε-stearolic acid) increases with the reaction time even with great excess of reagent (cf. B., 1931, 400). E. Lewkowitsch.

Synthesis of fatty acids of high mol. wt. and of their anhydrides. W. Bleyberg and H. Ulrich (Ber., 1931, **64**, [*B*], 2504—2513).—The prep. of fatty acids along the lines $R{\cdot}CO_2H \longrightarrow R{\cdot}CO_2Et \longrightarrow$

$R·CH_2·OH \longrightarrow R·CH_2I \longrightarrow R·CH_2·CH(CO_2Et)_2 \longrightarrow R·CH_2·CH(CO_2H)_2 \longrightarrow R·CH_2·CH_2·CO_2H$ is dissected. The difficulties in the reduction of ester to alcohol by Na and EtOH, due to hydrolysis of the ester, are overcome by dissolving the ester in light petroleum, b. p. 30—50° or 70—80°, containing an excess of Na wire and gradually adding the necessary amount of EtOH. After prolonged boiling, excess of 96% EtOH is added and the solution is boiled to hydrolyse residual ester. Bimol. products [glycols, acyloins, or diketones) are produced in only minor amount; the alcohols are therefore best purified by distillation in high vac. Difficulties encountered in applying this procedure to the higher esters (*e.g.*, Et behenate) are avoided by replacing EtOH by BuOH. In the malonic ester condensation EtOH is advantageously replaced by BuOH, since Et sodiomalonate dissolves readily in the last-named substance and the reaction with the sluggish iodides can be effected at a higher temp. Formation of ketones during the decomp. of the substituted malonic acids is avoided by conducting the operation at 140—150° at first in the vac. of a water pump and finally in high vac. and subsequent immediate distillation of the fatty acid in high vac. The transition from stearic to *n*-eicosoic acid is thus effected with an over-all yield of 77·4%. It appears characteristic of individual acids that they solidify from the molten state with a coarsely cryst. surface and loose texture, whereas mixtures of them have a microcryst. structure and are comparatively compact. Anhydrisation of the acids is effected by repeated treatment with Ac_2O and intermediate distillation, finally in high vac., of AcOH and excess of Ac_2O, after which the anhydrides are crystallised from light petroleum. The following data are recorded: arachidic acid, m. p. 76·1—76·3° (*anhydride*, m. p. 77·5—77·7°); behenic acid, m. p. 80·3—80·7° (*anhydride*, m. p. 81·7—81·9°; *Et* ester, m. p. 48·0—48·5°; *behenyl alcohol*, m. p. 70·0—70·5°, and *iodide*, m. p. 47·5—48·0°); lignoceric acid, m. p. 84·5—84·9° (*anhydride*, m. p. 86·0—86·3°; *Et* ester, m. p. 54·5—55·0°; *lignoceryl alcohol*, m. p. 75·2—75·5°, and *iodide*, m. p. 53·4—53·8°); cerotic acid, m. p. 87·7—87·9° (*anhydride*, m. p. 89·3—895°; *Et* ester, m. p. 59·5—59·8°; *cerotyl alcohol*, m. p. 79·3—79·6°, and *iodide*, m. p. 58·2—58·5°); *eicosanoctoic acid*, m. p. 90·3—90·5° (*anhydride*, m. p. 92·7—92·9°; *Et* ester, m. p. 59·5—59·8°; *eicosanoctyl alcohol*, m. p. 79·3—79·6°, and *iodide*, m. p. 62·8—63·2°); melissic acid, m. p. 91·9—92·1°.

H. WREN.

Constituents of petroleum. I. J. VON BRAUN [with R. DEUSER, A. HEYMONS, L. MANNES, W. MAY, M. REUTER, E. ANTON, W. KELLER, E. FRIEHMELT, and O. SCHORNING] (Annalen, 1931, **490**, 100—179).—The naphthenic acids from various sources are separated into definite fractions by lengthy processes of fractional distillation of them and their esters; complete separation from accompanying hydrocarbons and phenols is difficult. They are best characterised by conversion into the amine with 1 C less by action of dry N_3H in H_2SO_4 which gives yields of the order of 90%, whereas the yields by Hofmann's method are very poor in this field; the amines are more readily separated than the acids by distillation, and are finally purified by crystallisation of their oxalates, by which means products of definite empirical composition, nevertheless consisting of mixtures of isomerides, are obtained. The following tests of structure are applied to the acids: (1) chlorination of their ethylamides (cf. A., 1927, 547) whereby a distinction is made between primary, sec., and tert. bound CO_2H groups; attempts at oxidation of the Cl_2-acids to the next lower failed; (2) bromination by the Hell–Volhard–Zelinski method, removal of HBr from the bromo-ester by a tert.-amine, isomerisation of the αβ- to the βγ-acid and lactonisation of the latter by conc. H_2SO_4, and oxidation of the lactone; formation of succinic acid indicates the structure $R·[CH_2]_3·CO_2H$ in the original acid; (3) the alcohol produced by Na–EtOH reduction of the Et ester is converted into its bromide, which is combined with NMe_3, and the corresponding base distilled with conc. aq. KOH, and the olefine produced ozonised to the aldehyde, which on oxidation gives the next lower homologue of the original acid; (4) the amine (N_3H) is converted into its methiodide and the derived quaternary base treated as in (3); a ketone is thus produced from acids of the type $R{:}CH·CH_2·CO_2H$, and an acid from the type $R'·CH_2·CH_2·CO_2H$.

The modified Hofmann degradation used in (3) and (4) lessens the extremely marked tendency of the higher ammonium hydroxides to split off MeOH and regenerate the original amine (cf. A., 1927, 650); nevertheless this is still the principal reaction in many cases, and the process of forming the quaternary base and submitting it to decomp. often needs to be repeated more than once. This may lead to the fractionation of isomeric mixtures; thus the fraction $C_9H_{16}O_2$, b. p. 139—141°/12 mm., from Rumanian petroleum was converted by method (3) into the acid $C_8H_{14}O_2$, which was then converted into the amine (N_3H), the metho-hydroxide of which was distilled with KOH; the fraction that resisted decomp. appeared to be a chemical individual $C_5H_{10}{:}CH·CH_2·NMe_2$, b. p. 163° (*picrate*, m. p. 138—141°, sinters 136°; *methiodide*, m. p. 213—215°).

Various qualities of distilled, and one of crude, Rumanian petroleum, and also oils from California (distilled), Germany (crude), and Galicia (distilled) were examined. The naphthenic acids from all these sources had the same general characteristics; they belonged to the aliphatic (paraffin) class up to C_{6-7}, monocyclic from C_7 to C_{12}, and to the dicyclic series above C_{12} (at least to C_{22}, there being no definite evidence of the occurrence of more highly condensed systems). Acids of approx. the same empirical composition occur in corresponding fractions of the products from these widely differing sources. Among the distilled oils the Galician oil alone formed an exception to the above generalisations, and contained only aliphatic and monocyclic (above C_{11}) acids. In crude Rumanian oil the lower members, found in the distilled oils, are absent and more sec.-acids are present, suggesting that the lower members are the products of pyrogenic decomp. during refining.

From the fraction $C_{10}H_{18}O_2$, b. p. 148—155°/12 mm., from Rumanian oil, and corresponding fractions from Galician and Californian oils, a *ketone*, $C_8H_{14}O$,

b. p. 172—174° (*semicarbazone*, m. p. 163°; *di-p-nitrobenzylidene* derivative, m. p. 188—190°), was isolated by method (4); acids were also present in the first two oils that gave succinic acid by method (2). The ketone is concluded to be 3 : 3 : 4-*trimethyl*-cyclo*pentanone*, since, like all the other ketones isolated, it gave no evidence of the presence of a COMe group, and it is different from all the possible *cyclo*pentanone isomerides (cf. this vol., 1417). A mixture of monocyclic, $C_{11}H_{21}{\cdot}NH_2$, and dicyclic, $C_{13}H_{23}{\cdot}NH_2$, amines was obtained from the acids, b. p. 183—200°/12 mm., from the heavier Rumanian oils by action of N_3H; by method (4) the former is converted into a *ketone*, $C_{10}H_{18}O$, b. p. 201—204° (*semicarbazone*, m. p. 162°), identical with that from a similar fraction (b. p. 162—173°/16 mm.) from Californian oil, and the latter into a dicyclic *ketone*, $C_{11}H_{18}O$, b. p. 230—234° (*semicarbazone*, m. p. 169°; *oxime*, b. p. 155°/14 mm.). The next higher fraction from Californian oil gives by similar methods the *ketone*, $C_{12}H_{20}O$, b. p. 255—260° (*semicarbazone*, m. p. 162°).

Cyclic ureides, apparently individual substances, were isolated from two fractions by reduction to the alcohol, conversion into the bromide, condensation of the bromide with Et sodiomalonate, and treatment of the resulting ester with carbamide and NaOEt in EtOH. The *ureide*, $C_{14}H_{22}O_3N_2$, m. p. 230° [β-*bromo-allyl* derivative, m. p. 144—154° (from crude ureide)], from the fraction b. p. 148—155°/12 mm., and the *ureide*, m. p. 220°, from the fraction b. p. 190—210°/12 mm., both of Rumanian origin, are described. Campholic and fencholic acids readily give the corresponding amines (NH_2 replaces CO_2H) on treatment in conc. H_2SO_4 with N_3H in C_6H_6 or $CHCl_3$. The Cl_2-derivative, m. p. 47—48°, of *stearmethyl-amide*, m. p. 77—79°, b. p. 185°/0·2 mm., is hydrolysed by 90% aq. $PhSO_3H$ at 140—150° to dichlorostearic acid (*anilide*, m. p. 41—45°), but attempts to oxidise this to margaric acid by a variety of agents failed. H. A. PIGGOTT.

Structure of enol-acetates and the corresponding vinylamines. L. J. ROLL and R. ADAMS.—See this vol., 1419.

Lævulic acid. III. Hydrogenation of alkyl esters in presence of platinum catalyst. R. W. THOMAS, H. A. SCHUETTE, and M. A. COWLEY (J. Amer. Chem. Soc., 1931, **53**, 3861—3864).—The rate of catalytic reduction (Adams) of alkyl (Me, Et, Pr, Pr^β, Bu, Bu^β) lævulates in absence or presence of Et_2O at 22—24° varies inversely with the size of the alkyl group; the Pr (Bu) ester is reduced more rapidly than the Pr^β (Bu^β) ester. Distillation of Pr γ-hydroxy-*n*-valerate under atm. pressure gives *n*-valerolactone and PrOH, and a similar decomp. occurs when the Me and Et esters are distilled repeatedly at 2·5 mm. A little Et valerate is formed during the reduction of Et lævulate. H. BURTON.

Alkyl oxalates and oxamates. P. P. T. SAH and S. CHIEN (J. Amer. Chem. Soc., 1931, **53**, 3901—3903).—Me, Et, Pr, b. p. 214—215°, Pr^β, b. p. 193—194°, Bu, b. p. 247—249°, and Bu^β, b. p. 229—231°, oxalates (convenient method of prep. given) are converted by aq. NH_3 (*d* 0·9; 1 mol.) in EtOH into Me, m. p. 122—123°, Et, m. p. 114—115°, Pr, m. p. 90—92°, Pr^β, m. p. 86—87°, *Bu*, m. p. 82—84°, and Bu^β, m. p. 75—76°, oxamates, respectively. H. BURTON.

Alkyl derivatives of ethyl malonate and ethyl cyanoacetate. G. R. CLEMO and C. R. S. TENNISWOOD (J.C.S., 1931, 2549—2551).—An improved prep. for β-chloroethyl toluene-*p*-sulphonate is described. Action of β-cyanoethyl toluene-*p*-sulphonate on Et sodiomalonate gives (*a*) *Et* β-*cyano-ethylmalonate*, b. p. 165°/18 mm., 135°/0·2 mm. (yield 63%), converted by HCl in EtOH into Et propane-αγγ-tricarboxylate; or (*b*) *Et di*-(β-*cyano-ethyl*)*malonate*, m. p. 61·5°, b. p. 200—205°/0·2 mm. (yield 80%), converted by HCl in EtOH into Et pentane-αγγε-tetracarboxylate, and by KOH in EtOH into pentane-αγγε-tetracarboxylic acid, m. p. 184° (decomp.) (cf. J.C.S., 1896, **69**, 1509). A. A. LEVI.

Properties of conjugated compounds. XII. Addition of esters to butadiene esters and ketones: effect of constitution on the αβ,αδ-ratio. E. H. FARMER and T. N. MEHTA (J.C.S., 1931, 1904—1913).—The ratio αβ/αδ-addition of esters to various butadiene derivatives in presence of traces of NaOR has been determined either (*a*) by catalytic reduction and separation of the dibasic acids formed, or (*b*) by separation of the products of ozonolysis. The figures in brackets give the % of αβ-addition in each case. The additive products of Me malonate and Me sorbate (A., 1930, 1163) are now found to yield tricarballylic acid on ozonolysis, corresponding with 9% of the αβ-product. Me malonate and Me $\Delta^{\alpha\gamma}$-*n*-pentadienyl ketone afford a mixture, b. p. 170—175°/18 mm., of *Me* β-*acetonyl*-Δ^{γ}-*pentene*-αα-*dicarboxylate* [29% as β-propylglutaric acid by (*a*); 27% as tricarballylic acid by (*b*)] and *Me* ε-*acetyl*-β-*methyl*-Δ^{γ}-*pentene*-αα-*dicarboxylate*. Addition of Et malonate to Et β-methylsorbate (improved prep.) affords a mixture, b. p. 170—175°/10 mm., of *Et* β-*methyl*-Δ^{γ}-*hexenoate*-β-*malonate* [>7% by (*b*)] and *Et* βδ-*dimethyl*-Δ^{β}-*pentene*-αεε-*tricarboxylate*, whilst Et cyanoacetate and Et γ-methylsorbate give a product, b. p. 190—195°/18 mm. [70% by (*b*); 74·5% by hydrolysis and subsequent ozonolysis]. J. W. BAKER.

Conjugated compounds. XIII. Michael reaction and manner of formation of saturated double-additive products. E. H. FARMER and T. N. MEHTA (J.C.S., 1931, 2561—2568).—The possible modes of formation of saturated additive compounds from butadienoid esters and, *e.g.*, Et malonate are discussed. Crotonaldehyde (1 mol.) and Et malonate (3 mols.) in presence of EtOH–NaOEt (1 mol.) give a product which after hydrolysis with 35% HCl and re-esterification affords *Et* 3-*methyl*cyclo*hexanone*-5-*acetate* (I), b. p. 140°/11 mm. (*semicarbazone*, m. p. 152°), and *Et* β-*methylpimelate*-β′-*acetate* (II), b. p. 187—188°/11 mm. (free *acid*, m. p. 130°). Dieckmann condensation of (II) gives *Et* 3-*methyl*cyclo*hexanone*-6-*carboxylate*-5-*acetate*, b. p. 170—172°/11 mm. (*phenylhydrazone*, m. p. 111°), hydrolysed (with loss of the 6-CO_2H group) to 3-*methyl*cyclo*hexanone*-5-*acetic acid*. b. p. 185°/9 mm., m. p. 77° (*Ag* salt; *semicarbazone*, m. p. 218°), and

oxidised by 3% $KMnO_4$ to oxalic and β-methylglutaric acids. H. BURTON.

Thioketonic esters. I. Synthesis of ethyl thioacetoacetate and its derivatives. S. K. MITRA (J. Indian Chem. Soc., 1931, 8, 471—474).—Et β-chlorocrotonate (*cis* or *trans* form, or a mixture of both) with KSH, first at 0° and then under reflux, gives *Et thioacetoacetate* (I), orange, b. p. 75°/15 mm., which, since it decolorises I in EtOH, contains some of the enolic form, *Et β-thiolcrotonate.* With 10% H_2SO_4, KOH, or NaOH (I) yields $COMe_2$, H_2S, and CO_2. When boiled with 1 mol. of KOH in EtOH (I) gives a mixture of K thioacetoacetate and acetoacetate together with K_2S. With Na in Et_2O, but not with NaOEt in EtOH, (I) gives the *Na* salt, a hygroscopic powder; with $NHPh{\cdot}NH_2$, H_2S and a mixture of phenylmethylpyrazolone and the *substance* $\begin{matrix}NPh{\cdot}CO\\N{=}CMe\end{matrix}\!\!>\!C{:}C\!<\!\!\begin{matrix}CH_2{\cdot}NPh\\CMe{:}N\end{matrix}$ (II) are formed, the proportion of the latter increasing with the amount of $NHPh{\cdot}NH_2$ used. *p*-Sulpho- and *p*-nitro-phenylmethylpyrazolone were similarly prepared.

R. S. CAHN.

Mechanism of the Cannizzaro reaction with formaldehyde. H. S. FRY, J. J. UBER, and J. W. PRICE (Rec. trav. chim., 1931, 50, 1060—1065).—The view of Birstein and Labanov (A., 1927, 319) that the conversion of CH_2O into HCO_2Na and MeOH by the Cannizzaro reaction is represented by consecutive reactions (*a*) $CH_2O+NaOH\longrightarrow HCO_2Na+H_2$ and (*b*) $CH_2O+H_2\longrightarrow MeOH$ has been confirmed stoicheiometrically by addition to the reaction mixture of $CuSO_4$, the reduction of which to Cu competes with reaction (*b*). Determination of the free H_2 liberated (x), the H_2 equiv. (y) to the reduced Cu, and that (z) equiv. to the MeOH formed proves that, within experimental error, the sum $x+y+z$=the total quantity of H_2 formed by reaction (*a*), as ascertained by determination of the amount of HCO_2Na produced. The same data show that 76—83% of the initial CH_2O reacted in conformity with equation (*a*) and the remainder in conformity with (*b*), the sum of these quantities being equal to the whole of the CH_2O used.

J. W. BAKER.

Formaldehyde and its polymerides. F. WALKER (Ind. Eng. Chem., 1931, 23, 1220—1222).—A review.

Constitution of artificial resins. I. Condensation products from thiocarbamide, formaldehyde, and cuprous chloride. G. WALTER and K. OESTERREICH (Kolloidchem. Beih., 1931, 34, 115—162).—Yellow, viscous solutions with identical properties are obtained by interaction of $[CuThi_3]Cl$ $[Thi{=}CS(NH_2)_2]$ with CH_2O (6 mols.), or of equiv. amounts of CuCl, $CS(NH_2)_2$, and CH_2O, or of CuCl and mono- or *s*-di-(hydroxymethyl)thiocarbamide in H_2O. The presence of the CH_2 group (presumably in the combination $\dot{:}N{\cdot}CH_2{\cdot}N\dot{:}$) is proved by a Herzig–Meyer determination. Evaporation of the first yields a resin of the approx. composition $[CuThi_3]Cl,2CH_2O$, and flocculation with KCl of the second gives a ppt. of $[CuThi(H_2O)_2]Cl$, in marked contrast to the behaviour of an untreated solution of $[CuThi_3]Cl$. The third method, using cold freshly-prepared solutions, gives a final ratio of $1Cu : 3CS(NH{\cdot}CH_2{\cdot}OH)_2$, and polymerisation, *e.g.*, by heating, leads to a decrease of Cu in the ppt. formed with KCl. Identical ppts. are obtained from both mono- and di-hydroxymethyl derivatives after CuCl treatment. These relations are explained on the assumption that polymerisation occurs with the formation of cyclic structures (annexed formula) in to the normal chain polymerides, such structures being most probably through Cu into co-ordinated complexes with thiocarbamide.

$$\begin{matrix}NH{\cdot}CH_2{\cdot}N{\cdot}CH_2{\cdot}NH\\CS\qquad CS\qquad CS\\NH{\cdot}CH_2{\cdot}N{\cdot}CH_2{\cdot}NH\end{matrix}$$

The identity of the products from mono- and di-(hydroxymethyl)thiocarbamides is readily explained only by the initial formation of dicyclic products, and this is supported by analysis of the ppts. if it is assumed that Cu can only be linked to sec.-N.

Cryoscopic measurements of aged solutions of di-(hydroxymethyl)thiocarbamide indicate decomp. into simpler mols. (unidentified), and similar measurements after CuCl treatment suggest that polymerisation under mild conditions leads merely to an increase in the no. of dicyclic polymerides. More complex resins (tetracyclic ?) are produced with loss of CH_2O and H_2O by more prolonged heating. $HAuCl_4$, $HgCl_2$, and $Pb(NO_3)_2$ are without the action of Cu salts. Measurements of the conductivity of the various " resin " solutions and flocculation by various electrolytes of these and of $[CuThi_3]Cl$ are appended. In accordance with previous conductivity measurements, $[CuThi_3]Cl$ behaves as a colloid in H_2O.

H. A. PIGGOTT.

Action of sulphuric acid on aldehyde cyanohydrins. J. VERHULST (Bull. Soc. chim. Belg., 1931, 40, 475—496).—The compounds formed by the action of conc. H_2SO_4 on the cyanohydrins of $COMe_2$, COMeEt, $COEt_2$, and $COPr_2$ are acids of the type $CR_2(CO{\cdot}NH_2){\cdot}OSO_3H$ [*Na* salts (all $+1H_2O$)] and not $OH{\cdot}CR_2{\cdot}C({:}NH){\cdot}OSO_3H$ as previously described (this vol., 471). The cyanohydrins of CH_2O, MeCHO, EtCHO, PrCHO, $Pr^{\beta}CHO$, BuCHO, and $Bu^{\beta}CHO$ are similarly converted into the acids $CHR{\cdot}(CO{\cdot}NH_2){\cdot}OSO_3H$ [*Na* salts (all $+1H_2O$) (crystallographic data given in many cases)], which are hydrolysed much less readily both by $0{\cdot}2N$-HCl (with formation of H_2SO_4) and -NaOH (with production, in most cases, of mainly the salt $CO_2Na{\cdot}CHR{\cdot}OSO_3Na$) than those from the ketone cyanohydrins. Heptaldehyde cyanohydrin is converted directly by H_2SO_4 into α-hydroxyoctoamide. H. BURTON.

[Attempts to prepare] ketones and related products from paraffin hydrocarbons. J. F. MESMER and R. A. BAXTER (Colorado Sch. Mines Mag., 1931, 21, No. 6, 9—10).—In unsuccessful experiments CO_2 and CH_4 were passed over $ZnCO_3$ or $Zn(OAc)_2$ at 300° and 80 lb. pressure.

CHEMICAL ABSTRACTS.

Formation of unsaturated ketones from substituted aminomethylene ketones. E. BENARY (Ber., 1931, 64, [*B*], 2543—2545).—Addition of Me β-dimethylaminovinyl ketone in Et_2O to MgPhBr results mainly in the production of styryl Me ketone.

Similarly, Me β-dimethylamino-α-methylvinyl ketone and MgMeI or MgEtBr yield, respectively, Me α-methyl-Δ^{α}-propenyl ketone, b. p. 137°, and *Me α-methyl-Δ^{α}-butenyl ketone*, b. p. 55—60°/14 mm., obtained also from β-piperidino-α-methylvinyl Me ketone. β-Diethylaminovinyl Pr^{α} ketone and MgEtBr give *Pr^{α} Δ^{α}-butenyl ketone*, b. p. 68·72°/25 mm. Ph β-dimethylaminovinyl ketone is transformed by MgPhBr into PhOH, Ph_2, and Ph styryl ketone and by MgEtBr into *Ph Δ^{α}-butenyl ketone*, b. p. 250—252°/atm., 130—131°/22 mm. H. WREN.

Synthesis of *n*-propyl *n*-amyl ketone by Karrer and co-workers. S. A. BRYANT and G. R. CLEMO (J.C.S., 1931, 2080—2082).—Contrary to Karrer and others (A., 1929, 200) the ketone obtained by Bouveault and Locquin (A., 1905, i, 18) by hydrolysis of Et ethyl-*n*-hexoylacetate is Pr^{α} *n*-amyl ketone, the semicarbazone, m. p. 73—74°, of which is not depressed by that (also raised to m. p. 72° by repeated crystallisation) of the ketone prepared by Karrer's method (*loc. cit.*), but is depressed by the semicarbazone of Pr^{β} *n*-amyl ketone. Karrer's ketone is contaminated with Et *n*-hexoate, which is removed by treatment with KOH in MeOH. Recrystallisation of the semicarbazone, m. p. 65—66°, of the thus purified ketone (correct analysis) raises it to m. p. 73°, but this derivative now gives low C vals. on analysis. No such anomalies are observed with the p-*nitrophenylhydrazone*, m. p. 84—85°, which should be used in confirming the structure of the ketone obtained from lupinine. J. W. BAKER.

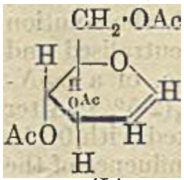
Ring structure of normal methylriboside. P. A. LEVENE and R. S. TIPSON (J. Biol. Chem., 1931, **93**, 623—630).—Methylriboside (I) (this vol., 938) is methylated (Me_2SO_4 and NaOH in $COMe_2$ followed by MeI and Ag_2O) to *trimethylmethylriboside*, b. p. 54°/0·05 mm., $[\alpha]_D^{24}$ −35·0° in H_2O, hydrolysed by dil. HCl to 2 : 3 : 4-*trimethylribose* (II), m. p. 85—86°, $[\alpha]_D^{27}$ (in H_2O) −51·7⟶−40·0°. Oxidation of (II) with Br–H_2O affords *trimethylribonolactone*, b. p. 93—95°/0·05 mm., $[\alpha]^{27}$ +69·3° in $CHCl_3$, whilst oxidation with HNO_3 (*d* 1·42) and subsequent esterification gives Me *i*-trimethoxyglutarate. (I) and its derivatives are, therefore, of the pyranose type.
H. BURTON.

"Active glucose"; concentration and reaction with mild oxidants. J. M. ORT (Proc. Staff Meetings Mayo Clinic, 1931, **6**, 295—296).—When "active glucose" has been destroyed by an oxidant, more of the active reductant begins to form at once, immediately reduces the excess of oxidant, and then accumulates until the concentration reaches the equilibrium vals. After zero time when the last trace of oxidant has been reduced the reduction potential P at any time T, the equilibrium concentration X_E, the rate of formation of active glucose R, the equilibrium potential P', and the potential at unit concentration of active glucose, P_0, are related by the expression $(P_0 - P)/(P_0 - P') = 1 + [\log(e^{TR/X_E} - 1) - \log e^{TR/X_E}/\log X_E]$. Approx. the same amount of active glucose (10^{-5} g.-equiv. per 60 g. of dextrose) is present at all vals. from 7 to 10. CHEMICAL ABSTRACTS.

Methylglucose of Pacsu. R. SCHINLE (Ber., 1931, **64**, [*B*], 2361—2363).—The methylglucose, m. p. 157° after slight softening at 150°, $[\alpha]^{20}$ +23·5° to +65·3° in H_2O, obtained by Pacsu (A., 1925, i, 1242) (improved prep.) is shown by direct comparison and by the identity of its phenylhydrazone, m. p. 177°, and phenylosazone, m. p. 205° when rapidly heated, to be 2-methylglucose (cf. Brigl and Schinle, this vol., 71; Levene and others, *ibid.*, 825).
H. WREN.

Syntheses of sugars. X. Preparation of 2 : 3 : 6-triacetyl-β-methyl-*d*-glucoside and its application to the synthesis of cellobiose derivatives. B. HELFERICH and H. BREDERECK (Ber., 1931, **64**, [*B*], 2411—2414).—β-Methyl-*d*-glucoside 2 : 3 : 6-triacetate is isolated by treating the mixture of acetates obtained by partial acyl migration from the 2 : 3 : 4-compound with CPh_3Cl (cf. A., 1930, 1411) whereby the desired compound is unchanged and can be separated from the other products by virtue of its solubility in H_2O. It condenses with acetobromoglucose in presence of Ag_2CO_3, $CaCl_2$, I, and $CHCl_3$ to β-methylcellobioside hepta-acetate (identified by microscopic m. p. and mixed m. p.) Glucose 1 : 2 : 3 : 6-tetra-acetate and acetobromoglucose yield cellobiose octa-acetate, and 4-methylglucose is obtained by methylation of β-methylglucoside 2 : 3 : 6-triacetate. H. WREN.

Structure of glucal. E. L. HIRST and C. S. WOOLVIN (J.C.S., 1931, 1131—1137).—Triacetylglucal (I) behaves normally (cf. A., 1930, 1411) with BzO_2H giving a mixture of dextrose and mannose (after deacetylation), isolated as osazone and phenylhydrazone, respectively. Simultaneous deacetylation and methylation of (I) with Me_2SO_4, and 30% NaOH in $COMe_2$ at 47°, followed by MeI and Ag_2O, gives *trimethylglucal*, b. p. 45°/0·03 mm., $[\alpha]_D^{18}$ +19·6° in H_2O (probably contaminated with a ψ-glucal derivative). This is oxidised by BzO_2H in H_2O to a trimethylglucose (further methylated to 2 : 3 : 4 : 6-tetramethylglucopyranose), and is converted by $2N$-H_2SO_4 into 3 : 4 : 6-trimethyl-2-deoxyglucose (II) (this vol., 71). These reactions prove the presence of a pyranose ring in glucal (as I), and that no migration of Ac groups occurs in the prep. of I by reduction of acetobromoglucopyranose. Oxidation of (II) with Br in H_2O at 35—40° affords 3 : 4 : 6-trimethyl-2-deoxygluconic acid (*phenylhydrazide*, m. p. 125°) as its lactone, the rate of hydrolysis of which in H_2O at 19° is the same as that of tetramethyl-δ-mannonolactone (30% of lactone at equilibrium). J. W. BAKER.



(I)

Hydrogenation of kojic acid and its relationship to the products of dismutation of the sugars. K. MAURER (Ber., 1931, **64**, [*B*], 2358—2360).—Hydroxyglucal tetra-acetate is treated with Cl_2 in anhyd. Et_2O until the yellow colour persists, the solution is rapidly evaporated in vac., and the product, dissolved in Et_2O, is treated with $NaHCO_3$. Acetylation with Ac_2O and pyridine followed by hydrolysis with NH_3–EtOH affords kojic acid (5-hydroxy-2-hydroxymethyl-4-pyrone) in good yield. Tetrahydrogenation of kojic acid in presence of colloidal Pd, followed by the action of $NHPh{\cdot}NH_2$, leads to a

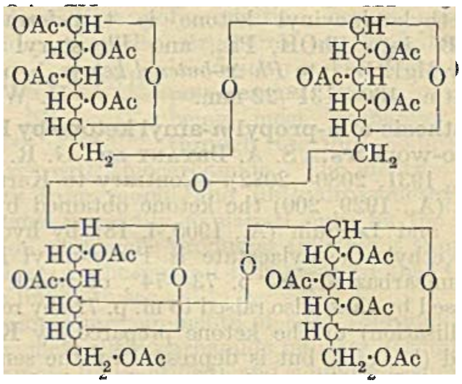
phenylosazone $C_{18}H_{22}O_2N_4$, m. p. 169°, which is the racemic form of the phenylosazone derived by Bergmann and Zervas (this vol., 939) from hydroxyglucal tetra-acetate. H. WREN.

Effect of a 2-*p*-toluenesulphonyl group on the reactivity of the halogen atom of a glucosidyl halide. T. M. REYNOLDS (J.C.S., 1931, 2626—2630).—3 : 4 : 6-Triacetyl-β-glucosidyl chloride and p-Me·C_6H_4·SO_2Cl in presence of pyridine and $CHCl_3$ give 2-p-*toluenesulphonyl*-3 : 4 : 6-*triacetyl-α-glucosidyl chloride* (I), m. p. 121—122°, $[\alpha]_D^{16.5}$ +134·8° in $CHCl_3$, the Cl atom of which is comparatively inactive. (I) is unaffected by Ag_2O or Ag_2CO_3 in cold MeOH, does not react with MeOH at 20—24°, but is converted by $AgNO_3$ and pyridine in boiling MeOH into 2-p-*toluenesulphonyl*-3 : 4 : 6-*triacetyl-β-methylglucoside*, m. p. 157—157·5°, $[\alpha]^{24}$ +3·4° in $CHCl_3$. α- and β-Glucosidyl halides when dissolved in pyridine show similar changes in rotation as in MeOH (cf. A., 1928, 873; 1929, 1167). H. BURTON.

Iodometric determination of lævulose. J. FIEHE and W. KORDATZKI (Z. Unters. Lebensm., 1931, **62**, 516—522).—Auerbach and Bodländer's method (A., 1924, ii, 127) may be used for the determination, by difference, of dextrose+lævulose if the iodometric determination is applied before and after destruction of the lævulose by heating 25 c.c. of 1% solution with 10 c.c. of 5*N*-HCl in boiling H_2O for 2·5 hr., 27 c.c. of 5*N*-NaOH then being added, the solution diluted to 100 c.c., and 20—40 c.c. neutralised and mixed with 50 c.c. of *N*-I and 133 c.c. of a 0·5*N*-mixture of $NaHCO_3$ (97·5%) and Na_2CO_3 (2·5%). After 2 hr. in the dark the residual I is titrated with 0·1*N*-$Na_2S_2O_3$. Under these conditions the influence of the decomp. products of the lævulose (humic and lævulic acids, HCO_2H, etc.) is minimised. In presence of 0·1*N*-NaOH the amount of I consumed may be high by >1 c.c. J. GRANT.

Action of perbenzoic acid on substituted glucals. II. P. A. LEVENE and R. S. TIPSON (J. Biol. Chem., 1931, **93**, 631—644).—Bromotetra-acetylgalactose, Zn dust, and 50% AcOH at 0° give *triacetylgalactal* (I), b. p. 134°/0·01 mm., m. p. 30°, $[\alpha]_D^{23}$ −12·4° in $CHCl_3$, converted by BzO_2H in $CHCl_3$ into 1-*benzoyl*-3 : 4 : 6-*triacetylgalactose*, m. p. 189°, $[\alpha]_D^{25}$ +24·0° in $CHCl_3$. This is acetylated by Ac_2O in pyridine at 0° to 1-*benzoyl*-2 : 3 : 4 : 6-*tetra-acetylgalactose*, m. p. 122°, $[\alpha]_D^{23}$ −2·98° in $CHCl_3$, also prepared (with $[\alpha]^{23}$ ±0·15° in $CHCl_3$) from AgOBz and bromotetra-acetylgalactose. Hydrolysis of (I) with $Ba(OH)_2$ in H_2O, or, better, with $Ba(OMe)_2$ in MeOH, gives *galactal* (*talal*), m. p. 100°, which with BzO_2H in H_2O–EtOAc gives mainly talose and a little galactose (p-*bromophenylhydrazone*, m. p. 168—169°). The C_3–OH group in "glucals" appears to have a directive influence since the major product always contains C_2– and C_3–OH groups *cis* to one another; with C_3–OMe or –OAc, *trans* addition of C_2–OH occurs. Various methods of prep. and interconversion of some of the rarer sugars (*e.g.*, gulose, idose, altrose) are predicted. H. BURTON.

Action of mercury salts on acetohalogeno-sugars. VIII. Synthesis of 1-β-methyl-6′-β-cellobiosidogentiobiose trideca-acetate. G. ZEMPLÉN and A. GERECS (Ber., 1931, **64**, [*B*], 2458—2461; cf. this vol., 716).—6-β-Cellobiosidoglucose acetate is converted by a 50% excess of 1-β-methylglucose triacetate in presence of $Hg(OAc)_2$ and boiling C_6H_6 into 1-β-*methyl*-6′-β-*cellobiosidogentiobiose trideca-acetate* (I), m. p. 236—237°, $[\alpha]_D^{19}$ −16·35° in $CHCl_3$.



(I.)

Hydrolysis with NaOMe yields a colourless, non-cryst. *powder*, m. p. 100—110° after softening at 70°, $[\alpha]_D^{21}$ −30·34° in H_2O. If only a 10% excess of the glucoside is employed, 1-β-*methyl*-6′-α-*cellobiosidogentiobiose trideca-acetate* is produced in considerable quantity, but it could not be isolated. H. WREN.

Behaviour of stachyose when heated in glycerol. S. MURAKAMI (Acta Phytochim., 1931, **5**, 267—270). Stachyose remains unchanged after heating for 2 hr. at 90—95° or 6 hr. at 140°. F. R. SHAW.

Constitution of myricitrin. S. HATTORI and K. HAYASHI (Acta Phytochim., 1931, **5**, 213—218).—Methylation of myricitrin with diazomethane and hydrolysis with 2% H_2SO_4 affords myricetin 5 : 7 : 3′ : 4′ : 5′-pentamethyl ether (I); the conclusion is reached that the rhamnose residue in the glucoside is in the 3-position [Perkin (J.C.S., 1902, **81**, 208) gives the 4′-position)]. Similarly, methylation with Me_2SO_4 and alkali in an atm. of H_2 results in a Me_6 derivative, hydrolysed to (I). F. R. SHAW.

Glucosides. IV. Aesculin. A. K. MACBETH (J.C.S., 1931, 1288—1290).—Aesculin is converted either by KOH and MeI in MeOH or by diazomethane in Et_2O into 7-*O*-methylaesculin, hydrolysed by 2% H_2SO_4 to methylaesculetin. Repeated and prolonged methylation of methylaesculin with MeI and Ag_2O affords pentamethylaesculin, which could not be crystallised, but is hydrolysed by 1% HCl in MeOH to tetramethylglucopyranose. In support of Head and Robertson's conclusions (this vol., 73), aesculin is 6-β-glucosidoxy-7-hydroxycoumarin, the sugar being a pyranose form. J. W. BAKER.

Synthesis of glucosides. VIII. Synthesis of monotropitoside (gaultherin). A. ROBERTSON and R. B. WATERS (J.C.S., 1931, 1881—1888).—Me salicylate condenses with *O*-tetra-acetyl-α-glucosidyl bromide in the presence of Ag_2O and quinoline to form its *O*-tetra-acetyl-β-glucoside, m. p. 158—160°, $[\alpha]_{5461}$ −48·35° in $COMe_2$, hydrolysed by NH_3 in MeOH at 0° to the β-glucoside, m. p. 196—197°, $[\alpha]_{5461}^{21}$ −68·83° in H_2O (probably identical with the compound, m. p. 105°, of Karrer and Weidmann, A.,

1920, i, 395). This with CPh_3Cl in dry pyridine gives the 6-*triphenylmethyl ether*, m. p. 149°, $[\alpha]_{5461}^{20}$ −5·14° in $COMe_2$, the 2 : 3 : 4-Ac_3 derivative, m. p. 125°, $[\alpha]_{5461}$ −34·84° in $COMe_2$, of which is hydrolysed by HBr in AcOH to the 2 : 3 : 4-O-*triacetyl*-β-*glucoside* of Me salicylate, m. p. 152—153°, $[\alpha]_{5461}^{20}$ −50·87° in Me_2CO. This condenses with *O*-triacetylxylosidyl bromide in the presence of Ag_2O in C_6H_6 at 33—35° (poor yield in $CHCl_3$) to *monotropitoside hexa-acetate* $o\text{-}CO_2Me\cdot C_6H_4\cdot O\cdot CH{<}\underset{\overline{\qquad\quad O\qquad}}{[CH\cdot OAc]_3}{>}CH\cdot$ $CH_2\cdot O\cdot CH{<}\underset{\overline{\qquad\quad O\qquad}}{[CH\cdot OAc]_3}{>}CH_2$, m. p. 189°, $[\alpha]_{5461}^{20}$ −85·8° in $CHCl_3$, identical with a specimen prepared by acetylation of the natural glucoside from *Gaultheria procumbens* (A., 1925, i, 347), and converted into a specimen identical with the latter on deacetylation with NH_3 in MeOH. Hence in primeverose the xylose and dextrose units are both pyranose and the glucosidic linkings are of the β-type. By similar methods the β-*xyloside* $+0{\cdot}5H_2O$ and anhyd., m. p. 173°, $[\alpha]_{5461}^{21}$ −46·01° in H_2O (Ac_3 derivative, m. p. 109—110°, $[\alpha]_{5461}^{1}$ −62·3° in $COMe_2$) and *rhamnoside* $+3H_2O$ and anhyd., m. p. 233° (decomp.), $[\alpha]_{5461}$ +22·64° in H_2O (Ac_3 derivative, m. p. 109°, $[\alpha]_{5461}^{21}$ −11·36° in $COMe_2$), of Me salicylate are also prepared. The former is partly hydrolysed by emulsin in H_2O at 37°, but the latter is unattacked. J. W. BAKER.

Behaviour of zinc chloride in the esterification of cellulose. W. FREY and E. ELOD (Ber., 1931, **64**, [*B*], 2556—2561).—The following evidence is adduced in favour of the view that the enhanced rate of formylation of cellulose in simultaneous presence of $ZnCl_2$ and HCl as compared with the sum of the rates in the presence of each catalyst singly is due to the formation of complexes of the type $[ZnCl_2,Cl]H$ or $[ZnCl_2\cdot O\cdot CO\cdot H]H$. HCO_2H containing $ZnCl_2$ can dissolve much greater amounts of HCl than in absence of the salt. The electrical conductivity of HCO_2H containing $ZnCl_2$ and HCl is much greater than the sum of the corresponding conductivities of the acid containing $ZnCl_2$ and HCl singly. Transport measurements show that Zn wanders to the anode. The strongly acidic nature of the complex is established by the coloration given by its solution to safranine compared with those imparted by HCl and H_2SO_4 of known concentration. Parallelism exists between the strength of the acids and the rate of dissolution of cellulose. H. WREN.

Synthetic cellulose and textile fibres from dextrose. H. HIBBERT and J. BARSHA (J. Amer. Chem. Soc., 1931, **53**, 3907).—The membrane formed by the action of *Acetobacter xylinum* on dextrose is a true cellulose, since various derivatives obtained from it are identical with those prepared similarly from cotton cellulose. The membranes formed similarly from lævulose, sucrose, mannitol, glycerol, and glyceraldehyde are probably all identical with cellulose.
H. BURTON.

Methylene ethers of carbohydrates. I. Cellulose methylene ether. F. C. WOOD (J.S.C.I., 1931, **50**, 411—418T).—Acid condensing agents cannot lead to a complete conversion of cellulose (or other insoluble carbohydrate) into its methylene ether by CH_2O, since it is unstable to acid and it is impossible to separate the unconverted portion. In presence of acid and controlled amounts of H_2O the product is absorbent or not to cuprammonium hydroxide or direct dyes according to whether the reaction is conducted in presence of large or small amounts of H_2O. This explains the discrepancy between Eschalier's and Bruckhaus' work. In Eschalier's original process, the two types of product have also been observed by the author. The hydroxymethyl structure for the products obtained by the action of H_2SO_4–CH_2O mixtures on cellulose is erroneous. Experiments are described on the methylenation of cellulose under alkaline conditions by a variety of agents. Under optimum conditions, *cellulose monomethylene ether*, $C_6H_7O_2(OH)(O_2CH_2)$, has been prepared by utilising Haworth's technique employed in the methylation of sugars. This ether has a fibrous structure, is stable to alkali, but unstable to mineral acid, thus resembling the *iso*propylidene sugars. It is probably a 2 : 3-monomethylene cellulose with the 6-OH group free. It may be methylated in the usual way without disturbing the methylene group, but the process is difficult. Monochlorodimethyl sulphate reacts with soda-cellulose, giving a mixed Me methylene ether, with the possible intermediate formation of chloromethylcellulose. Neither the *iso*propylidene derivative nor the true thiocarbonate could be obtained from soda-cellulose, CMe_2Cl_2, and $CSCl_2$, respectively.

Lichenin and lichenin nitrate. J. REILLY, (MISS) M. HAYES, and P. J. DRUMM (Proc. Roy. Irish Acad., 1931, **40**, **B**, 102—105).—Lichenin purified through its acetate gives a *pentanitrate*, similar in properties to cellulose nitrate. A. A. LEVI.

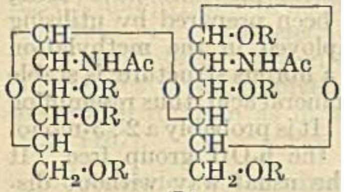
Pine-wood lignin. B. RASSOW and H. GABRIEL (Cellulosechem., 1931, **12**, 290—295).—The lignin (termed "glycol-lignin") is isolated in 22% yield from the air-dried wood-meal (5 g.) by extraction with 100 c.c. of glycol (previously treated at 160° with 0·1 c.c. of 25% HCl) at 165—170° for 5 min., precipitation from the extract with H_2O, subsequent dissolution in AcOH and re-precipitation, and extraction with Et_2O; other modifications of the purification process are described. The OMe and Ac contents, composition, colour reactions, and solubility of the lignins are given; the analytical results vary with the method of purification. H. BURTON.

Formula of fir-wood lignin. P. KLASON (Svensk Kem. Tidskr., 1931, **43**, 226—234).—By evaporation of the waste sulphite liquors almost to dryness at 80°, a brown residue is obtained sol. in H_2O with production of a non-dialysable solution. Addition of $C_{10}H_7\cdot NH_2$ to the solution gives a dark-coloured ppt. of a naphthylamine *salt*, $C_{38}H_{39}O_{13}NS$. The name *melaligninsulphonic acid* is proposed for the acid, which is regarded as a polymeride of β-ligninsulphonic acid, and *melalignin* for the corresponding lignin. The lignin present in wood is regarded as composed of 64·6% of α-lignin, $6C_{10}H_{12}O_4$, and 35·4% of β-lignin, $2C_9H_9O_4Ac,C_{10}H_{12}O_4$; it is shown from determinations of the quantities of CaO and SO_2 taking part in the sulphite process that the reactions involved are in harmony with the above formulæ.
H. F. HARWOOD.

Degradation of wood to cellulose and nitro-lignin. K. Kurschner (Cellulosechem., 1931, **12**, 281—286).—A lecture. H. Burton.

[Reaction of] monobromoamine with organo-magnesium halides. G. H. Coleman and C. B. Yager (Proc. Iowa Acad. Sci., 1930, **37**, 250).—The yields of primary amines are much smaller than with NH_2Cl. Chemical Abstracts.

Chitin and chitobiose. M. Bergmann, L. Zervas, and E. Silberkweit (Ber., 1931, **64**, [*B*], 2436—2440).—Chitin is converted by Ac_2O and conc. H_2SO_4 into *chitobiose octa-acetate* (I; R=Ac), m. p. 289° (corr., decomp.), $[\alpha]_D^{20}$ +50·3° in AcOH, hydrolysed by boiling dil. HCl to *d*-glucosamine hydrochloride. It is converted by 0·2*N*-KOH into *diacetylchitobiose* (I; R=H), m. p. above 185° (decomp.). When treated with NaOI in presence of sufficient alkali to hydrolyse the OAc groups, the octa-acetate affords *diacetylchitobionic acid* (II), converted by boiling Ac_2O into *hexa-acetylanhydrochitobionolactone* (III), m. p. 215° (corr.). Since only one double linking is hereby developed, it follows from analogy with the behaviour of glucosamic acid (this vol., 1402) that the OH group in position 4 or 5 is substituted by the second glucosamine residue, whilst the presence of the double linking in the 2 : 3-position is deduced from the enhanced instability of the compound towards dil. HCl (with which NH_4Cl is produced) and by its ozonolysis to acetoxamic acid. H. Wren.



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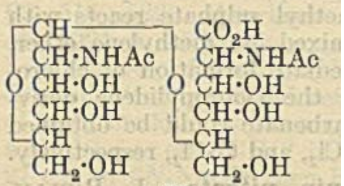

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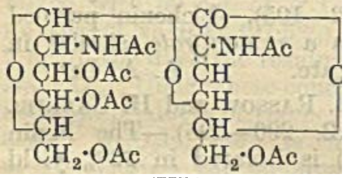

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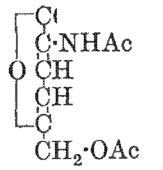
Preparation of glycine. H. Krause (Chem.-Ztg., 1931, **55**, 666).—A solution of 378 g. of $CH_2Cl·CO_2H$ in 1200 g. of H_2O (≯40°) is mixed with the theoretical wt. of Cu in the form of a paste of oxide and carbonate. After 2 days the blue solution is filtered, made up to 2000 g. with H_2O, and mixed with 2 litres of 9% aq. NH_3 (1/2 in excess of theory). After 24 hr. at room temp. the liquid is boiled for 3 hr. under reflux and finally conc. to 1200 g. The separation of Cu aminoacetate is facilitated by adding 1500 c.c. of 75% EtOH and, after washing and drying, the Cu compound (350—360 g.) is converted into glycine by the action of H_2S. H. J. Dowden.

Preparation of sarcosine. W. Cocker and A. Lapworth (J.C.S., 1931, 1894—1898).—Glycine, either pure or by hydrolysis of aminoacetonitrile H sulphate with 40% H_2SO_4 at 125° (cf. this vol., 943), is converted (93 and 88% yield, respectively) by cold *N*-NaOH and $PhSO_2Cl$ into its *N*-benzenesulphonyl derivative, readily methylated (95% yield) with 3*N*-NaOH and Me_2SO_4 to *N*-benzenesulphonylsarcosine. After hydrolysis of this with 40% H_2SO_4 at 125—130° the $PhSO_3H$ is readily removed as its Zn salt by addition of a saturated solution of $ZnSO_4$, the excess of which is removed by $BaCO_3$. Traces of Ba in the filtrate are removed by the requisite amount of dil. H_2SO_4 and evaporation affords crude cryst. sarcosine in 74% yield. The prep. of cryst. *N*-benzoylsarcosine in 50% yield by the action of BzCl and $NaHCO_3$ is described. J. W. Baker.

Glucosamic acid and its deamination. M. Bergmann, L. Zervas, and E. Silberkweit (Ber., 1931, **64**, [*B*], 2428—2436).—Glucosamic acid is converted by Ac_2O and anhyd. NaOAc into the lactone (I), m. p. 154° (corr.), which reduces Fehling's and ammoniacal Ag solutions, is optically inactive, and is transformed by catalytic hydrogenation and subsequent hydrolysis into the stereoisomeric *α-amino-δε-dihydroxy-n-hexolactone hydrochlorides*, m. p. 165° (corr.) and 173—175° (corr.), respectively. Partial hydrogenation yields the *lactone* (II), m. p. 113°



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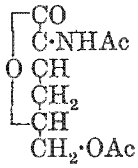

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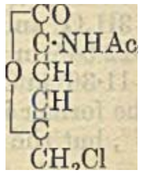
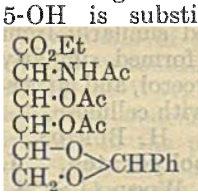


(III.)

(corr.), in which the double linking is in the 2 : 3-position, since it is hydrolysed by dil. HCl to NH_4Cl and α-keto-δε-dihydroxy-*n*-hexolactone [*phenylhydrazone*, m. p. 179° (corr.)] and converted by ozonisation into the *compound* (?) $NHAc·CO·CO·O·CH(CH_2·OH)·CH_2·CO_2H$, m. p. 131° (corr., decomp.), hydrolysed to acetoxamic acid [*phenylhydrazide*, decomp. 184° (corr.)]. The 4 : 5-position of the second double linking in (I) follows from the absence of an asymmetric C atom and the ready formation by means of conc. HCl of the *chlorohydrin* (III), m. p. 197°, which absorbs 2 mols. of H_2 and is easily converted by AgOAc into the original lactone. Further confirmation of the δ-lactonic structure is found in the transformation of the lactone by conc. AcOH and $NHPh·NH_2$ into the *compound* $NHPh·NH·CO·C(:N·NHPh)·CH_2·CH_2·C(:N·NHPh)·CH:N·NHPh$, m. p. 219 (corr., decomp.). [A *substance*, (?) $NHPh·NH·CO·C(:N·NHPh)·CH_2·CH_2·C(:N·NHPh)·CH_2·OH$, m. p. 193° (corr.), is also obtained.] The possible deamination of glucosamic acid to αδ-diketo-ε-hydroxy-*n*-hexoic acid is thus established. Elimination of H_2O in the 4 : 5-position during the acetylation of glucosamic acid is not observed when the 5-OH is substituted. Thus Et 5 : 6-benzylidene-



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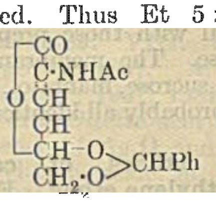

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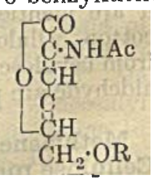

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glucosamate hydrochloride, Ac_2O, and anhyd. NaOAc afford the Ac_3 derivative (IV), m. p. 119° (corr.), and

the singly unsaturated *lactone* (V), m. p. 198° (corr.), $[\alpha]_D^{20}$ −30·1° in $CHCl_3$. Removal of the benzylidene group from (V) by cold HCl is immediately followed by loss of H_2O, disappearance of optical activity, and production of the *lactone* (VI; R=H), m. p. 158·5° (corr.), which yields an Ac derivative (VI; R=Ac), m. p. 115° (corr.), from which a chlorohydrin is not obtained by the action of conc. HCl. H. WREN.

Cobalt complexes of cysteine. M. P. SCHUBERT (J. Amer. Chem. Soc., 1931, **53**, 3851—3861).—Cysteine hydrochloride and $CoCl_2$ in presence of aq. KOH and N_2 give at p_H 11—12, *K cobaltobiscysteinate* (I), $Co(RSK)_2,2H_2O$ [in this and other formulæ R—$\cdot CH_2\cdot CH(NH_2)\cdot CO_2\cdot$], whilst at p_H 7—8 *Co'' cobaltobiscysteinate* (+2 and $4H_2O$) results. At p_H 5—6 in presence of O_2 the above reactants give the *complex* $Co(RSH)_3$ (+3 and $4H_2O$) [K_3 salt (II)], but at p_H 8—9 the *K* salt (+$4H_2O$) (III) of the *complex* $[Co(RSH)_2OH]_2,8H_2O$ [*Ba* salt (+$9H_2O$); unstable *trihydrochloride* (+H_2O); *picrate* (+$9H_2O$)] is formed. (I) is oxidised by H_2O_2 to an unidentified yellow complex. The ultra-violet absorption spectrum of (III) resembles that of K cobaltibisthiolacetate (this vol., 67), but that of (II) differs from that of cobaltitrisalanine. Co-ordination structures are suggested for (I), (II), and (III). H. BURTON.

Synthesis of carbamide from ammonium carbamate. B. NEUMANN.—See this vol., 1374.

Esterification of erythritol. J. SCHALIT (Wiss. Mitt. Oesterr. Heilmittelstelle, 1929, 42—44; 1930, 5—10; Chem. Zentr., 1931, i, 2602—2603).—Treatment of erythritol or its dichlorohydrin with palmitic or stearic acid leads to mixtures of esters. The quantities of the various esters obtained under different conditions are recorded. A. A. ELDRIDGE.

Reaction of chloropicrin with potassium iodide. G. D. SUICHER (J. Chem. Ind., Russia, 1930, 7, 1168—1169).—The reaction $CCl_3\cdot NO_2+4KI=CI_4+3KCl+KNO_2$ takes place with or without solvents; with less KI I-substituted derivatives of $CCl_3\cdot NO_2$ are not obtained. Interaction between $CCl_3\cdot NO_2$ and KBr is slow; CBr_4, $CBr_3\cdot NO_2$, $CClBr_2\cdot NO_2$, and other Br-substitution products are formed. CHEMICAL ABSTRACTS.

Formation and transformation of cyclic acid imides. W. HÜCKEL and H. MÜLLER.—See this vol., 1291.

Constitutional studies in the monocarboxylic acids derived from sugars. V. Hexonic and pentonic acid amides. Action of sodium hypochlorite on the isomeric trimethylarabonamides. R. W. HUMPHREYS, J. PRYDE, and E. T. WATERS (J.C.S., 1931, 1298—1304).—By the action of dry NH_3 in EtOH on the appropriate lactone (obtained by the action of Br and HBr in H_2O on the glucoside) the following pyranoid and furanoid amides have been obtained: 2 : 3 : 4 : 6-, m. p. 68°, $[\alpha]_D$ +60·4° in $COMe_2$ (previously described as the 2 : 3 : 5 : 6-compound, J.C.S., 1924, **125**, 1045), and 2 : 3 : 5 : 6-, m. p. 91°, $[\alpha]_D^{20}$ +39·2° in H_2O, *-tetramethylgluconamide*; 2 : 3 : 4 : 6-, m. p. 120°, $[\alpha]_D$ +37·9° in $COMe_2$ (A., 1925, i, 356), and 2 : 3 : 5 : 6-, m. p. 153° (slight decomp.), $[\alpha]_D$ +5·76° in $COMe_2$, *-tetramethylgalactonamide*; 2 : 3 : 4-, m. p. 96°, $[\alpha]_D$ +35·5° in EtOH, and 2 : 3 : 5-, m. p. 132°, $[\alpha]_D$ +19·3° in EtOH, *-trimethylarabonamide*. 2 : 3 : 4-Trimethylarabonamide is converted by alkaline NaOCl into the internal *urethane*, $NH<\genfrac{}{}{0pt}{}{[CH\cdot OMe]_3}{CO\text{———}O}>CH_2$ (I), m. p. 142°, $[\alpha]_D$ +42° in H_2O, the 2 : 3 : 5-compound similarly yielding 2-*keto*-4 : 5 : ω-*trimethoxy*-6-*methyltetrahydro*-1 : 3-*oxazine*, $NH<\genfrac{}{}{0pt}{}{[CH\cdot OMe]_2}{CO\text{———}O}>CH\cdot CH_2\cdot OMe$ (II), m. p. 76°, $[\alpha]_D$ +5·0° in H_2O, converted by 1% HCl in MeOH at room temp. into an isomeric *compound* (III), m. p. 63—65°, $[\alpha]_D$ −178° in H_2O, similar treatment in a sealed tube at 80° giving a substance, m. p. 45—47°, which is probably a mixture of (II) and (III). Considerable change in rotation occurs when either (II) or (III) is treated with 1% NaOH in H_2O, (III) giving a *substance*, $[\alpha]_D$ −41°, possibly a dimethyltetrose. J. W. BAKER.

Guanidine and nitrous acid. II. W. D. BANCROFT and S. L. RIDGWAY (J. Physical Chem., 1931, 35, 2950—2963; cf. this vol., 1280).—Guanidine and HNO_2 do not react, but in the presence of HCl or H_2SO_4 the reaction is slow up to a certain concentration, sp. for each acid. At higher concentrations they react slowly, liberating 2 atoms of N; the third atom is evolved more slowly. The influence of various factors affecting the reaction and preliminary experiments on the decomp. products are discussed. Various formulæ for guanidine are also considered. L. S. THEOBALD.

Ethylenic nitriles. α-Ethylcrotononitriles. P. BRUYLANTS and L. ERNOULD (Bull. Acad. roy. Belg., 1931, [v], 17, 1027—1040).—Quinoline at 140—145° converts β-chloro-α-ethylbutyronitrile into a mixture of approx. 40% of the form (I), b. p. 139—140°/758 mm., and 60% of the form (II), b. p. 155—156°/760 mm. (A., 1927, 652), of α-ethylcrotononitrile which are interconvertible by heating with NaOPh. They are converted by H_2SO_4 into the corresponding stereoisomeric amides, m. p. 93—94° and m. p. 118—119° (*loc. cit.*, m. p. 109°). Irradiation of the amide, m. p. 118—119°, causes some conversion into the other form (together with other changes), whilst the amide of lower m. p. undergoes no appreciable change. Hydrolysis of the nitrile (II) affords only α-ethylcrotonic acid (*trans*), m. p. 41—42°, whilst under certain conditions of (incomplete) hydrolysis (I) affords a mixture of this acid and α-ethyl*iso*crotonic acid (*cis*), m. p. −22·5° to −21·8°, separated by means of their Ca salts (A., 1904, 906). J. W. BAKER.

Ethylenic nitriles. β-Ethylcrotononitrile. P. BRUYLANTS (Bull. Acad. roy. Belg., 1931, [v], **17**, 1008—1026).—β-Hydroxy-β-chloromethyl-*n*-butane is converted by KCN in EtOH into β-*hydroxy*-β-*ethyl*-n-*butyronitrile* (I), b. p. 106—107°/14 mm., dehydrated by H_2SO_4 to a mixture of αβ- and βγ-unsaturated nitriles (some COMeEt is also formed) from which only one *form* (II), b. p. 162—162·5°/752 mm., of β-methyl-Δ^{α}-pentenonitrile is obtained when the βγ-nitrile is removed as its dibromide. HCl converts (I) into the corresponding β-*chloronitrile*, b. p. 77—78°/11 mm. (together with some unsaturated nitrile containing 81% of the βγ-form), which with

quinoline at 130° again gives only the form (II), together with less of the βγ-nitrile than is obtained in the H_2SO_4 dehydration (A., 1929, 1294). Oxidation of β-methyl-*n*-butyl alcohol (from trioxymethylene and *sec.*-BuBr) to the aldehyde is best effected by air and a divided Ag catalyst at 330° (A., 1921, i, 218), the *cyanohydrin*, b. p. 115—115·5°/12 mm., of which is dehydrated by P_2O_5 into a mixture of unsaturated nitriles from which, after removal of the βγ-form by Br, a second stereoisomeric *form*, (III), b. p. 142—143°/765 mm., of β-methyl-Δ$^{\alpha}$-pentenonitrile, together with (II) are isolated by fractional distillation. The two forms have also different vals. of *d* and *n* and differ in odour, and each is converted by cold conc. H_2SO_4 into the corresponding *amide*, m. p. 98—99° [*loc. cit.* from (II)] and m. p. 116—116·8° [from (III)]. Interconversion of these amides could not be effected by irradiation. J. W. BAKER.

Action of the Grignard reagent on amino-nitriles. T. S. STEVENS, J. M. COWAN, and J. MACKINNON (J.C.S., 1931, 2568—2572).—The following reactions occur between α-*tert.*-aminonitriles and Grignard reagents: NR‴R⁗·CR′R″·CO·R′′′′′ (I) ⟵ NR‴R⁗·CR′R″·CN+MgR′′′′′X ⟶ MgXCN +NR‴R⁗·CR′R″R′′′′′ (II) (cf. Bruylants, A., 1924, i, 984). (I) is produced [sometimes admixed with (II)] only when R′=R″=H. Thus, $NMe_2·CH_2·CN$ and MgMeI give NMe_2Et and $NMe_2·CH_2Ac$; with MgPhBr, $NMe_2·CH_2Bz$ results. $NEtPh·CH_2·CN$ and MgMeI afford *N*-ethylanilinoacetone, b. p. 143°/11 mm. (*phenylhydrazone*, m. p. 96°), also formed from NHEtPh and CH_2AcBr at 30°; α-piperidinopropionitrile and MgPhBr yield 1-α-phenylethylpiperidine (*picrate*, m. p. 140—142°); α-dimethylaminophenylacetonitrile with MgMeI, MgPhBr, and $CH_2Ph·MgCl$ furnishes α-phenylethyldimethylamine, benzhydryldimethylamine, and αβ-diphenylethyldimethylamine [*picrate*, m. p. 156—157° (softens at 130°); *hydrochloride*, m. p. 187—188°, converted by dry distillation into stilbene], respectively; α-dimethylamino-β-phenylpropionitrile [*hydrochloride*, m. p. about 170° (decomp.)] and MgPhBr give αβ-diphenylethylamine. Reaction (II) is correlated with the ψ-basic properties of the corresponding *tert.*-amino-alcohols. In accordance with this view, 1-cyanohydrastinine and 9-cyano-9 : 10-dimethyl-9 : 10-dihydroacridine are converted by MgMeI into 1-methylhydrastinine and 9 : 9 : 10-*trimethyl*-9 : 10-*dihydroacridine* (also obtained from MgMeI and methylacridine methiodide), respectively. H. BURTON.

***tert.*-Phosphines containing higher alkyl radicals.** I. K. JACKSON, W. C. DAVIES, and W. J. JONES (J.C.S., 1931, 2109—2112).—By the action of the appropriate Grignard compound on PCl_3 or $PPhCl_2$ in absence of air the following phosphines are prepared: *tri*-n-*hexyl*-, m. p. about 20°, b. p. 227°/50 mm. (*oxide*); *phenyldi*-n-*hexyl*-, b. p. 236°/50 mm. [*oxide*; *chloromercurate*, m. p. 140°; *methiodide*, m. p. 67° (*chloroplatinate*, m. p. 135°)]; *tri*-n-*heptyl*, m. p. about 20°, b. p. 260°/50 mm. (*oxide*); *phenyldi*-n-*heptyl*-, b. p. 260°/50 mm. [*chloromercurate*, m. p. 102°; *methiodide*, m. p. 87° (*chloroplatinate*, m. p. 105°)]; *tri*-n-*octyl*-, m. p. about 30°, b. p. 291°/50 mm.; *phenyldi*-n-*octyl*-, b. p. 277°/50 mm. [*oxide*; *methiodide*, m. p. 81° (*chloroplatinate*, m. p. 102°)], -*phosphine*. The physical properties of the trialkyl- and phenyldialkyl-phosphines are discussed, the b. p./50 mm. of the members of these two homologous series being represented (error ±2°) by $t=32·014M^{0·48587}-273$ and $t=41·583M^{0·44512}-273$, respectively (*M*=mol. wt.). J. W. BAKER.

Arsinosulphides of the fatty and aromatic series. A. E. KRETOV and A. Y. BERLIN (J. Gen. Chem. Russ., 1931, **1**, 411—418).—A series of arsinosulphides was prepared by the action of H_2S, KHS, or Na_2S on the corresponding chloroarsines. Arsinosulphides of the type RAsS are generally polymerised: those of the type $S(AsR_2)_2$ are monomerides. The following were obtained: β-*chlorovinyl*-; β-*hydroxyethyl*-, m. p. 66—70°; β-*acetoxyethyl*-, m. p. 69°; p-*cyanophenyl*-, m. p. 152°; β-*naphthyl*-, m. p. 154°; p-*chlorophenyl*-, m. p. 135°; p-*nitrophenyl*-, m. p. 210°; m-*nitrophenyl*-, m. p. 98—101°; p-*ethoxyphenyl*-, m. p. 127—129°, -*arsinosulphide*; p-*phenylenediarsinodisulphide*, m. p. 275—276°. E. B. UVAROV.

Action of boron fluoride on organic compounds. H. BOWLUS and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1931, **53**, 3835—3840).—The following *compounds* are obtained when BF_3 (1 mol.) is passed into the requisite substance (1 mol.) at 25°: $AcOMe,BF_3$, b. p. 110°/739 mm., m. p. 60°; $AcOEt,BF_3$, b. p. 119°/739 mm., m. p. 26°; HCO_2Et,BF_3, b. p. 102°/748 mm.; $AcOPr,BF_3$, b. p. 126°/743 mm.; $EtCO_2Et,BF_3$, b. p. 116°/747 mm.; Ac_2O,BF_3, m. p. 194°; NH_2Ac,BF_3 (decomp. on attempted distillation). BuOH and BF_3 give an oil which gradually decomposes to a mixture of aliphatic and aromatic hydrocarbons, whilst AcOH and $EtCO_2H$ yield the compounds $(AcOH)_2,BF_3$, b. p. 140°/746 mm., and $(EtCO_2H)_2,BF_3$, b. p. 62—63°/17 mm., respectively (cf. A., 1927, 836). The compound $MeCN,BF_3$ has b. p. 101°/752 mm., m. p. 87° (cf. A., 1891, 1441). Most of the above compounds are completely dissociated in the vapour phase. Cryst. additive compounds are formed from pyridine and 2 mols. of BF_3 and from quinoline and piperidine with 1 mol. of BF_3. The compound from 1 mol. of an alcohol (ROH) and 1 mol. of BF_3 is probably a co-ordination compound which subsequently ionises to $[RO \longrightarrow BF_3]^- + H^+$. The mechanism of acetal formation (A., 1930, 745, 1160) from C_2H_2,BF_3, and ROH is probably: (*a*) $C_2H_2 + 2H^+ + 2[RO \longrightarrow BF_3]^- \longrightarrow CHMe\left(\begin{smallmatrix}\nearrow BF_3\\ OR\end{smallmatrix}\right)$ (I); (*b*) (I) $\longrightarrow CHMe(OR)_2 + BF_3$. H. BURTON.

Co-ordination compounds of boron trifluoride with oxygenated carbon derivatives. G. T. MORGAN and R. TAYLOR (Chem. and Ind., 1931, 869).—BF_3 combines additively with the esters of aliphatic acids and the following have been obtained in the cryst. state: HCO_2Me,BF_3, m. p. 23·5°, b. p. 94°/772 mm.; HCO_2Et,BF_3, m. p. 3°, b. p. 103°/772 mm.; $AcOMe,BF_3$, m. p. 61·5°, b. p. 112°/772 mm.; $AcOEt,BF_3$, m. p. 31°, b. p. 123°/772 mm.; Ac_2O,BF_3, m. p. 190° (decomp.). E. S. HEDGES.

Decomposition of ortho-ethers of monosilane on heating under pressure, and the liberation of free silicon. III. B. N. DOLGOV and J. N. VOLNOV (J. Gen. Chem. Russ., 1931, **1**, 330—339).—Tetra-alkyl-

oxymonosilanes yield disilane derivatives on heating at 280° with H_2 under pressure, whilst at >280° unsaturated hydrocarbons and SiO_2 are produced. Under analogous conditions tetralkyloxymonosilanes decompose only at >280° to yield the corresponding phenol and amorphous Si. The ethers are less stable than are the corresponding silanes. Tetra*cyclo*hexyl orthosilicate decomposes at >380° to yield SiO_2 and *cyclo*hexene. R. Truszkowski.

Reactions of inorganic vanadium compounds with magnesium phenyl bromide. C. C. Vernon (J. Amer. Chem. Soc., 1931, **53**, 3831—3834).—Varying amounts of Ph_2 are formed when MgPhBr is treated with VCl_2, VCl_3, $VOCl_3$, V_2O_3, V_2O_4, or V_2O_5 in Et_2O (cf. A., 1928, 50). A small amount of a solid V-containing compound (hydrolysed by H_2O to Ph_2) was obtained in one experiment from MgPhBr and $VOCl_3$. V does not react with EtBr, EtI, $Pr^{\beta}I$, BuCl, PhBr, PhI, $PhSO_2Cl$, ethylene dibromide, or *p*-dibromobenzene in Et_2O, or with CH_2PhCl, AcCl, or Me_2SO_4 in absence of solvent. H. Burton.

Aromatic sulphonyl fluorides. Method of preparation. W. Davies and J. H. Dick (J.C.S., 1931, 2104—2109).—Aromatic sulphonyl fluorides are readily prepared (in glass vessels) by refluxing the sulphonyl chloride with 50% excess of KF in H_2O (the presence of H_2O is essential: NaF and ZnF_2 may be used) and thus are prepared a number of known sulphonyl fluorides (A., 1927, 963) and: *2-chloro-5-nitro*-p-*toluene*-, m. p. 84—85°; 1 : 3-dimethylbenzene-4 : 6-di- (*loc. cit.*, described as the 2 : 4-disulphonyl compound); *chlorobenzene*-2 : 4-*di*-, m. p. 88—89°; 1 : 3-*dichlorobenzene*-4 : 6-*di*-, m. p. 141—143°; 1 : 3 : 5-*trichlorobenzenedi*-, m. p. 109—110°; 1 : 3-*dimethoxy*-(?-*benzene*)-4 : 6-*di*-, m. p. 209—211°; *benzene*-1 : 3 : 5-*tri*-, m. p. 166—167°; *chlorobenzene*-2 : 3 : 6-*tri*-, m. p. 179—181°, -*sulphonyl fluoride*. These are all more stable to acid and neutral hydrolytic agents than are the corresponding chlorides, but are quantitatively hydrolysed to NaF and the sulphonate by NaOH and are thus a convenient source of definite ionisable F concentration. J. W. Baker.

Influence of directing groups on nuclear reactivity in oriented aromatic substitutions. II. Nitration of toluene. C. K. Ingold, A. Lapworth, E. Rothstein, and D. Ward (J.C.S., 1931, 1959—1982).—Accurate data for the proportions of isomerides (ratio of the magnitudes which individually relate to the effect of the substituent Me on the reactivity at different nuclear positions) and the speed of total substitution relative to that of C_6H_6 (reduced velocity, *i.e.*, sum of such magnitudes) have been determined for nitration of PhMe in $AcNO_3$ at 30° (in AcOH alone or in excess of Ac_2O as solvent) by refinement of methods previously employed (A., 1928, 164). Under these conditions the mean val. of the reduced velocity is 23, the mean proportions of *o*-, *m*-, and *p*-nitrotoluenes formed (by oxidation methods and by thermal analysis) are 58·4, 4·4, and 37·2%, respectively, whence the partial rate factors (*F*, previously designated coeff. of activation=the factor by which the introduction of the directing group increases the probability of substitution at that atom during a small element of time under the conditions of comparison) for the *o*-, *m*-, and *p*-positions are 40, 3·0, and 51, respectively ($\Delta E=+2{\cdot}21$, $+0{\cdot}66$, and $+2{\cdot}36$ kg.-cal., respectively; cf. below). Thus the inductive (+I) effect of the Me group activates all three positions in PhMe, the *o*- and *p*- to a much greater extent than the *m*-. Alteration of the nitrating medium to HNO_3 in $MeNO_2$ causes no change in either the reduced velocity (21) or in the *F* val. (37, 28, and 47, respectively). With $AcNO_3$ at 0°, a higher reduced velocity (27) and higher *F* val. (47, 3·0, 62) were obtained (*o* : *m* : *p*-isomerides=58·1 : 3·7 : 38·2). The significance of these results is discussed and it is tentatively suggested that *F* may vary with temp in such a way that $\Delta E=RT\log_e F$, the ΔE's being a measure of the internal activation by the substituent Me for the various nuclear positions in PhMe. J. W. Baker.

Action of magnesium on dibromotoluene and dibromo-*m*-xylene. J. S. Salkind, S. Kirillova, and N. Nikiforova (J. Gen. Chem. Russ., 1931, **1**, 193—198).—Mg and 3 : 4-dibromotoluene interact slowly and with difficulty; both Br atoms react, mainly forming org. Mg compounds and some tarry products. Tribromotoluene does not react. 4-Bromo-*m*-xylene gives dimethylbenzoic acid. 4 : 6-Dibromo-*m*-xylene reacts when the Mg is activated by I, forming 4-bromo-*m*-xylene and a Mg org. compound which gives 5-bromo-2 : 4-dimethylbenzoic acid on decomp. with H_2O. The presence of the second Me group in the C_6H_6 ring hinders the reaction, allowing only one Br atom to react. E. B. Uvarov.

Preparation of cinnamyl chloride and its Grignard reagent. H. Gilman and S. A. Harris (Rec. trav. chim., 1931, **50**, 1052—1055).—For the prep. of the compound $MgCl{\cdot}CHPh{\cdot}CH{:}CH_2$ in good yield the necessary cinnamyl chloride is best obtained by the action of $SOCl_2$ and pyridine in $CHCl_3$ on the alcohol. A prep. having a val. 76·8% by acid titration gave 57% by the I method (A., 1926, 535) and hence the observation that one RMgX mol. reacts with the ethylenic linking in another to form a new Grignard reagent which does not react with I (A., 1929, 802) is not confirmed. An efficient method for the conversion of a Grignard reagent into the carboxylic acid is described. J. W. Baker.

Tetraphenyl-*o*-xylylene. G. Wittig and M. Leo (Ber., 1931, **64**, [*B*], 2395—2405).—Me *o*-phthalate is readily transformed by LiPh in Et_2O into tetraphenyl-*o*-xylylene glycol, m. p. 203·5° (cf. Schlenk and Brauns, A., 1915, i, 519) (*Li* derivative). The superiority of LiPh over MgPhBr is shown by the smooth conversion by the former of Me diphenate into 2 : 2′-di(hydroxybenzhydryl)diphenyl, m. p. 252—253° (cf. A., 1926, 610). Similarly Me 2 : 2′-dimethoxydiphenate and LiPh afford 2 : 2′-*di-methoxy*-6 : 6′-*di(hydroxybenzhydryl)diphenyl*, m. p. 278—280° (Li_2 derivative), converted by boiling AcOH into the corresponding *anhydride*, $C_{40}H_{32}O_3$, m. p. 314—316°, whereas the glycol does not appear to be formed with MgPhBr. Phthalic anhydride and LiPh give resinous matter and triphenylcarbinol. Tetraphenyl-*o*-xylylene glycol cannot be converted into the corresponding Me_2 ether by MeOH containing HCl on account of its ready anhydrisation to tetra-

phenylphthalane; the crude Li derivative does not react with MeI at 100°, whilst at 160° or 200° tetraphenylphthalane is produced. Treatment of the glycol with K in dioxan yields the corresponding *K* derivative, readily transformed by MeI into *tetraphenyl-o-xylylene glycol Me ether*, m. p. 195—196°, converted by MeOH containing HCl into tetraphenylphthalane. Treatment of the ether with K gives the *compound* $CPh_2K\cdot C_6H_4\cdot CPh_2\cdot OK$, also obtained from tetraphenylphthalane and Na–K in dioxan and converted by EtOH into 2-benzhydrylhydroxybenzhydrylbenzene, m. p. 216·5—217°, from which 9 : 9 : 10-triphenyldihydroanthracene, m. p. 226—227°, is obtained by treatment with HCl in boiling AcOH.

Tetraphenyl-*o*-xylylene glycol does not react with *iso*amyl nitrite or Me orthosilicate, but is transformed by Et or Bu borate into the *Et* ester $C_6H_4<\begin{matrix}CPh_2\cdot O\\CPh\ \ O\end{matrix}>B\cdot OR$ (R=Et), m. p. 201—202·5° after softening, or *Bu* ester (R=Bu), m. p. 161—162°, hydrolysed by alkali to the glycol and converted by acid into tetraphenylphthalane; treatment of the ester with K–Na gives a mixture of the compounds $C_6H_4(CPh_2K)_2$ and $CPh_2K\cdot C_6H_4\cdot CPh_2\cdot O\cdot B(OR)\cdot OK$, from which 2-hydroxybenzhydrylbenzhydrylbenzene is obtained by alcoholysis (isolated as triphenyldihydroanthracene).

Tetraphenyl-*o*-xylylene glycol cannot be converted into its Me_2 ether by the use of CPh_3K or K phenyl diphenylyl ketone, which yield only the K_1 compound, whereas K 2-phenyl*iso*propyl affords the K_2 compound, transformed by MeI into *di(methoxybenzhydryl)benzene*, m. p. 179·5—180·5°, which is unexpectedly unstable. It is quant. decomposed by Na–K in dioxan into KOMe and $C_6H_4(CKPh_2)_2$ and converted by EtOH into *tetraphenyl-o-xylene*, m. p. 146·5°. K is eliminated by tetramethylethylene bromide, but, even at —50°, the expected di-radical becomes isomerised to 9 : 9 : 10-triphenyl-9 : 10-dihydroanthracene. Dry O_2 transforms the K compound into a mixture of substances which do not liberate I from HI and from which only triphenyldihydroanthracene could be isolated. H. WREN.

Apparatus for pyrolytic production of diphenyl. A. W. HIXSON, L. T. WORK, H. V. ALESSANDRONI, G. E. CLIFFORD, and G. A. WILKENS (Ind. Eng. Chem. [Anal.], 1931, 3, 289—291).—C_6H_6 is vaporised at 500° and passed through a steel tube immersed in molten Pb. The optimum temp. for the production of Ph_2 is about 740°. The conversion of C_6H_6 into Ph_2 decreases with increase in the rate of flow; the decrease is not so marked at atm. pressure as at higher pressures. Increased pressure causes better conversion at all rates of flow. H. BURTON.

Diphenyl and its derivatives. VIII. New 2 : 2′-disubstituted derivatives. L. MASCARELLI and D. GATTI (Atti R. Accad. Lincei, 1931, [vi], 13, 887—893).—The following 2 : 2′-derivatives of diphenyl were prepared according to the scheme $NO_2\cdot C_6H_4\cdot C_6H_4\cdot NO_2 \longrightarrow NH_2\cdot C_6H_4\cdot C_6H_4\cdot NO_2 \longrightarrow C_6H_4X\cdot C_6H_4\cdot NO_2$ —— $C_6H_4X\cdot C_6H_4\cdot NH_2$ —— $C_6H_4X\cdot C_6H_4X$ (X=halogen): *nitrochloro-*, m. p. 71°; *nitrobromo-*, m. p. 66—67°; *nitroiodo-*, m. p. 81—82°; *nitrohydroxy-* (*Ac* derivative, m. p. 102°); *chloroamino-*, m. p. 56—57°; *bromoamino-*, m. p. about 46—50°; *iodoamino-* (*Ac_2* derivative, m. p. 129—130°; *chloroiodo-*, m. p. 63—64°; *chlorobromo-*, m. p. 58°; *bromoiodo-*, m. p. 90°. T. H. POPE.

Diphenylene sulphide series. C. COURTOT and CHAIX (Compt. rend., 1931, 192, 1667—1669).—Alkali fusion at 250° of diphenylenesulphone or its substituted derivatives yields the corresponding diphenyl-2-sulphonic acid (*diphenyl-2-sulphonyl chloride*, m. p. 103°; *sulphonamide*, m. p. 120·5°; *dibromodiphenyl-2-sulphonyl chloride*, m. p. 93·5—94·5°; *sulphonamide*, m. p. 151—152°), hydrolysed by aq. HBr to the diphenyl (3 : 3′-*dibromodiphenyl*, m. p. 52·5—53°). G. DISCOMBE.

Polyphenyls. I. *sym*.-Diphenyldiphenyls. S. T. BOWDEN (J.C.S., 1931, 1111—1114).—When 2- or 3-iododiphenyl is heated with Cu-bronze at 255—260°, 2 : 2′-, m. p. 118—119°, and 3 : 3′, m. p. 86°, *-diphenyldiphenyl*, respectively, are obtained. 4 : 4′-Diphenyldiphenyl may be similarly prepared, but is best obtained (63% yield) by heating anhyd. $CuCl_2$, activated Mg, and 4-bromodiphenyl at 100°. It is also obtained in small yield by pyrolysis of Ph_2. J. W. BAKER.

Stereochemical studies on hydronaphthalenes and derivatives. II. Catalytic oxidation–reduction of hydronaphthalenes and sesquiterpenes. S. KIMURA.—See this vol., 1288.

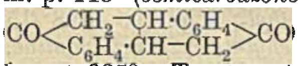
4 : 4-Derivatives of diphenyldidiphenylyl and didiphenylyl. R. PUMMERER and L. SELIGSBERGER (Ber., 1931, 64, [*B*], 2477—2486; cf. A., 1924, i, 381).—4 : 4′-Di-iododiphenyl and Ag powder at 240—250° give 4-iododiphenyl, unchanged material, a little didiphenylyl (4 : 4′-diphenyldiphenyl), and possibly a trace of diphenyldidiphenylyl. With Cu powder at 250° the I_2-derivative affords Ph_2, *p*-iododiphenyl, didiphenylyl, and diphenyldidiphenylyl. 4 : 4′-Di-iododiphenyl and 4-iododiphenyl with Ag powder at 280—300° give much Ph_2, I-compounds, and very impure $(C_6H_4Ph)_2$ and by Cu powder at 250—275° into Ph_2, $(C_6H_4Ph\cdot)_2$, and $Ph[C_6H_4]_4Ph$, m. p. 465° after softening at 435° (yield 24·4%). 4′-Iodo-4-methyldiphenyl, 4 : 4′-di-iododiphenyl, and Cu powder at 280—300°/200—300 mm. yield Ph_2, impure dimethyldidiphenylyl, and 4′′′′ : 4′′′′′-*dimethyldiphenyldidiphenylyl*, m. p. 469° after softening at 435°. 4′-Iodo-4-methyldiphenyl and Ag powder at 300° give 4-methyldiphenyl, m. p. 51°, whereas with Cu powder at 220°, 4′′ : 4′′′-*dimethyldidiphenylyl*, m. p. 334°, is obtained in 60—70% yield. It is oxidised by CrO_3 in boiling AcOH to 4′′-*methyldidiphenylyl-4′′′-carboxylic acid*, darkening without melting at 425° (*pyridine* compound; *Na* salt), and *didiphenylyl-4′′ : 4′′′-dicarboxylic acid*, decomp. 450° (*Na* salt; *Me_2* ester, decomp. 325—330°), which yields $(C_6H_4Ph\cdot)_2$ when heated at 500°/18 mm. or (with carbon and other products) when heated in boiling quinoline. 4-*Iododiphenyl-4′-carboxylic acid*, decomp. above 250° (*Na* salt unchanged below 400°), is prepared by oxidation of 4-iodo-4′-methyldiphenyl or from 4-*iododiphenyl-4′-nitrile*, m. p. 166° (from 4-iodo-4′-aminodiphenyl), and subsequent hydrolysis with conc. HCl in Et_2O. *Me* 4-*iododiphenyl-4′-*

carboxylate, m. p. 189°, is transformed by Cu powder at 270° into Me didiphenylyl-4'' : 4'''-dicarboxylate.

H. WREN.

Tribromonaphthalene obtained in bromination of naphthalene. J. S. SALKIND and M. V. BELIKOVA (J. Gen. Chem. Russ., 1931, **1**, 430—436).—Bromination of 1 : 4-dibromonaphthalene gives 1 : 4 : 6-tribromonaphthalene; similarly a SO_3H group takes the 6-position. A NO_2-group takes the 5-position. No clear explanation of this is available.

E. B. UVAROV.

Relative ease of formation of rings. III. New synthesis of chrysene. J. VON BRAUN and G. IRMISCH (Ber., 1931, **64**, [*B*], 2461—2465; cf. A., 1929, 561).—*meso*-βγ-Diphenyladipic acid (cf. Oommen and Vogel, A., 1930, 1435) is transformed by $SOCl_2$ into the corresponding chloride, which, with $AlCl_3$ in CS_2 or light petroleum, slowly affords 4-*keto*-2-*phenyl*-1 : 2 : 3 : 4-*tetrahydronaphthyl*-1-*acetic acid*, m. p. 148° (*semicarbazone*, m. p. 225°), and the *ketone*  (I), m. p. 295° after softening at 285°. Treatment of the ketone according to Clemmensen in presence of EtOH gives Et *meso*diphenyladipate, m. p. 114°, also obtained by use of EtOH and HCl in absence of Zn, but not from 4-keto-2-phenyl-1 : 2 : 3 : 4-tetrahydronaphthyl-1-acetic acid under analogous conditions. Reduction of the *meso*-ketone with P and HI at 170—180° gives the non-homogeneous *hydrocarbon* [as (I), but H_2 for O], dehydrogenated by PbO to chrysene, m. p. 248°. *r*-Diphenyladipyl chloride with $AlCl_3$ yields *r*-diphenyladipic acid, very little 4-keto-2-phenyl-1 : 2 : 3 : 4-tetrahydronaphthyl-1-acetic acid, and the r-*diketone* (cf. I), m. p. 182—184° (*semicarbazone*, m. p. 305°), converted by amalgamated Zn and HCl into a complex hydrocarbon. Reduction of the diketone by P and HI gives the r-*hydrocarbon*, b. p. about 140°/0·5 mm., m. p. 50—55°, dehydrogenated by PbO to chrysene.

H. WREN.

Polycyclic aromatic hydrocarbons. VII. 5 : 6-*cyclo*Penteno-1 : 2-benzanthracene, a cancer-producing hydrocarbon. J. W. COOK (J.C.S., 1921, 2529—2532).—The ketone formed from the interaction of hydrindene, 2-methyl-1-naphthoyl chloride, and $AlCl_3$ when heated gives a mixture of 5 : 6-*cyclo*penteno-1 : 2-benzanthrene (this vol., 612) (*picrate*, m. p. 195°; quinone, m. p. 184·5—185·5°), and (?) 6 : 7-cyclo*penteno*-1 : 2-*benzanthracene*, m. p. 164—165° (*quinone*, m. p. 182—184°), purified through the *picrate*, m. p. 180°. 1 : 2 : 5 : 6-Dibenzanthraquinone or 5 : 6-*cyclo*penteno-1 : 2-benzanthraquinone on oxidation with $KMnO_4$ in hot H_2SO_4 gives *anthraquinone*-1 : 2 : 5 : 6-*tetracarboxylic acid*, m. p. >360°, purified through the Me_4 ester, m. p. 292—293°, which is obtained from the Ag salt.

A. A. LEVI.

Coloured hydrocarbons. Violet hydrocarbon, $C_{36}H_{22}$. C. DUFRAISSE and M. BADOCHE (Compt. rend., 1931, **193**, 529—531).—$C_{36}H_{24}$ (this vol., 1151) with NaOEt gives a violet *hydrocarbon*, $C_{36}H_{22}$, m. p. 270—271°, considered to be phenylenediphenyldibenzbifulvene. The absorption spectrum was measured.

A. A. LEVI.

Aniline and methyl chloride. W. D. BANCROFT and B. C. BELDEN (J. Physical Chem., 1931, **35**, 3090—3091).—MeCl and NH_2Ph react slowly at room temp. yielding mainly NHPhMe,HCl and a trace of a magenta-coloured dye. Below 180°, MeCl and dry biuret do not react.

L. S. THEOBALD.

Condensation of ethyl propylacetoacetate with aromatic amines. I. G. V. JADHAV (J. Indian Chem. Soc., 1931, **8**, 681—684).—When Et *n*-propylacetoacetate is heated with NH_2Ar, a mixture of the carbamide $CO(NHAr)_2$ and the anilide CHPrAc·CO·NHAr is usually produced; long heating favours carbamide formation. The following are new: n-*propylacetoacet-anilide*, m. p. 96—97°; -o-, m. p. 105—106°, and -p-, m. p. 112—113°, -*toluidides*; -p-*anisidide*, m. p. 115°; -p-*phenetidide*, m. p. 115°; -m-4-*xylidide*, m. p. 100—101°; -p-*xylidide*, m. p. 113—114°. s-*Di*-m-4- and s-*di*-p-*xylylcarbamides* have m. p. 239—240° and above 275°, respectively.

H. BURTON.

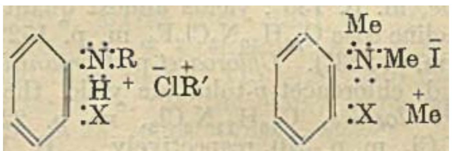
Polysulphides of arylthiocarbimides. T. G. LEVI (Gazzetta, 1931, **61**, 619—622).—Previous work on sulphides of arylthiocarbimides is discussed. The *hexasulphides* of phenyl- (m. p. 80—90°), *o*-tolyl-, and *p*-tolyl-thiocarbimides are obtained by the action of S_2Cl_2 on the NH_4 aryldithiocarbamates.

E. E. J. MARLER.

Polymorphism. II. Further researches on *o*-nitroaniline. N. H. HARTSHORNE and A. STUART (J.C.S., 1931, 2583—2591).—A third form, γ, of *o*-nitroaniline has been identified (cf. A., 1930, 764) and is apparently the most stable; it is that described by von Jaeger (Z. Krist., 1905, **40**, 114) and by Herrmann and Burak (A., 1929, 18). It has been prepared by stabilisation of the β-form on microscope slides, has m. p. 71·2—71·3°, and is monoclinic. Both α- and β-forms are also monoclinic, and optical properties for each of the forms have been determined. The β-form is preferentially deposited from a melt.

F. R. SHAW.

Steric hindrance. V. J. VON BRAUN and W. RUDOLPH (Ber., 1931, **64**, [*B*], 2465—2473; cf. A., 1930, 466).—The different behaviour of an *o*-substituent in Ar in the reactions Ar·NHR+ClX=Ar·NR·X+HCl and $Ar·NMe_2$+MeI=$Ar·NMe_3I$ is explained by a consideration of electrochemical as well as steric factors. In a compound I and II the electrochemical character of X as well as its steric effect on

(I.)  (II.)

the mobility of H (I) and the additive power of the *tert.*-N (II) must be considered. In (I) a negative X (Cl, Br) attracts the positive H into its field more powerfully and renders it less reactive with ClR' than does a positive X (Me); in (II) the influence of X on the Me of MeI is similar, *i.e.*, the final effect is that Cl or Br afford less "steric hindrance" than Me. In conformity with these views it is shown that *o*-fluorodimethylaniline adds MeI with great readiness, whereas *o*-fluoroimido-chlorides are very stable, and that strongly electronegative substituents make their

presence felt in the *m*- but not in the *p*-position, whereas the weakly positive Me group has scarcely any action.

The reaction of the Ac and chloroacetyl derivatives of the amines with PCl_5 is effected by admixture at $\not>$ 20° and keeping the Ac compounds for 3 hr. at 20° and for 1 hr. at 65°, and of the chloroacetyl compounds for 16 hr. at 20° and for ½ hr. at 60°. The following compounds are described: o-*fluorodimethylaniline*, b. p. 64—65°/13 mm. (*picrate*, m. p. 131°; *methiodide*, decomp. 21°), transformed by CH_2O into 2-*fluoro*-4-*hydroxymethyldimethylaniline*, b. p. 115—120°/0·1 mm. (*picrate*, m. p. 125°; *methiodide*, m. p. 110°); o-*fluoroacetanilide*, m. p. 80°, b. p. 140—142°/14 mm., converted into the *imide chloride* $C_6H_4F·N:CMeCl$, b. p. 70°/0·25 mm.; the *amidine* base $C_6H_4F·N:CMe·N(C_6H_4F)·CCl:CH_2$, m. p. 85° (non-cryst. *hydrochloride*); o-*fluorochloroacetanilide*, b. p. 150—151°/14 mm., m. p. 87°, and the *imide chloride* $C_6H_4F·N:CCl·CH_2Cl$, b. p. 83—85°/0·2 mm.; m-*fluoroacetanilide*, m. p. 88°, converted by PCl_5 into the corresponding *imide chloride*, b. p. 70°/0·25 mm., and, mainly, the *amidine*, $C_{16}H_{13}N_2ClF_2$, m. p. 74°; m-*fluorochloroacetanilide* and the corresponding *imide chloride*, b. p. 112—115°/0·55 mm., and the quinoline *base*, $C_{16}H_{10}N_2Cl_2F_2$, m. p. 186° (*hydrochloride*, decomp. 216° after darkening at 206°); the quant. behaviour of chloroacet-*m*-chloroanilide is described (cf. this vol., 236); *chloroacet*-m-*toluidide*, m. p. 88°, b. p. 154°/0·2 mm., and the *quinoline hydrochloride*, $C_{18}H_{17}N_2Cl_3$, m. p. 214°.

3-Nitro-*o*-toluidine is transformed through the corresponding *diazonium fluoborate*, decomp. 143° after softening at 120°, into 2-*fluoro*-3-*nitrotoluene*, b. p. 110—111°/12 mm., reduced by $SnCl_2$ to 2-*fluoro*-m-*toluidine*, b. p. 85—87°/12 mm. (*picrate*, m. p. 205°; *hydrochloride*, m. p. 197°). The *Ac* derivative, b. p. 167—170°/14 mm., is converted by PCl_5 into the *imide chloride*, C_9H_9NClF, b. p. 97°/high vac., and, mainly, the *chlorovinylamidine*, $C_6H_3MeF·N:CMe·N(CHCl:CH_2)·C_6H_3MeF$, m. p. 90° (non-cryst. *hydrochloride*). The Ac derivative of *vic*-*o*-xylidine yields the corresponding *imide chloride*, b. p. 108—110°/3 mm., and the *chlorovinyl* base, $C_{20}H_{23}N_2Cl$, m. p. 94° (non-cryst. *hydrochloride*). *p*-Fluoroacetanilide affords essentially the *chlorovinyl* base, $C_{16}H_{13}N_2ClF_2$, m. p. 101°, and a little imide chloride due probably to incomplete reaction. p-*Fluorochloroacetanilide*, m. p. 130°, yields almost quantitatively the quinoline *base* $C_{16}H_{10}N_2Cl_2F_2$, m. p. 152° (*hydrochloride*, m. p. 233°). *Chloroacet*-p-*chloroanilide*, m. p. 168°, and chloroacet-*p*-toluidide yield the *quinoline hydrochlorides*, $C_{16}H_{11}N_2Cl_5$, m. p. 226°, and $C_{18}H_{17}N_2Cl_3$, m. p. 270, respectively. H. WREN.

Affinity of organic residues. VIII. J. VON BRAUN, W. MAY, and R. MICHAELIS (Annalen, 1931, **490**, 189—200).—The relative strengths of attachment of the CH_2Ph residue in the substituted dibenzylmethylamines and dibenzyl sulphides are determined by the nature of the fission products with CNBr of substances containing two different radicals (cf. A., 1926, 1231); in both series the order of increasing affinity is: *p*-methylbenzyl, benzyl, *m*-methylbenzyl, *o*-methylbenzyl, and in the methylamine series *p*-methoxybenzyl, *p*-phenylbenzyl, *m*-methylbenzyl. The required substituted dibenzylmethylamines are separated by distillation from the mixture produced by combination of a benzylmethylamine with the benzyl chloride. For the prep. of the substituted dibenzyl sulphides a substituted benzyl chloride is treated with NH_4 dithiocarbamate in EtOH, the thiourethane produced hydrolysed by alkali, and the resulting mercaptan condensed with the second benzyl chloride. The following are described and appear to be new: p-*methyl*-, b. p. 82—84°/11 mm. (*picrate*, m. p. 145°; *hydrochloride*, m. p. 174°), and m-*methylbenzylmethylamine*, b. p. 86—88°/12 mm. (*picrate*, m. p. 133°; *hydrochloride*, m. p. 149°); 3 : 4′-*dimethyl*-, b. p. 173—175°/12 mm. (*methiodide*, m. p. 189°), 2 : 3′-*dimethyl*-, b. p. 173—175°/11 mm. (*methiodide*, m. p. 175°), 2 : 4′-*dimethyl*-, b. p. 178—180°/14 mm. (*methiodide*, m. p. 207°), 3-*methyl*-, b. p. 162—163°/11 mm., 4-*methoxy*-, b. p. 187—189°/14 mm., 2-*methyl*-, b. p. 164—166°/10 mm. (*methiodide*, m. p. 199°), 4-*methoxy*-4′-*methyl*-, b. p. 195—198°/15 mm., and 4-*methoxy*-4′-*phenyl*-*dibenzylmethylamine*, b. p. 222—224°/0·6 mm.; m-*methylbenzyl*-, b. p. 158—160°/11 mm., p-*methylbenzyl*-, b. p. 156—158°/13 mm., and *diphenylyl-methylcyanamide*, b. p. 218—220°/11 mm.; m-*methylbenzyl*-, m. p. 175°, and *anisyl*-, m. p. 142°, -*trimethylammonium bromides*; 2-*methyl*-, m. p. 177°, 3 : 3′-*dimethyl*-, m. p. 183°, 4 : 4′-*dimethoxy*-, m. p. 205°, and 4 : 4′-*dimethoxy*-4″-*methyl*-, m. p. 100—105° (impure ?), -*tribenzylmethylammonium bromides*; p-*methyl*-, m. p. 104°, and m-*methyl-benzyldithiourethane*, m. p. 68°; p-*methyl*-, b. p. 89—90°/11 mm., and m-*methyl-benzyl mercaptan*, b. p. 90°/12 mm. (*disulphides* oily in both cases); 2 : 3′-, 2 : 4′-, and 3 : 4′-*dimethyl*-, and 3-, and 2-*methyl-dibenzyl sulphides*; *benzyl*, b. p. 120—122°/14 mm., and o-, b. p. 148—150°/15 mm., and m-*methylbenzyl thiocyanate*, b. p. 148—150°/14 mm.; p-, m. p. 92°, and m-*methylbenzyl* β-*naphthyl ether*, m. p. 85°. *Anisylidenebenzylamine*, b. p. 216°/12 mm., is reduced by Na and EtOH to 4-*methoxydibenzylamine*, b. p. 206°/12(?) mm. (*hydrochloride*, m. p. 213°; *picrate*, m. p. 120°; *Bz* derivative, m. p. 65°). The Bz derivative is converted by PCl_5 (1 mol.) at 115—120° into benzylbenzamide and anisyl chloride (4-*methoxydiphenylamine*, m. p. 65°). H. A. PIGGOTT.

Ditolyl series. II. Resolution into optical antipodes of *dl*-2-nitro-2′-amino-6 : 6′-dimethyldiphenyl. A. ANGELETTI [with P. GUALA] (Gazzetta, 1931, **61**, 651—656).—Reduction of 2 : 2′-dinitro-6 : 6′-dimethyldiphenyl with NH_4HS gives 2-*nitro*-2′-*amino*-6 : 6′-*dimethyldiphenyl*, m. p. 122—123°, which is resolved by combination with *d*-tartaric acid, giving the d-*tartrates* of l-, $[\alpha]_D^{20}$ −40°, and d-2-*nitro*-2′-*amino*-6 : 6′-*dimethyldiphenyl*, $[\alpha]_D^{20}$ +40. The base is not easily racemised. E. E. J. MARLER.

Derivatives of naphthalene-2-sulphonic acid. F. FABROWICZ and W. LESNIANSKI (Rocz. Chem., 1931, **11**, 636—654).—4-*Benzeneazo*-α-*naphthylamine*-6- and -7-*sulphonic acids* yield on treatment in NaOH solution with $NaHSO_3$ 1 : 4-*diaminonaphthalene*-6- and -7-*sulphonic acids*, the former of which is oxidised by HNO_3 to 1 : 4-*naphthaquinone*-6-*sulphonic acid*. 1-Nitronaphthalene-6- and -7-sulphonic acids, m. p.

118—119° and 135—136°, respectively, yield on reduction with $(NH_4)_2S$ 1-*hydroxylaminonaphthalene*-6- and -7-*sulphonic acids*, whilst on treatment with NH_4HS followed by conc. HCl 4-*amino-α-naphthol*-6- and -7-*sulphonic acids* are obtained. These yield 4-*diazo-α-naphthol*-6- and -7-*sulphonic anhydrides* on treatment with Et nitrite, whilst on oxidation with conc. HNO_3 1 : 4-*diazonaphthol*-6- and -7-*sulphonic acids* are produced. Reddish-brown dyes are obtained by diazotising the above aminosulphonic acids and coupling with β-naphthol. R. TRUSZKOWSKI.

Effect of the lactonic ring on the colour of azo-dyes. D. CHAKRAVARTI (J. Indian Chem. Soc., 1931, **8**, 503—509).—Azo-derivatives of coumaric acid, although approx. the same colour as the corresponding coumarin derivatives, have a much greater affinity than the latter for fibres. The following dyes were prepared either by coupling diazotised arylamines with coumarin in NaOH solution, or by coupling diazotised 6-aminocoumarin (modified prep. from 6-nitrocoumarin, m. p. 185°) with phenols or coumarin derivatives in NaOH solution : 6-*azocoumarin*, yellow, m. p. above 300°; *coumarinazo*-o-*coumaric acid*, light brown, decomp. 177°; *azo*-o-*coumaric acid*, reddish-brown, m. p. above 300°; *coumarinazo*-4 : 7-*dimethylcoumarin*, greenish-yellow, m. p. 280°; *coumarinazo*-4 : 6-*dimethylcoumarin*, golden-yellow, m. p. 262°; *coumarinazo-4-methyl-α-naphthacoumarin*, orange, m. p. above 280°; *coumarinazo-7-hydroxy-4-methylcoumarin*, softening at 205°; *coumarinazo*-7 : 8-*dihydro-4-methylcoumarin*, brownish-black, softening at 282°; *coumarinazoresorcinol*, reddish-brown, m. p. 245°; *coumarinazodimethylaniline*, reddish-yellow, m. p. 231°; 8-p-*nitrobenzeneazo-6-iodocoumarin*, reddish-brown; *coumarinazo-6-iodocoumarin* (I), brown; 8-*coumarinazo-6-aldehydocoumarin* (II), brown; p-*nitrobenzeneazo*-7 : 8-*dihydroxy-4-methylcoumarin*, brown, softening at 292°. The colours developed on silk and wool are given for the above compounds and for benzene-, *o*-, *m*-, and *p*-nitrobenzene-, naphthalene-α- and -β-azocoumarin, diphenylbisazodicoumarin, benzeneazo-4 : 6-dimethylcoumarin, and the corresponding coumaric acids. Coumaric acids could not, however, be obtained from the azodimethylcoumarins. The acids from (I) and (II) probably exist in the quinonoid form. 6-Nitrocoumarin does not form azo-compounds. R. S. CAHN.

Attempts to prepare dyes from fluorenone. A. C. SIRCAR and K. C. BHATTACHARYYA (J. Indian Chem. Soc., 1931, 8, 637—643).—Fluorenone-2-diazonium chloride couples with the following substances yielding *azo*-compounds (m. p. given in parentheses) which dye wool evenly from a 1% H_2SO_4-bath in shades varying from orange-yellow to scarlet and bluish-violet : β-naphthol (192—194°); PhOH (213°); NMe_2Ph (193°); NEt_2Ph (above 310°); salicylic acid (216°); 3-hydroxy-β-naphthoic, naphthionic, α-naphthol-4-sulphonic, and β-naphthol-3 : 6- and -6 : 8-disulphonic acids (all above 310°). Arylidene-2-aminofluorenones, prepared from 2-aminofluorenone (I) and the requisite araldehyde (usually in EtOH), are not satisfactory dyes; the following are described : *benzylidene*, m. p. above 290°; o-, m. p. 230°, m-, m. p. above 290°, and p-, m. p. above 290°, -*hydroxybenzylidene*; o-, m. p. 152°, m-, m. p. 213°, and p-, m. p. above 290°, -*nitrobenzylidene*; p-*acetamidobenzylidene*, m. p. above 290°; p-*dimethylaminobenzylidene*, m. p. 256°; 2 : 4-*dihydroxybenzylidene*, m. p. above 290°, and 4-*hydroxy-3-methoxybenzylidene*, m. p. above 290°. 2-*Oxamido*-, -*phthalamido*-, -*malonamido*-, -*succinamido*-, and -*glutaramido-fluorenones*, all not melted at 290°, are obtained from 2 mols. of (I) and 1 mol. of the requisite acid chloride in $PhNO_2$. s-*Di-2-fluorenonylcarbamide* and -*thiocarbamide*, both m. p. above 290°, were prepared. None of these amides gives a sol. vat when reduced with hyposulphite. H. BURTON.

Chemical reactions induced by light. II. C. PICCININI and L. VECCHIOTTI (Gazzetta, 1931, **61**, 626—630; cf. A., 1930, 1180).—In a mixture of $PhNO_2$ and NH_2Ph exposed to sunlight for 5 months, azoxybenzene, *o*-hydroxyazobenzene, and traces of *p*-aminophenol are detected. The action is not due to the sun's heat and does not occur when luminous radiations are excluded. E. E. J. MARLER.

***p*-Alkylsulphonylphenylhydrazines.** E. KOENIGS and A. WYLEZICH (J. pr. Chem., 1931, [ii], **132**, 24—38).—*p*-Bromothiophenol is alkylated and the product oxidised by H_2O_2 to the sulphone, the Br in which is readily replaced by action of N_2H_4 in EtOH at 100—120°. The following are described : p-*bromophenyl*, methyl, *ethyl*, m. p. 56—57°, n-*propyl*, m. p. 52—53°, iso*propyl*, m. p. 67°, n-*butyl*, m. p. 61°, iso*butyl*, m. p. 49°, n-*hexyl*, m. p. 49°, *benzyl*, m. p. 159°, and *phenylethyl*, m. p. 86—87°, *sulphones*; p-*methyl*-, m. p. 135—136° (*benzylidene* derivative, m. p. 206—208°; indefinite compounds, m. p. 155—176°, with dextrose), p-*ethyl*-, m. p. 112—113°, p-n-*propyl*-, m. p. 104—105°, p-iso*propyl*-, m. p. 110—111°, p-n-*butyl*-, m. p. 139—140°, p-iso*butyl*-, m. p. 127—128°, p-iso*amyl*-, m. p. 143°, p-n-*hexyl*-, m. p. 125—126°, p-*phenyl*-, m. p. 202—203°, p-*benzyl*-, and p-*phenylethyl*-, m. p. 144—145°, -*sulphonylphenylhydrazines*; *methylenedi*-p-*bromophenyl sulphide*, m. p. 77°, *sulphone*, m. p. 209—210°; s-*ethylenedi*-p-*bromophenyl sulphide*, m. p. 177°, *sulphone*, m. p. 271—272°; s-*pentamethylenedi*-p-*bromophenyl sulphide*, m. p. 70—71°, *sulphone*, m. p. 151°. The disulphones did not react normally with N_2H_4 to give the hydrazine; in the case of the ethylene compound fission to *p*-methylsulphonylphenylhydrazine occurred. H. A. PIGGOTT.

***m*-Phenylenedihydrazine.** H. WIELAND, D. JUCHUM, and J. MAIER (Ber., 1931, **64**, [*B*], 2513—2516).—Resorcinol is converted by N_2H_4 pyrosulphite and N_2H_4,H_2O at 115—120° into m-*phenylenedihydrazine*, m. p. 124° (decomp.), stable when dry but unstable in aq. solution [*hydrochloride*; *sulphate*; *oxalate*, decomp. 138°; *dibenzylidene*, m. p. 254°, Ac_2 m. p. 227° (decomp. after darkening at 222°), Bz_2, decomp. 225°, derivatives; *disemicarbazide*, decomp. 272°]. Attempts to prepare compounds with a 10-membered hetero-ring were unsuccessful. With CH_2Ac_2, *m*-phenylidenedihydrazine affords m-*phenylene*-1 1′ *di*-3 : 5-*dimethylpyrazole*, $C_6H_4\left(\cdot N{<}\begin{matrix}N{=\!=}CMe\\ CMe{:}CH\end{matrix}\right)_2$, m. p. 106°. H. WREN.

Aromatic diazo-compounds. III. H. T. BUCHERER and A. FROHLICH (J. pr. Chem., 1931, [ii], **132**,

72—112).—Yellow-II (A., 1930, 1280; cf. Rowe etc., A., 1926, 625), the formation of which from yellow-I, the isomeride obtained by the action of KOH on *p*-nitrobenzenediazonium β-naphthol-1-sulphonate is discussed, can be esterified (*Et* ester, m. p. 179°) and benzoylated (*Bz* derivative, $C_{23}H_{17}O_6N_3$, m. p. 129°), and reduced to the corresponding NH_2-compound (III), m. p. 231°, without affecting the rest of the mol.; it does not, therefore, appear to contain the diazo-group. A crude reduction product of yellow-I gives (III) with HCl, and on diazotisation and coupling with R-salt gives a reddish-blue dye, converted into the red dye from (III) by HCl. The *substance*, m. p. 229° (IV), obtained by heating yellow-II with HCl at 150° is the simple decarboxylated derivative, and is free from phenolic groups; the corresponding NH_2-compound, m. p. 255°, is obtained both from (III) and HCl and from (IV) by reduction. Yellow-II is decomposed completely by 20% KOH at 150° under pressure, but at the b. p./1 atm. azobenzene, benzidine, NH_2Ph, phthalic acid, and 1 at. proportion of N_2 are produced; distillation with Zn dust gives NH_3 and NH_2Ph, and oxidation with alkaline $KMnO_4$ gives phthalic acid. More drastic conditions are needed for the fission of (III), which with boiling 80% KOH gives *p*-phenylenediamine, NH_3, and phthalic acid.

The action of weak acids in aq. solution (*e.g.*, $NaHCO_3$, H_2CO_3, H_3BO_3, AcOH, and dil. $H_2C_2O_4$) on the *anti*-diazotate of *p*-nitroaniline leads first to formation of the *syn*-diazotate, which apparently is partly hydrolysed to HNO_2 and *p*-nitroaniline, the NO_2-group being simultaneously replaced by OH; the products are 4 : 4′-dinitrodiazoaminobenzene, *p*-hydroxydiazobenzene (20%), and HNO_2. The *o*-NO_2-group is more easily removed, the yield of OH-compound in this case being 50% of theory. The reaction time only, and not the yield, is affected by temp. or pressure conditions, or by the nature of the acid used within the stated limits. An additional negative group in the *m*-position to the NO_2-group markedly increases the ease of its replacement by OH. Thus almost quant. conversion into OH-compound occurs with 2-nitroaniline-4-sulphonic acid, or with 2 : 4-dinitroaniline in about one twentieth the time taken with *o*-nitroaniline, the formation of a chromable azo-dye with R-salt in the latter case pointing to replacement of the *o*-NO_2-group. On the other hand, the *anti*-diazotate from 4-nitroaniline-2-carboxylic acid seems to be stable to $NaHCO_3$. The diazotates from 5- and 6-nitro-*o*-toluidines react with $NaHCO_3$ only very slowly. With HNO_2 the *syn*-diazotates can undergo both the above-mentioned reactions, and also replacement of the diazo- by the NO_2-group (examples: *o*-, *m*-, and *p*-nitroanilines, *p*-chloroaniline, and β-naphthylamine; 2-nitroaniline-4-sulphonic acid is converted mainly into OH-compound).

In spite of the above observations, the dyes obtained by coupling the *anti*-diazotate from *p*-nitroaniline with J- and γ-acids gave *p*-phenylenediamine on reduction, and are therefore *p*-nitro- and not *p*-hydroxy-azo-dyes. *o*-Hydroxyazo-dyes from K-acid, as expected, do not couple with this diazotate. The coupling of pyrogallol, salicylic acid, α-naphthol-3 : 6- and -3 : 8-disulphonic acids, α-naphthylamine-6- and -7-sulphonic acids (mixed), and resorcinol with the *anti*-diazotate proceeds exactly as with *p*-nitrobenzenediazonium chloride, and gives in most cases a mixture of *o*- and *p*-hydroxyazo-dye. Yellow-I is the compound (II) and yellow-II the 1-hydroxy-3-*p*-nitrophenyl-1 : 3-dihydrophthalazine-4-acetic acid of Rowe etc. (*loc. cit.*). H. A. PIGGOTT.

Reactivity of aromatic hydroxyl groups. II. H. L. BASSETT (J.C.S., 1931, 2516—2518).—The rate of reaction (cf. A., 1930, 1033) of certain halogenated phenols with AcBr in AcOEt increases with acidity of the phenol, with the exception of *o*- and *p*-iodophenols. The abnormal slowness of the *o*-substituted compounds may be due to steric hindrance, but it is modified by a *p*-Me group. F. R. SHAW.

Decomposition of phenol and naphthol ethers by concentrated hydrochloric acid. G. B. KOLHATKAR and R. P. GHASWALLA (J. Indian Chem. Soc., 1931, 8, 511—516).—The numbers quoted after the following ethers are the % hydrolysis taking place when the ethers are heated with 10*N*-HCl at 130° for 2 hr.; the numbers in parentheses and brackets refer to 5*N*-HCl at 130° and 10*N*-HCl at 100°, respectively, from 2 hr.: PhOMe, 33; PhOEt, 14·8; *m*-, *o*-, and *p*-nitroanisole, 6·4 (1·3) [1·29], 10·83 (1·95) [1·9], and 12·77 (2·4) [2·3], respectively; *m*-, *o*-, and *p*-chloroanisole, 3·55, 9·9, and 12·8, respectively; *m*-, *o*-, and *p*-bromoanisole, 2·33, 4·67, and 6·3, respectively; *m*-, *o*-, and *p*-tolyl Me ether, 11·4, 12·1, 16·1, respectively; *m*-, *o*-, and *p*-aminoanisole, 12, 35·5, 75 [33·25], respectively; *m*-, *o*-, and *p*-acetylanisole, 12, 53·8, 68·3 [8·8], respectively; 2 : 4- and 3 : 5-dinitroanisole, 3·3 and 3·7, respectively; 2 : 4 : 6-tribromoanisole, 3·7; *p*-nitrophenetole, 5·34; *p*-chlorophenetole, 6·3; *p*-bromophenetole, 3·5; *p*-methylphenetole, 5·4; α-naphthyl Me ether, 15·7; β-naphthyl Me ether, 26·8; *ar*-tetrahydro-α-naphthyl Me ether, 9·2. *p*-Nitrophenol can be determined by KBr–$KBrO_3$ mixture in the presence of its Me and Et ethers, since the latter are unaffected by the reagent. Other phenols were determined by bromination after removal of the ethers by Et_2O; this method is, however, inapplicable to *m*-bromophenol, 2 : 4 : 6-tribromophenol, and the aminophenols, and in these cases the undecomposed ether was extracted and weighed. Br, Cl, NO_2, and Me increase, whilst Ac and NH_2 decrease, the stability of the ethers; the order for position isomerides is regularly $p>o>m$; phenetoles are more stable than anisoles. R. S. CAHN.

Synthesis of thyronamine. R. STOHR (Z. physiol. Chem., 1931, **201**, 142—148).—4-*p*-Anisyloxybenzaldehyde (I) was obtained (*a*) from *p*-bromoanisole and PhOH by Harington's method (A., 1926, 724), (*b*) from *p*-bromonitrobenzene and quinol Me ether through the stages 4-*p*-anisyloxy-nitrobenzene, m. p. 111°, -aniline, m. p. 79° (lit. 81—82°) (*hydrochloride*, m. p. 212°), -*benzonitrile*, m. p. 109° (converted into the aldehyde with $SnCl_2$ and HCl by way of the aldimine–$SnCl_4$ additive product). Condensation of (I) with $MeNO_2$ in presence of KOH yields ω-*nitro*-4-p-*anisyloxystyrene* (II), m. p. 79°. Reduction of (II) with Zn dust and AcOH in EtOH

affords the *oxime*, which on reduction with Na–Hg in AcOH and EtOH gives 4-p-*anisyloxyphenylethylamine* (*hydrochloride*, m. p. 221·5°), which when heated with HI yields thyronamine. J. H. BIRKINSHAW.

Orientation in the aromatic ether series. J. REILLY, P. J. DRUMM, and B. DALY (Proc. Roy. Irish Acad., 1931, **40**, B, 90—93).—The product of nitration of phenyl *p*-tolyl ether is 4 : 2′-dinitro-4′-methyldiphenyl ether, since it is identical with the products of nitration of 4-nitrophenyl *p*-tolyl ether, or of Ph 3-nitro-*p*-tolyl ether. The product of nitration of 2-nitrophenyl *p*-tolyl ether is probably the 2 : 2′-$(NO_2)_2$-derivative. A. A. LEVI.

Sulphur isomerism of benzyl sulphide. O. HINSBERG (Ber., 1931, **64**, [*B*], 2500—2504; cf. A., 1929, 310, 1269).—The action of 70% $HClO_4$ on α-benzyl sulphide, m. p. 49°, in C_6H_6 yields β-*benzyl sulphide perchlorate*, decomp. 178°, benzyl disulphide, and dibenzyl. The perchlorate is transformed into the *hydrochloride*, m. p. 81°, which rapidly decomposes when preserved into HCl, and a liquid (? β-benzyl sulphide), isomerising to the α-sulphide, m. p. 49°, and the *picrate*, m. p. 140°. The perchlorate is converted by 1% KOH–MeOH slowly at room temp., more rapidly when heated, into the non-cryst. β-*benzyldibenzyl sulphide*, $CH_2Ph{\cdot}CHPh{\cdot}S{\cdot}CH_2Ph$, oxidised through the *sulphoxide* to β-*benzyldibenzylsulphone*, m. p. 122°. Prolonged contact of the perchlorate with 1—2% KOH–EtOH leads to the formation of α-*benzyldibenzyl sulphide*, m. p. 64°, oxidised by H_2O_2 in Ac_2O to the corresponding *sulphone*, m. p. 157°. H. WREN.

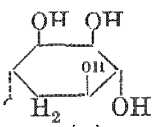
Crystalline form of diphenyldiphenylene-ethylene, diphenyldiphenylene-ethylene oxide, and of the "mixed crystals" formed therefrom. O. ZEDLITZ (Ber., 1931, **64**, [*B*], 2424—2428).—Crystallographic data are recorded for the materials (cf. Schlenk and Bergmann, A., 1928, 1031 *et seq.*; Kliegl, this vol., 1413). The substances represent three differing types of crystal which are assigned to the same class. The expression "mixed crystals" is not justified, since they are not isomorphous mixtures, but probably mol. compounds. H. WREN.

Action of oxalyl chloride on thymol, guaiacol, pyrocatechol, and quinol. J. MIKŠIĆ and Z. PINTEROVIĆ (Glasń. Hem. Drust. Ktal. Jugoslav., 1930, 6 pp.; Chem. Zentr., 1931, i, 2607).—Thymyl oxalate has m. p. 61°; guaiacyl oxalate has m. p. 127°; pyrocatechyl oxalate has m. p. 184°. Quinyl oxalate was not obtained. A. A. ELDRIDGE.

Dinaphthyl derivatives. A. KORCZYNSKI and T. TUCHOLSKI (Rocz. Chem., 1931, **11**, 655—663).—2 : 2′-Dimethoxy-αα-dinaphthyl yields an oily additive *product* on nitration in AcOH, which on keeping deposits 2 : 2′-*dimethoxy*-4 : 4′-*dinitro*-αα′-*dinaphthyl*, m. p. 244°, which on reduction yields the corresponding $(NH_2)_2$-derivative (Ac_2 derivative, m. p. 256°); this on diazotisation and coupling with H-acid yields a product, the K salt of which $(C_{42}H_{26}O_{10}N_6S_4K_6)$ forms colloidal solutions with H_2O. This dye is substantive for cotton, which is dyed a violet colour. R. TRUSZKOWSKI.

Derivatives of 1 : 2 : 3 : 4-tetrahydroxybenzene. I. W. BAKER and H. A. SMITH (J.C.S., 1931, 2542—2549).—2-*Hydroxy*-3 : 4-*dimethoxybenzaldehyde*, (I), m. p. 74° (*phenylhydrazone*, m. p. 156°), obtained from pyrogallol 1 : 2-Me_2 ether by the Gattermann reaction, may be methylated to 2 : 3 : 4-trimethoxybenzaldehyde (*phenylhydrazone*, m. p. 155—156°). Oxidation of (I) with H_2O_2 affords 1 : 2-dihydroxy-3 : 4-dimethoxybenzene (Bz_2 derivative, m. p. 96°), identical with the substance obtained by Ciamician and Silber (A., 1896, i, 608) from dill apiole. It is methylated to 1 : 2 : 3 : 4-tetramethoxy- and methylenated to 1 : 2 - methylenedioxy - 3 : 4 - dimethoxy - benzene (characterised by its Br_2-derivative). Nitration of pyrogallol 1 : 2-Me_2 ether gives 4-*nitro*-, m. p. 102—103° [methylated to the trimethyl compound (II)], and under different conditions to 4 : 6-*dinitropyrogallol* 1 : 2-*dimethyl ether*, m. p. 76°. Reduction of (II) yields 4-aminopyrogallol Me_3 ether, the hydrochloride of which is oxidised to 2 : 3-*dimethoxy*-p-*benzoquinone*, m. p. 66—67°. This is reduced by Zn and AcOH to 2 : 3-dimethoxyquinol (*diacetate*, m. p. 54—56°), which is methylated to 1 : 2 : 3 : 4-tetramethoxybenzene. Reduction of 3-nitroveratrole with Zn gives o-*azoxyveratrole*, m. p. 125—126°, and not the required hydroxylamine. F. R. SHAW.

Configuration of quercitol. H. KILIANI (Ber., 1931, **64**, [*B*], 2473—2476; cf. Karrer, A., 1926, 398).—Oxidation of quercitol with HNO_3 (*d* 1·38) does not appear to yield mannosaccharodilactone. The main product is K *l*-trihydroxyglutarate, $[\alpha]_D + 8{\cdot}55°$ in H_2O. Although the formation of *l*-saccharic acid could not be established, the configuration (I) is regarded as proved for quercitol. H. WREN.



(I.)

Preparation and utilisation of organomagnesium compounds without use of ether. I. Preparation of β-phenylethyl alcohol. P. SCHORIGIN, V. ISSAGULIANZ, A. GUSSEVA, V. OSSIPOVA, and C. POLJAKOVA (Ber., 1931, **64**, [*B*], 2584—2590).—MgPhCl is prepared by heating Mg turnings with PhCl at 160—165° in an Fe autoclave provided with mechanical stirring; the best yields, 70% calc. on PhCl or 59% calc. on Mg, are obtained by use of 1 g.-atom Mg and 1 mol. of PhCl. Ph_2 is invariably produced in amount increasing with that of PhCl. I accelerates the change without giving better yields, but affords a darker and more compact product; $NPhMe_2$ retards the reaction. The solubility of the product (g. per 100 c.c. calc. as MgPhCl) in $Et_2O+C_6H_6$ (1 : 1), *iso*amyl ether, benzyl Me ether, benzyl Et ether, and C_6H_6 is respectively 17, 16, 14·5, 14, and 3·6. The equilibrium 2MgPhCl $\rightleftharpoons$ $MgPh_2+MgCl_2$ lies towards the right. Dissolution of the MgPhCl in C_6H_6 and cautious addition of ethylene chlorohydrin at $\not>$ 35°, followed by distillation of the solvent, affords $CH_2Ph{\cdot}CH_2{\cdot}OH$ in 53% yield. Substitution of ethylene oxide in C_6H_6 for the chlorohydrin gives $CH_2Ph{\cdot}CH_2{\cdot}OH$ in 70% yield; separation of the product from Ph_2 is effected by treatment with $CaCl_2$ in C_6H_6. H. WREN.

Reduction of aromatic carbinols. A. VANSCHEIDT and B. MOLDAVSKI (J. Gen. Chem. Russ.,

1931, **1**, 304—324).—The reduction of aromatic carbinols by $SnCl_2$ and HI is shown to proceed in two stages: $CR_3\cdot OH+2HI \longrightarrow CHR_3+I_2+H_2$; I_2+SnCl_2+2HCl —— $2HI+SnCl_4$. Polyarylmethanes are produced in the cases of $CPh_3\cdot OH$, diphenyl-α-naphthylcarbinol, phenylxanthenol, $CHPh_2\cdot OH$, fluorenol, and others. Reduction of phenylfluorenol gives diphenyldidiphenylene-ethane. On continued boiling phenylfluorene is formed. Xanthhydrol gives dixanthyl. 9-Alkylfluorenols are unstable in presence of acids and of $SnCl_2$, but a mixture of $SnCl_2$ and HI in acetic acid reduces them, giving dimerides of the radicals, viz., *didiphenylenedimethylethane*, m. p. 209°, *didiphenylenediethylethane*, m. p. 210° (corr.), *didiphenylenedibenzylethane*, m. p. 203—203·5° (corr.). Reduction of phenylfluorenol with HI alone in the cold gives unstable fluorenyl iodide, giving difluorenyl on heating. Excess of HI reduces this to phenylfluorene. In the case of 9-ethylfluorenol an intermediate stage is the formation of ethylidenefluorene. In the reduction of alkylfluorenols dehydration is probably an intermediate stage. E. B. UVAROV.

Constitution of cholesterol. II. Metacholesterol. R. DE FAZI (Gazzetta, 1931, **61**, 630—635).—A new method of obtaining metacholesterol by the action of $CuSO_4$ on cholesterol is described. The work of Lifschütz (A., 1919, i, 591) is confirmed. Metacholesterol is formed when cholesterol is exposed to ultra-violet radiation, but Lifschütz' view that the antirachitic properties of irradiated chlolesterol are due to this is disputed. It is reconverted into cholesterol by KOH–EtOH. Its *Br_2* (m. p. 96—97·5°) and *Ac* (m. p. 112—113°) derivatives are described. The latter may be the Ac derivative of cholesterol. Oscillation of the double linking in cholesterol is suggested to account for its transformation into metacholesterol. E. E. J. MARLER.

Attempted use of the Friedel–Crafts reaction with unsaturated compounds. H. WIELAND and C. HASEGAWA (Ber., 1931, **64**, [*B*], 2516—2522).—Attempts to apply the Friedel–Crafts reaction to the synthesis of unsaturated ketones are not successful, probably owing to the sensitiveness of the ketones to $AlCl_3$. Cholesterol, AcCl, and $AlCl_3$ in CS_2 yield 6(?7)-*chlorocholestanyl acetate*, m. p. 151°, converted by short treatment with KOH–MeOH into 6(?7)-*chlorocholestanol*, m. p. 163°, which passes by loss of HCl into cholesterol. Under similar conditions, ergosterol becomes isomerised to a *compound*, $C_{27}H_{42}O$, m. p. 138—140°, $[\alpha]_D^{0}$ —61·1° in $CHCl_3$. αδ-Diphenyl-$\Delta^{\alpha\gamma}$-butadiene, AcCl, and $AlCl_3$ in C_6H_6, but not in CS_2, afford a *compound*, $C_{36}H_{33}O_2Cl$, m. p. 262°, whereas BzCl gives the *substance* $C_{36}H_{30}O$, m. p. 203°. Di*cyclo*pentadiene reacts energetically without giving homogeneous products, whereas distyryl ketone is unexpectedly passive. The base, m. p. 121°, obtained by the action of HCl and HCN on *cyclo*hexene in presence of $AlCl_3$ (cf. A., 1930, 464) does not give an Ac derivative or a nitrosoamine, is stable towards 2*N*-HCl at 180° and towards KOH–EtOH. Since it is converted smoothly by distillation with soda-lime into *cyclo*hexylamine, the constitution $C_6H_4{<}\begin{matrix}N(CH{:}N\cdot C_6H_{11})\cdot CH\cdot OH\\ CH(OH)\text{———————}N\cdot C_6H_{11}\end{matrix}$ is suggested. During the action a *substance*, $C_{25}H_{36}O$, m. p. 150°, is produced. H. WREN.

Photochemical activation of ergosterol. CASTILLE and RUPPOL (Bull. Acad. Roy. Méd. Belg., 1929, 799—821; Chem. Zentr., 1931, i, 3129).—Since the spectrum of ergosterol in hexane shows between 2600 and 3000 Å. four closely neighbouring bands, the three double linkings are considered to belong to one C_6H_6 ring; moreover, the secondary alcoholic group is immediately adjacent to the C_6H_6 ring. Changes caused by irradiation of ergosterol in various solvents were followed in air and in N_2, unchanged ergosterol being determined as digitonide, and unsaturation by Hübl's I method. In absence of O_2 isomerisation occurs. A. A. ELDRIDGE.

Constitution of irradiated ergosterol. A. CASTILLE (Bull. Acad. Roy. Méd. Belg., 1930, 319—325; Chem. Zentr., 1931, i, 3130).—The pairs *iso*ergosterol *B* and ergosterol *B*, and *iso*dihydroergosterol *A* and dihydroergosterol *A* show in the absorption spectra the differences characteristic of *cis–trans*-isomerism. *cis–trans*-Isomerism as between ergosterol and vitamin-*D* is postulated.

A. A. ELDRIDGE.

Ergosterol and certain derivatives. DE BOE (Bull. Acad. Roy. Méd. Belg., 1930, 336—375; Chem. Zentr., 1931, i, 3128—3129).—Fractional crystallisation of Reindel's *iso*ergosterol affords iso*ergosterol* B, m. p. 135—136°, α —66° (*Ac* derivative, m. p. 112°), giving in $CHCl_3$ a yellow colour with H_2SO_4 but no colour with $SbCl_3$ in $CHCl_3$ or $CCl_3\cdot CO_2H$; Liebermann test blue, becoming green and then brown; and *ergosterol* B, m. p. 145—146° (*Ac* derivative, m. p. 139°, affording the *iso*ergosterol *B* on saponification), yielding *iso*ergosterol *B* in air. The ultraviolet absorption spectra of the isomerides were studied. Benzoylergosterol has m. p. 164—165° when prepared from BzCl in pyridine at 0°; BzCl at 170° affords a Bz derivative, m. p. 125—126°, which on hydrolysis gives a mixture of ergosterol *B* and *iso*ergosterol *B*, from which it may be prepared. Windaus' ergosterol *C* is a mixture of *iso*ergosterol *B* and ergosterol *B*; ergosterol is named ergosterol *A*. Reduction of ergosterol *A* with Na and amyl alcohol afforded iso*dihydroergosterol* A, $C_{27}H_{44}O$, m. p. 173—174°, and dihydroergosterol *A*, $C_{27}H_{44}O$ m. p. 208—209 , the latter (the principal product) containing only one OH group. When similarly treated, ergosterol *B* is partly isomerised to α-*iso*-ergosterol *B*, m. p. 188—190° (*Ac* derivative, m. p. 112°, affording on hydrolysis *iso*ergosterol *B*). Dihydroergosterol *A* could not be isomerised with HCl (cf. Heilbron and Spring, A., 1930, 210).

A. A. ELDRIDGE.

Refraction of solutions of compounds with many acetylenic linkings. V. KRESTINSKI and N. PERSSIANZEVA (Ber., 1931, **64**, [*B*], 2363—2370).—Determination of *n* of αε-diphenyl-γ-methyl-$\Delta^{\alpha\delta}$-pentadi-inen-γ-ol, αε-diphenyl-γ-phenylacetylenyl-$\Delta^{\alpha\delta}$-pentadi-inen-γ-ol, αθ-diphenyl-γζ-dimethyl-$\Delta^{\alpha\eta}$-octadi-inene-γζ-diol, and αθ-diphenyl-γζ-diphenylacetylenyl-$\Delta^{\alpha\eta}$-octadi-inene-γζ-diol in AcOEt, *cyclo*hexanone, amyl alcohol, MeOH, C_6H_6, $COMe_2$, and NH_2Ph leads to the following conclusions. In all cases the observed

vals. of *M* are considerably greater than the calc., the differences increasing with increasing no. of CPh·C groups. The *EM* vals., which depend solely on the CPh:C groups, vary considerably from solvent to solvent in the limits, *e.g.*, for the *D* line from 2·25 in NH_2Ph to 4·00 in $COMe_2$. If the mean vals. for all experiments and solvents are chosen, the data EM_α 3·07, EM_D 3·29, EM_β 3·77, and EM_γ 4·30 may be adopted as mean val. of the increment for the CPh:C group. The influence of the solvent is very great, the compounds differing in this respect from the acetylenic and saturated γ-glycols; the lowest results are observed in NH_2Ph, the highest in $COMe_2$. Much smaller differences are observed with phenylacetylene. αε-*Diphenyl-γ-methyl-*$\Delta^{\alpha\delta}$*-pentadi-inen-γ-ol*, m. p. 110—111°, from AcOEt and Mg phenylacetylenyl bromide, αε-*diphenyl-ψ-phenylacetylenyl-*$\Delta^{\alpha\delta}$*-pentadi-inen-γ-ol*, m. p. 130°, from $CO(OEt)_2$, stereoisomeric αδ-*diphenyl-γζ-dimethyl-*$\Delta^{\alpha\eta}$*-octadi-inene-γζ-diols*, m. p. 105—106° and 92—96°, respectively, from acetonylacetone and Mg phenylacetylenyl bromide, and αθ-*diphenyl-γζ-diphenylacetylenyl-*$\Delta^{\alpha\eta}$*-octadi-inene-γζ-diol*, m. p. 136°, from Mg phenylacetylenyl bromide and Et succinate, are described. H. WREN.

Structure and optical rotation. I. Configurational relationship of disubstituted propionic acids containing a phenyl group. II. Optically active trisubstituted methanes containing a phenyl group. P. A. LEVENE and R. E. MARKER (J. Biol. Chem., 1931, **93**, 749—774).—The method previously used for correlation of the configurations of acids of the type $CHPhAlk{\cdot}CO_2H$ (I) is applied to the series $CHPhAlk{\cdot}CH_2{\cdot}CO_2H$ (II). Configuratively related members of (I) (this vol., 711, 821) rotate oppositely to the corresponding members of (II). The members of the configurativelv related pairs of acids [(I), Alk=Me and Et] and [(II), Alk=Me and Et] themselves rotate in opposite directions, indicating that the $\cdot CO_2H$ and $\cdot CH_2{\cdot}CO_2H$ groups are heavier than Me or Et, but lighter than Pr; the same conclusion is reached for the $\cdot[CH_2]_3{\cdot}CO_2H$ group. Rearrangement of the relative positions of the heavier and lighter alkyl groups in CHPhAlkAlk′ also leads to a change in rotation. The effect of a polar group or of a group absorbing in the near ultra-violet differs with its distance from the asymmetric C atom.

The *Et* ester, b. p. 111°/4 mm., $[\alpha]_D^{25}$ −7·41°, of l-β-*phenylbutyric acid*, b. p. 134°/4 mm., $[\alpha]_D^{26}$ −12·38° (from the *dl*-acid by resolution with quinine), is reduced by Na and EtOH in xylene to l-γ-*phenylbutyl alcohol*, b. p. 117°/8 mm., $[\alpha]_D^{25}$ −9·15°, which with PBr_3 gives l-γ-*phenylbutyl bromide*, b. p. 120°/17 mm., $[\alpha]_D^{25}$ −18·52°. The Grignard reagent from this is decomposed by ice and dil. HCl to l-β-*phenylbutane*, b. p. 68°/20 mm., $[\alpha]_D^{24}$ −6·82°. The *Et* ester, b. p. 110°/2 mm., $[\alpha]_D^{25}$ −7·41°, of l-β-*phenylvaleric acid*, b. p. 140°/4 mm., $[\alpha]_D^{25}$ −16·5° in C_6H_6, is similarly converted into l-γ-*phenylamyl alcohol*, b. p. 108°/1 mm., $[\alpha]_D^{25}$ −4·53° (*bromide*, b. p. 127°/15 mm., $[\alpha]^{25}$ −22·23°). The alcohol from Mg *l*-γ-phenylamyl bromide and paraformaldehyde is converted by PBr_3 into the bromide; the Grignard reagent from this is decomposed by ice to d-γ-*phenylhexane* (III), b. p. 103°/25 mm., $[\alpha]_D^{24}$ +0·57°. The *Et* ester, b. p. 123°/2 mm., $[\alpha]_D^{25}$ +3·45°, of d-β-*phenylhexoic acid*, b. p. 152°/4 mm., $[\alpha]^{25}$ +5·93°, is reduced to d-γ-*phenylhexyl alcohol*, b. p. 127°/5 mm., $[\alpha]_D^{25}$ +2·51° (*bromide*, b. p. 112°/2 mm., $[\alpha]_D^{25}$ +10·96°, convertible into (III)]. β-Phenylbutylamine, $[\alpha]_D^{24}$ −3·26°, is treated with NOCl in Et_2O at −50° and the resultant chloride converted into a Grignard reagent; decomp. of this with CO_2 and H_2O gives d-β-*phenylvaleric acid*, b. p. 142°/5 mm., $[\alpha]_D^{24}$ +2·86° in C_6H_6, and *l*-β-phenylbutane, $[\alpha]_D^{24}$ −1·92° (cf. above), respectively. d-β-*Phenylbutyric acid*, b. p. 135°/4 mm., $[\alpha]_D^{26}$ +0·96°, is similarly prepared from β-phenylpropylamine, $[\alpha]_D^{24}$ +9·86°. d-δ-*Phenylheptoic acid*, b. p. 162°/1 mm., $[\alpha]_D^{25}$ +2·12° (prepared from γ-phenylamyl bromide, $[\alpha]_D^{25}$ +11·05°, by the malonate method) (*Et* ester, b. p. 147°/1 mm., $[\alpha]_D^{25}$ +1·05°); d-ε-*phenylheptyl alcohol*, b. p. 145°/1 mm., $[\alpha]_D^{25}$ +1·47° (*bromide*, b. p. 131°/1 mm., $[\alpha]_D^{25}$ +2·45°); d-γ-*phenylheptane*, b. p. 105°/16 mm., $[\alpha]_D^{25}$ +0·97°; l-δ-*phenyloctoic acid*, b. p. 170°/1 mm., $[\alpha]_D^{25}$ −0·82° (from γ-phenylhexyl bromide, $[\alpha]_D^{25}$ −11·85°) (*Et* ester, b. p. 152°/1 mm., $[\alpha]_D^{25}$ −0·49°); l-ε-*phenyloctyl alcohol*, b. p. 147°/1 mm., $[\alpha]_D^{25}$ −1·1° (*bromide*, b. p. 146°/1 mm., $[\alpha]_D^{25}$ −2·18°); d-δ-*phenyloctane*, b. p. 119°/18 mm., $[\alpha]_D^{25}$ +0·62°; d-δ-*phenylhexoic acid*, b. p. 156°/1 mm., $[\alpha]_D^{25}$ +2·01° (from γ-phenylbutyl bromide, $[\alpha]_D^{25}$ +6·03°) (*Et* ester, b. p. 145°/1 mm., $[\alpha]_D^{25}$ +1·4°); d-ε-*phenylhexyl alcohol*, b. p. 127°/1 mm., $[\alpha]_D^{25}$ +1·96° (*bromide*, b. p. 133°/1 mm., $[\alpha]_D^{25}$ +2·03°), and d-β-*phenylhexane*, b. p. 100°/22 mm., $[\alpha]_D^{25}$ +1·96°, are described. β-Phenylhexoic acid, $[\alpha]_D^{23}$ −2·32°, is converted by the Hofmann method into l-β-*phenylamylamine*, b. p. 90°/3 mm., $[\alpha]_D^{25}$ −0·5° in 75% EtOH. H. BURTON.

Conjugated double linkings. XX. Perkin's synthesis. R. KUHN and S. ISHIKAWA (Ber., 1931, **64**, [*B*], 2347—2352).—Condensation does not occur between PhCHO, crotonic anhydride, and K crotonate or between crotonic acid, Ac_2O, and PbO, whereas in presence of *tert.* bases, particularly NEt_3, PhCHO and crotonic anhydride afford α-*vinylcinnamic* [α-*benzylidene-*Δ^β*-butenoic*] *acid*, m. p. 92° (corr.) [*dibromide*, m. p. 172° (corr.)], oxidised by $KMnO_4$ to BzOH and by CrO_3 to CO_2 and H_2O; it is hydrogenated in presence of Pd–$BaSO_4$ to α-benzyl-*n*-butyric acid [anilide, m. p. 89° (corr.)]. The corresponding *ozonide* is converted by boiling H_2O into PhCHO, CH_2O, and $H_2C_2O_4$. *p*-Nitrobenzaldehyde, crotonic anhydride, and NEt_3 at 100° give α-p-*nitrobenzylidene-*Δ^β*-butenoic acid*, m. p. 151·2° (corr.), and α-o-*chlorobenzylidene-*Δ^β*-butenoic acid*, m. p. 124·2° (corr.), is derived similarly from *o*-chlorobenzaldehyde. The mixed enolic anhydride, CHMe:CH·CO·O·C(OH):CH·CH:CH_2, is probably formed intermediately. H. WREN.

Isomerism of 9-fluorene derivatives. A. KLIEGL (Ber., 1931, **64**, [*B*], 2420—2423; cf. A., 1930, 918, 1031).—Mainly a reply to Bergmann (A., 1930, 1031). Re-examination of the β-fluorene-9-carboxylic acid of Schlenk and Bergmann established its identity with the purified, technical α-acid. 9-Methoxyfluorene-9-carboxylic acid has m. p. about 184° (vigorous decomp.) whether prepared from Na 9-methoxyfluorene and CO_2 or from diphenyleneacetic acid. The 9-benzhydrylfluorene obtained from $CHPh_2Na$ and

9-chlorofluorene has m. p. 217° when crystallised from $Pr^{\alpha}OH$ and subsequently from dioxan. The "isomeride" of m. p. 187—189° is a mol. compound of 9-benzhydrylfluorene and difluorenyl, prepared from its components in $Pr^{\alpha}OH$. The existence of dimorphous forms of diphenyldiphenylene-ethylene is admitted, but the product considered by Schlenk and Bergmann to be a stereoisomeride is a mixture of the ethylene and ethylene oxide. H. WREN.

Action of oxalyl chloride on fluorene-9-carboxylic acid. R. STOLLE and L. ESTER (J. pr. Chem., 1931, [ii], **132**, 1—14).—Interaction of fluorene-9-carboxylic acid with $(COCl)_2$ in complete absence of H_2O gives a very small yield of a cyclic *diphenylenyloxalacetic anhydride*, m. p. 311° (decomp.), to which the structure $(C_6H_4)_2C<\begin{matrix}CO\cdot O\\CO\cdot CO\end{matrix}$ is assigned on account of its reaction with pyridine to form 1 : 3 : 4-*triketo*-2 : 5-*bisdiphenylenyl*cyclo*pentane* (I), m. p. about 345°, CO (2 mols.), and CO_2; (I) is also obtained by interaction of fluorene-9-carboxylic acid, $(COCl)_2$, and pyridine, being then occasionally accompanied by a yellow *substance*, $C_{28}H_{16}O_3$, m. p. 283°, probably $(C_6H_4)_2C<\begin{matrix}CO\cdot CO\\O—C(C_6H_4)_2\end{matrix}$. Decomp. of (I) with warm 10% aq. NaOH gives fluorene-9-carboxylic acid, fluorene-9-glyoxylic acid, and decomp. products; with NH_2Ph it gives *fluorene-9-glyoxylanilideanil*, m. p. 245°, and with $NHPh\cdot NH_2$ the corresponding *phenylhydrazidephenylhydrazone*, m. p. 190° (decomp.), and fluorene-9-carboxyphenylhydrazide. *Et* -*diketo*-αα-*bisdiphenylenyladipate*, m. p. 213°, prepared in good yield by action of $(COCl)_2$ on Et potassiofluorene-9-carboxylate, could not be cyclised to (I), being hydrolysed to its components readily by alkalis, and with difficulty by acids. Attempts to hydrolyse *Et bisdiphenylenylacetonedicarboxylate*, m. p. 129° (from $COCl_2$ and Et potassiofluorene-9-carboxylate), failed; it is converted by Ac_2O and anhyd. NaOAc into 9 : 9-*diacetylfluorene*, m. p. 97°, in 90% yield. 2 : 7-*Dibromofluorene*-9-*carboxylic acid*, m. p. 240° (decomp.), prepared from MgEtBr and 2 : 7-dibromofluorene, gives with $(COCl)_2$ and pyridine the Br_4-derivative of (I). *Et fluorene-9-glyoxylate-anil*, m. p. 138°, is prepared by gently warming an equimol. mixture of NH_2Ph and Et fluorene-9-glyoxylate. H. A. PIGGOTT.

Abietic acid. P. LEVY [with H. TILLMANNS] (Ber., 1931, **64**, [*B*], 2441—2446).—Details are given for the conversion of abietic acid by HBr and HCl in AcOH into dibromodihydro-, m. p. 175—176°, and dichlorodihydro-abietic acid, m. p. 190—192° (decomp.) when slowly heated, respectively. Treatment of the Br_2-acid with KOH in EtOH yields a *monohydroxymonohydroabietic acid*, m. p. indef. 154°, not identical with the acid described by Rau and Simonsen (A., 1925, i, 687). Chlorohydroabietic acid, m. p. 192—195° when rapidly heated, is obtained from the Cl_2-acid and AcOH. When heated at 200° the Cl_2-acid gives abietic acid, whereas in boiling quinoline it gives a *product*, $C_{20}H_{30}O_2$, m. p. 187°, $[\alpha]_D^{15}$ −73·17°. Monohydroxymonohydroabietic acid, m. p. 225—227°, is smoothly prepared from the Cl-acid and moist Ag_2O. Abietic esters unite with H halides under the same conditions as the acid; *Me*, m. p. 148°, and *Et*, m. p. 138—140° (decomp.), *dibromodihydroabietate*, *Me*, m. p. 163—164°, and *Et*, m. p. 143—145°, *dichlorodihydroabietate* are described The Cl_2-esters are converted by short treatment with AcOH into *Me*, m. p. 126°, and *Et*, m. p. 82—84°, *monochloromonohydroabietate*, respectively. H. WREN.

4 - Methylthioldiphenylamine - 2′ - carboxylic acid and its derivatives. P. G. SERGEEV (J. Gen. Chem. Russ., 1931, **1**, 279—288).—4-*Methylthioldiphenylamine-2′-carboxylic acid*, m. p. 195—196°, is obtained by the action of 1-bromo-4-methylthiolbenzene on anthranilic acid, and of *p*-methylthiolaniline on *o*-chlorobenzoic acid. The following derivatives were prepared: *Ba* salt, 4-*methylthioldiphenylamine*, m. p. 84·5°; 3-*methylthiolacridone*, m. p. 260—261°; 4-*bromophenylmethylsulphoxide*, m. p. 86—87°; 4-*methylsulphoxidodiphenylamine-2′-carboxylic acid*, m. p. 181°; and 4-*methylsulphonyldiphenylamine-2′-carboxylic acid*, m. p. 186—186·5°. E. B. UVAROV.

Mixed glycerides of salicylic acid. IV. W. HUMNICKI (Rocz. Chem., 1931, **11**, 670—673).—αγ-Dichlorohydrin β-monosalicylate on treatment with Ag_2CO_3, AgOH, or $AgNO_3$ does not yield glyceryl β-salicylate. Merck's "glycosal" is glyceryl α-salicylate; on chlorination with SO_2Cl βγ-dichlorohydrin α-salicylate, m. p. 58°, is obtained. R. TRUSZKOWSKI.

Action of phenylcarbimide on aromatic hydroxy-acids. W. HUMNICKI (Rocz. Chem., 1931, **11**, 674—677).—*o*-, *m*-, and *p*-Hydroxybenzoic acids do not yield urethanes with PhCNO, the only product of reaction being $CO(NHPh)_2$, even in non-aq. media. The *phenylurethane* of salol, m. p. 111—112°, yields salol and $CO(NHPh)_2$ on dissolution in aq. solvents. R. TRUSZKOWSKI.

Preparation of *m*-hydroxybenzonitrile. J. B. CULBERTSON, E. L. CARPENTER, and E. K. NIELSEN (Proc. Iowa Acad. Sci., 1930, **37**, 248—249).—The reactions *m*-nitro⟶*m*-amino⟶*m*-hydroxy-benzaldehyde⟶oxime⟶nitrile were employed. Sn was removed by means of aq. NH_3 from a solution of the residue of an Et_2O extract of the hydroxyaldehyde, the aldehyde adsorbed by the ppt. being extracted with EtOH. The aldehyde was purified by crystallisation from CCl_4 after treatment with norite. On dehydration of the oxime with Ac_2O the Ac derivative is preferably hydrolysed with 10% KOH without previous isolation. CHEMICAL ABSTRACTS.

Physical properties of optical antipodes. A. N. CAMPBELL (Ber., 1931, **64**, [*B*], 2476—2477; cf. A., 1930, 1289).—A reply to Kortüm (this vol., 956). H. WREN.

Azomethines of homophthalimide and its *n*-aryl derivatives. A. MEYER and R. VITTENET (Compt. rend., 1931, **193**, 531—533).—Homophthalimide when condensed with the NO-derivatives of $NPhMe_2$, $NPhEt_2$, antipyrine, and *p*-tolylantipyrine gives p-*dimethylaminophenyl*-, m. p. 243°, p-*diethylaminophenyl*-, m. p. 196—197°, *antipyryl*-, m. p. 224—225° (decomp.), and p-*tolylantipyryl-iminophthalonimide*, m. p. 227—228°. The N-*Ph*, m. p. 210°, N-p-*tolyl*, m. p. 223—224°, N-α-*naphthyl*, m. p. 239—

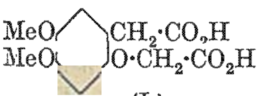
240°, and N-β-*naphthyl*, m. p. 180—181° (decomp.), derivatives of antipyryliminophthalonimide are similarly prepared from the corresponding *N*-arylated homophthalimides. A. A. LEVI.

Differing modes of reaction of magnesium phenyl bromide and lithium phenyl towards derivatives of naphthalic acid. G. WITTIG, M. LEO, and W. WIEMER (Ber., 1931, **64**, [*B*], 2405—2411).—The action of more than 4 mols. of MgPhBr on Me naphthalate leads to ill-defined mixtures, whereas from naphthalic anhydride 9 : 10-dihydroxy-9 : 10-diphenylacenaphthene, m. p. 155—156° (cf. Beschke, A., 1909, i, 917), is produced, reaction being thus accompanied by reduction. From 1 : 8-dibenzoylnaphthalene and MgPhBr an isomeric 9 : 10-*dihydroxy*-9 : 10-*diphenylacenaphthene*, m. p. 171—173°, is produced. Both glycols are converted by HCl in boiling AcOH into 9 : 9-diphenylacenaphthenone and by HCl in cold $CHCl_3$ into 9 : 10-*dichloro*-9 : 10-*diphenylacenaphthene*, m. p. 185° (decomp.), transformed by Cu powder into 9 : 10-*diphenylacenaphthylene*, m. p. 159·5—161°.

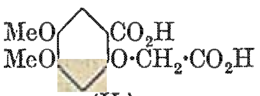
Naphthalic anhydride and 4 mols. of LiPh yield resins, whereas with 2 mols. of the reagent the lactone of 1-hydroxybenzhydrylnaphthalene-8-carboxylic acid, $C_{10}H_6\Big<{}^{CO}_{CPh_2}\Big>O$, m. p. 203—204°, is produced. This adds a further mol. of LiPh, yielding the *compound* $C_{30}H_{22}O$, (I) (? $C_{10}H_6\Big<{}^{CPh(OH)}_{CPh_2}\Big>O$), m. p. 202—203·5°, also obtained from excess of LiPh and Me naphthalate or 1 : 8-dibenzoylnaphthalene. Further reaction to form 1 : 8-di(hydroxybenzhydryl)naphthalene does not take place. (I) is converted by HCl in AcOH into the oxonium *salt*, $C_{10}H_6\Big<{}^{CPhCl}_{CPh_2}\Big>O,HCl$, m. p. 153—155°.

H. WREN.

Rotenone. XV. Structure of derric acid. F. B. LA FORGE (J. Amer. Chem. Soc., 1931, **53**, 3896—3901).—Derric acid is now considered to be (I) (cf. A., 1930, 1187) and rissic acid (Takei, this vol., 490) to be (II), since decarboxyrissic acid (III) (Takei,



(I.)



(II.)

loc. cit.) [*Br*-derivative, m. p. 150°; *Cl*-derivative, m. p. 146° (*Et* ester, m. p. 83°), from (III) and PCl_5; the NO_2-derivative, m. p. 214—215° (*Et* ester, m. p. 164—165°), is prepared from (II) and HNO_3, and is described by Takei as a nitrodimethoxybenzoic acid] is identical with 3 : 4-*dimethoxyphenoxyacetic acid*, m. p. 116—117°, obtained from Na 3 : 4-dimethoxyphenoxide and $CH_2I\cdot CO_2Et$ in EtOH. Takei's suggestion that (III) is 2 : 5-*dimethoxymandelic acid*, m. p. 101° (softens at 90°), is disproved by synthesis of the latter from 2 : 5-dimethoxybenzaldehyde by the usual method. 2 : 3-*Dimethoxymandelic acid* has m. p. 96°. H. BURTON.

***spiro*-Compounds. I.** P. K. PAUL (J. Indian Chem. Soc., 1931, **8**, 717—724).—cyclo*Pentane*-, m. p. 257°, cyclo*hexane*- (I), m. p. 266°, 3-*methyl*cyclo*hexane*-, m. p. 259°, and 4-*methyl*cyclo*hexane*-, m. p. 252°, -spiro-2′ : 4′-*dicyanocyclobutane*-2′ : 4′-*dicarboxylimides* are prepared by Kerr's method (A., 1929, 445) from the appropriate Guareschi imide and CH_2I_2. Hydrolysis of (I) with 2% NaOH gives cyclo*hexane*spiro-2′ : 4′-*dicarbamyl*cyclo*butane*-2′ : 4′-*dicarboxylic acid*, m. p. 180° (decomp.), whilst hydrolysis of the other imides with 10% KOH affords cyclo*pentane*-, m. p. 188°, 3-*methyl*cyclo*hexane*-, m. p. 211°, and 4-*methyl*cyclo*hexane*-, m. p. 204°, -spiro-2′ : 4′-*dicyano*-2′-*carbamyl*cyclo*butane*-4′-*carboxylic acids*. These products are hydrolysed further by 20% NaOH to cyclo*pentane*-, m. p. 190° (decomp.), cyclo*hexane*-, m. p. 190° (decomp.), 3-*methyl*cyclo*hexane*-, m. p. 173° (decomp.), and 4-*methyl*cyclo*hexane*-, m. p. 162° (decomp.), -spirocyclo*butane*-2′ : 2′ : 4′ : 4′-*tetracarboxylic acids*, which when heated at 5° above their m. p. give mixtures (*cis* and *trans*) of the corresponding 2′ : 4′-dicarboxylic acids, separable by treatment with AcCl (whereby the *cis*-form is removed as its anhydride). trans-cyclo*Hexane*-, m. p. 178°, and trans-3-*methyl*cyclo*hexane*-, m. p. 176°, -spirocyclo*butane*-2′ : 4′-*dicarboxylic acids*, and cis-cyclo*hexane*-, m. p. 159—162°, and cis-4-*methyl*cyclo*hexane*-, m. p. 180°, -spirocyclo*butane*-2′ : 4′-*dicarboxylic anhydrides* are described. The above compounds resemble in stability to alkalis the corresponding derivatives of norpinic acid described by Kerr (*loc. cit.*). H. BURTON.

Constituents of petroleum. I. J. VON BRAUN and others.—See this vol., 1396.

Autoxidation of benzaldehyde. E. RAYMOND.—See this vol., 1375.

Attempted isolation of copper benzaldehyde. D. B. BRIGGS, H. SAENGER, and W. WARDLAW (J.C.S., 1931, 2552—2555).—The substance obtained by Bernouilli and Schaaf (A., 1922, i, 1029) by the action of Cu on PhCHO in PhMe is not Cu benzaldehyde, but *benzaldehyde Cu benzoate*, $Cu(OBz)_2,PhCHO,H_2O$ (I). When crystallised from pyridine *dipyridine Cu benzoate*, $Cu(OBz)_2,2C_5H_5N,H_2O$, results, formulated $2[Cu(PhCHO)_2],5C_5H_5N$ by Schaaf (A., 1923, i, 799); when heated this compound loses 1 mol. of H_2O and 1 mol. of pyridine to give *monopyridine Cu benzoate*, $Cu(OBz)_2,C_5H_5N$. On prolonged heating $Cu(OBz)_2$ is left and on keeping with quinoline, C_5H_5N is replaced to give *monoquinoline Cu benzoate*. $Cu(OBz)_2$ when heated with PhCHO in PhMe produces (I). It is suggested that BzO_2H is formed as an intermediary. F. R. SHAW.

Condensation of aldehydes and ketones with ethyl chloroacetate. II. Aromatic aldehydes and ketones. B. N. RUTOVSKI and N. A. DAEV (J. Gen. Chem. Russ., 1931, **1**, 185—189).—Action of the Na compound of PhCHO on Et chloroacetate gives $CH_2Ph\cdot OH$, $CH_2Ph\cdot CHO$, and NaCl. The Na compound of $COPh_2$ gives $CHPh_2\cdot OH$, diphenylglycidic acid, and NaCl. The presence of electronegative Cl in the α position renders the H atom in the CH_2Cl group mobile, the reaction proceeding: $2CAr_2\cdot ONa + CH_2Cl\cdot CO_2Et \longrightarrow 2CHAr_2\cdot ONa \longrightarrow CHAr_2\cdot OH + CAr_2\Big<{}^{O}_{CH\cdot CO_2Et}$ E B UVAROV.

Action of phenylcarbimide on some aromatic amino-oximes. C. V. Gheorghiu (Bull. Soc. chim., 1931, [iv], 49, 1205—1210).—In contrast to the thiocarbimides (this vol., 210), phenylcarbimides yield products with amino-oximes, formed by addition of 2 mols. of PhNCO to 1 mol. of amino-oxime. Thus *p*-aminobenzaldoxime in C_6H_6 yields *dicarbanilido*-p-*aminobenzaldoxime*, NHPh·CO·NH·C_6H_4·CH:NO·CO·NHPh, m. p. 176—177° (decomp.); *dicarbanilido*-m-*aminobenzaldoxime*, m. p. 171° (decomp.), and -p-*aminoacetophenoneoxime*, m. p. 178—179° (decomp.), are similarly obtained in $COMe_2$, and *dicarbanilido*-m-*aminoanisaldoxime*, m. p. 170—171° (decomp.), and -*acetophenoneoxime*, m. p. 175—176°, in Et_2O. The dicarbanilido-*o*-aminobenzaldoxime, m. p. 195—196° (decomp.), obtained from *o*-aminobenzaldoxime in Et_2O is probably β-2-keto-3-phenyl-1 : 2 : 3 : 4-tetrahydro-4-quinazolylhydroxylaminecarbanilide, a structure which is supported by the fluorescence of its solution in H_2SO_4 on dilution with H_2O.

R. Brightman.

Condensation of aldehydes with hydrazones. V. Condensation of benzaldehyde with the phenylhydrazones of anis- and *p*-dimethylaminobenz-aldehydes. A. Giacalone (Gazzetta, 1931, 61, 639—642).—PhCHO condenses with anisaldehydephenylhydrazone, giving 4 : 4′-*di*-p-*methoxybenzylidenehydrazinotriphenylmethane*, m. p. 166—167°, and with *p*-dimethylaminobenzaldehyde giving 4 : 4′-*di*-p-*dimethylaminobenzylidenehydrazinotriphenylmethane*, m. p. 213—214°, the product in each case being identical with that obtained from the aldehyde R·C_6H_4·CHO and dihydrazinotriphenylmethane. Vanillin condenses with dihydrazinotriphenylmethane giving 4 : 4′-*di*-p-*hydroxy*-m-*methoxybenzylidenehydrazinotriphenylmethane* m. p. 154°, but vanillinphenylhydrazone does not condense with PhCHO.

E. E. J. Marler.

Behaviour of phenylhydrazones with condensing media. A. Giacalone [with A. Domenico] (Gazzetta, 1931, 61, 642—645).—When benzaldehydephenylhydrazone is heated with $ZnCl_2$ or dissolved in H_2SO_4, dibenzylidenedihydrazinotriphenylmethane and a salt of NHPh·NH_2 are formed, on account of partial hydrolysis of the hydrazone, the liberated PhCHO condensing with the remaining hydrazone. The phenylhydrazones of anisaldehyde and salicylaldehyde react similarly with $ZnCl_2$, but salicylaldehyde does not react with H_2SO_4, and anisaldehyde reacts only in presence of Et orthoformate.

E. E. J. Marler.

Action of bromine on *o*-tolylhydrazones and *o*-nitrophenylhydrazones. F. D. Chattaway and A. B. Adamson (J.C.S., 1931, 2787—2792).—The action of 2 mols. of Br on the *o*-tolylhydrazones of *o*-, *m*-, and *p*-nitrobenzaldehydes results in bromination in the ω-position and in the 3-position in the *o*-tolyl nucleus; excess of Br causes further substitution in the 5-position, and less Br gives mixtures of Br_2-derivative and unchanged hydrazone. The products described are: ω-*bromo*-m-*nitrobenzaldehyde*-3-*bromo*-, m. p. 164°, -3 : 5-*dibromo*-, m. p. 152°, ω-*bromo*-p-*nitrobenzaldehyde*-3-*bromo*-, m. p. 186°, and -3 : 5-*dibromo*-o-*tolylhydrazone*, m. p. 175°. These react with NH_3 to give respectively: 3-*bromo*-, m. p. 149°, 3 : 5-*dibromo*-o-*tolyl*-m-, m. p. 150°, 3-*bromo*-, m. p. 152°, and 3 : 5-*dibromo*-o-*tolyl*-p-*nitrobenzylhydrazidine*, m. p. 171°, and with NaOAc, m-*nitrobenz*-β-*acetyl*-3 : 5-*dibromo*-, m. p. 176°, and p-*nitrobenz*-β-*acetyl*-3-*bromo*-o-*tolylhydrazide*, m. p. 195°, are obtained. -*Bromo*-o-*nitrobenzaldehyde*-3-*bromo*-o-*tolylhydrazone*, m. p. 106° (3 : 5-*dibromo*-, m. p. 137°), is converted by NH_3 into 3-*keto*-1 : 2-endo-3′-*bromo*-o-*tolylimino*-2 : 3-*dihydro*-1 : 2-*benzisodiazole* 1-*oxide*, explodes 151° (3 : 5-*dibromo*-, explodes 145°), which is reduced to the corresponding *benzisodiazole*, m. p. 181°.

The compounds obtained from the nitrophenylhydrazones of PhCHO and nitrobenzaldehydes behave similarly: ω-*bromobenzaldehyde*-, m. p. 166°, ω-*bromo*-m-*nitrobenzaldehyde*-, m. p. 201°, and ω-*bromo*-p-*nitrobenzaldehyde*-4-*bromo*-2-*nitrophenylhydrazone*, m. p. 242°; 4-*bromo*-2-*nitrophenyl*-, m. p. 188°, 4-*bromo*-2-*nitrophenyl*-m-*nitro*-, m. p. 245° (decomp.) [*hydrochloride*, m. p. 235° (decomp.)], and 4-*bromo*-2-*nitrophenyl*-p-*nitro*-*benzenylhydrazidine*, m. p. 249°; m-*nitrobenz*-β-*acetyl*-4-*bromo*-2-*nitrophenylhydrazide*, m. p. 173°; ω-*bromo*-o-*nitrobenzaldehyde* 2-*nitrophenylhydrazone*, m. p. 137°, and 3-*keto*-1 : 2-endo-4′-*bromo*-2′-*nitrophenylimino*-2 : 3-*dihydro*-1 : 2-*benzisodiazole* 1-*oxide*, explodes at 142°.

F. R. Shaw.

Action of bromine and of chlorine on 2 : 4-dinitrobenzaldehyde-phenyl- and -*p*-tolyl-hydrazones. F. D. Chattaway and A. B. Adamson (J.C.S., 1931, 2792—2796).—Both Cl and Br substitute in the *o*- and *p*-positions in the Ph residue and in the *o*- and ω-positions in the *p*-tolyl residue of the hydrazones, chlorination proceeding further than bromination. The following are described: ω-*bromo*-2 : 4-*dinitrobenzaldehyde*-4-*bromo*-, m. p. 176° (decomp.), and -2 : 4-*dibromo*-, m. p. 202° (decomp.), ω-*chloro*-2 : 4-*dinitrobenzaldehyde*-2 : 4-*dichloro*-, m. p. 196° (decomp.), and -2 : 4 : 6-*trichloro*-*phenylhydrazone*, m. p. 129° (decompose when treated with NH_3 or NaOAc); ω-*bromo*-2 : 4-*nitrobenzaldehyde*-3-*bromo*-p-*tolylhydrazone*, m. p. 141° (-3 : 5-*dibromo*-, m. p. 152°), treated with NH_3 affords 6-*nitro*-1 : 2-endo-3′-*bromo*-p-*tolylimino*-3-*keto*-2 : 3-*dihydro*-1 : 2-*benzisodiazole* 1-*oxide*, explodes 133° (-3 : 5-*dibromo*-, explodes 142°), which is converted by EtOH into the *benzisodiazole*, m. p. 250° (-3 : 5-*dibromo*-, m. p. 279°); ω-*chloro*-2 : 4-*dinitrobenzaldehyde*-3-*chloro*-, m. p. 170° (decomp.), and -3 : 5-*dichloro*-p-*tolylhydrazone*, m. p. 151° (decomp.); 2 : 4-*dinitrobenzaldehyde*-2 : 4-*dibromo*-, m. p. 204°, and -2 : 4-*dichlorophenylhydrazone*, m. p. 207°, -3 *bromo*-, m. p. 179°, -3 : 5-*dibromo*-, m. p. 182°, -3-*chloro*-, m. p. 192°, and -3 : 5-*dichloro*-p-*tolylhydrazone*, m. p. 200°.

F. R. Shaw.

Colours produced by alcoholic alkali hydroxides and concentrated sulphuric acid on certain chloro- and bromo-nitro-3-hydroxybenzaldehyde-*p*-nitrophenylhydrazones. An electronic explanation. H. H. Hodgson and E. W. Smith (J.S.C.I., 1931, 50, 358—360T).—6-Chloro-2 : 4-dinitro-3-hydroxybenzaldehyde-*p*-nitrophenylhydrazone develops a vivid royal-blue colour on treatment with aq. NaOH, whereas 2-chloro-4 : 6-dinitro-3-hydroxybenzaldehyde-*p*-nitrophenylhydrazone gives only

a claret colour on warming, a behaviour which recalls that of 2 : 5-dichloro-6-nitrobenzaldehydephenylhydrazone, the only exception to Chattaway and Clemo's generalisation (J.C.S., 1923, **123**, 3043). The anomalous behaviour cited is connected with the presence of a Cl atom in position 2. An explanation of the variations of colour encountered, and also of the colours produced by conc. H_2SO_4 on the Br-products in terms of modern electronic theory is advanced, the variations depending on the extent of ionisation of the imino-H.

Production of phenylglyoxal. C. NEUBERG and E. HOFMANN (Biochem. Z., 1931, **239**, 495—497).—The method previously described (this vol., 486) is cheaper and better than that of Henze (this vol., 843). If desired the nitrosylsulphuric acid may be replaced by H_2SO_4 and $NaNO_2$. The yield is then 35—37%. *p*-Tolylglyoxal can be obtained in the same way from *p*-methylacetophenone. W. McCARTNEY.

Condensation of aromatic aldehydes with nitromethane in presence of alcoholic sodium hydroxide. N. A. LANGE and W. E. HAMBOURGER (J. Amer. Chem. Soc., 1931, **53**, 3865—3867).—Gradual addition of alcoholic NaOH to vanillin benzyl ether and $MeNO_2$ in EtOH below 15°, and subsequent acidification, gives a 97% yield of ω-nitro-4-benzyloxy-3-methoxystyrene, which could not be prepared by Kobayashi's method (A., 1928, 169). ω-Nitro-3 : 4-methylenedioxystyrene, m. p. 161·5° (corr.), is prepared similarly from piperonal in 74% yield. H. BURTON.

Synthesis of alkyl*cyclo*pentanones. J. VON BRAUN, W. KELLER, and K. WEISSBACH (Annalen, 1931, **490**, 179—188).—Alkylsuccinic acids, prepared from the appropriate cyanohydrin and Et sodiocyanoacetate (cf. Higson and Thorpe, J.C.S., 1906, **89**, 1465), are converted into Et esters, which are reduced to glycols (Na–EtOH); these are converted successively into the corresponding dibromides, dicyanides, and adipic acids, which are finally distilled with $FeSO_4$, or, alternatively, the dibromides are treated with Mg and CO_2. The following are described: *Et αβ-dicyano*-n-*hexoate*, b. p. 173—177°/12 mm.; *β-propyl-adiponitrile*, b. p. 174—176°/12 mm., and *-adipic acid*, m. p. 45—49°, b. p. 184—186°/0·1 mm.; 3-n-*propyl*cyclo*pentanone*, b. p. 190—191° (*oxime*, m. p. 121—122°; *semicarbazone*, m. p. 178—179°; p-*nitrobenzylidene* derivative, m. p. 222°); *Et αβ-dicyano-α-ethyl*-n-*butyrate*, b. p. 160—162°/13 mm.; *Et α-methyl-α-ethylsuccinate*, b. p. 120°/13 mm.; *βγ-di(hydroxymethyl)*-n-*pentane*, b. p. 141—143°/14 mm. (*dibromide*, b. p. 114—116°/13 mm.); *β-methyl-β′-ethyladipic acid*, m. p. 58—70°, b. p. 176—178°/0·7 mm. (probably a mixture of stereoisomerides) (*dinitrile*, b. p. 164—166°/13 mm.); 3-*methyl*-4-*ethyl*cyclo*pentanone*, b. p. 180° (*oxime*, b. p. 117—118°/11 mm.; *semicarbazone*, m. p. 208—209°; *bis*-p-*nitrobenzylidene* derivative, m. p. 192°); *Et H*, b. p. 154—156°/12 mm., and *Et₂*, b. p. 120—122°/14 mm., *α-methyl-α-ethylsuccinates*; *γ-methyl-γ-hydroxymethylpentan-α-ol*, b. p. 142—144°/14 mm. (*dibromide*, b. p. 114°/14 mm.); 3-*methyl*-3-*ethyl*cyclo*pentanone*, b. p. 174° (*semicarbazone*, m. p. 170°; p-*nitrobenzylidene* derivative, m. p. 180°); *Et H trimethylsuccinate*, b. p. 158°/14 mm.; *ββγ-trimethylbutan-αδ-diol*, b. p. 134—136°/12 mm. (*dibromide*, b. p. 106°/12 mm.). From the last-named dibromide by action of KCN and subsequent hydrolysis is formed a small amount of *δ-bromo-βγγ-trimethyl*-n-*valeric acid*, b. p. 114—116°/0·3 mm. (*Et* ester, b. p. 122°/12 mm.), in which the Br is not replaceable by Mg or org. bases. No definite ketonic product was isolated by action of Mg and CO_2 on the dibromide. Reduction of *iso*camphorphorone with Pd–H_2 gives 3 : 3 : 4-*trimethyl*cyclo*hexanone*, b. p. 184—188° (*oxime*, m. p. 100°; *semicarbazone*, m. p. 177°; *di*-p-*nitrobenzylidene* derivative, m. p. 226°), from which no recognisable products were obtained by oxidation with dil. aq. $KMnO_4$ at 3—4°.
H. A. PIGGOTT.

Orientation phenomena among the *cyclo*hexanones. I. R. CORNUBERT. **II.** R. CORNUBERT and R. HUMEAU. **III.** R. CORNUBERT and A. MAUREL. **IV.** R. CORNUBERT, R. HUMEAU, H. LE BIHAN, and A. MAUREL (Bull. Soc. chim., 1931, [iv], **49**, 1229—1238, 1238—1248, 1248—1259, 1260—1266).—I. The formation of the dissymmetric $\cdot CH_2\cdot CO\cdot CRMe\cdot$ and symmetric $\cdot CHR\cdot CO\cdot CHMe\cdot$ types of ketone in the alkylation or arylation of ketones $\cdot CH_2\cdot CO\cdot CHMe\cdot$ is an orientation phenomenon and is not due to transposition. Alkylation of *cyclo*hexanone affords successively (1) 2-alkyl*cyclo*hexanone; (2) a mixture of 85—90% of 2 : 2-dialkyl*cyclo*hexanone and 10—15% of 2 : 6-dialkyl derivatives; (3) 2 : 2 : 6-trialkyl- and (4) 2 : 2 : 6 : 6-tetra-alkyl-*cyclo*hexanone. The secondary and condensation reactions increase with concentration of the ketone and the temp. Similarly, alkylation or arylation of a 2-alkyl- or -aryl-*cyclo*hexanone affords 85—90% of the 2 : 2- and 10—15% of the 2 : 6-derivative, the relative percentages depending on the nature of the halogen atom in the alkyl halide, chlorides yielding more of the 2 : 6-derivative. Benzylation of 2-methyl*cyclo*hexanone affords a mixture of the 2-methyl-2 : 6- and -6 : 6-dibenzyl derivatives. The nature of the 2-alkyl group in the alkyl*cyclo*hexanone has little influence. Attempts at phenylation or *cyclo*hexylation failed. Alkylation of 3-methyl*cyclo*hexanone yields mainly the 3 : 6-, together with a trace of 3 : 6 : 6-derivative; the 2 : 3-derivative has not been detected. The 3-Me group can thus inhibit the formation of the 2 : 3 : 6-derivative if there is an alkyl group in the 6-position. Alkylation of 2 : 3-dimethyl*cyclo*hexanone affords 77% of the 2 : 2 : 3- and 23% of the 2 : 3 : 6-derivative. Alkylation of 4-methyl*cyclo*hexanone affords successively (1) 4-methyl-2-alkyl*cyclo*hexanone, (2) a mixture of 88% of 2 : 6- and 12% of 2 : 2-dialkyl derivatives, (3) 2 : 2 : 6-trialkyl-4-methyl-, and (4) 2 : 2 : 6 : 6-tetra-alkyl-4-methyl-*cyclo*hexanone, exactly as in the methylation of *cyclo*hexanone itself. The formation of the dissymmetric ketone is attributed to dehydration of the 2-methyl*cyclo*hexanol, $\cdot CH_2\cdot CH(OH)\cdot CHR\cdot$, yielding $\cdot CH_2\cdot CH\colon CHR\cdot$ and the readier sodiation of the group $>CHR$ than of $>CH_2$. The results are not interpreted by the theory of steric hindrance and the formation of sodio-derivatives $>C\cdot ONa$ is supported by the exclusive formation of 2 : 2 : 5-trimethyl*cyclo*hexanone by methylation of 2 : 5-dimethyl*cyclo*hexanone, whilst amyl formate and $NaNH_2$ yield the 2 : 5-dimethyl-6-hydroxymethylene derivative.

II. Variable results for the composition of the reaction mixture obtained in the alkylation of 2-methyl*cyclo*hexanones are attributed partly to viscous products which accompany the cryst. benzylidene compound in amounts decreasing as the difference in b. p. between methyl*cyclo*hexanone and the alkyl derivative increases and with the efficiency with which the methyl*cyclo*hexanone is eliminated with $NaHSO_3$. The viscous products are mixtures of the benzylidene derivatives of 2-methyl*cyclo*hexanone and its alkyl derivatives, the viscous product from 2 : 6-dimethyl*cyclo*hexanone affording with H_2 in presence of Ni and condensation with PhCHO the tetrahydropyrone of 2-methyl-6-benzyl*cyclo*hexanone. The formation of the tetrahydropyrone of 2-methyl*cyclo*hexanone and the reactivity of the latter with $NaHSO_3$, although destroyed on alkylation, limit the accuracy of the method of calculating the composition of the reaction mixture. There is no evidence that impurities in tho $NaNH_2$ effect transposition or that transposition occurs on working up or analysis. Me_2SO_4 yields 88% of 2 : 2- and 12% of 2 : 6-derivatives, MeI affording 89% and 11%, respectively. Benzylation of 2-methyl*cyclo*hexanone with CH_2PhBr affords 94% of dissymmetric and 6% of symmetric isomeride, CH_2PhCl yielding 89—90% and 11—10%, respectively.

III. Methylation of 3-methyl*cyclo*hexanone by $NaNH_2$ and Me_2SO_4 affords a series of fractions, b. p. 172—192°, from which have been obtained the oximes of 2 : 5-dimethyl*cyclo*hexanone, pulenone (2 : 2 : 5-trimethyl*cyclo*hexanone), and 2 : 2 : 5 : 6-tetramethyl*cyclo*hexanone, condensation with PhCHO in presence of HCl affording the benzylidene compound of pulenone and the tetrahydropyrones of 2 : 5-dimethyl- and 2 : 5 : 6-trimethyl-*cyclo*hexanone. The 3-Me group has an almost exclusively *p*-orienting influence and methylation of 2 : 5-dimethyl*cyclo*hexanone affords exclusively pulenone, the 2 : 5 : 6-trimethyl*cyclo*hexanone resulting partly from the formation of a 5 : 5-Na_2 derivative in the action of $NaNH_2$ on 3-methyl-, but mainly from the 2 : 3-dimethyl-*cyclo*hexanone which has not been characterised. Allylation of 3-methyl*cyclo*hexanone similarly affords successively 2-methyl-5-allyl- (with-probably, a little 3-methyl-2-allyl-) and 2-methyl-5 : 5-diallyl-, with possibly traces of 3-methyl-2 : 6-diallyl-*cyclo*hexanone. The 2-methyl-5-propyl*cyclo*hexanone obtained on hydrogenation affords with 2 mols. of PhCHO two isomeric tetrahydropyrones. Methylation of *l*-menthone affords 2 : 5-dimethyl- with possibly traces of 1 : 2-dimethyl-5-*iso*propyl*cyclo*hexanone, which unlike dihydrocamphorone does not give an abnormal benzylidene compound but a tetrahydropyrone in poor yield.

IV. Allylation of *cyclo*hexanone with 2 mols. of $NaNH_2$ and 2 mols. of allyl bromide affords 89% of 2 : 2-diallyl- and 11% of 2 : 6-diallyl-*cyclo*hexanone, allylation of allyl*cyclo*hexanone affording substantially the same mixture (86 : 14). Although the Na derivative of *cyclo*hexanone with allyl*cyclo*hexanone and subsequent treatment with allyl bromide gives three times the normal yield of diallyl*cyclo*hexanone, this observation is insufficient to prove the sodiating action of a Na derivative, and the formation of a benzylallyl*cyclo*hexanone when the allyl*cyclo*hexanone is replaced by benzyl*cyclo*hexanone cannot be attributed to sodiation by the sodio-derivative. The greater reactivity of Na in 2-sodio-2-methyl- than in 2-sodio-6-methyl-*cyclo*hexanone towards alkyl bromides, the reactivity to alkyl chlorides being similar, and the differing sodiating action of the sodiomethylalkyl*cyclo*hexanones are further factors in determining the proportions of the alkylated products. Methylation of 2 : 3-dimethyl*cyclo*hexanone affords 77% of 2 : 2 : 3-trimethyl- and 23% of 2 : 3 : 6-trimethyl*cyclo*hexanone. Benzylation of *cyclo*hexanone affords, in addition to benzyl*cyclo*hexanone, 2 : 2-dibenzyl*cyclo*hexanone, m. p. 53—54°, with a little benzyl*cyclo*hexylidene*cyclo*hexanone. 2-Benzyl*cyclo*hexanone gives 98·5—99·5% of 2 : 2-dibenzyl*cyclo*hexanone, with traces of the 2 : 6-dibenzyl derivative, m. p. 103—103·5°. R. BRIGHTMAN.

Condensation of ketones in the presence of hydrochloric acid under pressure. B. N. DOLGOV and I. N. VOLNOV (J. Gen. Chem. Russ., 1931, 1, 340—344).—The velocity of condensation and yield are increased considerably by the use of high pressures. The high pressures allow the use of large quantities of HCl necessary for condensation of the higher ketones. E. B. UVAROV.

ω-Substituted acetophenone derivatives. I. ω-Halogeno-derivatives of ω*m*- and ω*p*-dinitroacetophenone. J. W. BAKER (J.C.S., 1931, 2416—2426).—Of the ω-halogeno-derivatives of *m*- and *p*-nitroacetophenone only the I-compounds are attacked by $AcNO_3$. The resulting ω-NO_2-derivatives are stable only in absence of air and H_2O, whilst the ω-bromo-ω-nitro-derivatives, obtained indirectly, are more stable. These results are discussed on the basis of electronic theories. The action of Cl_2 on molten *m*-nitroacetophenone gives the ω-Cl-derivative, m. p. 103° (A., 1928, 1009), converted by KBr in EtOH and H_2O into the ω-Br-derivative, also obtained by the method of Evans and Brooks (A., 1908, i, 338). This is converted by KI in EtOH into *ω-iodo-*m*-nitroacetophenone*, m. p. 96°, the solution of which in Ac_2O and HNO_3, when evaporated in vac., gives *ω-iodo-*mω*-dinitroacetophenone*, analysed in a special apparatus, and hydrolysed to *m*-nitrophenylglyoxal (*semicarbazone*, m. p. 203°; osazone, m. p. 233°) (A., 1911, i, 987), *m*-nitrophenacyl acetate (*semicarbazone*, m. p. 177°) (A., 1908, i, 338), *m*-nitrobenzoic acid, and a little *m*-nitrobenzoylformic acid, m. p. 105° (A., 1880, 253), also obtained by oxidation of *m*-nitrophenylglyoxal with HNO_3. ω-Bromo-*p*-nitroacetophenone with KI in EtOH gives *ω-iodo-*p*-nitroacetophenone*, m. p. 97—98°, converted by Ac_2O and HNO_3 into (?) ω-iodo-*p*ω-dinitroacetophenone, which is hydrolysed by H_2O to (?) p-*nitrophenacyl acetate*, m. p. 124°, converted by NHPh·NH_2 in H_2O into the *phenylhydrazone*, m. p. 178°, of *p*-nitrophenacyl alcohol, and oxidised by HNO_3 to p-*nitrobenzoylformic acid*, m. p. 150° (previous softening). The *K* salt of ω*p*-dinitroacetophenone (A., 1903, i, 16) with Br in H_2O gives *p*-nitrobenzoic acid, whilst in anhyd. Et_2O it gives *ω-bromo-*ωp*-dinitroacetophenone*, m. p. 89—90°, converted by H_2O or KI into *p*-nitrobenzoic acid. *m*ω-Dinitrostyrene with Br in hot $CHCl_3$ gives *αβ-dibromo-α-nitro-β-*m*-nitrophenylethane*,

m. p. 158°, converted by NaOAc in EtOH into *ω-bromo-*m*ω-dinitrostyrene,* m. p. 114—115°. This with KOH in MeOH gives a small amount of *α-bromo-α-nitro-β-methoxy-β-*m*-nitrophenylethane,* m. p. 103—104°, and the Me_2 acetal of m*α*-dinitroacetophenone, which is hydrolysed to the ketone. The *K* salt of this with Br in anhyd. Et_2O gives *ω-bromo-*m*ω-dinitroacetophenone,* m. p. 87°, converted by H_2O or KI into *m*-nitrobenzoic acid. A. A. LEVI.

Reactivities of ω-halogen atoms in acetophenone. D. MATHESON and J. E. HUMPHRIES (J.C.S., 1931, 2514—2516).—The reactivities of Cl, Br, and I in the ω-position in COPhMe towards NH_2Ph in EtOH at 40° are in the order I>Br>Cl, the reaction being followed by the titration of the halogen acid liberated. The Cl-compound shows reactivity only when NH_2Ph is in excess. F. R. SHAW.

Ester–ester-enol isomerisation and the dimeric diphenylthioketen. A. SCHONBERG, L. VON VARGHA, and H. KALTSCHMITT (Ber., 1931, 64, [*B*], 2582—2584).—β-Thiol-β-phenylthiol-αα-diphenylethylene (this vol., 964) is isomerised in boiling ligroin to Ph *diphenyldithioacetate,* $CHPh_2 \cdot CS_2Ph$, m. p. 78—79°. When either substance or Ph diphenylthioacetate is heated at 250—280°, PhOH or PhSH is removed with production of dimeric *diphenylthioketen,*

$CPh_2{:}C{<}^{S}_{S}{>}C{:}CPh_2$, m. p. 257—258°. Hydrolysis of Ph diphenyldithioacetate with aq. H_2SO_4 in AcOH yields diphenylacetic acid, m. p. 146°. H. WREN.

Organic compounds of sulphur. XX. Sulphur analogues of hexaphenylethane. II. A. SCHONBERG, D. CERNIK, and W. URBAN (Ber., 1931, 64, [*B*], 2577—2581; cf. A., 1930, 1577).—Contrary to Bergmann (A., 1930, 1584), the action of thiobenzophenone on diazomethane in Et_2O yields the colourless 4 : 4 : 5 : 5-tetraphenyltrimethylene 1 : 3-disulphide, $CH_2{<}^{S \cdot CPh_2}_{S \cdot CPh_2}$, m. p. 199—200°, converted by LiPh into $CPh_2{:}CPh_2$. Below its m. p. it commences to decompose into thiobenzophenone, S, and $CH_2{:}CPh_2$. Similarly, thiobenzophenone is converted by diazoethane and Et diazoacetate into *2-methyl-4 : 4 : 5 : 5-tetraphenyltrimethylene 1 : 3-disulphide,* m. p. 170—172°, and *2-carboxyethyl-4 : 4 : 5 : 5-tetraphenyltrimethylene 1 : 3-disulphide,* respectively. These compounds, particularly that last-named, which decomposes in indifferent media at room temp. particularly in presence of light, are more thermolabile than the parent substance. Thiobenzophenone and diphenyldiazomethane afford tetraphenylethylene sulphide; it is assumed that 2 : 2 : 4 : 4 : 5 : 5-hexaphenyltrimethylene 1 : 3-trisulphide is intermediately formed, but is too unstable to permit isolation. H. WREN.

Derivatives of phenacyl sulphides and their properties. A. KRETOV, A. PANTCHENKO, and A. KONOVALTCHIK (J. Gen. Chem. Russ., 1931, 1, 396—400).—The action of Na_2S on ω-chlorodimethylacetophenone gives *dimethylphenacyl sulphide* (decomp. above 100°), of which the dioxime was not obtained. The *dioxime* of *p*-methylphenacyl sulphide has m. p. 149—150°, and the *monophenylhydrazone,* m. p. 137°. Bromination of phenacyl sulphide in cold glacial AcOH gives the *dibromide,* m. p. 101°. On further bromination and heating, decomp. takes place, BzOH being formed. *Phenacyl mercaptan* (an oil, distils under reduced pressure) is prepared by the action of $Na_2S_2O_3$ on ω-chloroacetophenone. Derivatives of phenacyl sulphides are analogous to the parent substances and give ketone reactions, but with greater difficulty. E. B. UVAROV.

Structures of enol-acetates and the corresponding vinylamines. L. J. ROLL and R. ADAMS (J. Amer. Chem. Soc., 1931, 53, 3469—3476).—Reduction of Et β-acetoxycrotonate (the enol-acetate of Et acetoacetate) in presence of PtO_2–Pt-black and AcOH gives Et butyrate. The enol-acetate, b. p. 120—122°/2 mm., of benzoylacetone has the structure CHBz:CMe·OAc, since it is reduced similarly to butyrophenone. The enol-acetate, b. p. 130—133°/2 mm., of α-phenylpentane-αγ-dione is reduced to a mixture of phenylbutylcarbinol and its acetate; the mixture is oxidised (after hydrolysis) by $K_2Cr_2O_7$ and dil. H_2SO_4 to valerophenone, which when reduced catalytically yields a similar mixture. Similarly, the enol-*acetate,* b. p. 136—139°/2 mm., of α-phenylhexane-αγ-dione affords a mixture of phenylamylcarbinol and its acetate, which on hydrolysis and oxidation yields Ph amyl ketone. Catalytic reduction of Et β-aminocrotonate in AcOH gives Et β-acetamidobutyrate, which on hydrolysis and subsequent distillation furnishes Et crotonate. Et *n*-butylacetoacetate and NH_3 in EtOH afford *Et -amino-α-*n*-butylcrotonate,* m. p. 31°, reduced catalytically (as above) in AcOH to *Et β-acetamido-α-butylbutyrate,* b. p. 158—160°/3 mm. β-Amino-α-butylbutyric acid (*hydrochloride,* m. p. 87—88°) passes at 220° into *α-butylcrotonic acid,* b. p. 160—163°/23 mm. H. BURTON.

Benzanthrone derivatives. I. New synthesis of benzanthrone derivatives. II. Derivatives of bromobenzanthrone. M. NAKANISHI (Bull. Inst. Phys. Chem. Res. Tokyo, 1931, 10, 883—896, 897—908).—I. Anthrone is condensed with crotonaldehyde to *compounds,* $C_{18}H_6O_2$, m. p. 242°, and $C_{18}H_{14}O$, m. p. 125—127°, both of which are converted by Br into *γ : 9-dibromo-9-butenyl-10-anthrone,* $C_{18}H_{14}OBr_2$, $CO{<}^{C_6H_4}_{C_6H_4}{>}CBr \cdot CH{:}CH \cdot CHMeBr$, m. p. 136°. The dibromide is oxidised by $KMnO_4$ to 9-bromo-10-anthrone-9-carboxylic acid, m. p. 146°, and gives by treatment with $AlCl_3$ in $PhNO_2$ at 200° *compounds,* $C_{18}H_9OBr$, m. p. 173°, and $C_{18}H_8OBr_2$, m. p. 258°, which yield bluish-violet vat dyes when boiled with NaOMe in MeOH, one Br atom being lost. No methylbenzanthrone is obtainable from crotonylideneanthrone itself.

II. Trinitrobenzanthrone, m. p. 247°, obtained from benzanthrone and HNO_3 of *d* 1·48, is stable to CrO_3 oxidation. The *Bz*-NO_2 group is reduced by NH_3 and H_2S, and the product, m. p. 236°, gives by CrO_3 oxidation 2 : 7-dinitroanthraquinone. Nitration of 3-bromobenzanthrone yields a NO_2-compound, m. p. 301—301·5°, reducible to 3-bromo-2(or 1)-aminobenzanthrone, m. p. 248—250° (Ac derivative, m. p. 278°). The bromonitro-compound is converted by PCl_5 into 2(or 1)-chloro-3-bromobenzanthrone 7 : 7-dichloride, m. p. 227°, and by NaOEt into a

green vat dye. The quinoline, m. p. 245°, from the bromoamino-compound gives with NaOEt an intense brownish-red vat dye. Alkaline fusion of 3-bromo-2(or 1)-nitrobenzanthrone gives a dinitrodibenzanthrone (green vat dye), whilst the bromoamine yields an azine (reddish-brown). C. HOLLINS.

Manufacture of halogenated cyclic ketones of the acenaphthene series. I. G. FARBENIND. A.-G., —See B., 1931, 1041.

Manufacture of ω-aminomethylbenzanthrone. I. G. FARBENIND. A.-G.—See B., 1931, 1041.

Anthraquinone series. Condensation of 3 : 5-dinitrophthalic acid with toluene. P. C. MITTER and R. GOSWAMI (J. Indian Chem. Soc., 1931, **8**, 685—688).—3 : 5-Dinitrophthalic anhydride and PhMe in presence of $AlCl_3$ give 3 : *5-dinitro-2-p-toluoylbenzoic acid*, m. p. 237°, reduced by $FeSO_4$ and aq. NH_3 to 3 : *5-diamino-2-p-toluoylbenzoic acid*, m. p. 170—171°. This is converted by conc. H_2SO_4 at 160—170° into 1 : *3-diamino-6-methylanthraquinone*, m. p. 265°, characterised by its conversion into 1 : 3-dihydroxy-6-methylanthraquinone. H. BURTON.

1 : 3-Dichloroanthraquinone. A. A. GOLDBERG (J.C.S., 1931, 2829—2830).—Phthalic anhydride condenses with *m*-dichlorobenzene to give dichlorobenzoylbenzoic acid, which in 5% oleum at 155—160° forms 1 : 3-dichloroanthraquinone, m. p. 209—210°. F. R. SHAW.

Synthesis of alizarin. V. I. MINAEV and B. P. FEDEROV (Bull. Inst. polytech. Ivanovo-Vosniesensk, 1930, **15**, 113—130).—Anthracene is chlorinated in $o-C_6H_4Cl_2$, yielding 90% of very pure 9 : 10-dichloroanthracene, which is sulphonated with oleum in $PhNO_2$; $PhNO_2$ is removed with steam and the 9 : 10-dichloroanthracene-2-sulphonic acid converted quantitatively with HNO_3 (*d* 1·2) into anthracene-2-sulphonic acid, which yields very pure alizarin in quant. yield on alkaline oxidative fusion.
CHEMICAL ABSTRACTS.

3-Iodoalizarin. A. G. PERKIN and C. W. H. STOREY (J.C.S., 1931, 2620—2624).—2-Hydroxy- (Hardacre and Perkin, A., 1929, 319) and 2 : 7-dihydroxy- are the only 2-hydroxy-anthraquinones with the 3-position free which are iodinated in pyridine, the latter giving *3-iodo-2 : 7-dihydroxyanthraquinone*, m. p. 305—307° (*Ac_2* derivative, m. p. 218—221°). Alizarin is inert, but alizarin 1-Me ether is converted into *3-iodoalizarin 1-Me ether*, m. p. 235—237°, demethylated to *3-iodoalizarin*, m. p. 227—229° (*Ac* derivative, m. p. 205—207°), which dyes yellower shades than alizarin. Iodination of 1-bromo-2-hydroxyanthraquinone gives the 3-iodo-2-hydroxy-compound (I) with elimination of Br; but when excess of I is used, a red *substance*, m. p. 289—290°, is produced, related to, but not formed by the action of I on, (I). F. R. SHAW.

Polycyclic aromatic hydrocarbons. VI. 3 : 4-Benzphenanthrene and its quinone. VII. 5 : 6-*cyclo*Penteno-1 : 2-benzanthracene, a cancer-producing hydrocarbon. J. W. COOK (J.C.S., 1931, 2524—2528, 2529—2532).—VI. The Pschorr synthesis with α-(2-naphthyl)-*o*-aminocinnamic acid (cf. A., 1912, i, 547) gives a mixture of 1 : *2-benz-4-anthroic acid* (I), m. p. 281—282°, and 3 : *4-benz-1-phenanthroic acid* (II), m. p. 240—241°, separated through the Na and K salts. When oxidised with CrO_3, (I) affords 1 : *2-benzanthraquinone-4-carboxylic acid*, m. p. 292—293° (decomp.), which passes into the quinone on heating, whilst (II) is converted into 3 : *4-benz-9 : 10-phenanthraquinone*, m. p. 187—188°, which reacts readily with *o*-phenylenediamine to form 1 : *2-benz-3* : 4-(1′ : 2′-naphtha)phenazine, m. p. 189—190°. (I) is converted by Cu powder into 3 : *4-benzphenanthrene*, m. p. 68°, purified through its *picrate*, m. p. 126—127°. 1 : 2-Benzanthracene picrate, m. p. 141·5—142·5°, contains 1 mol. of picric acid (cf. Elbs, A., 1886, 1037).

VII. 5 : 6-*cyclo*Penteno-1 : 2-benzanthracene (III) (this vol., 612) (*picrate*, m. p. 195°; *quinone*, m. p. 184·5—185·5°) shows pronounced cancer-producing activity. The isomeric 6 : 7-cyclo*penteno-1 : 2-benzanthracene*, m. p. 164—165° (*quinone*, m. p. 182—184°), purified through its *picrate*, m. p. 180°, is formed at the same time. The constitution of (III) is proved by the oxidation of the quinone to *anthraquinone-1 : 2 : 5 : 6-tetracarboxylic acid*, m. p. above 360° (*Me_4* ester, m. p. 292—293°), identical with that obtained from 1 : 2 : 5 : 6-dibenzanthraquinone.
F. R. SHAW.

Constitution of corchoritin, a new crystalline bitter [substance] from jute seeds. I. N. K. SEN (J. Indian Chem. Soc., 1931, **8**, 651—665).—The mother-liquors from the crystallisation of corchorin (A., 1930, 826; this vol., 337) contain a little *corchoritin* (I), $C_{12}H_{18}O_3$ ($+0·5H_2O$), m. p. (anhyd.) 218—220° (decomp.) (sinters at 130°), $[\alpha]_D^{??}$ (anhyd.) −35·1° in EtOH (*monoacetate*, m. p. 120—122°; *phenylurethane*, m. p. 254—266°). (I) is unsaturated, is not a glucoside, contains a lactone grouping, does not give an oxime, and when hydrolysed with EtOH–KOH affords, after acidification with AcOH, a small amount of a *substance*, m. p. 182° (decomp.), isomeric with (I). Treatment of (I) with conc. HCl at room temp. gives *anhydrocorchoritin*, m. p. 97—98° (decomp.), whilst catalytic reduction (Pd) in MeOH affords *dihydrocorchoritin*, m. p. 191°. Distillation of (I) with Zn dust in H_2 yields gaseous and liquid products together with a $C_{10}H_8$-like *substance*, m. p. 135° [*picrate*, m. p. 107°; *NO_2-derivative* (?), m. p. 150° (decomp.)], whilst oxidation with alkaline $KMnO_4$ gives AcOH, oxalic and pyruvic acids. *o*-Phenylenediamine hydrochloride and (I) in AcOH give a blood-red coloration; the reaction is used for detecting traces of (I). H. BURTON.

Constitution of bile-pigments. VI. Synthesis of mesobilirubinogen, neobilirubic acid, mesobilirubin, a neoxanthobilirubic acid, and 1 : 8-dihydroxytripyrrodienes. H. FISCHER and E. ADLER (Z. physiol. Chem., 1931, **200**, 209—231; cf. this vol., 967).—Me xanthobilirubate gives with SO_2Cl_2 a colourless *Cl_6-derivative*, decomp. 167°; the free acid does not yield a cryst. derivative. Bromination of bilirubic acid with 1 mol. of Br gives xanthobilirubic acid (I), which on bromination yields mesobilirubin (II) (as hydrobromide) (mesobilirubin ester, m. p. 216°). Reduction of (II) with Na–Hg affords mesobilirubinogen, with HI in AcOH neo-

bilirubic acid (III) and bilirubic acid, fusion with resorcinol neoxanthobilirubic acid (IV). Reduction of (IV) with Na–Hg gives (III). Condensation of (IV) with CH_2O gives (II). Bromination of (I) at −20° also gives (II), which is unchanged by HBr in AcOH. Bromination of (I) gives as by-product an *isomeride* of (II), m. p. 305—310° (decomp.), absorption bands at 695 and 635 mμ (*Me ester hydrochloride*, m. p. 235—240°). Resorcinol fusion and Na–Hg reduction give the same products as those obtained from (II).

Bromination of 5-hydroxy-3 : 3′ : 5′-trimethyl-4-ethyl-4′-β-carboxyethylpyrromethene yields a mesobilirubin *isomeride*, decomp. 327° (*Me* ester, m. p. 222°). 5-Carboxy-2-formyl-4-methyl-3-β-carboxyethylpyrrole with cryptopyrrole and HBr gives the unstable 5-*carboxy*-4 : 3′ : 5′-*trimethyl*-4′-*ethyl*-3-β-*carboxyethylpyrromethene hydrobromide*, which with $CH_2Br{\cdot}CO_2H$ gives 5-*bromo*-4 : 3′ : 5′-*trimethyl*-4-*ethyl*-3-β-*carboxyethylpyrromethene hydrobromide* (V), m. p. 160° (decomp.). KOAc with (V) yields 5-*hydroxy*-4 : 3′ : 5′-*trimethyl*-4-*ethyl*-β-*carboxyethylpyrromethene*, m. p. 282°. 5-*Hydroxy*-3-*carbethoxy*-4-*methyl*-2-*chloromethylpyrrole* (VI) condenses with opsopyrrole (boiling C_6H_6) to form 1 : 8-*dihydroxy*-3 : 6-*dicarbethoxy*-2 : 4 : 7-*trimethyl*-5-*ethyltripyrrene*, m. p. 283° (decomp.). (VI) condenses with opsopyrrolecarboxylic acid forming 1 : 8-*dihydroxy*-3 : 6-*dicarbethoxy*-2 : 4 : 7-*trimethyl*-5-β-*carboxyethyltripyrrene*, m. p. 245°. (VI) heated in boiling MeOH with opsopyrrole gives 5-*hydroxy*-3-*carbethoxy*-4 : 3′-*dimethyl*-4′-*ethylpyrromethene*, m. p. 210°, which condenses with PhCHO to form [*di*-(5-*hydroxy*-3-*carbethoxy*-4 : 3′-*dimethyl*-4′-*ethyl*)*pyrromethene*]*phenylmethane*, absorption bands 640 and 530 mμ. J. H. Birkinshaw.

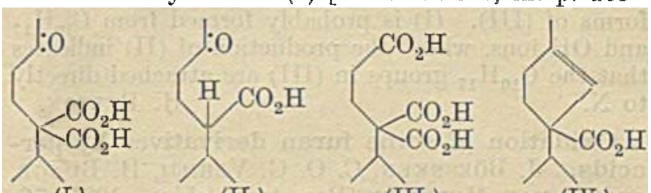
New source of hydrocarotene. O. Rygh, A. Rygh, and P. Laland (Z. physiol. Chem., 1931, **200**, 261—262).—Hydrocarotene was isolated in small amount from the juice of citrus fruits. It had no antiscorbutic action. J. H. Birkinshaw.

α- and β-Carotene. R. Kuhn and E. Lederer (Z. physiol. Chem., 1931, **200**, 246—254).—Carotene isolated from ovaries, grass, spinach, or nettles contained none of the α-form. In the leaf of germinating seeds and in evergreens the β-form predominated. The two forms were not separable by fractional crystallisation, but repeated precipitation of the β-form with I led to the isolation of the pure α-form, $[\alpha]_D$ +364°, absorption bands at 511 and 478 mμ. Both forms show autoxidation at about the same rate. The ratio of the solubilities in C_6H_6 at 0° is α : β=3 : 1 The rotation of α-carotene in C_6H_6 is independent of concentration, but varies with the solvent. J. H. Birkinshaw.

α-Carotene from palm oil. R. Kuhn and H. Brockmann (Z. physiol. Chem., 1931, **200**, 255—258).—The carotene of palm oil shows the greatest optical activity of all natural carotene mixtures. Pure α-carotene was separated from the mixture by adsorption of the β-carotene on fuller's earth. J. H. Birkinshaw.

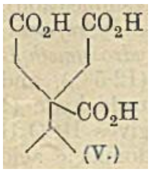
Elasticity of guttapercha hydrocarbon. A. W. K. de Jong (Rec. trav. chim., 1931, **50**, 1011—1017).—Thin films of guttapercha hydrocarbon obtained by slow evaporation of a C_6H_6 solution consist of microscopic rosettes of needles, and, after stretching, show straight extinction with polarised light between crossed Nicols. The changes during gradual stretching have been examined microscopically. Films obtained by rapid evaporation from light petroleum solutions were also examined. J. W. Baker.

Autoxidation of αβ-unsaturated ketones. III. Degradation and constitution of piperitolenic acid. W. Treibs (Ber., 1931, **64**, [*B*], 2545—2552; cf. this vol., 1299).—Treatment of the lactone, m. p. 26—28°, obtained by the autoxidation of piperitone (this vol., 94) with MeOH and H_2SO_4 affords *Me piperitolenate*, b. p. 212—215°, slowly oxidised by boiling HNO_3 (*d* 1·26) to a compound containing N and finally to *iso*propylsuccinic acid. Gentle oxidation of it with $KMnO_4$ does not permit the isolation of the expected dihydroxydihydro-acid, whereas more drastic oxidation affords the *Me H* ester of the ketodicarboxylic acid (I) [*semicarbazone*, m. p. 165°

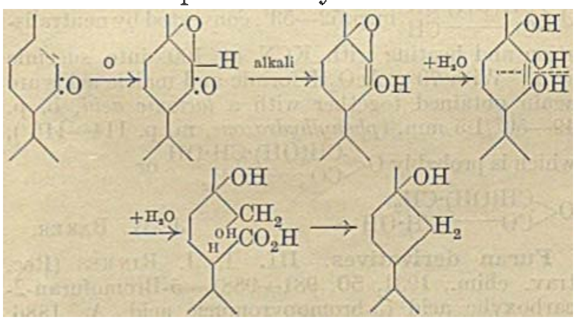


(I.) (II.) (III.) (IV.)

(decomp.)], converted when heated in vac. into the *Me* ester of the ketomonocarboxylic acid (II), b. p. 113°/13 mm. (*semicarbazone*, m. p. 128—130°). The free ketodicarboxylic acid (I) is oxidised by alkaline NaOBr to CBr_4 and the *tricarboxylic acid* (III), m. p. 160—162° (decomp.), whereas, under like conditions, the ketocarboxylic acid (II) affords α-*iso*propylglutaric acid, m. p. 95°. To piperitolenic acid the constitution (IV) is therefore ascribed. The lactone of m. p. 26—28° (see above) is converted by boiling HNO_3 (*d* 1·15) into a substance containing N and finally into AcOH, *iso*butyric, oxalic, and *iso*propylsuccinic acid, and a *tricarboxylic acid* (V), m. p. 169—170° (decomp.), which yields an *anhydride*, m. p. 145—146°. The course of the autoxidation of piperitone in presence of alkali is represented by the scheme:



(V.)



Protracted heating of piperitolenic acid at its b. p. does not cause loss of CO_2, whereas after addition of solid KOH it gives an unsaturated *hydrocarbon*, b. p. 154°, which resinifies when preserved. H. Wren.

Isomerisation of pinene in presence of alumina. P. A. MULCEY (Bull. Inst. Pin, 1931, 177—181, 201—206).—No camphene is obtained by the action of Al_2O_3 on pinene at its b. p. Pinene vapour, passed over Al_2O_3 at 310—425°, gives dipentene and much smaller amounts of *l*-limonene, α-terpinene, terpinolene, and light C_6H_6 hydrocarbons. No camphene is detectable. C. HOLLINS.

Preparation of bornyl mono- and di-hydrogen orthophosphates. K. P. JACOBSOHN and L. JACOBSOHN (Compt. rend. Soc. biol., 1930, **105**, 154—156; Chem. Zentr., 1931, i, 3363).—Neuberg's method (A., 1928, 88) gives both compounds; $(C_{10}H_{17})_2HPO_4$ has m. p. 221°. A. A. ELDRIDGE.

Structure of ferrocyanides. H. W. POST (J. Amer. Chem. Soc., 1931, **53**, 3904—3905).—The formation of *iso*borneol (I) and *iso*bornylamine (II) during alkaline hydrolysis of compounds of the type $(C_{10}H_{17})_2H_2Fe(CN)_6$ (III) (this vol., 736) appears to involve the existence of completely and partly ionised forms of (III). (I) is probably formed from $C_{10}H_{17}$ and OH ions, whilst the production of (II) indicates that the $C_{10}H_{17}$ groups in (III) are attached directly to N. H. BURTON.

Oxidation of some furan derivatives by per-acids. J. BÖESEKEN, C. O. G. VERMJI, H. BUNGE, and C. VAN MEEUWEN (Rec. trav. chim., 1931, **50**, 1023—1034).—The initial stage in the oxidation of furan derivatives with peracids is the formation of an oxide at one of the double linkings, and this then polymerises (especially in AcOH) or is hydrated and further oxidised. Furan with 6—10% AcO_2H in AcOH gives only an amorphous resin, $(C_4H_5O_2)_n$, mol. wt. 780, but with BzO_2H in $CHCl_3$ the *monobenzoate*, m. p. 98—100°, of 1 : 2-dihydroxy-1 : 2-dihydrofuran is obtained. With 70% AcO_2H in AcOH, 2-methylfuran affords *5-keto-4-hydroxy-2-methyl-4 : 5-dihydrofuran*, m. p. 87—89° (*phenylhydrazidephenylhydrazone*, m. p. 109—110°) (together with 90% resinification), whilst furfuryl alcohol gives *5-keto-4 : 5-dihydrofuran*, m. p. 150—153° (4%), (?) *5-keto-2-hydroxymethyl-2 : 5-dihydrofuran*, b. p. 55°/0·5 mm. (12·5%), and 80% resinification. Oxidation of furfuraldehyde (1 mol.) with 6—10% AcO_2H (2 mols.) gives HCO_2H (1 mol.), maleic acid (7%), and aldehydomaleic acid $O{<}\begin{matrix}CH(OH){\cdot}CH\\ CO{——}CH\end{matrix}{\cdot}$ m. p. 52—53°, converted by neutralisation and heating with KCN at 100° into succinic acid. With 70% AcO_2H formic and maleic acids are again obtained together with a *lactonic acid*, b. p. 49—50°/1·5 mm. (*phenylhydrazone*, m. p. 114—116°), which is probably $O{<}\begin{matrix}CH(OH){\cdot}C{\cdot}OH\\ CO{——}CH_2\end{matrix}$ or $O{<}\begin{matrix}CH(OH){\cdot}CH_2\\ CO{——}CH{\cdot}OH\end{matrix}{\cdot}$ J. W. BAKER.

Furan derivatives. III. I. J. RINKES (Rec. trav. chim., 1931, **50**, 981—988).—5-Bromofuran-2-carboxylic acid (5-bromopyromucic acid, A., 1886, 446) with HNO_3 (*d* 1·51) in Ac_2O at −10° gives *2-bromo-5-nitrofuran*, b. p. 118°/15 mm., m. p. 48°, converted by activated Cu powder at 190° into *5 : 5′-dinitro-2 : 2′-difuryl*, m. p. 213—214°, identical with the by-product obtained in the nitration of furan (A., 1905, i, 224). Decarboxylation of 3-nitro-2-methylfuran-5-carboxylic acid (I) (this vol., 95) affords *3-nitro-2-methylfuran*, f. p. 8·0°, which with HNO_3 and H_2SO_4 gives a small yield of *3 : 5-dinitro-2-methylfuran*, m. p. 74°, best obtained by similar nitration of (I). 2-Nitro-3-methylfuran (*loc. cit.*) is converted by HNO_3 (*d* 1·2) at 100° into the 2 : 5-$(NO_2)_2$-compound, m. p. 89—90°. Et 3-methylfuran-2-carboxylate with HNO_3 and Ac_2O at −10° gives the 5-NO_2-derivative, m. p. 61°, the free *acid*, m. p. 160°, of which is decarboxylated to *5-nitro-3-methylfuran*, m. p. 291°. J. W. BAKER.

Orientation in the furan nucleus. H. GILMAN and G. F. WRIGHT (Iowa State Coll. J. Sci., 1931, **5**, 85—88).—Di-iodofuran can be prepared from dehydromucic acid and converted into a Grignard reagent by treatment with activated Mg–Cu alloy; this renders possible the substitution of a variety of radicals on the furan ring. The following compounds have been prepared: *Et 5-acetamido-3(4)-bromofuroate*, m. p. 112°; *Et 5-acetamido-3(4)-nitrofuroate*, m. p. 138°; *5-iodo-2-furoic acid*, m. p. 192°. CHEMICAL ABSTRACTS.

Catalytic hydrogenation of furfuraldehyde. R. L. VAN PEURSEM (Proc. Iowa Acad. Sci., 1930, **37**, 225).—With Ni the max. yield (5%) of furfuryl alcohol is obtained at 200°, and with Cu at 215°. CHEMICAL ABSTRACTS.

Mechanisms of addition and substitution reactions of furfuraldehyde and its derivatives. H. GILMAN, G. F. WRIGHT, J. B. DICKEY, and A. P. HEWLETT (Proc. Iowa Acad. Sci., 1930, **37**, 247—248).—Substitution is preceded by 1 : 2-, 1 : 4-, or 1 : 6-addition. Ring fission, ring closure, and rearrangement involving unsaturated linkings accompany some of the transformations. CHEMICAL ABSTRACTS.

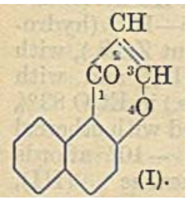
Cannizzaro reaction with furfuraldehyde. H. GILMAN and W. M. SELBY (Iowa State Coll. J. Sci., 1930, **5**, 15—18).—Yields are recorded. CHEMICAL ABSTRACTS.

Polymeric 2-furfuryl mercaptan. H. GILMAN and A. P. HEWLETT (Iowa State Coll. J. Sci., 1930, **5**, 19—23).—In 1 year a white solid, m. p. 135°, probably $(C_5H_6OS)_7$, was obtained. When kept, Et furoate is gradually converted into a substance of higher b. p. Furan compounds tend to remain unchanged when highly purified and preserved in sealed containers. CHEMICAL ABSTRACTS.

Coumaryl-6-thiocarbimide. B. B. DEY and T. R. SESHADRI (J. Indian Chem. Soc., 1931, **8**, 527—530).—6-Aminocoumarin (I) and boiling CS_2 in EtOH slowly, or with a little S more rapidly, give *6 : 6′-dicoumarylthiocarbamide* (II), m. p. 250—252°. This with boiling Ac_2O gives *coumaryl-6-thiocarbimide* (III), m. p. 186—187°, and 6-acetamidocoumarin. When treated with $CSCl_2$ in dry C_6H_6, (I) forms an unstable substance, probably the thiocarbamyl chloride, which with H_2O gives the hydrochloride of (II) and (III), which was better obtained from $CSCl_2$ and (I) (3 mols.) in aq. suspension at 60°. (III) is slowly transformed into (I) by AcOH, and on boiling with (I) in EtOH gives (II). *Coumaryl-6-thiocarbamide*, m. p. 234—235° (decomp.), is formed from (III) and

aq. NH_3 in boiling EtOH. *Phenyl-6-coumarylthiocarbamide*, m. p. 169—170° (decomp.), obtained from (*a*) (III) and NH_2Ph, and (*b*) PhNCS and (I) in boiling EtOH or C_6H_6, decomposes into (I) on melting. With $NH_2{\cdot}NHPh$ in boiling C_6H_6 (III) gives *phenyl-6-coumarylthiosemicarbazide*, m. p. 171—172°, and with boiling EtOH *Et coumaryl-6-thiocarbamate*, m. p. 167—168°. With boiling PhMe and $AlCl_3$ (I) yields 6-*thio*-p-*toluamidocoumarin*, m. p. 253—254°. The following compounds were prepared by similar methods: 6 : 6′-*di*-(4 : 7-*dimethylcoumaryl*)-, m. p. 258—260°; 4 : 7-*dimethylcoumaryl*-, m. p. 241° (decomp.), *phenyl*-4 : 7-*dimethylcoumaryl-thiocarbamide*, m. p. 192° (decomp.); 4 : 7-*dimethylcoumaryl-6-thiocarbimide*, m. p. 235°. R. S. Cahn.

Chromone group. IV. 1 : 4-βα-Naphthapyrones. B. K. Menon and K. Venkataraman (J.C.S., 1931, 2591—2596).—1 : 4-βα-*Naphthapyrone* (I), m. p. 103°, is obtained when the oxymethylene ketone from 1-acetyl-β-naphthol (II) and Et formate is treated with H_2SO_4 in EtOH. Treatment of (II) with Ac_2O and NaOAc at 170° gives 2-acetyl-3-methyl-1 : 4-βα-naphthapyrone, converted by NH_3 in EtOH into 3-methyl-1 : 4-βα-naphthapyrone, m. p. 168° (lit. 164°). 2-Acylation does not occur with aromatic anhydrides; βα-naphthaflavone, 4′-*methoxy*- (III), m. p. 165°, and 3′ : 4′ : 5′-*trimethoxy*-, m. p. 159°, -βα-*naphthaflavones* are prepared in poor yield from Bz_2O, anisic and trimethylgallic anhydrides, respectively. 4′-*Methoxy*-, m. p. 143°, 3′ : 4′-*dimethoxy*-, m. p. 157°, and 3′ : 4′-*methylenedioxy*-, m. p. 169°, -βα-*naphthaflavanones*, prepared from (II) and anisaldehyde, veratraldehyde, and piperonal, respectively, in presence of aq. EtOH–NaOH, are converted by PCl_5 in C_6H_6 into (III), 3′ : 4′-*dimethoxy*-, m. p. 168°, and 3′ : -*methylenedioxy*-, m. p. 225—226°, -βα-*naphthaflavones*, respectively. 4′-*Hydroxy*- and 3′ : 4′-*dihydroxy*-βα-*naphthaflavones*, prepared by demethylation of the corresponding OMe-derivatives, have m. p. 283—285° and 302—304°, respectively. Colour reactions of these substances are given. H. Burton.



(I).

Synthesis of anthocyanins. VI. Synthesis of chrysanthemin chloride. S. Murakami, A. Robertson, and R. Robinson. **VII. Four isomeric β-glucosides of pelargonidin chloride.** A. León, A. Robertson, R. Robinson, and T. R. Seshadri. **VIII. Synthesis of oenin chloride.** L. F. Levy, T. Posternack, and R. Robinson. **IX. Synthesis of oxycoccicyanin chloride. Distribution number of anthocyanins.** L. F. Levy and R. Robinson. **X. Synthesis of 3-β-galactosidylcyanidin chloride, which is believed to be identical with idæin chloride, and of 3-β-galactosidylpeonidin chloride.** (Miss) K. E. Grove and R. Robinson. **XI. Fisetinin chloride.** E. L. Fonseka and R. Robinson. **XII. Fisetinidin and luteolinidin chlorides.** A. León and R. Robinson. **XIII. 5-β-Glucosidyl- and 5-lactosidylhirsutidin chlorides.** L. F. Levy and R. Robinson (J.C.S., 1931, 2665—2671, 2672—2701, 2701—2715, 2715—2722, 2722—2730, 2730—2732, 2732—2737, 2738—2742; cf. A., 1928, 895).—VI. Chrysanthemin chloride (I) is shown by synthesis to be 3-β-glucosidylcyanidin chloride. Mecocyanin chloride is 3-(glucosidylglucosidyl)cyanidin chloride, since it resembles (I) in colour reactions and yields (I) on hydrolysis. Similarly, keracyanin and prunicyanin are probably 3-biosides. Cyanin (II), peonin, pelargonin, and malvin may, however, be diglucosides. (II) is considered to be probably cyanidin 3 : 5-diglucoside because of its resemblance to fisetinin chloride in colour reactions, its stability to oxidising agents, and its partial hydrolysis. The Na_2 salt of ω-chloro-3 : 4-dihydroxyacetophenone (improved prep.) with Ac_2O in cold C_6H_6 gives ω-*hydroxy*-3 : 4-*diacetoxyacetophenone* (III), m. p. 86—87° (reduces cold Fehling's solution in presence of a little EtOH), isolated as *$CaCl_2$ compound*, $2C_{12}H_{12}O_6,CaCl_2$, m. p. 126—127°, from which it is regenerated by H_2O. (III) with *O*-tetra-acetyl-α-glucosidyl bromide and Ag_2CO_3 in dry $CHCl_3$ gives ω-O-*tetra-acetyl*-β-*glucosidoxy*-3 : 4-*diacetoxyacetophenone*, m. p. 105—105·5°, which, when condensed with *O*-benzoylphloroglucinaldehyde and HCl in dry $CHCl_3$–EtOH or EtOAc, hydrolysed by NaOH, treated with HCl, and subsequently with picric acid, affords 3-β-*glucosidoxy*-5 : 7 : 3′ : 4′-*tetrahydroxyflavylium picrate*, $+4H_2O$, m. p. 170—175° or higher according to the rate of heating (vigorous decomp. 190—193°), identical with the picrate prepared from "asterin" chloride and chrysanthemin chloride, and converted by HCl in MeOH into the corresponding *chloride*, identical in crystal form, solubility, distribution no., and colour reactions in buffered solutions with natural chrysanthemin chloride from four different sources.

VII. The 5-, 7-, and 4′-β-glucosides of pelargonidin chloride are synthesised (cf. *loc. cit.*), and the first mentioned is identified with pelargonenin chloride, which differs from the other glucosides in colour reactions. Pelargonin is pelargonidin 3 : 5-diglucoside, since it is stable to very dil. aq. $FeCl_3$; its methylation (A., 1928, 1255) and that of monardein are discussed on the basis of this constitution. 6-Orcylaldehyde, ω-hydroxy-*p*-acetoxyacetophenone (I), and HCl in dry EtOAc give 3 : 7 : 4′-*trihydroxy*-5-*methylflavylium chloride*, $+H_2O$, and a small amount of xanthylium salt. γ-Orcylaldehyde led similarly to 3 : 5 : 4′-*trihydroxy*-7-*methylflavylium chloride*, $+2H_2O$. 4 : 6-Dihydroxy-2-methoxybenzaldehyde (prepared from phloroglucinol methyl ether), CH_2PhBr, and K_2CO_3 in boiling $COMe_2$ yield 2-*hydroxy*-4-*benzyloxy*-6-*methoxybenzaldehyde*, m. p. 101—102°, the constitution of which is proved by condensation with (I) to a flavylium salt. 6-Methylphloroglucinaldehyde benzyl ether, (I), and HCl in dry EtOAc give 3 : 4′-*dihydroxy*-7-*benzyloxy*-5-*methoxyflavylium chloride*, hydrolysed by conc. HCl in hot AcOH to 3 : 7 : 4′-*trihydroxy*-5-*methoxyflavylium chloride*, $+1{\cdot}5H_2O$. Condensation of 6-hydroxy-2-benzoyloxy-4-methoxybenzaldehyde with (I), hydrolysis of the product with NaOH in an atm. of H_2, and subsequent treatment with HCl affords 3 : 5 : 4′-*trihydroxy*-7-*methoxyflavylium chloride*. ω-4-Diacetoxyacetophenone and hot aq. KOH give ω : 4-*dihydroxyacetophenone*, m. p. 177—178° after sintering at 170° [*K* salt (II), $+2H_2O$ (lost at 120°), turns brown at 235° and decomp. at 275°;

Ag salt, decomp. in warm H_2O; *osazone*, m. p. 212—214°], which, when condensed with 2-*O*-benzoylphloroglucinaldehyde (III) (modified prep.), yields 5-*O*-benzoylpelargonidin chloride. (II) and α-tetra-acetylglucosidyl bromide (IV) in aq. $COMe_2$ give *ω-hydroxy-4-tetra-acetylglucosidoxyacetophenone*, m. p. 149—150° (reduces cold Fehling's solution and hot ammoniacal $AgNO_3$), which with (III) and HCl in dry Et_2O–$CHCl_3$ yields 5-O-*benzoyl*-4′-O-*tetra-acetylglucosidylpelargonidin chloride*, darkens at 182°, sinters at 193°, decomposes at 198°, transformed by successive treatment with NaOH and HCl into 4′-β-*glucosidylpelargonidin chloride*, $+2{\cdot}75H_2O$, decomp. 184° (corresponding *picrate*, decomp. 146—148°), which gives pelargonidin chloride on hydrolysis. The *Ag* salt of (III) (modified prep.) [but not the *K* salt (decomp. above 70°)] and (IV) in dry C_6H_6 give a poor yield of 2-*benzoyl*-4-β-*tetra-acetylglucosidylphloroglucinaldehyde* (V), m. p. 144—145°, which was better obtained from (III), (IV), and KOH in aq. $COMe_2$. This with MeI and Ag_2CO_3 in $COMe_2$ gives 2-*benzoyl*-4-β-*tetra-acetylglucosidyl*-6-O-*methylphloroglucinaldehyde*, m. p. about 120° after sintering at about 85°, hydrolysed by HCl in aq. EtOH at 50—60° or KOH in cold EtOH to 4-β-*glucosidyl*-2-O-*methylphloroglucinaldehyde* (VI), m. p. 237—239° (decomp.) after sintering at 235° ($FeCl_3$ colour, brownish-red), stable to dil., but decomposed by conc., acids. 6-*O*-Benzoyl-2 : 4-*O*-dimethylphloroglucinaldehyde also loses the Bz group on treatment with HCl. The constitution of (VI) is proved by its prep. from aq. KOH and 4-β-*tetra-acetylglucosidyl*-2-O-*methylphloroglucinaldehyde*, m. p. 147—148° [obtained from 2-*O*-methylphloroglucinaldehyde, (IV), and KOH in aq. $COMe_2$]. (V), ω : 4-dihydroxyacetophenone, and HCl in dry $CHCl_3$–Et_2O give 3 : 4′-*dihydroxy*-5-*benzoyloxy*-7-β-*tetra-acetylglucosidylflavylium chloride*, decomp. 184—186° after sintering at 177°, transformed by KOH in MeOH in an atm. of N_2 and subsequent treatment with HCl and picric acid into 7-β-*glucosidylpelargonidin picrate*, $+1{\cdot}5H_2O$, m. p. 180° (decomp.) after sintering at 120° (corresponding *chloride*, $+3H_2O$). 2 : 4-O-*Dibenzoylphloroglucinaldehyde*, m. p. 139—140°, obtained as a by-product in varying yield in the prep. of the 2-*O*-Bz compound, was prepared from phloroglucinaldehyde, BzCl, and KOH in aq. $COMe_2$ and from the 2-*O*-Bz compound by benzoylation in alkaline aq. $COMe_2$ or, better, in pyridine, and its constitution proved by methylation with MeI and Ag_2CO_3 in $COMe_2$ to 2 : 4-*dibenzoyl*-6-O-*methylphloroglucinaldehyde* (VII), m. p. 133—134°, hydrolysed by aq. KOH to the 2 : 4-$(OH)_2$ compound. *Tribenzoylphloroglucinaldehyde* has m. p. (anhyd.) 121—122°, and $+0{\cdot}5H_2O$, m. p. 80° (rapid heating) or about 118° (slow heating) after sintering at 80°. (VII) with tetra-acetylglucosidyl bromide and Ag_2CO_3 in dry C_6H_6 gives (?) 2 : 4-*dibenzoyl*-6-β-*glucosidylphloroglucinaldehyde*, m. p. 145° after sintering at 85° and becoming glassy at 110° (yields only BzOH on hydrolysis and does not give a cryst. Ac derivative), and with (IV) and KOH in aq. $COMe_2$ gives (?) 2 : 4-*dibenzoyl*-6-*tetra-acetyl*-β-*glucosidylphloroglucinaldehyde*, (?) $+3{\cdot}5H_2O$, m. p. 144—145°, also obtained together with a *substance*, m. p. 224—226°, from (VI), (IV), and Ag_2O in quinoline. The product (which could not be purified), obtained on hydrolysis of the last-mentioned aldehyde by cold alcoholic KOH in an atm. of N_2, when treated with ω-4-dihydroxyacetophenone and HCl in cold EtOH yields 5-β-*glucosidylpelargonidin chloride*, identical in m. p., solvent of cryst., crystal form, and colour reactions with pelargonenin chloride. This salt and the 4′- and 7-glucosides are decolorised by very dil. $FeCl_3$ in 1% HCl in 35 min., but callistephin, pelargonin, monardin, and salvidin chlorides were stable under these conditions. γ-Orcylaldehyde Me_2 ether, prepared by MeI and K_2CO_3 in $COMe_2$, has m. p. 91—92° (lit. 90—91°). The colour reactions of pelargonin and the 3-, 5-, 7-, and 4′-glucosides and 7- and 5-Me ethers of pelargonidin are recorded for various reagents and buffered solutions.

VIII. Oenin chloride (from purple-black grapes) and (probably) "primulin" chloride are shown by synthesis to be 5 : 7 : 4′-trihydroxy-3′: 5′-dimethoxy-3-β-glucosidylflavylium chloride (3-β-glucosidylmalvidin chloride). Syringic acid with Ac_2O and a few drops of pyridine at 100° gives little Ac derivative (I) and much *anhydride* (II), m. p. 195—197° (hydrolysed by hot 2*N*-NaOH with or without $ZnCl_2$), with boiling Ac_2O much (I) and little (II), and with *N*-NaOH (2·5 mols.) and Ac_2O (1·5 mols.) in Et_2O 83% of (I). Acetylsyringoyl chloride treated with ethereal diazomethane in a little $CHCl_3$ at −10° affords *ω-diazo-4-acetoxy*-3 : 5-*dimethoxyacetophenone* (III), m. p. 134° (decomp.), which is transformed into an amorphous substance (reducing Fehling's solution) by dil. aq.-alcoholic KOH, but with AcOH at 70° yields ω : 4-*diacetoxy*-3 : 5-*dimethoxyacetophenone*, m. p. 123°, hydrolysed by KOH in MeOH to the corresponding ω : 4-$(OH)_2$-compound (IV), m. p. $+ ?H_2O$ 93—95°, anhyd. 132° (*K* salt). Benzoylsyringoyl chloride (modified prep.), m. p. 125° (lit. 118°), affords the *diazo-ketone* (V) corresponding with (III), m. p. 168—172° (decomp.), which with cold abs. HCO_2H gives 4-*benzoyloxy*-ω-*formoxy*-3 : 5-*dimethoxyacetophenone*, cryst., and, best with hot 50% HCO_2H, yields ω-*hydroxy*-4-*benzoyloxy*-3 : 5-*dimethoxyacetophenone*, m. p. 175—177°. This with BzCl and pyridine gives the ω : 4-Bz_2 compound, m. p. 128°, and with Ac_2O and a drop of pyridine *ω-acetoxy*-4-*benzoyloxy*-3 : 5-*dimethoxyacetophenone*, m. p. 143° (rapidly reduces hot Fehling's solution), also obtained from (V) and hot AcOH. The ω-OH-compound with *O*-tetra-acetyl-α-glucosidyl bromide and Ag_2O in dry C_6H_6, first at 40° and then under reflux, gives a poor yield of 4-*benzoyloxy*-ω-O-*tetra-acetyl*-β-*glucosidoxy*-3 : 5-*dimethoxyacetophenone*, m. p. 80—90°, whence a monoglucosidic pyrylium salt, doubtless oenin, was obtained. (III) with anhyd. HCO_2H affords *ω-formoxy-4-acetoxy*-3 : 5-*dimethoxyacetophenone*, m. p. 152·5°, which with boiling 50% EtOH gives -*hydroxy*-4-*acetoxy*-3 : 5-*dimethoxyacetophenone* (VI), $+ ?H_2O$, m. p. anhyd. 119—120°, also obtained from (III) and 50% HCO_2H [ω-*Bz* derivative, m. p. 158—159°. from (III) and BzOH at 110—120°, or (VI), BzCl, and pyridine]. (VI) gives, in the usual way, *tetra-acetyl*-β-*glucosidoxy*-4-*acetoxy*-3 : 5-*dimethoxyacetophenone*, m. p. 83—85° (decomp.) (possibly the Ac_3 compound), which with *O*-benzoylphloroglucinaldehyde and HCl in dry EtOAc at 15° yields 7-*hydroxy*-

5-benzoyloxy-3-O-tetra-acetyl-β-glucosidoxy-4′-acetoxy-3′ : 5′-dimethoxyflavylium chloride, $+2H_2O$. This on hydrolysis with 10% aq. NaOH in an atm. of N_2 and subsequent ring-closure by HCl gives 3-β-glucosidylmalvidin chloride, $+3H_2O$. This and the corresponding picrate [$+1{\cdot}5H_2O$, or, (?) if not pure, $+4H_2O$] are identical in m. p., crystal form, solvent of cryst., distribution no., solubility, absorption spectrum, colour reactions in buffered solutions, and various chemical reactions with oenin derivatives. The crude anthocyanin from "Fogarina" grapes contains, besides oenin, malvidin, delphinidin, and probably petunidin.

IX. The prep. of ω-chloroacetovanillone and thence of 4-hydroxy-ω-acetoxy-3-methoxyacetophenone is improved. The latter substance with hot 16% aq. NaOH gives *ω : 4-dihydroxy-3-methoxyacetophenone*, + $?H_2O$, m. p. 158—160° (*Na* salt, $+1{\cdot}5H_2O$) (reduces cold Fehling's solution). The 4-*Ac* derivative of this, m. p. $+0{\cdot}5H_2O$ 88—90°, anhyd. 96°, prepared by shaking the aq. suspension with Ac_2O (1·5 mols.) in $CHCl_3$ (reduces cold Fehling's solution, gives no colour with $FeCl_3$, and insol. in NaOH, whereby its constitution is proved), affords the ω : 4-Ac_2 derivative, m. p. 76° (lit. 73°), when heated with Ac_2O, and when condensed with *O*-tetra-acetyl-α-glucosidyl bromide in the usual way yields *ω-O-tetra-acetyl-β-glucosidoxy-4-acetoxy-3-methoxyacetophenone*, m. p. 74—76° (possibly partly deacetylated), which with 2-*O*-benzoylphloroglucinaldehyde and HCl in EtOAc gives *7-hydroxy-5-benzoyloxy-3-O-tetra-acetylglucosidoxy-4′-acetoxy-3′-methoxyflavylium chloride*, $+1{\cdot}5H_2O$ (possibly an Ac_2 compound), whence by hydrolysis and subsequent ring closure *3-β-glucosidylpeonidin chloride*, $+2H_2O$, and the corresponding *picrate*, $+4{\cdot}5H_2O$, decomp. 165—180° after darkening at 110°, were obtained. These are identical with the corresponding salts of oxycoccicyanin. The glucoside is affected by $FeCl_3$ less than oenin, but more than callistephin; it is stable to very dil. $FeCl_3$, whereas peonidin is rapidly oxidised. The distribution nos. of oxycoccicyanin, natural and synthetic oenin chlorides between amyl alcohol and H_2O at different concentrations indicate that the anthocyanins exist as double mols. in the latter and single mols. in the former solvent; this is possibly connected with the difficulty of cryst. of anthocyanins and anthocyanidins from aq. acids and with the blueing effect of tannin on oenin solutions.

X. ω-Hydroxy-3 : 4-diacetoxyacetophenone (modified prep.), m. p. 86—87°, *O*-tetra-acetyl-α-galactosidyl bromide, and Ag_2CO_3 in warm dry C_6H_6 give the *ω-O-tetra-acetyl-β-galactoside*, amorphous, which with *O*-benzoylphloroglucinaldehydo and HCl in dry EtOAc yields 7 : 3′ : 4′-*trihydroxy-5-benzoyloxy*-3-β-*galactosidoxyflavylium chloride*, transformed by 8% aq. NaOH and subsequent acidification into 3-β-*galactosidylcyanidin chloride* (I), $+H_2O$, identical with idæin chloride. ω-Hydroxy-4-acetoxy-3-methoxyacetophenone gives similarly the ω-O-*tetra-acetyl*-β-*galactoside*, 7 : -*dihydroxy-5-benzoyloxy*-3-β-*galactosidoxy*-3′-*methoxyflavylium chloride*, amorphous, $+2H_2O$, and 3-β-*galactosidylpeonidin picrate* $+H_2O$, and *chloride* (II), $+2{\cdot}5H_2O$. The absorption curves (visible region) and alkali colour reactions are identical for (I) and oxycoccicyanin chloride (III), and for (II) and chrysanthemin chloride (IV), whilst the distribution nos. are controlled more by the carbohydrate component, being almost identical for (I) and (II), and for (III) and (IV). According to distribution experiments, association occurs between (I) and (IV) when mixed in aq. solution.

XI. The alkali colour reactions of 3-β-glucosidylfisetinidin chloride (I), which has been synthesised, are similar to those of cyanin chloride, thus confirming the diglucoside structure of the latter. In the cyanidin, peonidin, and malvidin, but not always in the pelargonidin, series, substitution in position 3 has a large effect on these colour reactions only if the OH group in position 5 is free. ω-Hydroxy-3 : 4-diacetoxyacetophenone, *O*-tetra-acetylglucosidyl bromide, and Ag_2CO_3 in warm C_6H_6 give the *ω-tetra-acetyl-β-glucoside*, which with β-resorcylaldehyde and HCl in dry EtOAc at 0° yields the flavylium salt, transformed by 8% NaOH in an atm. of H_2 and subsequent acidification into *fisetinin chloride* [=(I)], $+1{\cdot}5H_2O$ (corresponding *picrate*, $+5H_2O$), generally similar to chrysanthemin chloride.

XII. Under standard conditions, *luteolinidin* (I), *fisetinin* (II), chrysanthemin, cyanin, malvin, and oenin chlorides (which do not possess a free OH group in position 3) are stable to $FeCl_3$, whilst cyanidin, fisetinidin, *cyanidin 5-glucoside* (III), and malvin 5-glucoside (in which the OH in position 3 is free) are unstable; the 3 : 5-diglucoside structure for cyanin is thus confirmed. (I) and (II) have been synthesised in a pure state and solutions of (III) have been prepared by two methods. By the Schotten–Baumann method β-resorcylaldehyde yields the 4-*Bz* derivative, m. p. 103°, the constitution of which is proved because its *Me ether*, m. p. 85—86°, gives 4-hydroxy-2-methoxybenzaldehyde on hydrolysis (contrast phloroglucinaldehyde). 3 : 4-Diacetoxyacetophenone (improved prep. from the ω-Cl-derivative), *O*-benzoylphloroglucinaldehyde, and HCl in dry EtOAc give *benzoyl-luteolinidin chloride*, $+H_2O$, which on debenzoylation and acidification affords (I), $+1{\cdot}5H_2O$ (corresponding *picrate*, $+0{\cdot}5H_2O$, decomp. above 210°). ω : 3 : 4-Triacetoxyacetophenone, β-resorcylaldehyde, and HCl in dry EtOAc give (II), $+H_2O$. The colour reactions of (I) and (II) in buffered solutions are recorded. Partial hydrolysis of cyanin yielded, with difficulty, the 5-monoglucoside, the colour reaction of which with Na_2CO_3 is not in agreement with the 3 : 5-dimonoside structure for cyanin, which is, however, considered correct.

XIII. The 5-glucoside (I) and 5-lactoside (II) of hirsutidin (malvidin 7-Me ether) have been synthesised. The latter, but not hirsutin (hirsutidin diglucoside), very readily gives a cryst. ψ-base. The prep. of 2-*O*-benzoyl-4-*O*-methylphloroglucinaldehyde, m. p. 109° (obtained only in small yield by diazomethane), is modified. 2-*O*-Tetra-acetyl-β-glucosidyl-4-*O*-methylphloroglucinaldehyde (from 4-*O*-methylphloroglucinaldehyde), m. p. 177°, ω-hydroxy-4-acetoxy-3 : 5-dimethoxyacetophenone, and HCl in dry EtOAc give *3-hydroxy-5-o-tetra-acetyl-β-glucosidoxy-4′-acetoxy-7′ : 3′ : 5′-trimethoxyflavylium chloride*, partly deacetylated, + $?H_2O$, which on hydrolysis and acidification affords *5-β-glucosidylhirsutidin*

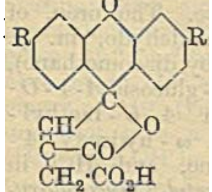
chloride, $+2{\cdot}5H_2O$. 4-*O*-Methylphloroglucinaldehyde, *O*-hepta-acetyl-α-lactosidyl bromide, and KOH in aq. $COMe_2$ at 5—10° afford 2-*O-hepta-acetyl-β-lactosidyl-4-O-methylphloroglucinaldehyde*, m. p. 164°, which with ω : 4-dihydroxy-3 : 5-dimethoxyacetophenone led to 3 : 4′-*dihydroxy-5-O-hepta-acetyl-β-lactosidoxy-7 : 3 : 5′-trimethoxyflavylium chloride*, isolated as Ac_2 derivative, $+4{\cdot}5H_2O$, and 5-β-*lactosidylhirsutidin chloride*, $+5H_2O$ (ψ-*base*, $+6H_2O$, decomp. 150—165° after darkening at 102°).

Many colour reactions are detailed for all the above flavylium compounds and their mutual relationship is discussed. R. S. CAHN.

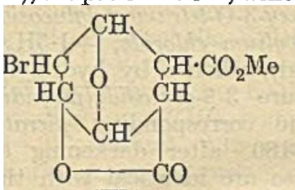
Yellow colouring matter of Khapli wheat, *Triticum dicoccum*. J. A. ANDERSON and A. G. PERKIN (J.C.S., 1931, 2624—2625).—A small amount of a flavone-like colouring matter, termed *tricin*, $C_{15}H_8O_5(OMe)_2$, m. p. 288° (Ac_2, m. p. 211—213°, and Ac_3, m. p. 251—254°, derivatives), has been isolated from the leaves. Tricin is demethylated to *tricetin*, decomp. slowly above 330° (Ac_4, m. p. 260—261°, and Ac_5, m. p. 244°, derivatives), which when fused with KOH at 200° gives phloroglucinol and an acid resembling gallic acid. Tricetin is not 5 : 7 : 3′ : 4′ : 5′-pentahydroxyflavone. H. BURTON.

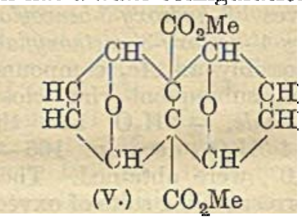
Diphenylene oxide monosulphonic acid and the corresponding sulphone. J. ZEHENTER (J. pr. Chem., 1931, [ii], 131, 331—336).—2 : 2′-Dihydroxydiphenyl is converted by 0·5 mol. of 17—18% oleum at 180—190° into *diphenylene oxide sulphonic acid*, $SO_3H{\cdot}\genfrac{}{}{0pt}{}{C_6H_3}{C_6H_4}{>}O$ (I) $+H_2O$, m. p. 133—135°, and anhyd., m. p. 163—165° ($K+H_2O$ and anhyd., $Na+H_2O$ and anhyd., $Ca+6{\cdot}5H_2O$ and anhyd., and $Cu+6H_2O$ and anhyd., salts) (separated by its solubility in H_2O), and *bisdiphenylene oxide sulphone*, $SO_2\left({\cdot}\genfrac{}{}{0pt}{}{C_6H_3}{C_6H_4}{>}O\right)_2$, m. p. 208—209°, together with a little diphenylene oxide. Further treatment of (I) with 20% oleum at 120° affords the disulphonic acid obtained by Hoffmeister (A., 1871, 123), isolated as its Ba salt, $+H_2O$ and $+4{\cdot}5H_2O$. J. W. BAKER.

Effect of unsaturated chromophores on pyronine dyes. I. B. B. DIKSHIT and J. D. TEWARI (J.C.S., 1931, 2511—2514).—*Aconiteins* (I) and *tricarballyleins* (*dihydroaconiteins*) (II) are prepared, usually by methods previously described (A., 1927, 969, 977; 1929, 1186), from aconitic and tricarballylic acids, respectively, and the following substances; the m. p. quoted first in brackets is that of (I), the other that of (II): PhOH [250° (decomp.); 220° (decomp.)]; resorcinol [190° (decomp.); 207° (decomp.)]; pyrocatechol [150°; 180° (decomp.)]; phloroglucinol [blackens at 195°; 119°]; *m*-diethylaminophenol [112°; 140° (decomp.) (shrinks at 130°)]; *m*-dimethylaminophenol [118° (decomp.); 138°]; *m*-phenylenediamine (condensed at 150—160° in presence of dry HCl) [248°; 198—200° (decomp.) (blackens at 190°)]; *o*-cresol (195° (decomp.)]; 168° (decomp.); *m*-cresol [126° (decomp.); 220° (decomp.)]; pyrogallol [above 300°; 236° (decomp.) (darkens at 195°)]; tetrabromoresorcinol [decomp. above 170°; 187° (decomp.) (darkens at 177°)]; tetraiodoresorcinol [decomp. above 187°; 215° (decomp.)]. The absorption maxima show that the aconiteins are more intensely coloured than their dihydro-derivatives. H. BURTON.


(I.)

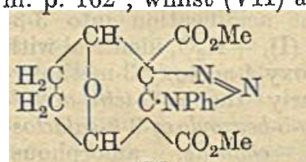
Syntheses in the hydroaromatic series. O. DIELS and K. ALDER. XII, XIII. "Dien syntheses with heterocyclic oxygen compounds. 2. Furan [with H. NIENBURG and O. SCHMALBECK]. **3. Coumalin** [with K. MULLER] (Annalen, 1931, 490, 243—257, 257—266).—XII. (cf. A., 1929, 570). Furfuryl acetate and maleic anhydride in Et_2O give (after some days) 3 : 6-*endoxo-3-acetoxymethyl-Δ*^{4}*-tetrahydrophthalic anhydride*, m. p. 114°, reduced catalytically (Pd) in MeOH to a *compound*, $C_{12}H_{16}O_7$, m. p. 142—143°. Furan (I) and aq. maleic acid afford 3 : 6-*endoxo-Δ*^{4}*-tetrahydrophthalic acid* $(+H_2O)$ (II), m. p. 103—105° (decomp.) (after sintering at 95°) with regeneration of (I), re-solidifying with m. p. 135°, best prepared by hydrolysis of its anhydride (*loc. cit.*). 4-*Bromo-5-hydroxy-3 : 6-endoxohexahydrophthalic acid* (III), m. p. 205°, from (II) and Br in H_2O, loses 1 mol. of H_2O when dried at 100°/high vac. over P_2O_5, and when treated with MeOH–HCl or Et_2O–diazomethane passes into the *bromolactonic* (cis-) *ester* (IV), m. p. 175°. Treatment of (IV) with HBr in AcOH at 100° gives a *bromolactonic acid* (as IV), m. p. 231—232°, which has a *trans*-configuration,

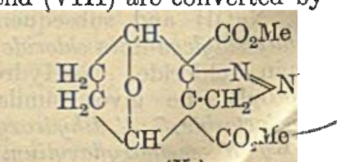

(IV.)


(V.)

since it yields a *Me* ester, m. p. 167—168°; similar treatment of (III) at 160—170° affords phthalic acid. Catalytic reduction (Pd–$CaCO_3$) of (III) in aq. EtOH–KOH and dehydration of the resultant product with AcCl gives the *lactonic acid* (IV, where $CHBr=CH_2$ and Me=H), m. p. 174—175°.

Me acetylenedicarboxylate and (I) at 100° afford a mixture of Me 3 : 6-endoxo-3 : 6-dihydrophthalate (not characterised) and *Me* 1 : 4 : 5 : 8-*diendoxo-1 : 4 : 5 : 8 : 9 : 10-hexahydronaphthalene-9 : 10-dicarboxylate* (V), m. p. 148° (decomp.) [free *acid* (VI), m. p. 158° (decomp.), formed from (I) and acetylenedicarboxylic acid]. Catalytic reduction (Pd) of the phthalate in $COMe_2$ gives *Me* 3 : 6-*endoxo-Δ*^{1}*-tetrahydrophthalate* (VII), m. p. 51—52° [free *acid* (VIII), m. p. 167—168° (decomp.)], oxidised by O_3 to oxalic and succinic acids. Phenyl azide and (VII) afford the *triazole* (IX), m. p. 162°, whilst (VII) and (VIII) are converted by


(IX.)

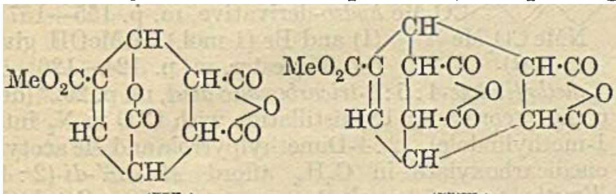

(X.)

an excess of diazomethane in Et_2O into the *pyrazoline* (X), m. p. 112—113°.

Catalytic reduction (Pd) of (V) in MeOH yields *Me* 1 : 4 : 5 : 8-*diendoxodecahydronaphthalene*-9 : 10-*dicarboxylate*, m. p. 158—160° [free *acid*, m. p. 245—246°, obtained by reduction of (VI)], hydrolysed by EtOH–KOH to the *Me H* ester, m. p. 212°.

Me cis-3 : 6-*endoxohexahydrophthalate* (*norcantharidate*), m. p. 80—85°, prepared from the Me H ester (*loc. cit.*) and diazomethane, is converted by $NaNH_2$ in Et_2O into the Me ester of trans-*norcantharidic acid*, m. p. 179—180°

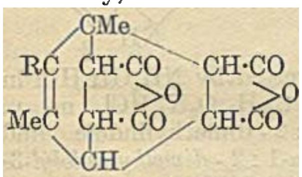
XIII. Me coumalate and maleic anhydride in boiling PhMe give about 30% of the *compound* (XI), m. p. 198°, converted by successive treatment with H_2O and MeOH–HCl into Me trimesate. When the reaction is carried out in boiling xylene, about 30% of the *compound* (XII), m. p. 331° (corresponding



(XI.) (XII.)

Me_5 ester, m. p. 137—138°), is formed after 24 hr., whilst (XI) results after 5 hr. (XI) is dehydrogenated by Br (2 mols.) at 200° to trimesic acid.

Dimethylcoumalin heated with maleic anhydride gives the *compound* (XIII, R=H), m. p. 274° (corresponding Me_4 ester, m. p. 155°), whilst *iso*dehydracetic acid similarly affords the *compound* (XIII, R=CO_2H), m. p. 325° (corresponding Me_5 ester, m. p. 204°). Similarly, coumalin furnishes the *dianhydride* (XII, CO_2Me=H), m. p. 349° (decomp.) [corresponding Me_4 ester (XIV), m. p. 130—131°], also formed from maleic anhydride and *cis*-$\Delta^{3:5}$-*cyclo*hexadiene-1 : 2-dicarboxylic anhydride. Coumalin and maleic anhydride



(XIII.)

in boiling PhMe give an *adduct*, $C_9H_6O_5$, m. p. 187°, which reacts further with maleic anhydride in boiling xylene yielding the above dianhydride. Catalytic reduction (Adams) of (XIV) in AcOH affords *Me* 3 : 6 - endo - αβ - *dicarbomethoxyethylenehexahydrophthalate*, m. p. 157°, convertible into the *trans*-modification, m. p. 112°, by the usual method.

H. Burton.

Azopyrrole-blacks. III, IV. A. Quilico and M. Freri (Atti R. Accad. Lincei, 1931, [vi], **13**, 282—287, 377—382; cf. A., 1930, 793).—III. In glacial AcOH solution 1-methylpyrrole readily reacts with diazotised (1) *p*-nitroaniline to give a black product, less intensely coloured and with a higher O content than that from pyrrole, and (2) 2 : 4-dinitroaniline to give a black product in lower yield and with 3—4% more C. In aq. solution made acid with AcOH, 1-methylpyrrole and diazotised *p*-nitroaniline give 2-*p*-nitrobenzeneazo-1-methylpyrrole (cf. Ciusa, A., 1921, i, 365). 3-Methylpyrrole yields similar black products, but 2 : 4-dimethylpyrrole and diazotised *p*-nitroaniline in glacial AcOH give quantitatively 3-p-*nitrobenzeneazo*-2 : 4-*dimethylpyrrole*, m. p. 208°. 2-Methylpyrrole and diazotised *p*-nitroaniline yield (1) in dil. EtOH acidified with AcOH, 5-*p*-nitrobenzeneazo-2-methylpyrrole (?) and (2) in glacial AcOH, a brown oxidation or resinification product completely sol. in dil. alkali solution and containing less C and more N than the corresponding azopyrrole-black should do.

T. H. Pope.

Cobalt nitrosodithiocarbamates. L. Cambi and A. Gagnasso [with A. Tanara] (Atti R. Accad. Lincei, 1931, [vi], **13**, 404—406).—The action of $Co(OAc)_2$ (1 mol.) on NH_4 or NH_2Me_2 dimethyldithiocarbamate (>2 mols.) in an atm. of NO at 0° yields *Co nitroso*-NN- *dimethyldithiocarbamate*, $[(NMe_2\cdot CS_2)_2Co\cdot NO]$. *Co nitroso*-N-*piperidyldithiocarbamate*, $[(C_5H_{10}N\cdot CS_2)_2Co\cdot NO]$, is similarly obtained. Both are highly stable as crystals.

T. H. Pope.

Reactivity of conjugated systems. IV. Condensation of alkylidene-ketones with cyanoacetamide. C. Barat (J. Indian Chem. Soc., 1931, 8, 699—710).—The activity of αβ-unsaturated ketones, CHR⁚CH·CO·R′, towards cyanoacetamide is enhanced when R=alkyl as compared with R=aryl (A., 1930, 925); the difference is ascribed to the smaller vol. of the alkyl group. Michael condensation (*A*) of ethylideneacetophenone and cyanoacetamide gives mainly 3-*cyano*-2-*keto*-6-*phenyl*-4-*methyl*-2 : 3 : 4 : 5-*tetrahydropyridine* (I), m. p. 248—250°, and some 3-cyano-6-phenyl-4-methyl-2-pyridone [also formed by oxidation of (I) with HNO_2], whilst Knoevenagel condensation (*B*) affords 3-*cyano*-6-*hydroxy*-2-*keto*-6-*phenyl*-4-*methylpiperidine* (II), m. p. 177—178°, dehydrated by HCl in CCl_4 to (I). Hydrolysis of (I) or (II) with conc. HCl at 120—125° gives γ-*benzoyl*-β-*methylbutyric acid*, m. p. 72—73°, also obtained by heating γ-*benzoyl*-β-*methylpropane*-αα-*dicarboxylic acid*, m. p. 141—142° (decomp.), prepared from Et malonate and the above ketone. Similarly, ethylidene-*p*-methylacetophenone (*dibromide*, m. p. 120—121°) affords (*A*) 3-*cyano*-2-*keto*-6-p-*tolyl*-4-*methyl*-2 : 3 : 4 : 5-*tetrahydropyridine*, m. p. 255—256°, and (*B*) 3-*cyano*-6-*hydroxy*-2-*keto*-6-p-*tolyl*-4-*methylpiperidine*, m. p. 163—164°, both hydrolysed to γ-p-*toluoyl*-β-*methylbutyric acid*, m. p. 105—106°, also obtained from γ-p-*toluoyl*-β-*methylpropane*-αα-*dicarboxylic acid*, m. p. 125° (decomp.). Ethylideneacetone gives (*A*) 3-*cyano*-2-*keto*-4 : 6-*dimethyl*-2 : 3 : 4 : 5-*tetrahydropyridine*, sublimes when heated, and (*B*) 3-*cyano*-6-*hydroxy*-2-*keto*-4 : 6-*dimethylpiperidine*, m. p. 173—175°. Mesityl oxide condenses (*A* or *B*) with cyanoacetamide forming 3-*cyano*-6-*hydroxy*-2-*keto*-4:4:6-*trimethylpiperidine*, m. p. 273—275°, dehydrated to 3-*cyano*-2-*keto*-4 : 4 : 6-*trimethyl*-2 : 3 : 4 : 5-*tetrahydropyridine*, m. p. 252—254°, which is unaffected by HNO_2. *cyclo*Hexenyl Me ketone (III) gives (*A* or *B*) 4-*cyano*-3-*keto*-1-*methyl*-3 : 4 : 5 : 6 : 7 : 8 : 9 : 10-*octahydro*iso*quinoline*, m. p. 358—360° (N-*Me ether*, m. p. 122—123°), hydrolysed by 75% H_2SO_4 to 3 - *hydroxy*-1-*methyl* - 5 : 6 : 7 : 8 : 9 : 10 - *hexahydro*iso - *quinoline*, m. p. 231—232° (decomp.), converted by successive distillation with Zn dust and PbO into 1-methyl*iso*quinoline [*picrate*, m. p. 209—210°; *chloroplatinate*, m. p. 200—202° (decomp.)]. Hydrolysis of the product from (III) and Et malonate gives

1 : 3-*dihydroxy*-5 : 6 : 7 : 8 : 9 : 10-*hexahydronaphthalene*, m. p. 115°. H. BURTON.

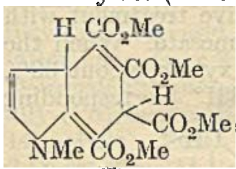
Dihalides of pyridine. D. M. WILLIAMS (J.C.S., 1931, 2783—2787).—Pyridine dichloride, *dibromide* (I), m. p. 62—63°, *bromochloride*, m. p. 107—108°, iodochloride (II), and *iodobromide*, m. p. 116—117°, are prepared from pyridine and the requisite halogens in CCl_4; (II) is the most stable. The dissociation of (I) in CCl_4 is extremely small. Conductivity measurements with (II) in pyridine at 25° indicate the structure C-H-N:I:Cl; 2 of the valency electrons of the I atom are assumed to have entered the core. H. BURTON.

Action of ammonia on pyridine and 2-methylpyridine in presence of dehydrogenating catalysts. II. J. P. WIBAUT and L. M. F. VAN DE LANDE (Rec. trav. chim., 1931, **50**, 1056—1059).—The yield of 2-aminopyridine obtained by the action of NH_3 on pyridine in presence of a Ni–Al_2O_3 catalyst (A., 1929, 1313) is decreased by carrying out the reaction at 320—360°/60—100 atm., the formation of 2 : 2′-dipyridyl being favoured under these conditions. With 2-methylpyridine and NH_3 in the presence of a Ni–asbestos catalyst at 430° a small yield of an *amino-2-methylpyridine*, b. p. 209—215° [*chloroplatinate*, m. p. 218—219° (decomp.); *picrate*, m. p. 203—204°], not identical with the 6-NH_2 compound, is formed. J. W. BAKER.

Biuret reaction. VI. Aminohydroxy-compounds which show the biuret reaction. M. TOMITA. **VII. Primary–quaternary bases which give the biuret reaction.** T. FUKAGAWA (Z. physiol. Chem., 1931, **201**, 38—40, 40—46; cf. A., 1930, 585).—VI. Compounds containing the group ·CH(OH)·CH(NH_2)· give the biuret reaction.

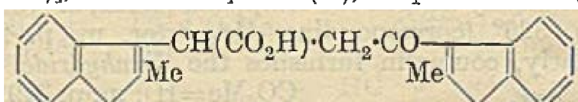
VII. γ-Chloro-β-hydroxypropylphthalimide (I) when heated with pyridine yields *γ-phthalimido-β-hydroxypropylpyridylium chloride* (II), m. p. 238—239° [*picrate*, m. p. 227—228°; *chloroplatinate*, m. p. about 218° (decomp.)]. (II) with moist Ag_2O forms the *betaine*, C_5H_5:N·CH_2·CH(OH)·CH_2·NH·CO·C_6H_4·CO·O [open-chain *dipicrate*, m. p. 223—224° (decomp.)]. (II) when boiled with 20% HCl affords *γ-amino-β-hydroxypropylpyridylium chloride hydrochloride*, m. p. 229°, giving the biuret reaction. With quinoline at 130—140° (I) gives *γ-phthalimido-β-hydroxypropylquinolylium chloride*, m. p. 265—266° (*picrate*, m. p. 242°; *chloroplatinate*, m. p. 239°; *dipicrate* of betaine compound, m. p. 230°; *γ-amino-β-hydroxypropylquinolylium chloride hydrochloride*, m. p. 271—272°, gives no biuret reaction owing to decomp.). With *iso*quinoline at 130° (I) gives the corresponding iso*quinolyl chloride*, m. p. 255° (*picrate*, m. p. 197—198°; *chloroplatinate*, m. p. 227°; *dipicrate* of betaine compound, m. p. 192—193°; *hydrochloride* of NH_2-compound, m. p. 253, gives no biuret reaction owing to decomp.). J. H. BIRKINSHAW.

Syntheses in the hydroaromatic series. O. DIELS and K. ALDER. **XIV, XV. "Dien"-syntheses with heterocyclic nitrogen compounds. 2. Syntheses with pyrrole and acetylenedicarboxylic acid and its esters** [with H. WINCKLER]. **3. Indole** [with W. LUBBERT and (in part) H. WINCKLER, E. HEINRICH, W. LÜCK, and W. ECKARDT] (Annalen, 1931, **490**, 267—276, 277—294).—XIV. *N*-Methylpyrrole and acetylenedicarboxylic acid in Et_2O give *α-N-methylpyrryl-2-maleic acid*, m. p. 222—223° (decomp.), and (mainly) its *anhydride*, m. p. 164°. Catalytic reduction of the acid (as Na salt) affords α-*N*-methylpyrryl-2-succinic acid [*Me* ester, m. p. 72°, also formed by esterification of the acid obtained from the adduct (A., 1929, 819) from *N*-methylpyrrole and maleic anhydride]. Prolonged interaction of *N*-methylpyrrole and Me acetylenedicarboxylate (2 mols.) gives the *indole* (I), m. p. 145—148°, reduced in presence of (*a*) colloidal Pd and MeOH and (*b*) Pt-black and AcOH to (*a*) a *dihydro*-, m. p. 114—116°, and (*b*) the *hexahydro*-derivative, m. p. 155—157°. (I) and Br (1 mol.) in MeOH give the *Me*$_3$ ester, m. p. 124—126°, of 1-*methylindole*-4 : 5 : 6-*tricarboxylic acid*, m. p. 292° (decomp.) (converted by distillation with CaO in N_2 into 1-methylindole). 2 : 4-Dimethylpyrrole and Me acetylenedicarboxylate in C_6H_6 afford *Me αα-di*-(2 : 4-*dimethylpyrryl*-5-)*succinate*, m. p. 165°. Catalytic reduction (Pd) of the adduct (this vol., 849) from 2-methylpyrrole and Me acetylenedicarboxylate gives Me α-2-methylpyrryl-5-succinate (*loc. cit.*).



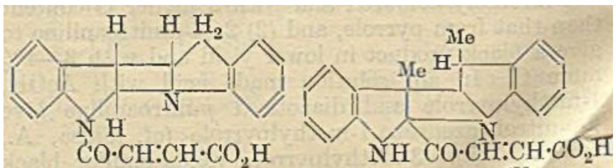
(I).

XV. 2-Methylindole and maleic anhydride in C_6H_6 give *α-2-methylindolyl-3-succinic anhydride*, m. p. 169° [free *acid*, m. p. 212° (decomp.) (*Me* ester, m. p. 103°)], and the *compound* (II), m. p. 235—236° (*Me*



(II).

ester, m. p. 155—156°, converted by NH_2OH,HCl in MeOH into a *compound*, $C_{23}H_{24}O_3N_4$,HCl, m. p. 245—246°). Similarly, 1 : 2-dimethylindole and maleic anhydride afford *α-1 : 2-dimethylindolyl-3-succinic anhydride*, m. p. 196—197° {free *acid*, m. p. 233° [*Me* ester (III), m. p. 139°]}, and the *compound* (II, NH=NMe), m. p. 253°. *Me* 1 : 2-*dimethylindolyl-5-ethylene-αβ-dicarboxylate*, m. p. 129°, from 1 : 2-dimethylindole and Me acetylenedicarboxylate, is reduced catalytically (Pd) in MeOH to (III). Indole (or di-indole) and maleic anhydride in AcOEt give the *compound* (IV), m. p. 157° (*Me* ester, m. p. 151°), converted by an excess of diazomethane into a *substance*, $C_{22}H_{20}O_3N_4$, m. p. 172°. Catalytic reduction (Adams) of (IV) in MeOH furnishes a *dihydro*-derivative, m. p. 169—170° (prepared also from di-indole and succinic anhydride in AcOEt), hydrolysed by 30% KOH to indole and succinic acid. Similar hydrolysis of (IV) yields indole and



(IV.) (V.)

an *acid*, $C_{12}H_{11}O_4N$, m. p. 197° (*Me*$_2$ ester, m. p. 74°). 3-Methylindole and maleic anhydride react

slowly in presence of a little conc. H_2SO_4, forming the *compound* (V), m. p. 246° [an *isomeride* (VI), m. p. 194°, is produced from di-3-methylindole and maleic anhydride in C_6H_6], hydrolysed to di-3-methylindole and fumaric acid, and converted by diazomethane into a *substance*, $C_{24}H_{24}O_3N_4$, m. p. 179°. Catalytic reduction (Pd) of (V) or (VI) gives the same *dihydro*-derivative (+EtOH), m. p. 207° (*Me* ester, m. p. 150°), also prepared from di-3-methylindole and succinic anhydride in AcOEt. H. BURTON.

Polymerisation of indole. III. Polymerisation mechanism in hydrochloric acid solution. O. SCHMITZ-DUMONT and H. H. SAENGER (J. pr. Chem., 1931, [ii], **132**, 39—58; cf. this vol., 1165).—The reversibility of the polymerisation of indole into di-indole hydrochloride in aq. HCl is proved by the complete conversion of the latter by shaking with dil. HCl and Et_2O into indole. The lack of relationship between HCl concentration and the position of equilibrium is probably explained by the mechanism $C_8H_7N,HCl+C_8H_7N \rightleftharpoons (C_8H_7N)_2,HCl$. Addition of indole in EtOH to a mixture of conc. HCl and EtOH gives an immediate precipitation of di-indole hydrochloride, and no tri-indole is formed. Tri-indole is formed by combination of equiv. proportions of indole and di-indole hydrochloride (but not the base) at 100°, and also by careful neutralisation of a suspension of di-indole hydrochloride in H_2O with dil. KOH; it is the stable polymeride at room temp., and its formation is not reversible. Measurements are made of the solubilities of di- and tri-indole hydrochlorides in aq. HCl of varying concentration, and of di-indole hydrobromide in HBr. The solubility of the first decreases with increasing HCl concentrations; consequently the velocity of formation of tri- from di-indole hydrochloride, which increases with increasing HCl concentration at first, and then diminishes, is explained as a result of the opposing catalytic (due to p_H) and solubility effects. The formation of di-indole hydrobromide only with comparatively dil. HBr is a consequence of its even lower solubility in aq. HBr. H. A. PIGGOTT.

Indole derivatives of mixed function. Q. MINGOIA (Gazzetta, 1931, **61**, 646—650; cf. A., 1929, 579).—In the prep. of 3-chloroacetylindole by the action of AcCl on magnesylindole, some *2-chloroacetylindole*, m. p. 230° (*Ag* derivative), is formed, giving when fused with KOH indole-2-carboxylic acid. Magnesylskatole with AcCl gives *2-chloroacetyl-3-methylindole*, m. p. 115—120°, converted by KOH into *2-chloroacetyl-3-methylindolylcarbinol*, m. p. 198—200° (*Ag* derivative; *Ac_2* derivative, m. p. 168°), and reacting with NH_3 in a sealed tube to give *2-aminoacetyl-3-methylindole*, m. p. 250—252° (decomp.) (*Ag* derivative; *picrate*, m. p. 170°). *3-Aminoacetylindole*, m. p. 237° [*Ag* derivative; *picrate*, m. p. 200° (decomp.)], is similarly obtained from 3-chloroacetylindole. E. E. J. MARLER.

Configurations of aldoximes. T. W. J. TAYLOR, D. H. G. WINCKLES, and M. S. MARKS (J.C.S., 1931, 2778—2783).—Quinoline-2-aldoxime (I) (A., 1903, i, 53) has a configuration (probably) similar to that of α-benzilmonoxime, since it furnishes a series of metallic (*Co*, Cu , and Fe˙˙) complexes. The regeneration of (I) by hydrolysis of its *Ac* derivative, m. p. 128—130° (decomp.), with aq. Na_2CO_3 supports the view that when AcOH is eliminated from an acetylaldoxime (with nitrile formation), the H atom and OAc group are *anti* to one another. Metallic complexes are not obtained from the α-furfuraldoxime of Brady and Goldstein (A., 1927, 973), whilst the *Cu* and *Co* complexes from the β-form (*loc. cit.*) resemble those from β-benzaldoxime and are unlike those from α-benzilmonoxime (II).

β-Benzilmonoxime and $Cu(OAc)_2$ react slowly in EtOH forming a Cu complex which is decomposed by acid to (II); the production of a Co complex from the β-oxime is accelerated by ultra-violet light, indicating that the change β-oxime ⟶ (II) occurs during these reactions. H. BURTON.

Doebner's reaction. II. G. CARRARA (Gazzetta, 1931, **61**, 623—626; cf. A., 1928, 1024).—The mechanism of the reaction between benzylideneaniline and pyruvic acid is discussed, and the hypothesis of Ciusa and Musajo (A., 1930, 222) is criticised. E. E. J. MARLER.

Quinoline derivatives. XXXIII. 4-Amino-2-phenyl-6- and -8-methylquinoline. H. JOHN (J. pr. Chem., 1931, [ii], **132**, 15—23).—The following are described: 2-phenyl-6-methylquinoline-4-carboxylic acid [*chloride*, m. p. 199° (decomp.); *β-hydroxyethylamide*, m. p. 191°; *Me*, m. p. 85°, and *β-chloroethyl*, m. p. 81°, esters; *hydrazide*, m. p. 216° (*CHPh:*, m. p. 234°, and *CMePh:*, m. p. 227°, derivatives); *azide*, decomp. 210°]; 4-amino-2-phenyl-6-methylquinoline (from -4-carboxylic acid by means of azide and urethane) [*picrate*, m. p. 208°; *Ac_2*, m. p. 247°, *N-CO_2Et* (from azide), m. p. 178°, and *NN'-carbonyl* (from azide), m. p. 189°, derivatives]; *4-carbimido-2-phenyl-6-methylquinoline*, m. p. 214° (decomp.); *1-(2'-phenyl-6'-methyl-4'-quinolyl)-3-methyl-5-pyrazolone*, m. p. above 300°; 2-phenyl-8-methylquinoline-4-carboxylic acid [*chloride*, m. p. 245° (decomp.); *amide*, m. p. 241° (*NN'-carbonyl* derivative, m. p. 210°, from chloride and carbamide); *diethylamide*, m. p. 107°; *β-hydroxyethylamide*, m. p. 198°; *Me*, m. p. 86°, *Et*, m. p. 70°, and *β-chloroethyl*, m. p. 84°, esters; *hydrazide*, m. p. 222° (*CHPh.*, m. p. 226°, and *CMePh:*, m. p. 215°, derivatives); *azide*, decomp. 90°]; *4-amino-2-phenyl-8-methylquinoline*, m. p. 125° [*Ac*, m. p. 212°, *Ac_2*, m. p. 293°, *N-CO_2Et*, m. p. 134° (from azide), and *NN'-carbonyl*, m. p. above 300° (from azide), derivatives]; *4-carbimido-2-phenyl-8-methylquinoline*, m. p. 261° (decomp.); and *1-(2'-phenyl-8'-methyl-4'-quinolyl)-3-methyl-5-pyrazolone*, m. p. above 300°. H. A. PIGGOTT.

Constitution of the bases formed by the action of phosphoryl chloride on acetanilide and phenacetin. O. G. BACKEBERG (J.C.S., 1931, 2814—2817).—The products obtained by Silberstein (G.P. 137,121) from the action of PCl_5 on NHAcPh and phenacetin are shown to be, besides the corresponding substituted acetamidines, 4-anilino- (I), m. p. 156° (*hydrochloride*, m. p. 266°), and *4-p-phenetidino-6-ethoxy-2-methylquinoline* (II), m. p. 225° (*hydrochloride*, m. p. 264°), respectively, the latter also being prepared from 4-chloro-6-ethoxyquinaldine and *p*-phenetidine. (I) when heated under pressure with fuming HCl

gives 4-hydroxy-2-methylquinoline and (II) similarly treated loses OEt-groups, but the $(OH)_2$-compound cannot be isolated. 4-Hydroxy-6-ethoxy-2-methylquinoline (*hydrochloride*, m. p. 241—243°) is converted by PCl_5 into 4-*chloro*-6-*ethoxy*-, m. p. 78°, and by fuming HCl into 4 : 6-*dihydroxy*-2-*methylquinoline*, $+H_2O$, m. p. 308° (decomp.). F. R. SHAW.

Manufacture of aminoalkoxy-compounds useful as antiseptics. SOC. CHEM. IND. IN BASLE.—See B., 1931, 1027.

Acridine. VII. Nitration of acridone. VIII. Nitration of 10-methylacridone and preparation of 3 : 7-diamino-10-methylacridinium chloride. K. LEHMSTEDT (Ber., 1931, **64**, [*B*], 2381—2386, 2386—2394).—VII. Acridone, prepared by the action of NaOCl on thioacridone, is converted by HNO_3 (*d* 1·5) and AcOH in presence of conc. H_2SO_4 at ≯30° into 3-nitro- (identified as 3-nitro-5-*p*-dimethylaminophenylacridine, m. p. 225°) and 1-nitro-acridone, m. p. 258—259°. Further nitration of 3-nitroacridone affords mainly 3 : 7-dinitroacridone [identical with the product of Bogert and others (A., 1930, 1047); 3 : 7-dinitro-5-*p*-dimethylaminophenylacridine, decomp. 328° (corr.)] and a little 3 : 9(or 1 : 7)-dinitroacridone, m. p. 302°, also prepared by nitrating 1-nitroacridone. Acridone-1-carboxylic acid is nitrated to 7-*nitroacridone*-1-*carboxylic acid*, decomp. 345°, decarboxylated at 355° to 3-nitroacridine.

VIII. [With H. HUNDERTMARK.] Acridine is heated with Me_2SO_4 at 100° and the product after treatment with 2*N*-NaOH is oxidised with CrO_3 in AcOH, whereby 10-methylacridone, m. p. 199°, is obtained in good yield. Nitration in AcOH with HNO_3 (*d* 1·4) at 100° gives 3-*nitro*-10-*methylacridone*, m. p. 276° (also prepared from 3-nitroacridone, NaOMe, and MeI in EtOH), and 1-*nitro*-10-*methylacridone*, m. p. 168° (obtained also by methylation of the $1-NO_2$-compound). 3 : 7-*Dinitro*-10-*methylacridone*, m. p. 350° (decomp.), is obtained from the $3-NO_2$-compound, conc. H_2SO_4, and HNO_3 (*d* 1·4) or from 10-methylacridone, conc. H_2SO_4, and HNO_3 (*d* 1·51) (also from 3 : 7-dinitroacridone and Me_2SO_4). Reduction of 3-nitro-10-methylacridone by HCl and $SnCl_2$ affords 3-*amino*-10-*methylacridone*, m. p. 205°, transformed by 20% HCl at 220° into 3-*hydroxy*-10-*methylacridone*, m. p. 275° (decomp.), converted by NaOMe and Me_2SO_4 into 3-*methoxy*-10-*methylacridone*, m. p. 139° (*picrate*). Similarly 3 : 7-dinitro-10-methylacridone is reduced by Sn and HCl to 3 : 7-*diamino*-10-*methylacridone*, m. p. 245—247° (*hydrochloride*), which with Zn dust and conc. HCl yields 3 : 7-*diamino*-10-*methyl*-5 : 10-*dihydroacridine*, oxidised to 3 : 7-*diamino*-10-*methylacridinium chloride*, $C_{24}H_{14}N_3Cl,HCl,4H_2O$. H. WREN.

Determination of the constitution of bases obtained from protein. I. Isolation of substituted piperazines and a new method for their synthesis. F. WREDE, E. BRUCH, and W. KEIL (Z. physiol. Chem., 1931, **200**, 133—144).—Treatment of gliadin according to Troensegaard's method (this vol., 245) gave three bases isolated as the chloroaurates: 2-iso*propylpiperazine* (I) [*chloroaurate* ($B,2HAuCl_4$), darkens at 230°, decomp. 243°; *hydrochloride*, m. p. 280° (darkens); *picrate*, decomp. about 250°; *chloroplatinate*; Bz_2 derivative, m. p. 225° (uncorr.)]; *base*, $C_5H_{11}ON$ (II) [*chloroaurate* ($B,HAuCl_4$), sinters at 164°, m. p. 174°], and 2-*methylpiperazine* (III) [*chloroaurate* ($B,2HAuCl_4$), darkens at 225°, decomp. 235°; *chloroplatinate*, blackens at 270°, Bz_2 derivative, m. p. 150° (uncorr.)].

Electrolytic reduction of diketopiperazines under stated conditions gave piperazine and homologues; 3 : 5-diketopiperazine gave piperazine, 3 : 5-diketo-2-methylpiperazine gave (III), and 3 : 5-diketo-2-*iso*propylpiperazine gave (I). The base (I) was previously isolated by Troensegaard (this vol., 1173). J. H. BIRKINSHAW.

***cyclo*Dipeptides of asparagine. II.** R. NUCCORINI and C. RAVENNA (Gazzetta, 1931, **61**, 657—664; cf. A., 1930, 617).—The product obtained by heating asparagine in glycerol contains a small amount of the diamide of the α-*cyclo*dipeptide of aspartic acid. Treatment of the remainder of the product with $Ba(OH)_2$ yields the β-dipeptide and a small amount (not rigorously identified) of the α-dipeptide of aspartic acid. It is suggested that in the original reaction there are formed (*a*) either the hypothetical β-*cyclo*dipeptide, converted by $Ba(OH)_2$ into the β-dipeptide or its anhydride, which is known to give rise to the β-dipeptide (cf. A., 1922, i, 180), and (*b*) the diamide of the α-*cyclo*dipeptide, by elimination of H_2O from the NH_2 and CO_2H groups of 2 mols. of asparagine, hydrolysis of this giving the α-*cyclo*-dipeptide, converted by $Ba(OH)_2$ into the α-dipeptide. E. E. J. MARLER.

Racemisation. X. Action of alkali on diketopiperazines and peptides. P. A. LEVENE, R. E. STEIGER, and R. E. MARKER (J. Biol. Chem., 1931, **93**, 605—621).—The anhydride of *d*-alanyl-*d*-alanine (I) is racemised to the extent of 80% by 0·2*N*-NaOH (2 mols.) at 25° during 48 hr.; some hydrolysis occurs, but (I) is unaffected under the same conditions. Racemisation of *d*-leucyl-*d*-leucine anhydride by NaOH in aq. pyridine (cf. A., 1930, 788) is complete after 6 hr. Diketopiperazines are rapidly and completely racemised by alkali whenever hydrolysis does not occur. The figures quoted in parentheses after the following peptides (improved methods of prep. given) are the percentage racemisations taking place when they are treated (at 25°) with 0·2*N*- (2 mols.) and *N*-NaOH (10 mols.), respectively, after 8 days: *d*-leucyl-*d*-leucine (—, 0); *d*-leucyl-*d*-leucyl-*d*-leucine (0, 4); l-*alanyl*-d-*leucyl*-d-*leucine* (0, 5), $[\alpha]_D^{25}$ +62·2° in 1·01*N*-NaOH [prepared from l-α-*bromopropionyl*-d-*leucyl*-d-*leucine*, m. p. 180° (decomp.), $[\alpha]^{25}$ +46·35° in EtOH]. H. BURTON.

Catalytic reduction of pyridine derivatives. Methyl- and phenyl-pyridine, quinoline, pyridylpyrrole, nicotyrine, and nicotine. J. OVERHOFF and J. P. WIBAUT (Rec. trav. chim., 1931, **50**, 957—980).—Catalytic reduction (Adams) of these substances under slight pressure at 40—50° in either AcOH or as their hydrochlorides in EtOH gives the following results. In agreement with Skita 1916, i, 835), the velocity of reduction of pyridine, 2- and 3-, 2 : 4-di-, and 2 : 4 : 6-tri-methylpyridine to the corresponding piperidines decreases with increasing substitution. Quinoline (in EtOH) affords

cis- and *trans*-decahydroquinoline (A., 1927, 572). Only the pyridine ring is reduced in monosubstituted phenyl- or benzyl-pyridines, 2-phenyl-, 2- and 4-benzyl-pyridine giving the corresponding piperidines, whilst 4-phenylpyridine is not reduced. When more than one substituent Ph group is present, the Ph nucleus is also partly reduced or undergoes fission; 2 : 6-di-, 2 : 4 : 6-tri-, 2 : 3 : 5 : 6-tetra-, and penta-phenylpyridine give, respectively, 2 : 6-*di*(cyclo*hexyl*)*piperidine*, m. p. 63°, 2 : 4 : 6-*tri*(cyclo*hexyl*)-*pyridine*, m. p. 47°, a *substance* $C_{29}H_{39}N$, m. p. 224—225°, and a *substance*, $C_{29}H_{45}N$, m. p. 250—252°, probably a tetra(*cyclo*hexyl)pyridine. *N*-2-Pyridyl-pyrrole undergoes fission into piperidine and pyrrolidine, but 2-(2′-pyridyl)pyrrole hydrochloride is reduced in EtOH to 2-(2′-*piperidyl*)*pyrrole*, m. p. 93° (*benzenesulphonyl* derivative, m. p. 125°), further reduced in AcOH to 2-(2′-*piperidyl*)*pyrrolidine* (*picrate*, m. p. 215°), whilst 3-(2′-pyridyl)pyrrole (only in EtOH) affords 3-(2′-*piperidyl*)*pyrrole*, m. p. 88—89° (*hydrochloride*, m. p. 207—208°). Reduction of nicotine causes fission of the pyrrole ring giving the octahydro-compound [3-δ-methylamino-*n*-butyl-piperidine (I)], which is the only product isolated, although in AcOH the large excess of H_2 absorbed indicates the occurrence of a side-reaction. Reduction of 2-(2′-pyridyl)- and 2-(3′-pyridyl)-*N*-methylpyrrole is effected only with carefully purified materials in AcOH, and whilst the former gives 2-(2′-*piperidyl*)-1-*methylpyrrolidine*, b. p. 225—228° (*picrate*, m. p. 189—190°), the latter gives only (I), fission of the reduced pyrrole nucleus taking place.

J. W. Baker.

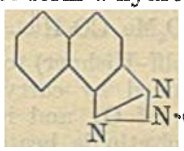
Quinazolines. II. Interaction of 2 : 4-dichloroquinazoline in alcohol with salts and bases. N. A. Lange and F. E. Sheibley (J. Amer. Chem. Soc., 1931, 53, 3867—3875).—The formation of 2-chloro-4-ethoxyquinazoline (I) from 2 : 4-dichloroquinazoline (II) and KCN in EtOH suggests that the reaction (II) +EtOH ⟶ (I)+HCl occurs; the HCl then reacts with the KCN. The possible replacement of KCN by other salts and bases is studied. (I) is formed from (II) and EtOH in presence of KCNO or Na_2CO_3, but with NaOAc a mixture of (I), AcOEt, benzoylenecarbamide [2 : 4-dihydroxy-quinazoline] (III), and 2(?)-*chloro*-4(?)-*hydroxy-quinazoline*, m. p. 211° [hydrolysed by dil. HCl to (III)], is obtained. (II) and NH_2Ph in EtOH give the *hydrochloride*, m. p. 317° (softens at about 304°), of 2 : 4-*dianilinoquinazoline* (not obtained free from EtOH except as a glass), m. p. 65° (indef.) [*sulphate*, m. p. 295°; *acetate* (+H_2O), m. p. 148°; *nitrate*, m. p. 223°; *oxalate*, m. p. 253°; *picrate*, m. p. 275° (softens at about 250°)]. *o*-, *m*-, and *p*-Aminobenzoic acids and (II) in EtOH afford the *hydrochlorides*, m. p. 271° (softens at 210°), 344°, and 347°, of 2 : 4-dianilinoquinazoline-2′ : 2″-, -3′ : 3″-, and -4′ : 4″-dicarboxylic acids (impure *Cu* salt), respectively. The *hydrochloride* of Me 2 : 4-dianilinoquinazoline-2″-dicarboxylate melts partly at 181° (decomp.) shrinking at about 160°, and completely at 261°. 4-Chloroquinazoline and NH_2Ph at 100° give the *hydrochloride*, m. p. 251°, of 4-*anilinoquinazoline*, m. p. 221—222° (*picrate*, m. p. 233°).

H. Burton.

Disulphonic derivatives of 2-phenyl-αβ-naphth-1 : 2 : 3-triazole. A. Neri (Gazzetta, 1931, 61, 597—604).—The Na_2 salt of 2-p-*sulphophenyl*-3 : 4-*naphth*-1 : 2 : 3-*triazole*-1-*sulphonic acid* (I) is obtained by the action of NH_3–$CuSO_4$ on the Na_2 salt *hexahydrate* of p-*sulphobenzeneazo*-α-*naphthylamine*-4-*sulphonic acid* (from Na sulphanilate and Na naphthionate). (I) is oxidised by CrO_3 to the Na sulphonate of 2-phenyl-αβ-napthtriazolequinone already described (A., 1929, 1184). The Na_2 salt of 2-p-*sulphophenyl*-3 : 4-*naphth*-1 : 2 : 3-*triazole*-7-*sulphonic acid* (II) is similarly obtained from p-*sulphobenzeneazo*-3-*naphthylamine*-7-*sulphonic acid*, prepared from sulphanilic acid and β-naphthylamine-6-sulphonic acid. Oxidation of (II) with CrO_3 gives unsatisfactory results. Treatment of 2-phenyl-αβ-naphth-1 : 2 : 3-triazole with excess of conc. H_2SO_4 gives a *disulphonic acid* (*Ba* salt +$4H_2O$; *K_2* salt; *Na_2* salt) not identical with (I) or (II). The free *acid* does not crystallise. Oxidation with CrO_3 gives small amounts of a *quinone*.

E. E. J. Marler.

Diethylaminoethyl ester of 2-phenyl-αβ-naphth-1 : 2 : 3-triazole-7′-carboxylic acid. A. Neri (Gazzetta, 1931, 61, 610—614).—Novocaine when diazotised and coupled with β-naphthylamine gives the *hydrochloride* of *diethylaminoethyl* p-*azo*-β-*naphthylaminobenzoate* (I) (non-cryst. *base*), converted by NH_3–$CuSO_4$ into *diethylaminoethyl* 2-*phenyl*-αβ-*naphth*-1 : 2 : 3-*triazole*-4′-*carboxylate*, (II), m. p. 162°, which does not form a hydrochloride.


$\cdot C_6H_4\cdot CO_2\cdot[CH_2]_2\cdot NEt_2$

Similarly, the *Na* 4-*sulphonate* of (I) is prepared from novocaine and naphthionic acid, and yields the *Na sulphonate* of (II), which is not sufficiently sol. in H_2O for its physiological action to be tested.

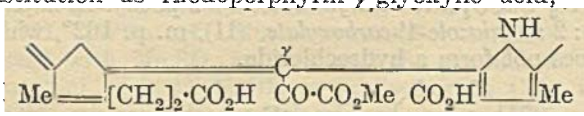
E. E. J. Marler.

Porphyrin syntheses. XL. Synthesis of deoxophylloerythrin. H. Fischer and J. Riedmair (Annalen, 1931, 490, 91—99).—Et 2-formyl-4-methyl-3-bromovinylpyrrole-5-carboxylate with cryptopyrrolecarboxylic acid in presence of HBr and AcOH gives 5-*carbethoxy*-4 : 3′ : 5′-*trimethyl*-3-*bromovinylpyrromethene*-4′-*propionic acid hydrobromide*, and with hæmopyrrolecarboxylic acid gives 5-*carbethoxy*-4 : 4′ : 5′-*trimethyl*-3-*bromovinylpyrromethene*-3′-*propionic acid hydrobromide* (I); the corresponding 5-*carboxy*-derivative [to (I)] (II) is similarly prepared. Fusion of (II) with 5-bromo-4 : 3′-dimethyl-3 : 4′-diethyl-5′-bromomethylpyrromethene hydrobromide and succinic acid gives mainly ætioporphyrin, deoxophylloerythrin (0·5% of theory), and an unidentified porphyrin, thus confirming the structure assigned to deoxophylloerythrin [cf. formula (II), this vol., 496]. A similar condensation could not be effected using (I) in the place of (II).

H. A. Piggott.

Chlorophyll. XVIII. Preparation and constitution of chlorophyll porphyrins. H. Fischer, L. Filser, W. Hagert, and O. Moldenhauer. **XIX. Chlorophyll *a*.** H. Fischer, O. Sus, and G. Clebs [with L. Filser and H. Siebel] (Annalen,

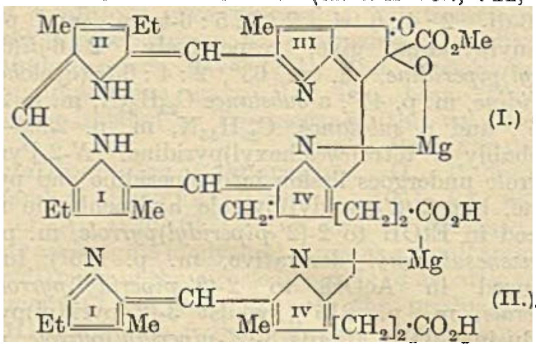
1931, 490, 1—38, 38—90).—XVIII. Phylloerythrin, like chlorophyll, gives with MeOH–KOH in N_2 verdoporphyrin, accompanied by phyllo-, rhodo-, and pyrroporphyrins; in O_2 rhodoporphyrin-γ-carboxylic acid and chloroporphyrin e_5 are also formed. Phylloerythrin is formed by action of O_2 and AcOH on phæoporphyrin a_5, and is converted by further treatment with this reagent into rhodoporphyrin-γ-carboxylic acid by ring-fission at the CO·CH_2 linking. The similar behaviour of other chlorophyll derivatives, *e.g.*, phæophytin (from which verdoporphyrin is formed in good yield with MeOH–KOH in N_2) and chloroporphyrin e_5, indicates the presence of the phylloerythrin structure. Phæophytin $a+b$, chlorophyllide $a+b$, phæophorbide a, and its Me ester all give phylloerythrin with 20% HCl in air or N_2, the formation of which in absence of air is probably accompanied by disproportionation. In absence of air phæophytin $a+b$ and phæophorbide a are degraded by MeOH–HCl to rhodoporphyrin Me_2 ester and chloroporphyrin e_4 ester. The intramol. migration of O that characterises many of these reactions explains the occurrence of *phæoporphyrin* a_7 (*mono*)*Me ester* [*Me_3* ester, m. p. 253° (decomp. into rhodoporphyrin and its Me_2 ester) (diazomethane or MeOH–HCl)] as the least sol. fraction of the reduction of phæophytin or phæophorbide a with HI in AcOH. Its constitution as rhodoporphyrin-γ-glyoxylic acid,



is proved by its reduction (Wolff–Kishner) to phylloporphyrin. Its yield is improved by carrying out the HI reduction in a stream of O_2, and it is the principal product when phæophytin is heated with AcOH in O_2 and the product reduced by addition of HI. When heated to 250° it gives rhodo- and, on longer heating, phyllo-porphyrin; it is also degraded to rhodoporphyrin by HBr–AcOH, MeOH–KOH at 155°, or by hot 95% HCO_2H or AcOH.

Chloroporphyrin e_5 gives pyrro- and rhodo-porphyrins with AcOH–air. Both phæophorbide a and methylphæophorbide a are decarboxylated by heating alone at 200°, or with pyridine at 160° (cf. A., 1930, 225); the products are reduced by HI to phylloerythrin and its ester. The conversion of phæoporphyrin a_5 into chloroporphyrin e_6 and phylloerythrin (this vol., 744) is also effected by HCl–Et_2O. A good yield of chloroporphyrin e_5 is obtained from e_6 by oxidation with air in AcOH. The *Fe* salt (hæmin ?) of phylloerythrin immediately gives the hæmochromogen spectrum with N_2H_4,H_2O, and is hydrolysed to phylloerythrin by dil. H_2SO_4 or HBr in AcOH. It is reduced by Na and amyl alcohol to deoxyphylloerythrin, traces of pyrro- and rhodo-porphyrins, and the *Fe* salt of decarboxylated chlorin e; similar treatment of natural chlorin e results in almost complete destruction. A product with all the properties of ψ-phylloerythrin is obtained by crystallisation of phylloerythrin with one tenth its weight of chloroporphyrin e_6 from pyridine–Et_2O. Phyllo- and ψ-phyllo-erythrin do not react with PhCHO or its p-NO_2-derivative in alkaline solution, but are converted into chloroporphyrin e_5. The action of Ag_2O on chlorin e in pyridine gives an *Ag* derivative. The spectra of phylloerythrin and other porphyrins in $Et_2C_2O_4$ are described; in the case of the first-named combination with the solvent appears to occur.

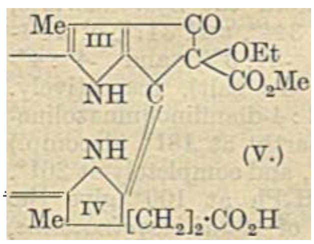
XIX. The slightly modified formulæ (I or II) are proposed for chlorophyll and are discussed and compared with Conant's formula (cf. this vol., 744, 745;



(I.) (II.)

Conant, *ibid.*, 1075) in the light of allomerisation and the phase test. The action of KOH in PrOH on phæoporphyrin a_5 or of KOH in amyl alcohol on chloroporphyrin e, in both cases in air, leads to oxidation to a green chlorin-like *rhodoporphyrin-γ-carboxyanhydride* (III) [*Me* ester, m. p. 256° (diazomethane)], whereas in N_2 the former reaction results in simple hydrolysis to chloroporphyrin e_5. Energetic treatment with alkali converts (III) into rhodoporphyrin and its γ-carboxylic acid, and action of HI in AcOH on the Me ester gives rhodoporphyrin Me ester, and the propionic acid residue does not, therefore, take part in the anhydride formation in (III); either or both of the first two decomp. products are also obtained by use of conc. aq. HCl or of HBr in AcOH. The structure of (III) is confirmed by its formation by heating rhodoporphyrin-γ-carboxylic acid (IV) to 250°. The action of cold pyridine converts it into an unidentified porphyrin [*Me* ester, m. p. 250° (diazomethane)] spectroscopically intermediate between (IV) and phylloporphyrin. Oxidation of phæoporphyrin with H_2O_2 and H_2SO_4 gives (IV) with phæoporphyrin a_7 as by-product; the latter also gives (III) with KOPr and is regarded as an intermediate in the first method.

Me and Et chlorophyllides give phæoporphyrin a_5 exclusively on reduction with HI, whereas after allomerisation with O_2 or with air in MeOH they afford spectroscopic traces of phylloporphyrin with phæoporphyrin a_7 as main product, and some a_5. The chlorophyllides are unchanged by MeOH. Allomerisation of Et chlorophyllide with benzoquinone in EtOH in absence of air also occurs with absorption of 1 mol. O_2, but the product with HI gives *phæoporphyrin* a_6 [*Me* ester, m. p. 284° (*oxime*)], to which formula (V) is assigned;



(V.)

this is decomposed by 10% KOH in MeOH to an unidentified porphyrin. It is therefore considered that whilst allomerisation with O_2 is a complex process which involves fission of the homocyclic nucleus, the product obtained with benzoquinone is a simple dehydro-derivative; this explains

the spectroscopic differences observed by Conant. Allomerisation with benzoquinone in EtOH is suppressed by traces of $H_2C_2O_4$, and reduction of the product obtained in $COMe_2$ gives phæoporphyrin a_5.

The phase test (cold KOH–MeOH) in presence of air gives with Et chlorophyllide the usual unstable chlorins which rapidly pass into a purpurin, and on reduction of the total product with HI rhodoporphyrin is formed; in N_2, however, chlorin e_7 (reduced by HI to chloroporphyrin e_5) and a little rhodin g are formed as in the hot quick hydrolysis. Using 25% KOH in PrOH under Conant's conditions a *purpurin*, $C_{33}H_{34}O_5N_4$ (*Me* ester, m. p. 254°), probably closely related to (III), results. Et chlorophyllide allomerised with benzoquinone in EtOH gives products converted by HI reduction into rhodoporphyrin whether the KOH hydrolysis is carried out in air or in its absence. It is concluded that the mechanism of the phase test consists in simple hydrolysis of the homocyclic ring. The change of the unstable chlorins into purpurins is reversible (*e.g.*, with phæopurpurin 7 Me_2 ester). Hydrolysis of chlorin e Me_3 ester with KOH–MeOH in N_2 gives chlorin e_7 and the purpurin previously obtained by hot, quick hydrolysis. Similar hydrolysis of phæophytin $a+b$ in N_2 gives a mixture of stable chlorins (e_6 and e_7), the latter of which is distinguished from the product obtained in air (phæopurpurin 7) by reduction with HI which gives chloro-e_6 and rhodoporphyrins, respectively. Degradation of dimethylphæopurpurin 7 with pyridine or "pyridine–soda" gives *ψ-verdoporphyrin* Me_2 ester, m. p. 277° (corr.), which with HI in AcOH gives rhodo-, and on energetic decomp. with alkali gives phyllo-porphyrin. The decarboxylation by heat of phæoporphyrin a_5 Me Et ester gives phylloerythrin Et ester.

H. A. PIGGOTT.

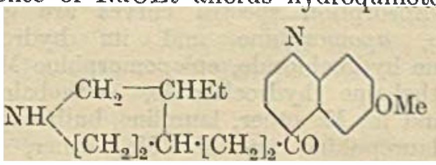
Action of fuming hydriodic acid on lupanine. K. WINTERFELD, A. KNEUER, and F. W. HOLSCHNEIDER (Ber., 1931, **64**, [*B*], 2415—2419; cf. this vol., 371).—Treatment of *r*-lupanine in the manner adopted for *d*-lupanine affords β-lupinane and other non-identified products (cf. Clemo and others, this vol., 970). *d*-Lupanine hydrochloride is transformed by PCl_5 into *dichlorolupanine*, $C_{15}H_{22}ON_2Cl_2$, m. p. 112—113°, $[\alpha]_D$ +82·5° in 96% EtOH *d-Lupanine H tartrate* has m. p. 194°.

H. WREN.

***Cinchona* alkaloids. XXV. Complete synthesis of the *Cinchona* alkaloids, hydroquinine and hydroquinidine.** P. RABE, W. HUNTENBURG, A. SCHULTZE, and G. VOLGER (Ber., 1931, **64**, [*B*], 2487—2500; cf. A., 1922, i, 360, 361).—Acetoacet-*p*-methoxyanilide, obtained from the ester and *p*-anisidine alone or in presence of solvent naphtha, is almost quantitatively converted by 90% H_2SO_4 at 100° into *2-hydroxy-6-methoxy-4-methylquinoline*, m. p. 253° (*hydrochloride*), transformed by PCl_5 and $POCl_3$ at 115° into *2-chloro-6-methoxy-4-methylquinoline*, m. p. 145° (corr.), which yields 6-methoxy-4-methylquinoline, m. p. 52°, when acted on by Al powder in 75% AcOH or by H_2 in presence of Pd and KOH–EtOH at 50—55°. Condensation of 6-methoxy-4-methylquinoline with boiling PhCHO in presence of anhyd. $ZnCl_2$ affords *6-methoxy-4-styrylquinoline*, m. p. 75° (corr.) (*sulphate*), oxidised by $KMnO_4$ in aq. pyridine to 6-methoxyquinoline-4-carboxylic acid (Et ester, m. p. 69°).

4-Methyl-3-ethylpyridine and CCl_3·CHO in presence of anhyd. $ZnCl_2$ at $\not>$ 86° yield 3-ethyl-4-γ-trichloro-β-hydroxy-*n*-propylquinoline, m. p. 139° (corr.), transformed by NaOEt in 99·5% EtOH into 3-ethylpyridyl-4-acrylic acid, m. p. 248° (corr., decomp.) [*hydrochloride* $+H_2O$, m. p. 190° (corr., decomp.) after loss of H_2O at 110—120°]. The hydrochloride is reduced by H_2 in 4% aq. HCl in presence of highly active Pt sponge to a mixture of β-3-ethyl-4-piperidylpropionic acid hydrochlorides. The mixture of the corresponding Et β-3-ethyl-4-piperidylpropionates, b. p. 114—117°/0·3 mm., is treated with *d*-tartaric acid in anhyd. EtOH, whereby *Et β-3-ethyl-4-piperidylpropionate H* d-*tartrate*, m. p. indef. 123—124° (decomp.), $[\alpha]_D^{18}$ +6·6° in EtOH, is obtained; it is converted into Et β-3-ethyl-4-piperidylpropionate, b. p. 112—114°/0·1 mm., $[\alpha]_D^{18}$ +19·0° (*Bz* derivative, b. p. 197—200°/0·2—0·3 mm.), identical with the product obtained by alkaloidal degradation.

Condensation of the Bz derivative with Et quinate in presence of NaOEt affords hydroquinotoxin (I),


(I.)

isolated as the Bz_2 *d*-tartrate, m. p. 170° (decomp.), $[\alpha]_D^{18}$ −39·5° in EtOH and $CHCl_3$ (1 : 2 vol.). *N-Bromohydroquinotoxin*, m. p. 117° after softening, is transformed into hydroquininone, m. p. 99—100°, identical with the product obtained by the oxidation of hydroquinine. Hydroquinotoxin is transformed into *C*-bromohydroquinotoxin dihydrobromide, and thence into hydroquininone. Hydrogenation of cryst. hydroquininone in presence of Pd yields hydroquinidine, whereas from the oily mixture of the ketonic and enolic forms of hydroquininone hydroquinine is obtained.

H. WREN.

Titration of quinine in ultra-violet light. J. GRANT (Analyst, 1931, **56**, 653—654).—If quinine be dissolved in an excess of H_2SO_4 and the excess of acid titrated in a dark room under a vertical beam of ultra-violet light, free quinine is liberated at the end-point. This produces a marked decrease in the fluorescence, which, however, is not sharp unless carried out in presence of controls. The titration must be made in a beaker to avoid fluorescence due to the glass itself.

T. McLACHLAN.

***Strychnos* alkaloids. LXII. Relationships of the C_{19} acids from brucidine and dihydrobrucidine.** H. LEUCHS, F. KRÖHNKE, and H. S. OVERBERG (Ber., 1931, **64**, [*B*], 2539—2543; cf. this vol., 970).—Oxidation of dihydrobrucidine with CrO_3 yields, in addition to diketodihydronucidine (*loc. cit.*), minor amounts of an NH_2-acid, $C_{19}H_{24}O_4N_2,2H_2O$, m. p. 258—260° (decomp.), $[\alpha]^{20}$ +185·4°/*d* (*perchlorate*, $[\alpha]_D^{20}$ +141·1°/*d*), and an isomeric *acid* ($+3H_2O$), $[\alpha]_D$ +51·7°/*d*. Hydrogenation of either acid in presence of PtO_2 yields the *acid* $C_{19}H_{26}O_4N_2$, $[\alpha]_D$ +104·4°/*d* (*perchlorate*, $[\alpha]_D$ +74·9°/*d*), also obtained from the isomeric acids, $C_{19}H_{22}O_4N_2$, prepared by the oxid-

ation of brucidine (this vol., 855). The respective pairs must therefore be geometrical isomerides. Reduction of the acids $C_{19}H_{22}O_4N_2$ by Na–Hg is confined to the C:CH·CO_2H group and yields 2-keto-nucidine-3-acetic acid (isolated as the *perchlorate*, $C_{19}H_{24}O_4N_2,HClO_4$, $[\alpha]_D^{20}$ +50·3°/*d*), catalytically reduced to the acid $C_{19}H_{26}O_4N_2$. H. WREN.

Transposition of 2-benzeneazomorphine into 2-benzeneazo*apo*morphine. A. NEU (Gazzetta, 1931, **61**, 604—609; cf. A., 1930, 230).—2-Benzeneazomorphine dissolves in H_2SO_4 to give 2-benzeneazo*apo*morphine, identical with that obtained by the action of benzenediazonium chloride on *apo*morphine. 2-p-*Chlorobenzeneazomorphine* is similarly transformed into 2-p-*chlorobenzeneazo*apo*morphine*, identical with that obtained from *p*-chlorobenzenediazonium chloride and *apo*morphine. Neither Cl-compound melts below 300°. The structure of these compounds is discussed. E. E. J. MARLER.

Absorption spectra of phenanthripyridine alkaloids. A. GIRARDET (J.C.S., 1931, 2630—2637).—Absorption spectra curves are given for thebaine, *apo*morphine and its hydrochloride, aporphine hydrochloride, epi*apo*morphine Me_2 ether, morphothebaine hydrochloride, *iso*thebaine, pukateine and its Me ether, laureline, bulbocapnine Me ether, laurepukine and its Me_2 ether, glaucine, dicentrine, domesticine Me ether, and corydaline. The effects of combinations of the substituents OH, OMe, :O_2CH_2, are discussed. H. BURTON.

Homologues of resorcinolarsinic acid and of 4-acetamido-2-hydroxyphenylarsinic acid (Fourneau 270). P. M. BARANGER (Bull. Soc. chim., 1931, [iv], **49**, 1213—1222).—The introduction of Me or Et *para* to the OH in *p*-amino- or *p*-acetamido-2-hydroxyphenylarsinic acid destroys the therapeutic val., the ratio maximum tolerated dose/curative dose decreasing to less than unity. A similar effect is observed with 2 : 4-dihydroxyphenylarsinic acid. The following are described: *p*-methoxyaceto-, b. p. 258°/160 mm., b. p. 146°/15 mm., m. p. 38—39° (yield 96%) (semicarbazone, m. p. 202°); *p-methoxypropio-*, b. p. 149—150°/19 mm., m. p. 20·5° (yield, 93%) (*semicarbazone*, m. p. 177°), *p*-methoxybutyro-, b. p. 158—159°/19 mm., m. p. 21—22° (yield, 91%) (*semicarbazone*, m. p. 183°), and p-*methoxyvalero-phenone*, b. p. 167°/25 mm. (80%) [*semicarbazone*, m. p. 220° (decomp.)]; *p*-heptoylanisole, b. p. 203°/25 mm. (yield 99%) (semicarbazone, m. p. 130°). Reduction of the above gives the alkylanisoles in the yield indicated; the latter are demethylated with gaseous HBr in boiling AcOH. *p*-Ethyl- (86%), b. p. 83—84°/16 mm., *p*-propyl- (70%) b. p. 107°/22 mm., *p*-butyl- (90%), b. p. 130°/33 mm., p-iso*amyl-* (56%), b. p. 121°/14 mm., p-*heptyl-anisole* (78%), b. p. 164°/23 mm.; *p*-ethyl- (93%), m. p. 45—46°, b. p. 217°, *p*-propyl- (90%), m. p. 20—21°, b. p. 120°/19 mm., *p*-butyl- (94%), b. p. 138—139°/18 mm., p-iso*amyl-* (80%), b. p. 126°/14 mm. and *p*-heptyl-phenol (87%), b. p. 176°/24 mm., m. p. 26°.

Nitration of the *p*-alkylphenols with dil. HNO_3 in C_6H_6 or AcOH at 0° affords the 2-nitro-4-alkylphenol, reduced to the 2-amino-4-alkylphenol with alkaline $Na_2S_2O_4$. 3-Nitro-*p*-cresol (95%), m. p. 32°; 2-*nitro-4-propyl-* (72%), b. p. 124°/3 mm., -4-*butyl-* (71%), b. p. 125°/3·5 mm., -4-*heptyl-phenol* (87%), b. p. 149—150°/3 mm., m. p. 38°; 3-amino-*p*-cresol (85%), m. p. 135° [*Ac* derivative, m. p. 159—160° (decomp.)], 2-*amino-4-ethyl-* (100%), m. p. 137—138° (decomp.) [*Ac* derivative, m. p. 104—105° (decomp.)], -4-*propyl-* (100%), m. p. 143° (decomp.) [*Ac* derivative, m. p. 130° (decomp.)], -4-*butyl-* (100%), m. p. 138° (decomp.) [*Ac* derivative, m. p. 91—92° (decomp.)], and -4-*heptyl-phenol* (100%), m. p. 130° (decomp.) [*Ac* derivative, m. p. 112° (decomp.)], are thus obtained in the yield indicated and are converted into the 5-nitro-2-amino-4-alkylphenols by distillation and nitration of the *p*-ethenylphenols. 3-Ethenylamino-*p*-cresol (85%), b. p. 110—111°/18 mm., 2-*ethenylamino-4-ethyl-* (90%), b. p. 130°/25 mm., -4-*propyl-* (92%), b. p. 136°/18 mm., -4-*butyl-* (93%), b. p. 146—148°/18 mm., -4-*heptyl-phenol* (85%), b. p. 187°/18 mm., 6-*nitro-3-ethenyl-amino-*p-*cresol* (100%), m. p. 132°; 6-*nitro-3-amino-*p-*cresol* (70%), m. p. 199—200° (decomp.) [*Ac* derivative, m. p. 242°], 5-*nitro-2-ethenylamino-4-ethylphenol* (100%), m. p. 69°; 5-*nitro-2-amino-4-ethyl-* (100%), m. p. 155—156° (decomp.) (*Ac* derivative, m. p. 196°), -4-*propyl-*, m. p. 125—126° (decomp.) [*Ac* derivative, m. p. 160° (decomp.)], and -4-*heptyl-phenol*, m. p. 76° (decomp.); 5-*nitro-2-ethenylamino-4-propyl-*, an oil, and -4-*heptyl-phenol*, m. p. 119—120° (decomp.), are described.

4-*Nitro-2-hydroxy-5-methylphenylarsinic acid*, obtained from 6-nitro-3-amino-*p*-cresol by Bart's reaction (yield 30%), is reduced to 4-*amino-2-hydroxy* [*Na* salt; *Ac* derivative (*Na* salt)], converted into 2 : 4-*dihydroxy-5-methylphenylarsinic acid* (*Na* salt). 4-Nitro-2-hydroxy-, 4-*amino-2-hydroxy-* [*Na* salt; *Ac* derivative (*Na* salt)], and 2 : 4-*dihydroxy-5-ethylphenylarsinic acid* (*Na* salt) are similarly obtained. The Bart reaction was unsuccessful when applied to the corresponding 4-propyl- and -heptyl-5-nitro-2-aminophenols. R. BRIGHTMAN.

Aromatic arsenic compounds containing sulphur groups attached to the nucleus. III. 3 : 3′-Diamino-4 : 4′-dithiolarsenobenzene, the thiol analogue of salvarsan. H. J. BARBER (J.C.S., 1931, 2556—2561).—4-Chloro-3-nitrophenylarsinic acid and KSH in aq. EtOH give impure 3-*nitro-4-thiolphenylarsenic disulphide* (I), oxidised by HNO_3 (*d* 1·52) to 3-*nitro-4-sulphophenylarsinic acid* (II) and by I in presence of KI and $NaHCO_3$ to 2 : 2′-*dinitro-4 : 4′-diarsinodiphenyl disulphide* (III). Reduction of (I) with alkaline $Na_2S_2O_4$ gives 3 : 3′-*diamino-4 : 4′-dithiolarsenobenzene* (IV), whilst with $Fe(OH)_2$, 3 : 3′-*diamino-4 : 4′-diphenyldiarsenic trisulphide* results. The last-named is also reduced by $Na_2S_2O_4$ in presence of $MgCl_2$ to (IV). 3-Nitro-4-thiocyanophenylarsinic acid is oxidised by HNO_3 (*d* 1·52) to (II) and a little (III). H. BURTON.

10-Chloro-5 : 10-dihydrophenarsazine and its derivatives. XVI. 10-Alkyl-5 : 10-dihydrophenarsazines as convenient sources of aliphatic dichloroarsines. C. S. GIBSON and J. D. A. JOHNSON (J.C.S., 1931, 2518—2523).—Treatment of 10-chloro-5 : 10-dihydrophenarsazine with the appropriate Mg alkyl halide gives 10-Me, -Et-, -Pr-, -*Pr*^{β}-,

m. p. 87—88°, -*Bu*-, m. p. 94—95°, -*Bu*$^{\beta}$-, m. p. 73—74°, -sec.-*Bu*-, m. p. 85—86°, -n-*amyl*-, m. p. 90—92°, and -*α-ethylpropyl*-, m. p. 110—111°, -5 : 10-dihydrophenarsazines. These are decomposed by dry HCl at 110—130° forming dichloroalkylarsines (65—85% yield); the following are prepared: $MeAsCl_2$, b. p. 132·5° (all b. p. are at 760 mm. except where stated otherwise), m. p. —42·5°; $EtAsCl_2$, b. p. 155·3°; *$PrAsCl_2$*, b. p. 175·3°, m. p. —28·2°; *$Pr^{\beta}AsCl_2$*, b. p. 168·6°; $BuAsCl_2$, b. p. 194·1°; *$Bu^{\beta}AsCl_2$*, b. p. 77·8°/20 mm; sec.-*$BuAsCl_2$*, b. p. 181·8°, and *dichloro-n-amylarsine*, b. p. 212·9°, m. p. —45·5°. Mol. heats of vaporisation and Trouton's const. at 760 mm. are calc., and other physical data recorded, for these dichloroarsines. *2-Methyl-10-propyl-5 : 10-dihydrophenarsazine* has m. p. 83·5—84·5°. H. BURTON.

Phenarsazine derivatives. I. P. G. SERGEEV and I. M. GORSKI (J. Gen. Chem. Russ., 1931, **1**, 263—271).—Action of KCNS on 10-chloro-9 : 10-dihydrophenarsazine gives 10-*thiocyano*-9 : 10-*dihydrophenarsazine*, m. p. 229—230° (two forms). Boiling with xylene and treatment with NaOH and AcOH gives phenarsazinic acid. Diphenylthiocyanoarsine under the same conditions is unchanged, but with boiling H_2O gives diphenylarsine oxide. The acid is also obtained by heating phenarsazine cyanide or thiocyanate with tetralin. Phenarsazine chloride when heated with tetralin gives the hydrochloride of phenarsazinic acid. The following mechanism is suggested for the transformation of phenarsazine derivatives: $NH[C_6H_4]_2AsX \xrightarrow{O} NH[C_6H_4]_2As(O)X \longrightarrow (NH[C_6H_4]_2As(OH)_2)X$. E. B. UVAROV.

Organo-chromium compounds and their relation to the complex chemistry of chromium. F. HEIN (J. pr. Chem., 1931, [ii], **132**, 59—71).—A lecture. In a summary of partly unpublished researches it is shown that the Cr complexes that react with MgPhBr with formation of organo-chromium compounds are in general non-electrolytes.

H. A. PIGGOTT.

Germanium. VII. Organic compounds of germanium. R. SCHWARZ and M. LEWINSOHN (Ber., 1931, **64**, [*B*], 2352—2358).—*Ge tetra-p-tolyl*, m. p. 224°, prepared from $GeCl_4$ and Mg *p*-tolyl bromide in Et_2O, is converted by Br in $C_2H_4Br_2$ into *Ge tri-p-tolyl bromide*, m. p. 128°, and thence by PhBr and Na in xylene into *Ge Ph tri-p-tolyl*, m. p. 191°. The last-named compound with Br in boiling CCl_4 affords *Ge Ph di-p-tolyl bromide*, m. p. 119°, which with MgEtBr gives *Ge Ph di-p-tolyl Et*, b. p. 220°/13 mm., m. p. 55°, transformed by Br_2 in CCl_4 into *Ge Ph p-tolyl Et bromide*. Similarly, $GeCl_4$ and Mg *p*-diphenylyl bromide yield *Ge tetra-p-diphenylyl*, m. p. 270—272°, whence *Ge tri-p-diphenylyl bromide*, m. p. 242°, *Ge tri-p-diphenylyl Et*, m. p. 154—156°, non-homogeneous *Ge di-p-diphenylyl Et bromide*, and non-homogeneous *Ge di-p-diphenylyl Et Pr^{β}*. $GePh_4$ with twice its wt. of $GeCl_4$ at 210—290° affords *Ge Ph trichloride*, b. p. 105—106°/112 mm.; attempts to prepare the corresponding tribromide yield the *dibromide*, b. p. 205—207°/12 mm., and (?) $Ge_2Ph_4Br_2$, m. p. 165°. $GePh_2Br_2$ and $MgPr^{\beta}Br$ give *$GePh_2Pr^{\beta}Br$*, b. p. 225—235°/13 mm., which yields *$GePh_2EtPr^{\beta}$*, b. p. 175—190°, whence *$GePhEtPr^{\beta}Br$*, b. p. 130—135°/13 mm. Treatment of the last-named salt with Ag *d*-bromocamphorsulphonate in H_2O gives *$GePhEtPr^{\beta}$ bromocamphorsulphonate*, decomp. 230°, $[\alpha]_D^{20}$ +95·08° in H_2O. Ge tetra-*p*-tolyl and Br in CCl_4 afford *Ge di-p-tolyl dibromide*, b. p. 230—233°/13 mm. Excess of Na and $GePhCl_3$ in boiling xylene afford the *compound* $(GePh)_6$, possibly $\mathrm{GePh}{<}\genfrac{}{}{0pt}{}{\mathrm{GePh{\cdot}GePh}}{\mathrm{GePh{:}GePh}}{>}\mathrm{GePh}$.

H. WREN.

Mercuration of higher aromatic hydrocarbons. I. M. GOSWAMI and H. N. DAS-GUPTA (J. Indian Chem. Soc., 1931, **8**, 475—478).—The following compounds were prepared by heating the appropriate hydrocarbon and $Hg(OAc)_2$ in AcOH at 110—140°, filtering, concentrating, and adding $CaCl_2$ in AcOH: *acenaphthene mercurichloride*, m. p. 148° (decomp.), which with Ag_2O in boiling EtOH gives some *mercurihydroxide*, m. p. 184° after sintering at 175°; *fluorene mercurichloride*, m. p. 130—132° (decomp.), giving similarly the *mercurihydroxide*, m. p. 145—147°, in poor yield; *anthracene mercurichloride*, m. p. 181—183° (decomp.), decomposed by Ag_2O; *phenanthrene mercurichloride*, m. p. 155—157° (decomp.), decomposed by Ag_2O. The mercuri-hydroxides liberate NH_3 from NH_4Cl and absorb CO_2. The position of the Hg is unknown. R. S. CAHN.

Mercuric derivatives of dihydric bromophenols. M. AMADORI (Atti R. Accad. Lincei, 1931, [vi], **13**, 371—374).—With dibromo-pyrocatechol and -resorcinol, $Hg(OAc)_2$ gives the *compounds* $C_6H_2O_2Br_2Hg$ and with the Br_3-derivatives, the *compounds* $C_6HO_2Br_3Hg$. T. H. POPE.

Mercury and halogen derivatives of 2-phenylcinchonic acid. M. DOMINIKIEWICZ (Rocz. Chem., 1931, **11**, 664—669).—The following substances are described: 3-*hydroxy*- and -*acetoxy-mercuri-2-phenylcinchonic acids*, 3-*iodo-2-phenyl*- and 3-*bromo-2-phenylcinchonic acids*, m. p. 227—228° and 231°. The iodo-derivative yields *o*-iodobenzoic and 5-iodo-6-phenylpyridine-2 : 3 : 4-tricarboxylic acid on oxidation with $KMnO_4$. R. TRUSZKOWSKI.

Organic derivatives of silicon. XLV. Fission of aromatic Si–R linkings by aluminium chloride. W. E. EVISON and F. S. KIPPING (J.C.S., 1931, 2774—2778).—Treatment of a mixture of $SiPh_2Cl_2$ (1 mol.) and $AlCl_3$ (1 mol.) with EtBr (5 mols.) gives HBr, $SiCl_4$, $SiPhCl_3$, and Et derivatives of C_6H_6. $SiPh_2Cl_2$ and $AlCl_3$ react at 70° giving $SiCl_4$ and a solid (probably $AlPhCl_2$) which is converted by H_2O and AcCl into C_6H_6 and COPhMe, respectively; the reactions $SiPh_2Cl_2 + AlCl_3 = AlPhCl_2 + SiPhCl_3$; $SiPhCl_3 + AlCl_3 = SiCl_4 + AlPhCl_2$, probably occur. $SiCl_4$ is also produced when $SiPh_4$, $Si(CH_2Ph)_4$, or trianhydrotrisdiphenylsilicanediol is treated with $AlCl_3$ in $CHCl_3$, whilst octaphenyl*cyclo*silicotetrane similarly gives a product, hydrolysed by H_2O to a solid (which probably contains some silico-oxalic acid).

H. BURTON.

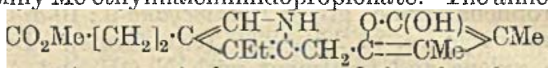
Tribenzylsilicane. W. E. EVISON and F. S. KIPPING (J.C.S., 1931, 2830—2831).—*Tribenzylsilicane* (I), m. p. 91°, has been isolated from a crude specimen of $Si(CH_2Ph)_4$ (A., 1928, 908). Tribenzyl-

silicyl oxide and H_2 are produced from (I), $COMe_2$, and KOH solution. H. BURTON.

Aromatic tin compounds containing halogen in the nucleus. A. N. NESMEJANOV and K. A. KOTSCHESCHKOV (J. Gen. Chem. Russ., 1931, **1**, 219—232).—Such compounds are obtained by the reduction of org. Hg compounds by Sn^{II} salts (cf. this vol., 503). Compounds of the type $(XC_6H_4)_2SnX'_2$, where X, X′ are halogens, so prepared are: *stannic di-p-chlorophenyl dichloride*, m. p. 86·5°, dibromide; *Sn di-p-bromophenyl dichloride*, m. p. 103°, *dibromide*, m. p. 82°; *Sn di-p-iodophenyl dichloride*, m. p. 147°, *dibromide*, m. p. 102°. The corresponding *di-iodides*, prepared by the action of NaI on the dichloride in hot EtOH, have m. p. 46—47° (X=Cl), 79—80° (X=Br), 88·5° (X=I). The action of alkali on these gives the corresponding *oxides* (infusible). H_2S in alkaline solution gives *sulphides* of the type $(XC_6H_4)_2SnS$, m. p. 179° (X=Cl), 228—229° (X=Br), 248° (X=I). Compounds of the type $XC_6H_4{\cdot}SnX'_3$ were obtained by heating the corresponding di-compound with Sn^{IV} halide in a sealed tube; *stannic p-chlorophenyl trichloride*, m. p. 39°, *p-bromophenyl trichloride*, m. p. 64·5—65°, *p-iodophenyl trichloride*, m. p. 55—56°, *p-iodophenyl tribromide*, m. p. 80—80·5°. Hydrolysis of the above trichlorides gives the corresponding infusible *acids*, $XC_6H_4{\cdot}SnOOH$. *Sulphides* of the type $(XC_6H_4Sn)_2S_3$ are obtained by the action of H_2S on acid aq. solutions of the trichlorides: m. p. 295° (decomp.) (X=Cl), 250° (decomp.) (X=Br), infusible (X=I). The action of Cl_2 in cold $CHCl_3$ on $(C_6H_4I)_2SnCl_2$ gives *stannic didichloroiododichloride*, m. p. 82—82·5°; and on $C_6H_4I{\cdot}SnCl_3$ gives *stannic dichloroiodotrichloride*, m. p. 50—70° (decomp.). E. B. UVAROV.

Action of acetic anhydride on amino-*tert.*-acids and dipeptides. Catalytic effects. Hydrolysis of *N*-acetyldipeptides. P. A. LEVENE and R. E. STEIGER (J. Biol. Chem., 1931, **93**, 581—604).—When pure α-amino*iso*butyric acid (I) is heated with Ac_2O at 150° (bath) a mixture of the corresponding azlactone and a *lactone* (II), $C_{10}H_{16}O_3N_2$ (alternative formulæ suggested), m. p. 143—144° (all m. p. are corr.) after slight previous sintering, is produced; if (I) contains traces of Cl and NH_3, the products formed are high-mol. solids. *dl-iso*Valine also gives some solid material in addition to azlactone, irrespective of the presence or absence of impurities. (II) is hydrolysed by H_2O at 25° to *α-(α-acetamidoisobutyryl)aminoisobutyric acid* (III), m. p. 223—225° (decomp.) [prepared by acetylation of α-(α-amino*iso*butyryl)amino*iso*butyric acid (IV), which is not hydrolysed by H_2O at 100°], and at 100° to an equimol. mixture of (I) and *α-acetamidoisobutyric acid*, m. p. 195—196° after previous sintering; the same mixture is formed from (III) and H_2O at 100°. When (IV) is heated with AcOH α-amino*iso*butyric anhydride is produced; the rate of dehydration depends on the amount of impurity (NH_3). *dl*-α-Amino-α-phenylpropionic acid and Ac_2O at 150° give the azlactone (V) of *dl*-α-acetamido-α-phenylpropionic acid (VI), m. p. 202—203° (lit. 192—193·5°). (V) and aq. NH_3 afford dl-*α-acetamido-α-phenylpropionamide*, m. p. 191—192° after previous sintering, whilst (V) and (I) in AcOH yield α-(dl-*α-acetamido-α-phenylpropionamido*)*isobutyric acid*, m. p. 214—215° (slight decomp.), readily hydrolysed by H_2O at 100° to (I) and (VI). Glycyl-α-amino*iso*butyric acid and Ac_2O in AcOH give *α-(acetamidoacetamido)isobutyric acid*, m. p. 190—191°, which is not readily hydrolysed by H_2O at 100°. H. BURTON.

Chromoproteins. I. Chromophoric group of the *Rhodymenia palmata*. P. A. LEVENE and A. SCHORMULLER (J. Biol. Chem., 1931, **93**, 571—579).—Peptic digestion of the seaweed followed by amyl alcohol extraction and Et_2O precipitation yields "phycobylin" (cf. A., 1928, 533; 1930, 488). Me-esterification gives a product resembling phycoerythrobilinic ester (cf. *ibid.*). The "phycobilin," however, contains 45% of the total N as NH_2-N and hence is termed "chromoproteinic acid." Reduction of this by HI yields a *substance*, $C_{17}H_{23}O_4N$, containing a little NH_2-N, whilst oxidation with CrO_3 yields mainly Me ethylmaleinimidopropionate. The annexed



structure is tentatively suggested for the phycoerythrobilinic ester. F. O. HOWITT.

Effect of alkali on protein. I. Optical behaviour of "racemic protein." F. A. CSONKA and M. J. HORN (J. Biol. Chem., 1931, **93**, 677—684).—Digestion of wheat gluten, caseinogen, and egg-albumin by 0·5*N*-NaOH at 38° yields optically-active products which with boiling 20% HCl lose their activity. This disagrees with Dakin's keto–enol theory of protein racemisation (A., 1913, i, 208). F. O. HOWITT.

Degradation of proteins. II. Colour reaction of glycine and other amino-acids with sodium hypochlorite and phenols. O. FURTH, A. FRIEDRICH, and R. SCHOLL (Biochem. Z., 1931, **240**, 50—61).—The blue colour obtained with glycine is very sensitive (down to 0·002%) but is not sp. It is given by other NH_2-acids and protein solutions, but much more faintly. The reaction is given very much more powerfully with NH_3 and NH_4 salts and the colour with NH_2-acids is due to the NH_3 liberated by hydrolysis, glycine being most easily hydrolysed. The pigment [using $(NH_4)_2CO_3$, NaOCl and PhOH] $C_{24}H_{17}O_6N_3Cl_4$ loses one third of its N in boiling alkali and gives with diazomethane a methoxymethylimide derivative. P. W. CLUTTERBUCK.

Structure of proteins. IX. Degradation of caseinogen by warming with glycerol and the structure of the degradation products. A. FODOR and S. KUK. **X.** A. FODOR (Biochem. Z., 1931, **240**, 123—139, 140—148).—IX. Examination of various fractions is described and a double *tetrapeptide* is isolated, $C_{41}H_{67}O_{12}N_9,2H_2O$, possessing 2 free CO_2H and a free NH_2 group and formulated as prolylpyrrolidonyl-lysyl-leucine united to prolylpyrrolidonylalanyl-leucine through the two pyrrolidonyl groups.

X. A theoretical paper on the chemical structure of proteins based on the author's experiments on the ready dissociation of gelatin and caseinogen in glycerol into polypeptide components.

P. W. CLUTTERBUCK.

Formation of biocolloids. I, II. S. J. von Przylecki and R. Majmin (Biochem. Z., 1931, **240**, 98—122).—The extent of union of coagulated protein and starch varies with the p_H and is least at the isoelectric point. Ions which decrease the charge on the protein also decrease the amount of combined starch. Change of p_H does not, however, affect the amount of dextrin combined with protein. Reversibility of the union is not obtained on the acid side, but is obtained at the isoelectric point and above. Certain protein sols strongly decrease the amount of bound starch. When both components are employed as sols, the union of protein and starch and of protein and dextrin is readily detected in alcoholic solution at $p_H > 4·7$. In concentrations of EtOH in which separately the protein sol is stable whereas starch sol owing to its feeble charge is coagulated, in mixtures no coagulation occurs, the protein combining with the starch. Salts which decrease the charge on the protein also decrease its protective action.

P. W. Clutterbuck.

[Action of ammono-bases and sodium on] proteins in liquid ammonia. I. E. W. McChesney and C. O. Miller (J. Amer. Chem. Soc., 1931, **53**, 3888—3896).—Proteins are partly ammonolysed by ammono-bases in liquid NH_3, the extent depending on the base and temp.; H_2O-insol. proteins (fibrin, silk-fibroin) thereby become H_2O-sol. Treatment of silk-fibroin with Na in liquid NH_3 and esterification of the resultant product gives high-mol. products which yield cryst. picrates; methylation of the product with MeI in C_6H_6 affords an oil. Salt formation, ammonolysis, and reduction appear to occur when proteins are treated with Na in liquid NH_3. Glycyl-*dl*-alanine (*Et* ester *picrate*, m. p. 97—98°) and NHAcMe are practically unaffected by Na in liquid NH_3, whilst 2 : 5-diketopiperazine and Et aminoacetate are converted partly into bases.

H. Burton.

Myosalvarsan, a reagent for protein and for testing colloid stability. W. Milbradt (Z. physiol. Chem., 1931, **200**, 166—168).—Myosalvarsan is a sensitive precipitant for proteins in presence of weak acid. The ppts. are dissolved by oxidising and reducing substances. It is proposed to use myosalvarsan as a reagent for quant. measurements of protein stability and as a qual. test for protein in urine.

J. H. Birkinshaw.

Determination of residual nitrogen by direct Nesslerisation. A. Lublin (Z. physiol. Chem., 1931, **201**, 1—8).—Folin's method (A., 1919, ii, 308) is modified (*a*) by the use of $CCl_3·CO_2H$ instead of Na tungstate for precipitation of proteins, (*b*) by the use of H_2O_2 instead of $CuSO_4$ in ashing. In this way clouding during Nesslerisation is avoided. A standard carbamide solution is similarly treated.

J. H. Birkinshaw.

Analysis of gaseous hydrocarbons. R. Rosen and A. E. Robertson (Ind. Eng. Chem. [Anal.], 1931, **3**, 284—289).—An apparatus for the prep. of synthetic mixtures of C_2H_6, C_3H_8, and butane, and the distillation of the condensed mixtures at 760 mm., is described. Graphs are constructed connecting data and composition, and used for the determination of the above gases in stabiliser gases; when the last-named contain C_3H_6, a correction (curve given) is made for the butane content. The method compares favourably with that of Podbielniak (B., 1929, 799).

H. Burton.

Analysis of three hydrocarbons by combustion. K. A. Kobe (Ind. Eng. Chem. [Anal.], 1931, **3**, 262—264).—Equations are developed for use in conjunction with the method employed (cf. this vol. 457) for the determination of mixtures of H_2, CO, and CH_4. The method is applicable to hydrocarbons, H_2, CO, CO_2, O_2, CH_2O, and Me_2O.

H. Burton.

Analysis of organic compounds by chromic acid. R. Kuhn and F. L'Orsa (Z. angew. Chem., 1931, **44**, 847—853).—Experimental details are given for the determination of C and H alone, or with certain combinations of the following groups: Ac, OEt, OMe, Me·C, by oxidation with CrO_3 to AcOH and CO_2; the necessary calculations are described and examples given.

R. S. Cahn.

Determination of halogens in organic compounds. M. B. Shchigol (Farm. Zhur., 1929, 509—513).—The compound is reduced by Zn and AcOH in presence of NaOAc and $CuSO_4$, first in the cold for 1 hr. and then under a reflux condenser for 5—10 min. The halide is determined volumetrically.

Chemical Abstracts.

Determination of halogens in organic compounds using sodium sulphide. A. E. Kretov, A. N. Pantschenko, and K. K. Savitsch (J. Gen. Chem. Russ., 1931, **1**, 419—422).—0·2 g. of substance is dissolved in 5 c.c. of EtOH, 7—8 c.c. of a solution containing 0·5—0·6 g. of $Na_2S,9H_2O$ in EtOH are added, and the mixture is heated for 30 min. under reflux at 100°, cooled, diluted with H_2O to 100 c.c., feebly acidified, and boiled until all the EtOH is expelled. Residual H_2S is oxidised by adding 3 c.c. of 30% H_2O_2 to the alkaline solution, which is then boiled a few min. to destroy excess of H_2O_2, and ionic halide is determined by Volhard's method. When coloured solutions are obtained after the action of H_2O_2, they should be further oxidised by $KMnO_4$ to the disappearance of the coloration. The above method is applicable to halogens present in aliphatic but not aromatic groups; when they are present in both the nucleus and the side-chain of aralkyl compounds only those of the side-chain are determined.

R. Truszkowski.

Determination of nitrogen in nitro- and azo-compounds by the Kjeldahl method. B. G. Šimek (Chem. Listy, 1931, **25**, 322—325).—Azo- and NO_2-compounds are first reduced by boiling for 30 min. with alkaline-alcoholic $Na_2S_2O_4$, and then treated as usual with conc. H_2SO_4.

R. Truszkowski.

Analysis of volatile compounds containing carbon, hydrogen, and nitrogen. W. Scholl and R. O. E. Davis (Ind. Eng. Chem. [Anal.], 1931, **3**, 276—278).—An apparatus for the combustion of volatile org. compounds, and subsequent analysis of the mixture of CO_2, N_2 and H_2O vapour produced, is described. All reagents are used in the solid form.

H. Burton.

Determination of sulphur in organic substances by means of the calorimetric bomb. II. F. Garelli and B. Saladini (Annali Chim. Appl., 1931, **21**, 443—446; cf. B., 1931, 661).—Addition of a combustible liquid to the material renders possible the complete combustion of substances of low calorific power and tardy combustibility, such as thiocarbamide, "saccharin," etc., and also of explosive substances like picryl chloride which alone do not undergo combustion. S (0·1 g.) is burnt entirely to SO_3 if 0·5 c.c. of PhMe or decahydronaphthalene is added to it. T. H. Pope.

Determination of sodium in organic compounds. Use of uranyl acetate–[magnesium acetate] method. D. L. Tabern and E. F. Shelberg (Ind. Eng. Chem. [Anal.], 1931, **3**, 278—279).—Na barbiturates can be analysed (for Na) either electrometrically or by Kahane's method (A., 1930, 726), but not (generally) by conversion into Na_2SO_4. Kahane's method is applicable to Na salts of other org. acids. H. Burton.

Modification of Pregl's micro-methoxyl apparatus. D. R. Rigakos (J. Amer. Chem. Soc., 1931, **53**, 3903—3904).—Illustrations of 2 modifications are given. H. Burton.

Determination of phenols in aqueous solution. Adaptation of bromine method to include range of 1—75 parts per million. J. A. Shaw (Ind. Eng. Chem. [Anal.], 1931, **3**, 273—274).—The dil. aq. solution is acidified with H_2SO_4, the phenol extracted with Et_2O, and then removed from the extract with 10% NaOH. The alkaline solution is then acidified and analysed as described previously (B., 1929, 771). H. Burton.

Gravimetric determination of phenol and salicylic acid by Lautemann's Red. M. François and (Mlle.) L. Seguin (Bull. Soc. chim., 1931, [iv], **49**, 1222—1229).—PhOH, salicylic acid, and Na salicylate are determined by dissolving 0·2 g. in 5 c.c. of NaOH (*d* 1·33), and 100 c.c. of H_2O and adding at 95° 1 c.c. at a time of *N*-I solution in KI, until a brown coloration persists. After boiling and cooling, excess of I is removed with Na_2SO_3 and the Lautemann's Red, $C_{12}H_4O_2I_4$, formed from 2 mols. of PhOH, is collected on a double 11-cm. filter, dried at 100°, and weighed. Bi salicylate is similarly determined after decantation from $Bi(OH)_3$. Salicylic acid in aspirin, salol, and Me salicylate are similarly determined, the ester being first hydrolysed by the NaOH. Determination of phenolphthalein by this method gave unsatisfactory results. R. Brightman.

Argentometric determination of aldehydes. W. Ponndorf (Ber., 1931, **64**, [*B*], 1913—1923).—MeCHO may be determined by oxidation with precipitated Ag_2O, the change being accelerated by heating the mixture and addition of alkali hydroxide when the concentration of aldehyde has become small. Unused Ag_2O is titrated with KI and unused Ag_2O dissolved in H_2SO_4 is determined in presence of starch iodide (this vol., 1259). Uniformity in operation is difficult to secure and the process is not applicable to slowly-reducing aldehydes (PhCHO) or to MeCHO in small amount. In a second method Ag_2O is precipitated simultaneously with $Mg(OH)_2$. With 5—45 mg. of MeCHO the enlargement of the active surface permits the determination to be effected at room temp. and with only slight alkalisation. CH_2O is similarly determined, but an experimental factor is required for dextrose. For more slowly reducing aldehydes (EtCHO or PhCHO) the reaction is accelerated by using a larger proportion of Ag_2O and more alkali hydroxide. In the case of 0·1—0·4 mg. of MeCHO, colloidal Ag_2O is used, prepared by adding NaOH to a solution of $AgNO_3$, $Al_2(SO_4)_3$, and Na_2SiO_3. For smaller amounts, retardation of the change is avoided by using SiO_2 as protective colloid; determination is effected in the absence of light. The colloidal condition of the Ag produced permits its direct titration with I and the intense colour of the solution renders a very rapid colorimetric or volumetric process applicable. H. Wren.

Determination of organic acids. III. Use of the *iso*amyl ether–water system in the partition method. IV. Provisional identification and determination of two fatty acids in a mixture. C. H. Werkman (Iowa State Coll. J. Sci., 1930, **5**, 1—3, 121—125).—*iso*Amyl ether is preferred to Et_2O or $Pr^{\beta}{}_2O$ on account of its smaller solubility in H_2O. Data are given for the pairs: acetic–propionic, –butyric, –lactic; propionic–butyric and –lactic acids. When the partition coeff. for Et_2O–H_2O indicates either of two binary mixtures, coeffs. using $Pr^{\beta}{}_2O$ and *iso*amyl ether are determined. Chemical Abstracts.

Determination of salicylic acid in the presence of mineral acids (sulphuric and hydrochloric), and the simultaneous determination of all these acids together. O. A. Kulskaja (Ukrain. Chem. J., 1931, **6**, [Sci.], 1—8).—Seubert's method (A., 1882, 106) for the determination of PhOH gives good results (mean error 0·3%) for the determination of salicylic acid, in the presence or absence of HCl or H_2SO_4. HCl is determined by Volhard's method, and total acidity by titration against NaOH, the H_2SO_4 content being calc. by difference. R. Truszkowski.

Colour reaction of adrenaline and adrenalone. M. Paget (Bull. Sci. pharmacol., 1930, **37**, 537—538; Chem. Zentr., 1931, i, 3136).—Adrenaline hydrochloride solution (2—3 c.c., 0·5%) with aq. NH_4 molybdate (1 c.c., 10%) gives a reddish-brown coloration which on addition of 6—7 drops of NaOH solution becomes green and fluorescent. 0·1% adrenaline solution gives an amber-yellow colour, changing with NaOH to green. 0·5% adrenalone solution gives with 1 drop of molybdate solution a yellow ppt., becoming orange on further addition of the reagent and then dissolving to a dichromate-coloured liquid which gives no green fluorescence with NaOH. 0·1% adrenalone solution gives a canary-yellow colour which is unchanged by NaOH. A. A. Eldridge.

Alkaloidal reagents. I. Introduction. J. C. Munch, F. C. Crossley, and W. H. Hartung (J. Amer. Pharm. Assoc., 1931, **20**, 1037—1041).—As a preliminary to a systematic study of alkaloidal reactions, standard methods of prep. of alkaloidal

reagents and test solutions and a standardised procedure of testing have been developed.

E. H. SHARPLES.

Sensitivity of alkaloid reagents. I. SANSONI (Ind. Chim., 1931, **6**, 149—153; Chem. Zentr., 1931, i, 2907).—The sensitivity is increased by causing reaction to take place at the interface of two liquids and using a light or dark background.

A. A. ELDRIDGE.

Silicotungstates and double mercuric iodides of the amine-oxides of alkaloids: use in the determination of these bases. M. POLONOVSKI, M. POLONOVSKI, and J. CAPPELAERE (J. Pharm. Chim., 1931, [viii], **14**, 328—337).—The silicotungstates of vegetable alkaloids and alkaloidal amine-oxides, with the exception of eserine, have the general composition $SiO_2,12WO_3,2H_2O$,4alkaloid,nH_2O. The eserine compound contains only 2 mols. of alkaloid. On ignition a residue of $SiO_2,12WO_3$ is left. Eserine and its amine-oxide both form $(HgI_2)_3$,(alkaloid,HI$)_2$. The quantity of eserine and its amine-oxide may be determined therefore in a mixture of the two. The m. p. of the silicotungstates of various alkaloids (and their amine-oxides) are: eserine, 197—198° (244°); strychnine 310° (310°); atropine 195° (187°); hyoscyamine 215° (212°); scopolamine 202° (decomp.) (chars about 200°); morphine, above 300° (above 300°). The silicotungstates are precipitated from a boiling solution in presence of a little HCl. The HgI_2 compounds are determined by precipitation, washing with 5% H_2SO_4, and dissolving in a little HNO_3-H_2SO_4 (1 : 2). Excess of H_2O is added, followed by $0{\cdot}1N$-$KMnO_4$ until a permanent colour is obtained, 10 drops of 10% Na nitroprusside are added, and the whole is titrated with $0{\cdot}1N$-NaCl until the cloudiness disappears.

T. McLACHLAN.

Biuret reaction of proteins. L. SCHULHOF (Magyar Chem. Fol., 1931, **37**, 10—16, 32—40, 50—55; Chem. Zentr., 1931, i, 2645—2646).—Cu complexes of biuret, gelatin, casein, gliadin, Witte's peptone, ovalbumin, serum-albumin, and serum-globulin were examined spectrophotometrically. In the visible spectrum the extinction coeffs. are of the same order of magnitude, but otherwise show marked differences. The extinction coeff. of proteins half- or quarter-saturated with $Cu(OH)_2$ did not give homologous vals.; hence the biuret reaction gives different complexes. The equiv. wts. of the various proteins with respect to $Cu(OH)_2$ show marked differences.

A. A. ELDRIDGE.

Determination of tryptophan and tyrosine. G. A. DA SILVA (Biochem. J., 1931, **25**, 1634—1640).—Any cystine which may escape decomp. by alkaline hydrolysis interferes with the determination of tyrosine. Histidine is precipitated with tryptophan by $HgSO_4$. The error can be obviated by determining total N and NH_2-N at the same time as the colorimetric or bromination determinations are made.

S. S. ZILVA.

Biochemistry.

Inhalation, retention, and exhalation of dusts and fumes by man. II. Concentrations below 50 mg. per cubic metre. C. E. BROWN (J. Ind. Hygiene, 1931, **13**, 285—291).—The retention of marble dust and MgO varies from 45 to 60% during normal breathing at rest with a concentration of 50—10 mg., but approaches 100% below 10 mg. per cu. m. Retention is decreased by 10% on inhalation of air containing 5% of CO_2.

P. G. MARSHALL.

Respiration, and function of hæmoglobin in *Planorbis corneus* and *Arenicola marina*. M. A. BORDEN (J. Marine Biol. Assoc., 1931, **17**, 709—738).—The blood-vol., O_2 consumption, combined and total blood-O, and O_2 capacity of the blood have been determined for these marine animals. Experiments are described which show that, during anaerobiosis, *Planorbis* goes into debt for O_2, whilst only partial debt is observed in *Arenicola*. Hæmoglobin functions as a transporter of O_2 for the former, and for the latter during low O_2 pressure.

A. COHEN.

Determination of minute volumes by the acetylene method during work by normal and men. A. GROLLMAN, S. PROGER, and H. (Arch. exp. Path. Pharm., 1931, **162**, 463— The C_2H_2 method for determining the rate of of the blood has been examined and adapted for more general application.

W. O. KERMACK.

Role of certain dietary factors in the formation of erythrocytes. B. C. GUHA and L. W. MAPSON (Biochem. J., 1931, **25**, 1674—1686).—There is a diminished red-cell count in rats suffering from vitamin-B_2-, but not from -B_1-deficiency. Autoclaved marmite, but not Cu, glutamic acid, extra Fe, or alkaline hæmatin, raises the blood count produced by this deficiency. An aq. extract of ox-liver after having the vitamin-B_2 activity destroyed by autoclaving in alkaline medium exerts a powerful influence on the formation of erythrocytes in rats suffering from vitamin-B_2 deficiency.

S. S. ZILVA.

Acid-denaturation of hæmoglobin. N. U. MELDRUM (Biochem. J., 1931, **25**, 1498—1512).—Acid methæmoglobin exists at p_H vals. at which the protein is entirely precipitable. Curves are given for the amount of sol. native protein obtained from methæmoglobin solutions brought to different p_H. Acid methæmoglobin precipitated at neutrality and dissolved in min. excess of alkali is entirely reprecipitated on neutralising with acid. A solution of methæmoglobin made alkaline after having been acid shows the spectrum of alkaline methæmoglobin irrespective of whether the protein is sol. or insol. at the isoelectric point. Determination of the alkaline methæmoglobin in such solutions yields curves which coincide with those obtained after "reversion" (A., 1925, i, 1475). Solutions are obtained at acid p_H which show spectra identical

with that of carboxyhæmoglobin but ppt. entirely on neutralisation. Determination of the amount of native protein measured by the intensity of this spectrum yields curves similar to those obtained when the natural protein is determined as alkaline methæmoglobin or when it is subjected to "reversion." It has been confirmed that the temp. at which denaturation takes place has little effect on the yield of native material after treatment with alkali and that the extent of denaturation is unaffected by length of treatment with acid after the first few min.

S. S. ZILVA.

Effect of acid-denaturation on the combining power of fibrinogen. M. FAY and B. M. HENDRIX (J. Biol. Chem., 1931, **93**, 667—675).—Fibrinogen from ox-blood is denatured by HCl at p_H 2·5—3·5 for 12—15 hr. at 12—14°, the isoelectric point being changed from p_H 4·7 to 5·2 and the acid- and base-combining powers diminished. F. O. HOWITT.

Blood-protein precipitants. E. K. DOAK, G. BOONE, and F. PAQUIN, jun. (J. Lab. Clin. Med., 1931, **16**, 594—596).—There appears to be no const. variation in the concentrations of the non-protein-N of filtrates of (normal, nephritic, or eclamptic) blood precipitated by Na_2WO_4 and H_2SO_4, molybdic acid, tungstomolybdic acid reagents, or Folin's reagents for unlaked blood. Ergothioneine was not found. Tyramine was found in traces in blood of eclampsia.

CHEMICAL ABSTRACTS.

Serum-proteins. A. SCHMITZ (Biochem. Z., 1931, **241**, 271—272).—The results of Lustig on the globulin and albumin fractions of serum (A., 1930, 1607; this vol., 505, 640) are critically discussed.

P. W. CLUTTERBUCK.

Finger-blood method for micro-Kjeldahl [determination of] non-protein-nitrogen. T. L. CANNIFF (Proc. Soc. Exp. Biol. Med., 1930, **28**, 348).—Blood (0·1 c.c.) is treated with Folin's H_2WO_4 reagent (10 c.c.) and centrifuged after 2—3 min.; the determination is performed on 5 c.c. and the NH_3 in the distillate determined colorimetrically. Finger-blood gives higher results than venous blood.

CHEMICAL ABSTRACTS.

Determination of xanthine and hypoxanthine in blood. W. H. COLE, W. H. ELLETT, and N. A. WOMACK (J. Lab. Clin. Med., 1931, **16**, 918—923).—Oxalated blood is incubated for 24 hr. with xanthine-oxidase (from milk), and the uric acid determined before and after treatment. The normal ratio of xanthine base to uric acid is 2 : 1.

CHEMICAL ABSTRACTS.

Ergothioneine content of the blood in health and disease. H. B. SALT (Biochem. J., 1931, **25**, 1712—1719).—The contents of uric acid and of ergothioneine are given. A differential method for the determination of the latter compound was employed. S. S. ZILVA.

Histamine and histamine-like substances in blood. O. E. GUTTENTAG (Arch. exp. Path. Pharm., 1931, **162**, 727—738).—Blood or its EtOH extracts cause contraction of the guinea-pig's isolated small intestine and uterus, which is not abolished by atropine or by the action of NaOH: they do not lower the blood-pressure of the atropinised cat or contract the isolated rat's uterus. Histamine is therefore considered absent from blood. F. O. HOWITT.

Diazotisable constituent of blood. A. FRIEDRICH and A. LEIMDORFER (Biochem. Z., 1931, **240**, 430—440; A., 1924, i, 1126).—From blood corpuscles two diazotisable constituents can be obtained. One, which reacts at once with the diazotising reagent and yields a dinitrophenylhydrazone, is probably the parent substance of the chromogenic constituent. The other constituent accumulates slowly as a result of decomp. (possibly oxidation) of some material originally present. Long boiling with conc. alkali or mild oxidation with $KMnO_4$ seems to accelerate its formation. W. McCARTNEY.

Determination of blood-fat, with observations on several species in post-absorptive conditions. H. E. HIMWICH, H. FRIEDMAN, and M. A. SPIERS (Biochem. J., 1931, **25**, 1839—1844; cf. A., 1925, **i**, 1485).—The experimental error of the method is $\pm$11 mg. per 100 c.c. The average val. for dogs in the post-absorptive state is 673 mg. per 100 c.c. The level of blood-fat varies by $\pm$3·6% in the course of an observation period of 8 hr. The vals. for blood-fat in post-absorptive conditions vary widely in the dog; the average vals. differ in various species. The method does not determine the fatty acids which exist in the blood as soaps, but only those as esters. S. S. ZILVA.

Individual variation of fasting blood-sugar. G. W. HOLT and E. M. GREISHEIMER (Proc. Soc. Exp. Biol. Med., 1931, **28**, 764—765).—In normal man the day-to-day individual variation is as great as the group variation. CHEMICAL ABSTRACTS.

Blood-sugar curves with acid and alkaline diets after administration of sugar by mouth. E. T. MINKER-BOGDANOVA (Russ. J. Physiol., 1931, **14**, 1—9).—Small alterations in the acidity and alkalinity of the diet of children do not appreciably affect the height of the blood-sugar curve after the administration of dextrose by mouth provided that the diet contains sufficient carbohydrate, but if the diet contains little carbohydrate and much meat abnormally high curves are obtained.

W. O. KERMACK.

Interferometric determination of alcohol in [normal] blood. J. C. BOCK (J. Biol. Chem., 1931, **93**, 645—655).—Blood is deproteinised with H_2MoO_4, distilled, and EtOH determined in the distillate by means of the interferometer. F. O. HOWITT.

Occurrence and determination of oxalic acid in blood. W. MERZ and S. MAUGERI (Z. physiol. Chem., 1931, **201**, 31—37).—Determination of $H_2C_2O_4$ in the Et_2O extract is untrustworthy, as the extraction is incomplete. Trustworthy results are obtained by precipitation with lime-water after deproteinisation of the blood with $CCl_3{\cdot}CO_2H$. $MgSO_4$ is added to protect the ppt. with hydroxide or phosphate during washing. The titration follows Leulier's method (A., 1929, 614). $H_2C_2O_4$ is regularly present in normal ox-blood. J. H. BIRKINSHAW.

Existence in blood of iron not combined with hæmoglobin. G. DOMINICI (Rend. Accad. Med. Torino, 1929, 6 pp.; Chem. Zentr., 1931, i, 3480).—

Normally the blood-non-hæmoglobin-Fe amounts to 0·92—3·12 mg. per 100 c.c. The val. increases in disease, particularly in that of the blood or liver.
A. A. ELDRIDGE.

Relation of the concentration of calcium to that of protein and inorganic phosphate in the serum. I. GREENWALD (J. Biol. Chem., 1931, **93**, 551—561).—The equation, serum-Ca=[5+0·875(protein, mg. per 100 c.c.)] mg. per 100 c.c., has been applied to normal and pathological sera and only in a few instances yields vals. more accurate than those from other equations previously suggested (A., 1927, 416; 1929, 1478). An attempt to derive an equation agreeing with all types of sera was unsuccessful. F. O. HOWITT.

Hæmoglobin and total phosphorus in the blood of cows and bulls. C. M. MCCAY (J. Dairy Sci., 1931, **14**, 373—378).—The hæmoglobin, Fe, and P contents of the blood of lactating cows is not affected by the level of protein feeding or by changes from winter conditions to pasture or sunlight. The blood of cows contains 10·9±0·86 g. and of bulls 12·8±0·8 g. of hæmoglobin per 100 c.c.
A. G. POLLARD.

Blood of normal sheep. A. TRAUTMANN, P. LUY, and J. SCHMITT (Biochem. Z., 1931, **241**, 260—270).—Many determinations on the blood of more than 100 sheep and a few goats are tabulated and differences due to age, sex, etc. noted. The following figures give the range of vals. for the different animals and the figures in parentheses the mean determination: Ca, 8—12 mg. per 100 c.c. (10·44); P, 5—10 mg. per 100 c.c. (7·43); sp. gr. at 18°, 1·0212—1·0293 (1·0250); p_H 7·4—7·58 (7·48); serum viscosity, 1·53—2·18 (1·70); blood viscosity, 4·0—5·4 (4·72); lowering of f. p. of venous blood, —0·535° to —0·60° (—0·567°); venous blood-sugar, 40—100 mg. per 100 c.c. (63·9); residual N, 13·2—40·6 mg. per 100 c.c. (28·1); plasma alkali reserve, 38·8—57·5 vols. CO_2 as $NaHCO_3$ per 100 c.c. of plasma (47·86).
P. W. CLUTTERBUCK.

Refinement of Hastings and Sendroy's determination of p_H of blood. J. W. SCHOONOVER and G. E. WOODWARD (J. Lab. Clin. Med., 1931, **16**, 621—624).—The tubes are graded according to internal diameter, and the p_H of the saline indicator is adjusted with 0·01*N*-NaOH containing suitable amounts of phenol-red and NaCl. CHEMICAL ABSTRACTS.

Tonicity of blood of aquatic animals. W. J. DAKIN and E. EDMONDS (Austral. J. Exp. Biol., 1931, **8**, 169—187).—The mangrove crab, *Helœcius cordiformis*, has the power of regulating its blood salinity. The body-wall of *Onchidium* acts like a semipermeable membrane. A. LAWSON.

Phosphatases of blood. J. ROCHE (Bull. Soc. Chim. biol., 1931, **13**, 840—855).—The optimum p_H of the phosphatases of the erythrocytes, leucocytes, and serum of the horse have been determined; whereas the last two are identical, that of the first varies with the nature of the substrate. It is suggested that animal phosphatases are divisible into at least 2 groups, the first those from the erythrocytes, and the second those from serum, leucocytes, kidney, and intestine. Bone-phosphatase is possibly a third group. C. C. N. VASS.

Effect of anticoagulants on serum-enzymes and on complement. K. YANAGISAWA (J. Biochem. Japan, 1931, **13**, 11—42).—Heparin has no effect on guinea-pig serum-butyrase, -lecithinase, -cephalinase, -glycerophosphatase, -tryptase, -peptase, -nuclease, -amylase, or the glycolytic enzyme systems. Its effect on hæmolysis is discussed.
CHEMICAL ABSTRACTS.

Muscle coagulins. A. FISCHER (Biochem. Z., 1931, **240**, 357—363).—Aq. extracts of the breast-muscle tissue of the hen contain material which reduces the time of coagulation of hen's blood from several hr. (or days) to about 3 min., and although the extracts are sensitive to O_2 and very rapidly lose their activity, the dry material obtained by evaporation retains its power for more than 2 years. H_2O_2 and $KMnO_4$ destroy the activity of the aq. extracts, not at once, but suddenly after 24 hr. or longer. The aq. extracts are unstable and deposit flocculent matter, even at 0°, and the rate of deposition increases with rise of temp., becoming almost instantaneous at 56°. The active material passes to the deposit when solutions are boiled or heated for a long time at 56°. Heparin retards the deposition and at the same time reduces the activity, but has no effect on the activity of the deposited materials. W. MCCARTNEY.

Mechanism of the inhibition of blood coagulation. A. FISCHER (Biochem. Z., 1931, **240**, 364—380; cf. preceding abstract).—Small amounts of substances (such as heparin, germanin, sulphosalicylic acid, and many others) which inhibit the coagulation of blood not only inhibit also precipitation of protein (globulin), but even cause peptisation of protein already precipitated. Heparin inhibits the precipitation at dilutions of $1:3\times10^6$ or less. Still smaller amounts of the substances, on the other hand, assist both precipitation of protein and coagulation of blood. The substances also cause a shift to the acid side in the isoelectric point of the protein and of the optimum point for coagulation of the blood. The mols. of all the substances which inhibit blood coagulation consist of a large org. complex to which strongly electronegative groups (*e.g.*, SO_3H) are attached. It is concluded that as regards their effects on precipitation of protein and on coagulation of blood the mechanism of action of the substances is the same and that a relation exists between blood coagulation and the synthesis and degradation of protein by the cells.
W. MCCARTNEY.

Influence of lactic acid on hæmolysis. J. SLADEK, I. A. PARFENTIEV, and B. SOKOLOV (J. Pharm. Exp. Ther., 1931, **43**, 245—250).—The hæmolysis of red blood-cells of rabbits in hypotonic NaCl solution is reduced by small concentrations of Na lactate. Thus with 0·4% aq. NaCl the degree of hæmolysis was reduced when the concentration of Na lactate was of the order of 0·1, whilst with lower concentrations of NaCl larger quantities of Na lactate were required. At p_H 7·0 Na lactate alone inhibits hæmolysis when present in concentrations greater than about 0·5%, whilst at p_H 5·0 about 1% Na lactate is required, and hæmolysis when it occurs is accompanied

by the decomp. of the hæmoglobin. The effect of Na lactate cannot be accounted for solely by the changes of osmotic pressure involved. W. O. KERMACK.

Spectrographic analysis of human tissues. J. H. SHELDON and H. RAMAGE (Biochem. J., 1931, **25**, 1608—1627).—195 specimens of different human tissues, both healthy and diseased, were examined. Cu, which is universal, occurs in greater concentration in fœtal tissues than in adult, and reaches its max. amount in the fœtal liver, where the percentage may be as much as ten times in excess of that present in the maternal liver. Mn occurs occasionally in many tissues, but is chiefly conc. in the liver, pancreas, suprarenal, and kidney. Fœtal bile contains a higher proportion than adult. In blood it is confined to the serum. Rb is almost as widely distributed as Cu and occurs in greatest concentration in the heart and in striated muscle. Ag, which is distributed to a smaller extent, is a normal constituent of the thyroid and the tonsil. Pb, Sr, and Li occur only occasionally. S. S. ZILVA.

Absorption spectrum of medullated and non-medullated nerves. B. R. MONAGHAN and F. O. SCHMITT (Proc. Soc. Exp. Biol. Med., 1931, **28**, 705—708).—Non-medullated nerves (claw of *Homarus* and *Limulus*) exhibited a spectrum characteristic of hæmochromogen compounds. The muscles of *Homarus*, *Limulus*, and green frog exhibit the spectrum typical of cytochrome. The sciatic nerves of frogs perfused with Ringer solution before dissection did not show the spectra of cytochrome or hæmochromogen, but showed bands due to carotenoid pigment (estimated, 0·5 mg. of carotene per g. of dry nerve), which may play an important part in the oxidative processes. CHEMICAL ABSTRACTS.

Chemical nature of the tigroid. A. SZENT-GYÖRGYI (Nature, 1931, **128**, 761).—Experiments suggest that tigroid is a reserve polysaccharide of the nervous tissues, similar to but not identical with glycogen. L. S. THEOBALD.

Collagen substances in human arteries at various ages. A. M. TROITZKA-ANDREEVA (Arkh. biol. Nauk, 1930, **30**, 519—526).—The collagen gradually increases in amount with increasing age. No relation of the process to senile atherosclerosis could be demonstrated. CHEMICAL ABSTRACTS.

Composition of human fat. A. J. MCAMIS and W. E. ANDERSON (Proc. Soc. Exp. Biol. Med., 1931, **28**, 749).—Fat from the abdominal wall of an obese female child (3 yr.) contained unsaponifiable matter 0·4%, saturated fatty acids 31·0%, and unsaturated fatty acids 60·0% (I val. 102). CHEMICAL ABSTRACTS.

Differentiation of various types of fats by means of dyes. L. D. HERBERT (J. Lab. Clin. Med., 1931, **16**, 926—929).—A routine method for the detection of fatty acids, neutral and acid fats, neutral Ca soaps, meat fibres, and cholesterol in fæces is described. CHEMICAL ABSTRACTS.

Hydrocarbon in ishinagi-liver oil. M. TSUJIMOTO (Bull. Chem. Soc. Japan, 1931, **6**, 237—239).—A crude *hydrocarbon*, *M* ~612 (camphor), 644 (C_6H_6) [*polybromide*, blackens and sinters at 170° after darkening from 130°; *polyhydrochloride*, m. p. 128—129° (decomp.) after sintering above 120°], is isolated in small amount from the unsaponifiable matter of the liver oil of *Stereolepsis ishinagi*, Hilgendorf. H. BURTON.

Lipins in the embryonic chicken liver. H. KIRKMAN (J. Amer. Inst. Homœopathy, 1931, **24**, 508—510).—Osmiophilic granules, presumably fat or lipin, appear in the hepatic cells at the 7th or 8th day of incubation. CHEMICAL ABSTRACTS.

Lipins of bone-marrow. L. T. CHENG (Z. physiol. Chem., 1931, **201**, 209—218).—The lipins of various samples of bone-marrow were examined. The fatty acids consist principally of palmitic, stearic, and oleic acids with a small amount of arachidic acid. A fatty acid of high mol. wt. may be present. The lipins in the gelatinous marrow are more unsaturated than those in the fatty marrow. The lipins of fatty ox-marrow are more unsaturated than those of body-fat. J. H. BIRKINSHAW.

Factors affecting size and iodine content of the thyroid in fowls. E. M. CRUICKSHANK (Proc. IV World's Poultry Cong., 1930, 237—241).—The max. I content is reached in 25—30 weeks; the seasonal variation in thyroid wt. is from 0·085 g. (March—July) to 0·13 g. (Jan.—March). CHEMICAL ABSTRACTS.

Distribution of protein in squab and pigeon flesh. R. C. ELMER, F. C. HILBERG, and P. E. HOWE (Proc. IV World's Poultry Cong., 1930, 301—307).—The protein content is similar to that of chicken and lower than that of beef muscle. Squab flesh contains the higher proportion of sol. protein-N and H_2O. CHEMICAL ABSTRACTS.

Hydroid pigments. *Sertulariidæ*. N. M. PAYNE (J. Marine Biol. Assoc., 1931, **17**, 739—749).—The pigments of various species of *Sertulariidæ* are H_2O-sol. and belong to the flavone series. Their solubilities, coloured metal-salt additive compounds, and behaviour as indicators are described. A. COHEN.

[Origin of] arcaine. L. ZERVAS and M. BERGMANN (Z. physiol. Chem., 1931, **201**, 208; cf. this vol., 1178).—Since arginine can form ornithine and diguanidovaleric acid (A., 1928, 874), the latter may be the precursor of arcaine. J. H. BIRKINSHAW.

Occurrence of choline in the placenta. E. KOTTLORS (Zentr. Gynakol., 1929, 2987—2990; Chem. Zentr., 1931, i, 2890).—During pregnancy the choline content of the placenta is approx. const. (60—90 mg. per kg.). A. A. ELDRIDGE.

Composition and formation of bone skeletal substance. T. GASSMANN (Z. physiol. Chem., 1931, **201**, 284).—A reply to Klement (this vol., 861). The disappearance of Ca, PO_4''', and CO_3'' in the ratio 10 : 6 : 1 from rhachitic bones can be accounted for only on the assumption of a complex of the constitution postulated by the author (A., 1913, ii, 320). J. H. BIRKINSHAW.

Distribution of non-electrolytes between the blood and the cerebrospinal fluid. J. R. COCKRILL (Arch. Neurol. Psych., 1931, **25**, 1297—1305).—Dextrose, creatinine, uric acid, and urea are unequally distributed between the H_2O of the cerebrospinal

fluid and that of the plasma in man. The amounts in the neural fluid are 50—80% of those in the plasma. Urea is also present in dissimilar concentration in the cerebrospinal fluid and plasma of normal cats and cats with experimental uræmia. Plasma dialysed *in vitro* against cerebrospinal fluid from the same subject does not show this unequal distribution.

CHEMICAL ABSTRACTS.

Inorganic constituents of cerebrospinal fluid. I. Calcium and magnesium. R. A. McCANCE and E. WATCHORN (Quart. J. Med. 1931, **24**, 371—379).—The Mg concentration is very const. ($3 \cdot 33 \pm 0 \cdot 19$ mg. per 100 c.c.); it is not altered by presence of excess of protein, by syphilis, or by wide variations in the serum val. Not more than 80% of the serum-Mg is unfilterable. CHEMICAL ABSTRACTS.

p_H of the cerebrospinal fluid. R. CERNATESCO and A. MAYER (Ann. Sci. Univ. Jassy, 1931, **16**, 551—554).—The mean p_H (quinhydrone electrode) is 7·08, and does not vary with time or on dilution of the fluid. The H electrode does not yield satisfactory results, possibly because of loss of CO_2.

H. F. GILLBE.

Determination of bile acids in bile. S. NAKAGAWA and H. FUJIKAWA (J. Biochem., Japan, 1930, **12**, 399—410).—If the bile is made strongly alkaline with aq. NH_3 and a little Na_2CO_3 to facilitate filtration it can be treated with animal charcoal in the extraction of the bile acids with EtOH. The red colour produced by H_3PO_4 and furfuraldehyde is practically sp. for bile acids and is probably a reaction of cholic acid. Good results are obtained with human or dog's bile, but for rabbit's bile the results are low.

CHEMICAL ABSTRACTS.

Effect of bile acids on the salt excretion in the liver bile. Y. KAWADA (J. Biochem., Japan, 1931, **13**, 133—144).—Na cholate when fed to dogs (0·05 g. per kg.) increases the ash and dry residue of fistula liver bile; the excretion of H_3PO_4 and Ca in the bile is increased. CHEMICAL ABSTRACTS.

Fluorescence spectra of pigments of the urobilin group. C. DHÉRÉ and J. ROCHE (Compt. rend., 1931, **193**, 673—676).—Examined in the solid state, by means of a C arc or in ultra-violet light (λ 365 mμ), mesobilirubin, mesobilirubinogen, and urobilin show a red fluorescence, whilst EtOH solutions of mesobiliviolin, mesobilirubinogen, and urobilin with the addition of $Zn(OAc)_2$ show yellowish-green fluorescence for the first two cases, and green in the case of urobilin. The spectra of EtOH solutions containing $Zn(OAc)_2$ and a trace of AcOH show in the case of mesobiliviolin three absorption bands having axes at 629·2, 572·5, 505·1 mμ, and four fluorescence bands at I 640·4, II 592·3, III 553·0, IV 515·5 mμ, the order of decreasing intensity being I, IV, III, II. Mesobilirubinogen under the same conditions has three absorption bands at 629, 576, 507·5 mμ, and four fluorescence bands I 633·1, II 600·7, III 550·6, IV 520·9 mμ, I and II being very weak. Urobilin under the above conditions shows an absorption spectrum similar to the first two, the bands at 631 and 582 mμ being less marked. The fluorescence bands occur at I 502, and II 633, changing to 637 mμ. The EtOH solutions of the $HgCl_2$ complexes formed by mesobiliviolin give absorption bands at 611, 563, 507 mμ, and fluorescence bands at 640 and 554 mμ, whilst the mesobilirubinogen Hg complex has absorption bands at 620, 570, 515 mμ, and fluorescence bands at 635·5, and 554·5 mμ, those in the orange range being strong, and in the green range weak. Under the same conditions urobilin and hydrobilirubin give no apparent fluorescence. A. LAWSON.

Conductivity of cod-liver oil. J. W. BUTLER (Proc. Iowa Acad. Sci., 1930, **37**, 316—317).—The conductivity increases with rise of temp. Sharp breaks in the rectilinear temp.-log resistance curves occurred at different temp. in different tests. The resistance became unstable at about 85°. Exposure to air caused marked changes. No relation between the electrical conductivity and vitamin content was observed. Cod-liver oil is not photo-electric under the action of ultra-violet light.

CHEMICAL ABSTRACTS.

Gastric analysis in childhood. H. DIETRICH and D. C. SHELBY (Amer. J. Dis. Children, 1931, **41**, 1086—1099).—The fractional method is employed; vals. for free HCl and total acidity show wide variations in normal children. CHEMICAL ABSTRACTS.

Composition of vixen milk. E. G. YOUNG and G. A. GRANT (J. Biol. Chem., 1931, **93**, 805—810).—The composition of the milk and colostrum is given.

F. O. HOWITT.

Citric acid in human milk. E. JERLOV (Svenska Lakartid., 1929, 17 pp.; Chem. Zentr., 1931, i, 2899).—Citric acid is not detectable in human milk before the third day after parturition; thereafter it increases, the quantity varying from 0·35 to 1·25 g. per litre.

A. A. ELDRIDGE.

Effect on milk yield of feeding irradiated yeast. H. M. KROON (Milch. Zentr., 1931, **60**, 325—328).—By feeding with irradiated yeast cows which had calved 3 weeks previously the weekly milk yield was increased by 25—30%, although there was no effect on the fat content of the milk. P. G. MARSHALL.

Influence of sunlight on milk. H. R. WHITEHEAD (Biochem. J., 1931, **25**, 1647—1652); cf. A., 1930, 947).—The oxidation of fat in whole milk under the influence of sunlight causes the development of a poorly poised reducing potential of small capacity which can be detected either by its effect on methylene-blue or by electrometric measurement. Some samples of separated milk also show a fall in potential with a subsequent drift to more positive potentials. Ultra-violet radiation or radiation from electric lamps does not produce these effects.

S. S. ZILVA.

Modification of Rothera's test for acetone substances in the urine. S. G. ROSS (J. Lab. Clin. Med., 1931, **16**, 908).—The urine is treated with solid Na nitroprusside and $(NH_4)_2SO_4$.

CHEMICAL ABSTRACTS.

Fermentable sugar in normal urine. V. J. HARDING and D. L. SELBY (Biochem. J., 1931, **25**, 1815—1838).—Fermentable sugar is absent from normal fasting urine. After dextrose ingestion in the morning under fasting conditions no increased amount of fermentable sugar can be detected in the urine.

There are small amounts of fermentable sugar in the post-prandial afternoon urine of 50% of cases. Fermentable urinary sugar occurs after large amounts of fruit, orange juice, honey, or invert-sugar taken fasting, although in the first case this did not occur after dextrose in the morning or after ordinary mixed meals. 50 or 25 g. of pure lævulose given as a lævulose tolerance test in the morning or in the afternoon at 4 p.m. give rise to fermentable urinary sugar. 50 g. of dextrose at 4 p.m. frequently give rise to glycosuria in individuals showing none under the fasting conditions of the morning test. This is least likely to occur if the noon meal is high in carbohydrate, and most likely if the meal is high in protein or in fat. The blood-sugar curves at 4 p.m. taken under ordinary conditions of diet all possess a higher peak than the corresponding fasting morning tolerance curves. The peak often rises above the usual renal threshold of sugar. The nature of the noon meal affects the blood-sugar curve after 50 g. of dextrose at 4 p.m. A high-carbohydrate meal gives rise to the lowest curve, a high-fat meal to a high-peak curve, sometimes remaining high at the end of 2 hr. There was ketosis in 6 out of 8 experiments after a high-fat noon meal. A high-protein noon meal gives a high-peak blood-sugar curve. All tolerance curves at 4 p.m. are higher than the morning tolerance curve in the same individual. There is no afternoon glycosuria in the urine after oral administration of lævulose. The non-occurrence of glycosuria after the usual morning dextrose tolerance test cannot be taken as a criterion of its continued non-occurrence throughout the day. S. S. ZILVA.

Determination of urinary sugar. J. E. COOK and A. STEINER (J. Lab. Clin. Med., 1931, **16**, 629—631).—The amount of $CuSO_4$ required to produce turbidity in urine containing 5% NaOH is measured. CHEMICAL ABSTRACTS.

Detection of lactosuria by the Castellani–Taylor mycological method. F. W. WILLWAY (J. Trop. Med., 1931, **34**, 133—134).—Urine which reduces Fehling's solution and is fermented by *B. coli* but not by *B. paratyphosus* contains lactose. The method is very sensitive. CHEMICAL ABSTRACTS.

Urinary composition and acid–base equilibrium. III. S. M. NEUSCHLOSZ (Biochem. Z., 1931, **240**, 286—294; this vol., 644).—The processes formerly used were inadequate, since the buffering effect of the org. acids of the urine was not taken into account. Results obtained by an appropriately modified procedure agree better with theory than did former results, but do not affect the dependence of the vals. on the [H˙] of the urine or the relations between the vals. W. MCCARTNEY.

Urinary acidifiers and alkalinisers. V. E. HENDERSON and J. M. SCOTT (Canad. Med. Assoc. J., 1931, **24**, 833—834).—Acidity is produced by administration of NaH_2PO_4, NH_4OBz, or NH_4Cl, and alkalinity by that of acetates or citrates. CHEMICAL ABSTRACTS.

Micro-determination of fixed bases, calcium, and sulphates in urine. W. S. HOFFMAN (J. Biol. Chem., 1931, **93**, 787—796).—Protein, inorg. and org. phosphates, fat, and some of the urinary pigments are removed by boiling with $FeCl_3$ in presence of NH_4OAc and filtering. The filtrate is ashed and SO_4 determined by the method of Stadie and Ross (A., 1926, 100) or directly on the filtrate by the method of Fiske (A., 1921, ii, 556). Ca is determined in the filtrate by precipitation as CaC_2O_4 and titration by $KMnO_4$. Comparative data are given. F. O. HOWITT.

Determination of total fixed base, sodium, and potassium in urine. A. FØLLING (Skand. Arch. Physiol., 1931, **61**, 27—34; Chem. Zentr., 1931, i, 3030).—The total base (in 2 c.c.) and the Na+K (in 10 c.c.) are determined by Stadie's benzidine method; the Na (in 5 c.c.) is precipitated as $NaZn(UO_2)_3(OAc)_9,9H_2O$, and determined titrimetrically. A. A. ELDRIDGE.

Determination of magnesium and of calcium in urine by the step photometer. C. URBACH (Biochem. Z., 1931, **241**, 222—225, 226—227).—The methods are described and claimed to be superior to the colorimetric methods. The errors are ±6·2% for Mg and ±3% for Ca determinations. P. W. CLUTTERBUCK.

Determination of ammonia in urine by extraction. G. HAMMARSTEN (Skand. Arch. Physiol., 1931, **61**, 49—63; Chem. Zentr., 1931, i, 3030).—In order to avoid high vals. resulting from decomp. of nitrogenous substances, especially urea, the NH_3 is extracted with Et_2O at room temp., and again extracted with $0·1N$-H_2SO_4, the excess of which is then titrated. A. A. ELDRIDGE.

Colorimetric determination of uric acid in urine. H. B. SALT (Biochem. J., 1931, **25**, 1720—1723).—A modification of Folin's method which obviates turbidity in the final colours is described. S. S. ZILVA.

Direct determination of urea in urine. S. W. COLE (Biochem. J., 1931, **25**, 1653—1655).—A modification of Marshall's method (A., 1913, ii, 640) in which a stronger enzyme prep. is used and the medium is maintained under optimal conditions of reaction. It is possible to complete the determination in 20 min., and the results are accurate to within 2%. S. S. ZILVA.

Glucose tolerance in pernicious anæmia. T. A. C. RENNIE (J. Lab. Clin. Med., 1931, **16**, 557—560).—Low vals. are often observed. CHEMICAL ABSTRACTS.

Certain lipoidal fractions of the adenocarcinoma of the rat. A. BOLAFFI (Atti R. Accad. Lincei, 1931, [vi], **13**, 298—300).—The aq. $COMe_2$ (*d* 0·85) extract of a tumour (rat adenocarcinoma, Ehrlich strain) has been analysed, together with the whole bodies of both normal and tumour rats. The total matter extracted by the solvent is reduced in the cancerous rat and still more in the cancerous tissue from that given by the normal rat. The soaps present in the appreciably lower proportion of neutral fats in the affected animals are in relatively higher amount, the K soaps especially showing a marked increase. The cancerous rats contain 2—3 times as much as the healthy ones of a base, which is united to the lipins and gives a cryst. salt with $HgCl_2$ and is precipitated by phosphotungstic acid. A phos-

phatide (1% P, I val. 58·7) is more abundant in the healthy than in the diseased animal or the tumour itself. A sulphophospholipin (S 1·5, P 1·06%), containing a base (? choline or cholamine), a highly unsaturated acid (probably linolenic) radical, and possibly lignoceric acid, occurs in higher concentration in the tumour than in the whole affected organism; the normal rat contains only traces. T. H. POPE.

Lipin content of malignant tumours. E. BIERICH, A. DETZEL, and A. LANG (Z. physiol. Chem., 1931, **201**, 157—166).—Carcinomatous tissue has a very high content of cholesteryl esters (*C*) and a slightly increased phospholipin content (*P*) as compared with normal tissue. In benign tumours both (*C*) and (*P*) are lower; in both types of tumour the quotient (*P*/*C*) is small. J. H. BIRKINSHAW.

Carbohydrate metabolism in malignant tumours. I. S. YUN and Y. C. LEE (Trans. Japan. Path. Soc., 1930, **20**, 734—737).—Hyperglycæmia usually occurs in sarcoma rabbits after inoculation of tumour tissue. The sensitivity to adrenaline, insulin, and pilocarpine is described. The variations in blood-sugar may be caused by glycolysis of tumour tissue *in vivo*. CHEMICAL ABSTRACTS.

Capacity of extracts of minced normal and malignant tissue to take up oxygen. K. VIETORISZ and A. SZENT-GYORGYI (Biochem. Z., 1931, **240**, 480—487).—The ability of suspensions of minced normal (liver, heart, muscle, testis, kidney, brain) and diseased (Ehrlich mouse carcinoma, Jensen rat sarcoma, Rous chick sarcoma) tissue before and after successive centrifuging and filtration to take up O_2 and to oxidise succinic acid has been investigated. In all cases both respiratory and oxidising powers are reduced by centrifuging and (except in the cases of the otherwise untreated heart muscle and testicular tissues) further great reduction results from filtration, but if the suspensions are ground with sand the effect of centrifuging and filtering is usually considerably less pronounced. The filtrates from the rat sarcoma and the mouse carcinoma give negative results when injected into rats and mice, respectively. Probably the respiratory power of the filtrates varies in proportion to their turbidity and is a function of the "optically visible parts" of the protoplasm. W. MCCARTNEY.

Tissue proteases. III, IV, V. Proteolytic enzymes of human malignant tumours. H. KLEINMANN and E. WERR (Biochem. Z., 1931, **241**, 108—139, 140—180, 181—217).—Existing knowledge of the proteolytic enzymes of normal and malignant tissues is reviewed and the proteolytic enzymes of human malignant tissue (carcinoma, sarcoma) are compared qualitatively and quantitatively with those of normal tissue. A detailed description of the nephelometric micro-method for investigation of tissue proteases is given. It is the only sure method of separation of the action of tryptase and ereptase and enables the degradation of proteins to be followed, not in terms of hydrolysis products, but in terms of the degradation of the substrate itself. Methods for the enzymic degradation of gelatin, caseinogen, edestin, and serum-albumin are developed. Acid and alkaline, aq. and glycerol enzyme extracts of the tissues were tried, but acid glycerol extracts proved most useful. The cathepsin, trypsin, and ereptase contents of the extracts were obtained. Extracts of tumour tissue were quantitatively compared with extracts of ox spleen and of human tissue (spleen, liver, kidney, brain, muscle, skin). Both normal and tumour tissue contain chiefly cathepsin with small amounts of trypsin. A kinetic study of the degradation of gelatin and caseinogen by cathepsin of normal and tumour tissue did not detect any difference between them. All the extracts of normal and tumour tissue showed two optima at p_H 3 and 5 against caseinogen. Strong extracts (of ox spleen and human parenchymatous organs) showed a third smaller optimum at p_H 8 (due to trypsin). Against gelatin, only the strong extracts showed any action, but after activation by H_2S all the extracts showed an optimum at p_H 4. All the extracts attacked edestin, the optimum being at p_H 4, but only the strong extracts attacked serum-albumin. All the extracts showed activation with H_2S and HCN when gelatin was used as substrate, but with the other proteins such activation did not occur. After purification of the enzyme, the cathepsin of the eluate is still activated by H_2S, but not by HCN. Tumour tissue extracts are purified by the same methods as for normal tissue extracts and the purified enzyme gives the same p_H-activity curve as the unpurified and is activated only by H_2S with gelatin as substrate. All the evidence goes to show that neither qual. nor quant. differences exist between the extracts of normal and malignant tumour tissue as to their proteolytic powers. P. W. CLUTTERBUCK.

Autolysis in malignant and normal rabbit tissues. H. I. PRICE (Biochem. J., 1931, **25**, 1491—1497).—Robin's observation (Bull. Acad. Med., 1919, **81**, 799) that the percentage ratio of protein-N to total N is lower in the "relatively healthy" region than in either the most cancerous region or the normal tissue does not manifest itself in freshly-excised tissue. After death H_2O disappears from the growth into the surrounding tissue. A malignant growth does not liberate proteolytic enzymes into the surrounding tissues. S. S. ZILVA.

Demonstration of a tumour-inhibiting substance in filtrate of Rous chicken sarcoma and in normal chicken sera. M. J. SITTENFIELD, B. A. JOHNSON, and J. W. JOBLING (Proc. Soc. Exp. Biol. Med., 1931, **28**, 577—520).—The supernatant liquid after precipitation of the tumour-producing agent at p_H 4 contained a substance which reduced the percentage of tumours developed by inoculated chickens, but did not prevent the growth of living tumour cells. The substance was precipitated with the globulin fraction of the supernatant liquid. CHEMICAL ABSTRACTS.

Effect of arsenic and hydrocyanic acid on the respiration of malignant tumours. K. VIETORISZ (Biochem. Z., 1931, **240**, 488—489).—The respiration of malignant tumours is affected by H_3AsO_3 and by HCN in the same way as is that of normal tissues. W. MCCARTNEY.

Hydrogen-ion concentration of blood in untreated cancer cases and its relation to prognosis. G. E. Woodward, J. W. Schoonover, E. G. Fry, E. G. Torrance, and E. McDonald (J. Lab. Clin. Med., 1931, **16**, 704—712).—The p_H of normal plasma or blood varies from 7·35 to 7·38. In skin and superficial cancer it is 7·38, and in untreated advanced cancer 7·44. Chemical Abstracts.

Metabolism in celiac disease. O. MacRae and N. Morris (Arch. Dis. Childhood, 1931, **6**, 75—93).—In celiac disease the ability of the intestines to absorb Ca, P, dextrose, and protein is impaired, probably owing to increased alkalinity of the contents, deficiency of bile salts, and lack of vitamin-*D*. Chemical Abstracts.

Anæsthesia in diabetes. Carbon dioxide-combining power of blood-plasma before and after ethylene anæsthesia in diabetics protected with insulin. I. I. Lehmann (Anesth. and Analg., 1931, **10**, 142—144).—No post-operative CO_2 val. approaching that of acidosis was found. Chemical Abstracts.

Lactic acid in the blood of children. J. S. Leopold and A. Bernhard (Amer. J. Dis. Children, 1931, **41**, 758—765).—The venous blood-lactic acid of normal children is 9—18 (average 14·8) mg. per 100 c.c. High vals. are associated with pneumonia, rheumatic fever, chorea, and high temp. No quant. relationship between the lactic acid concentration and the blood-sugar or -CO_2-combining power is observed. Chemical Abstracts.

Cause of exophthalmic goitre. W. S. Reveno (Arch. Int. Med., 1931, **48**, 592—597).—It is suggested that in exophthalmic goitre toxic substances of intestinal origin damage the thyroid gland so that the metabolism of tyrosine becomes abnormal, an excess of thyroxine, adrenaline, and tyramine being produced. W. O. Kermack.

Iodine in exophthalmic goitre. J. Lerman and J. H. Means (Amer. J. Med. Sci., 1931, **181**, 745—755).—I produces its characteristic effects independently of the type of compound (EtI, KI, or Lugol's solution) or the manner of administration. Chemical Abstracts.

Hypocalcæmia following experimental hyperparathyroidism and its possible significance. A. Bodansky and H. L. Jaffe (J. Biol. Chem., 1931, **93**, 543—549).—Discontinuance of parathyroid hormone treatment in young guinea-pigs is followed by a hypocalcæmia accompanied by changes in the P balance probably due to a rapid deposition of Ca in the bones depleted during the period of injection. A hypo-function of the glands induced by the hormone treatment may also play a part. F. O. Howitt.

Iron metabolism in liver disease with icterus. T. Brugsch (Med. Klinik, 1931, **27**, 536—539; Chem. Zentr., 1931, i, 3021—3022).—The high Fe content of the skin is due to deposition of Fe from the blood. The accumulation of Fe in the liver in icterus does not lead to increased elimination in the urine and bile. The intercutaneous $K_4Fe(CN)_6$ reaction may be produced by the oxidation of considerable quantities of bilirubin in the skin. A. A. Eldridge.

Detection of bilirubin in the skin in icterus. K. Jegorov (Deut. med. Woch., 1931, **57**, 539—540; Chem. Zentr., 1931, i, 3030).—The use of $K_4Fe(CN)_6$ and of diazobenzenesulphonic acid for the detection of bile colouring-matters in the tissues is described. A. A. Eldridge.

Methylene-blue as reagent for bilirubin. M. Roch (Med. Klinik, 1931, **27**, 589—590; Chem. Zentr., 1931, i, 3030).—Franke's methylene-blue reaction for the detection of bilirubin in urine is trustworthy. The colour change is attributed to a physical process. A. A. Eldridge.

Carbohydrate metabolism in Mongolian idiots as evidence of endocrine dysfunction. W. D. O'Leary (Amer. J. Dis. Children, 1931, **41**, 544—551).—The high dextrose tolerance resembles that of a hypo-functioning endocrine system. Following glandular therapy the tolerance becomes normal or lowered and the curves resemble those of mild diabetes or hyper-function of the thyroid and pituitary glands. Chemical Abstracts.

Blood-calcium in mental diseases. J. S. Hepburn and A. H. Neibaum (J. Amer. Inst. Homeopathy, 1931, **24**, 559—560).—In dementia præcox blood-Ca is high (*e.g.*, more than 11 mg. per 100 c.c.); in general paresis vals. were 10·5—11·0, and in epilepsy 10·0 or less. Chemical Abstracts.

Blood of leucæmic subjects. Variation of lipins in leucæmia. S. Marino (Arch. Farm. sperim., 1931, **53**, 17—52).—Diminished amounts of total fatty acids and cholesterol in the blood are found in chronic aleucæmic myelosis, whilst $COMe_2$-sol. fatty acids and phospholipins are unchanged. In chronic leucæmic myelosis and lymphadenosis the variations are irregular and bear no relation to the no. of leucocytes. R. K. Callow.

Elimination of phenolsulphonephthalein by the kidney. Influence of pathologic changes in the liver. J. P. Hanner and G. H. Whipple (Arch. Int. Med., 1931, **48**, 598—610).—When phenolsulphonephthalein is injected into a dog about 10% may be recovered from the bile in about 2 hr. and 75—78% appears in the urine. In the case of dogs with livers poisoned by $CHCl_3$ or P, secretion of the compound in the bile does not occur, and 90—97% is excreted in the urine. Only 3—5% of the phthalein taken by mouth appears in the urine. Reabsorption from the intestine therefore takes place only to a small extent, and abnormally high excretion of the phthalein in the urine by humans is indicative of hepatic disease. W. O. Kermack.

Water economy in disturbed liver function. I. Effect of the oral administration of water on the intermediate water metabolism and excretion in patients with liver disease and in dogs with damaged livers. S. Abe (Tohoku J. Exp. Med., 1931, **17**, 174—218).—In normal man the serum-protein, -NaCl, and blood-hæmoglobin are minimal following the ingestion of H_2O within 30 min. Changes in blood concentration are recorded. In liver disease or injury there may be prolonged hydræmia. Chemical Abstracts.

Absence of blood-uric acid in a case of liver damage. H. TAUBER (J. Amer. Inst. Homeopathy, 1931, **24**, 515—516).—During the last 7 weeks of life the urine (*d* 1·013—1·025; 270—550 c.c. per day) contained total N 3·30—4·75 g., urea 4·50—8·10 g., tyrosine 120 mg., and marked amounts of bile, urobilin, and urobilinogen, but no albumin. The blood contained dextrose 55—62, non-protein-N 25—27, urea-N 5—8, and creatinine 1·3—1·6 mg., but $<0·5$ mg. of uric acid, per 100 c c.

CHEMICAL ABSTRACTS.

Metabolism in myotonia atrophica. S. MORGULIS and A. YOUNG (Arch. Int. Med., 1931, **48**, 569—575).—A patient suffering from myotonia atrophica excreted in the urine an abnormally high quantity of creatine and an abnormally low quantity of creatinine, the total creatine and creatinine being approx. equal to the normal. A diet rich in arginine did not increase urinary creatine, but creatine taken by the mouth was rapidly and almost quantitatively excreted in the urine, about 16% appearing as creatinine.

W. O. KERMACK.

Metabolism in nephrosis. D. M. COWIE, K. M. JARVIS, and M. COOPERSTOCK (Amer. J. Dis. Children, 1930, **40**, 465—483).—A child with nephrosis associated with a high basal metabolic rate was free from œdema when a positive N balance of 1—3·76 g. was maintained. During this period the urinary albumin markedly decreased. The blood-protein rose to 5 g. per 100 c.c. before œdema permanently disappeared.

CHEMICAL ABSTRACTS.

Lipin nephrosis. IV. Extraction of the serum-lipins by ether. A. MACHEBŒUF and R. WAHL. **V. The physico-chemical equilibrium and the role of plasma-lipins.** A. MACHEBŒUF and G. SANDOR (Bull. Soc. Chim. biol., 1931, **13**, 736—744, 745—757).—IV. Extraction with Et_2O of normal and pathological sera does not remove the total lipin content even when the extraction is performed every 2 days for a period of 5 months. The greater is the protein content of the serum the less readily are the lipins extracted. Lipins are less readily extracted from normal than from pathological sera.

V. Comparison of the hydrophilic powers of normal and pathological sera at p_H 7·4, on the basis of dialysis, suggests that the combination of proteins and lipins, such as occurs in lipin nephrosis, liberates more free, non-diffusible, ionic valencies than an equal wt. of normal protein. The buffering action of the proteins admixed with lipins from lipin nephrosis is greater than that of an equal wt. of protein from normal sera, whilst the isoelectric points are identical.

C. C. N. VASS.

Absorption of calcium from the gall bladder. E. ANDREWS and L. HRDINA (Amer. J. Med. Sci., 1931, **181**, 478—482).—In cystic duct obstruction in dogs the relatively high Ca content of the cystic bile is gradually, or in the presence of infection rapidly, lowered.

CHEMICAL ABSTRACTS.

Cholesterol and œdema. J. K. CALVIN and A. H. GOLDBERG (Amer. J. Dis. Children, 1931, **41**, 1066—1080).—The hypercholesterolæmia of renal disease is probably the result of a disturbance in fat metabolism accompanying the nephrotic syndrome. The blood-cholesterol is high during, and sometimes after, œdema; the ascitic fluid- and bile-cholesterol is low.

CHEMICAL ABSTRACTS.

Peroxidase reaction in pus. S. KONNO (Tohoku J. Exp. Med., 1931, **17**, 31—38).—The peroxidase reaction in pus from acute otitis media is usually similar to that of normal leucocytes. In chronic otitis media crystals are frequently found inside and outside the pus cells.

CHEMICAL ABSTRACTS.

Pus and its calcium content. T. OYAMA (Tohoku J. Exp. Med., 1930, **16**, 438—485).—The Ca content of pus from abscesses does not exceed 12% unless bone is involved, when it may exceed 13—15%.

CHEMICAL ABSTRACTS.

Diastatic enzyme content of skin and blood. Its biochemical importance in skin diseases. I. Diastatic enzyme in the skin of healthy persons. II. Diastase in the skin in skin diseases and in diabetes. III. Diastase in blood. B. OTTENSTEIN (Biochem. Z., 1931, **240**, 328—343, 344—349, 350—356).—I. The diastase content of the surface layer of the living undamaged human skin *in situ* can be measured by allowing the enzyme to pass during 5 min. into distilled H_2O at room temp. and determining the amount of enzyme in the solution so formed by a combination of the methods of Rona and Eweyk (A., 1924, i, 1264) and of Hagedorn and Jensen, using glycogen as substrate. The content varies according to the location of the skin and is dependent on the blood supply and on the amount of sweat secreted at the place concerned. The vals. also vary from person to person and, in the same person, from time to time. When carbohydrate is consumed or injected the amount of diastase in the dialysate increases and at the same time the reaction of the solution becomes more acid. Injection of insulin causes increase which changes to decrease in the diastase content. When the permeability of the skin is increased by the action of KOH the amount of diastase in the dialysate increases. Irradiation of the skin with ultra-violet light decreases the diastase content greatly. The significance of the results is discussed.

II. In ichthyosis the diastase content of the skin increases and in other skin diseases (eczema, dermatitis, psoriasis, etc.) abnormal contents are found after intravenous injection of dextrose or intramuscular injection of insulin. In diabetes the content is high, but falls together with the sugar content of the blood after administration of insulin.

III. In healthy persons the blood contains 130—170 mg. of diastase per 100 c.c., whilst in diabetics much lower vals. are found, especially when no insulin has been administered. The diastase content of persons suffering from certain skin diseases is also low.

W. MCCARTNEY.

Chloride metabolism in congenital pyloric stenosis. N. MORRIS and S. GRAHAM (Arch. Dis. Childhood, 1931, **6**, 27—36).—Intravenous administration of NaCl tends to restore the reduced Cl content of the tissues; it may lead to excessive retention. Restoration of the blood-Cl to the normal level may be associated with a low urinary output with no reduction in the degree of alkalosis.

CHEMICAL ABSTRACTS.

Chemical analysis of blood in general and urologic surgery. V. C. Myers (J. Lab. Clin. Med., 1931, **16**, 751—759).—A discussion of prognosis.
Chemical Abstracts.

Metabolism in typhoid. Trial of a causal treatment. J. Kleeberg (J. Egypt. Med. Assoc., 1931, **14**, 543).

Pond life, with special reference to the possible causation of the swarming of phytoplankton. S. C. Akehurst (J. Roy. Microscop. Soc., 1931, [iii], **51**, 237—265).—Phytoplankton can be classified as a starch group and an oil group, according to the nature of their food reserve. The author suggests that the excretory products of each class are toxic to that class, but form an accessory food for the other class.
C. W. Gibby.

Action at a distance on the development of sea-urchin's eggs. J. Magrou, M. Magrou, and P. Reiss (Compt. rend., 1931, **193**, 609—612).—The development of sea-urchin's eggs proceeds abnormally when the egg suspension is separated by a thin sheet of quartz from an aq. medium containing reduced phenosafranine, dextrose in presence of $KMnO_4$, or a bacterial suspension. Experiments with thin sheets of different materials indicate that the essential requirement for a positive result is that the two media should be separated by a good insulator. The action appears to depend on a difference in oxidation–reduction potential on the two sides of the insulating sheet.
W. O. Kermack.

Is there a parallelism between function and metabolism in vegetative organs? F. Matakas (Arch. exp. Path. Pharm., 1931, **162**, 395—419).—Experimental and clinical observations indicate a negative answer.
W. O. Kermack.

Sex differences from the point of view of biochemistry. I. T. Tadokoro (J. Fac. Sci. Hokkaido, 1930, **1**, 1—179).—A comprehensive statistical survey of sex differences in physiology, anatomy, and general metabolism. The muscle-tissue of females in various types of fish and animals shows a greater reducing power than that of males, whilst the latter has a greater peroxidase activity, which is diminished by castration. Female bone invariably contains more Ca and less P than male bone, whilst the collagen of the latter is richer in NH_2-acids, particularly arginine. Female muscle has a higher power of swelling in aq. KCl than male muscle owing to its different protein composition; acetylation reveals a larger OH-group content in female than in male muscle-protein, which may account for this phenomenon. The female proteins have a higher P content and greater solubility but a lower S content; their isoelectric point is more acidic and they exhibit a lower rotation in alkaline solution. The lesser pigmentation of the female in general is explained by the decreased peroxidase activity combined with the fact that the chromogen of melanin is fat-sol. and melanin formation is therefore delayed. Female fat contains a higher percentage of unsaturated fatty acids and unsaponifiable matter than male fat, but it has a lower sap. val. The absorption spectrum of male fat is shorter than that of female, but its n is always higher.
P. G. Marshall.

Thermodynamic theory of excitation of nerves. N. Raschevsky (Physical Rev., 1930, [ii], **35**, 1435).
L. S. Theobald.

Liver metabolism. I. Continuous determination of the gas exchange of perfused isolated organs in a closed system. III. Gas exchange and equilibrium in the perfused isolated innervated or non-innervated liver. H. Staub (Arch. exp. Path. Pharm., 1931, **162**, 420—427, 433—451).—I. The apparatus described uses an artificial lung, measures the rate of perfusion, and allows a continuous series of observations to be made.

III. The O_2 consumption of the dog's liver perfused with dil. ox blood has a mean val. of 26·5 c.c. per kg. per min. The mean CO_2 production is 20·2 c.c. per min. and the R.Q. is 0·44—1·04. Factors such as duration of previous fasting, the intactness or otherwise of the nerve supply, or the rate of blood-flow appear to have no significant effect. The liver loses glycogen, giving up dextrose to the blood and the liver- and blood-fat usually fall. The addition of dextrose to the perfusion fluid causes the R.Q. to rise with increase of CO_2 production and a negative carbohydrate balance is observed. The fat balance becomes positive. With 0·362% of dextrose in the blood, glycogen is deposited in the liver. The effect of the addition of glycine to the perfusion fluid has also been determined.
W. O. Kermack.

Measurement of oxygen consumption, respiratory quotients, and reduction of methylene-blue by tissues and by yeast. P. Ambrus, I. Banga, and A. Szent-Gyorgyi (Biochem. Z., 1931, **240**, 473—477).—In the Barcroft apparatus the absorption of CO_2 is greatly facilitated by suspending filter-paper soaked in 20% aq. NaOH in the manometer tube. An apparatus for determining the absorbed CO_2 is described. The uptake of O_2 by minced muscle-tissue can be determined by measuring the corresponding dehydrogenation, and a procedure in which the reduction of methylene-blue provides this measure is described. Probably because of the time required for diffusion when methylene-blue and yeast suspensions react anaerobically for the first time, the period of reduction is always greater then than when the mixture is shaken with air until the dye is completely reoxidised and the experiment repeated. No decrease in the reduction period occurs when further repetitions are made.
W. McCartney.

Importance of lactic acid for the respiration of minced heart-muscle. I. Banga, L. Schneider, and A. Szent-Gyorgyi (Biochem. Z., 1931, **240**, 478—479).—The consumption of O_2 by minced pig-heart-muscle is increased by addition of lactic acid and inhibited by addition of $CH_2I{\cdot}CO_2H$, but the inhibition is only slight with concentrations of $CH_2I{\cdot}CO_2H$ which suppress production of lactic acid. It is concluded that the inhibiting effect of $CH_2I{\cdot}CO_2H$ on the respiration is not due to the accompanying inhibition of lactic acid production and that in minced heart-muscle lactic acid is not an indispensable intermediate oxidation product. The result also supports the view that oxidative and fermentative degradation proceed, for the most part, in different ways.
W. McCartney.

Influence of the co-enzyme of lactic acid formation on the hydrolysis of carbohydrate phosphoric esters in muscle extracts. K. LOHMANN (Biochem. Z., 1931, **241**, 50—66).—Frog's muscle extract after keeping at 20° for 3 hr. is no longer able to hydrolyse hexose-mono- and -di-phosphate and glycogen, but is reactivated by addition of adenylpyrophosphate. The dialysed extract can be reactivated by adding Mg+adenylpyrophosphate. Hydrolysis of diphosphate does not require added inorg. phosphate, but that of monophosphate is accelerated by addition of inorg. phosphate. Inactivated but not dialysed extracts can dephosphorylate hexosediphosphate to some extent without lactic acid formation. With dialysed extracts such dephosphorylation occurs only after addition of Mg salts.

P. W. CLUTTERBUCK.

Comparative investigation of the co-enzymes of lactic acid formation and of alcoholic fermentation. K. LOHMANN (Biochem. Z., 1931, **241**, 67—86).—The co-enzyme of lactic acid formation can be precipitated in neutral solution from the deproteinised extract of fresh muscle as the sparingly sol. Ba salt. Its activity in both crude and purified preps. runs parallel with the pyrophosphate fraction. The co-enzyme of lactic acid formation of yeast can be similarly precipitated from AcOH solution as the Pb salt. Euler's cozymase can act as co-enzyme of lactic acid formation in inactivated frog's muscle extracts, but not in dialysed extracts. The cozymase is very much more active as co-enzyme of alcoholic fermentation than adenylpyrophosphate. Cozymase then requires the presence of hexosediphosphate, whereas the pyrophosphate does not. The org. components of the co-enzyme system of lactic acid formation and alcoholic fermentation are not identical, but both systems require the presence of Mg salts.

P. W. CLUTTERBUCK.

Relation between chemical exchange and increase of osmotic pressure in muscle. O. MEYERHOF and A. GROLLMAN (Biochem. Z., 1931, **241**, 23—35).—The increase of osmotically active mols. as determined by changes of f. p. during fatigue of muscle is always 30% greater than is accounted for by known chemical changes. The f.-p. change is independent of muscle structure. At least $\frac{1}{4}$ of the excess is explained by side reactions, *e.g.*, increase of NH_2-N and hydrolysis of glycogen. The osmotic activity of the hydrolysis products appearing in muscle is the same as in aq. solution and it must be concluded that other still unknown reactions occur.

P. W. CLUTTERBUCK.

Rigor in muscle and co-enzyme. H. K. BARRENSCHEEN, L. FREY, and O. RENTH (Biochem. Z., 1931, **240**, 394—408).—In frog and guinea-pig muscle *rigor mortis* and also rigor caused by heat, caffeine, Et_2O, and $CHCl_3$ lead to complete or almost complete disappearance of the "pyrophosphate fraction" and hence also of the co-enzyme. This disappearance shows itself in the production and accumulation of methylglyoxal from added Mg hexosediphosphate and, in some cases at least, in inability of juice from the muscles in rigor to activate yeast free from co-enzyme. The rigor produced by heat, Et_2O, and caffeine also leads to accompanying production of the difficultly hydrolysable phosphoric esters. Such production does not result from *rigor mortis* or from the rigor caused by $CHCl_3$ or by the prolonged action of caffeine. The results confirm views previously expressed (this vol., 647).

W. MCCARTNEY.

Elimination of pentose in muscular work. G. EMBDEN and M. LEHNARTZ (Z. physiol. Chem., 1931, **201**, 149—156).—The stimulation of frog's gastrocnemius to exhaustion produces a large increase in "alcohol-sol." pentose. When both muscles were equally stimulated one, examined after 2 hr. in O_2, contained more pentose than the other, examined immediately, even under conditions where re-formation of $H_4P_2O_7$ occurs during recuperation. A loaded muscle after immersion in liquid air contains more alcohol-sol. pentose than an unloaded muscle when so treated. This also applies when the contraction of the loaded muscle is augmented by electrical stimulation at the moment of immersion. The appearance of pentose is regarded as due to hydrolysis of pentosephosphoric acid.

J. H. BIRKINSHAW.

Effect of repeated contractions of muscle on its lipin content. K. W. BUCHWALD and C. F. CORI (Proc. Soc. Exp. Biol. Med., 1931, **28**, 737—740).—The cholesterol, phospholipin, and total fatty acid content of the rat gastrocnemius remained unchanged during prolonged and severe muscular work. In the frog in summer the fatigued muscles of one leg contained 19·7% (dry wt.) less fatty acids than the resting muscles of the other leg.

CHEMICAL ABSTRACTS.

Precursor of ammonia produced in blood and muscle. E. FREUND and B. LUSTIG (Biochem. Z., 1931, **240**, 326—327; cf. this vol., 641).—The authors' views concerning the existence of NH_3 in blood and muscle are based on the facts that fresh material deproteinised in the cold gives no brown colour with Nessler's reagent, although 0·1% of added NH_3 gives the colour distinctly, that material which has been kept or has been heated in vac. gives the colour distinctly, and that when the green ppt. given with the reagent is removed a brown colour corresponding in depth with the amounts of NH_3 usually reported is obtained. Hence the criticisms of Parnas (this vol., 1319) are inapplicable.

W. MCCARTNEY.

Ammonia production induced by long keeping of frogs' muscles in Barkan solution. G. EMBDEN and M. LEHNARTZ (Z. physiol. Chem., 1931, **201**, 273—283).—Prolonged oxybiotic work of frog muscles in Barkan solution induces considerable NH_3 formation, only in part accounted for by deamination of the adenylic acid complex. Unstimulated muscles show a similar behaviour; the O_2 supply has no influence. The effect is probably due to autolytic processes.

J. H. BIRKINSHAW.

Action of bromoacetic acid poisoning on ammonia formation in frog's muscle. G. EMBDEN and L. NORPOTH (Z. physiol. Chem., 1931, **201**, 105—132).—In $CH_2Br\cdot CO_2H$ poisoning of frogs after severing the plexus ischiadicus to inhibit the onset of rigor only a small amount of NH_3 is formed in the corresponding gastrocnemius. In normal innerv-

ated muscle a large increase of NH_3 is associated with rigor. Direct and indirect stimulation of muscle after $CH_2Br\cdot CO_2H$ poisoning causes a much greater NH_3 production than in normal muscle. The contraction following fatigue and the gradual death of the muscle after contraction are associated with further NH_3 production. A small number of isolated stimuli causes NH_3 production independent of temp.

J. H. BIRKINSHAW.

Action of bromoacetic acid poisoning on the phosphocreatine metabolism of skeletal muscle. L. NORPOTH (Z. physiol. Chem., 1931, **201**, 133—141).—Considerable hydrolysis of phosphocreatine accompanies $CH_2Br\cdot CO_2H$ rigor. After section of one ischiadicus the innervated muscle long before onset of rigor was richer in phosphocreatine than the control. The action of $CH_2Br\cdot CO_2H$ on the innervated muscle does not cause phosphocreatine hydrolysis.

J. H. BIRKINSHAW.

Influence of protein level on rate of growth in chickens. G. F. HEUSER and L. C. NORRIS (Proc. IV World's Poultry Cong., 1930, 328—342).—Although the wt. after 20 weeks was the same for protein ration levels of 13 and 20%, growth in the first 10 weeks was greater on the 20% level and in the second 10 weeks on the 13% level.

CHEMICAL ABSTRACTS.

Creatine-creatinine metabolism. K. EIMER (Z. ges. exp. Med., 1931, **75**, 428—442; Chem. Zentr., 1931, i, 2898).—Part of the urinary creatinine is probably a metabolic product of chemical processes in the musculature.

A. A. ELDRIDGE.

Glycogen in liver cultures. L. DOLJANSKI (Compt. rend. Soc. Biol., 1930, **105**, 504—506; Chem. Zentr., 1931, i, 2898).—Pure cultures of liver cells retain *in vitro* the ability to produce glycogen. The glycogen disappears on rapid growth of the tissue, but again appears when growth is retarded.

A. A. ELDRIDGE.

Metabolism of tartrates. I. Colorimetric determination of tartaric acid. F. P. UNDERHILL, F. I. PETERMAN, and A. G. KRAUSE. **II. Behaviour of tartrate in the organism of the rabbit, dog, rat, and guinea-pig.** F. P. UNDERHILL, C. S. LEONARD, E. G. GROSS, and T. C. JALESKI. **III. Behaviour of tartrates in the human body.** F. P. UNDERHILL, F. I. PETERMAN, T. C. JALESKI, and C. S. LEONARD (J. Pharm. Exp. Ther., 1931, **43**, 357—358, 359—380, 381—398).—II. To the colourless neutral solution to be tested glacial AcOH (1 c.c.) and colourless 5% Na metavanadate solution (4 c.c.) are added and H_2O to 50 c.c. After shaking, the red colour which develops in 10 min. is compared with that in standards similarly treated containing known quantities of tartrate. The method has been adapted for use with urine, blood, grape juice, and baking-powder.

II. When tartrate is administered to rabbit, dog, or cat, either by mouth or parenterally, 90—100% is excreted in the urine. In the case of the guinea-pig, tartrate introduced parenterally is eliminated quantitatively by the kidneys, but introduced by mouth only a small percentage appears in the urine and none in the fæces. It appears, therefore, to be changed in the intestinal tract of the guinea-pig. Neither in the case of the rabbit nor of the dog does the diet appreciably affect the behaviour of administered tartrate. The rabbit is more susceptible than is the dog to the toxic effects of tartrate on the kidney.

III. In man, tartrate ingested by mouth is excreted in the urine to an extent of less than 20% and none appears in the fæces even after purgative doses. Destruction of the tartrate apparently takes place through bacterial action in the large intestine.

W. O. KERMACK.

Catabolism of fat directly incorporated into the animal body. I. T. BABA (Tohoku J. Exp. Med., 1931, **17**, 154—167).—Intravenous infusion of a fat emulsion into dogs on a fat-free meat and thyroxine diet quickly lowers the R.Q. (min. 0·707).

CHEMICAL ABSTRACTS.

Blood-phosphorus in fat absorption. B. VAHLQUIST (Biochem. J. 1931, **25**, 1628—1633).—There is a regular increase in the phosphatides of the plasma of dogs after fat ingestion; those of the corpuscles remain practically unchanged. During fat absorption the non-lipoid P of plasma is slightly increased; that of the corpuscles is unaltered. The hypothesis that the fat absorbed from the intestine is transformed into phosphatides of the red corpuscles is therefore not upheld.

S. S. ZILVA.

Has the pancreas any influence on the resorption of fat apart from its external lipolytic secretion ? M. NOTHMANN and H. WENDT (Arch. exp. Path. Pharm., 1931, **162**, 472—479).—In depancreatised dogs to which olive oil has been administered by mouth, the total fats in the small intestine consisted of $<4\%$ fatty acids, whilst in the large intestine the fatty acids varied from about 14 to 25%. This relatively high figure is probably the result of bacterial action. It is improbable that the pancreas has any effect on the resorption of fat other than through its lipolytic activity.

W. O. KERMACK.

Biochemistry of sulphur. XI. Substitution of dithioethylamine (cystineamine) for cystine in the diet of the white rat. M. X. SULLIVAN, W. C. HESS, and W. H. SEBRELL (U.S. Publ. Health Rep., 1931, **46**, 1294—1301).—A basal diet containing 4% of caseinogen was established on which young male rats gradually gained in wt. Substitution of 0·5% of cystine or cystineamine dihydrochloride for an equal amount of maize starch produced an increased growth rate which was similar up to 6 weeks, but thereafter the latter was effective only to about $\frac{2}{3}$ the extent of the former.

P. G. MARSHALL.

Sulphur metabolism of the dog. IX. Synthesis of phenol sulphate and indoxyl sulphate. T. S. HELE (Biochem. J., 1931, **25**, 1736—1744).—Synthesis takes place when the Na_2SO_4 is administered orally or subcutaneously and the PhOH or indole orally. When ethereal sulphate is formed from PhOH or indole at the expense of endogenous S, this S can be replaced at least in part by SO_4''. The ethereal sulphate is formed by the union of SO_4'' with phenolic compounds.

S. S. ZILVA.

Presence of phenaceturic acid in the urine of domestic animals. Z. HUBER (Ann. Sci. Univ.

Jassy, 1931, **16**, 497—514).—In dog, cat, rabbit, and poultry the benzene ring is completely destroyed, and in the pig and horse it is partly destroyed. In the ox and sheep it remains intact and is excreted in the urine as hippuric and phenaceturic acids, of which the latter frequently preponderates. H. F. GILLBE.

Effect of fasting and subsequent administration of protein on the formation of mercapturic acid. E. ABDERHALDEN and E. WERTHEIMER (Z. physiol. Chem., 1931, **201**, 267—272; cf. this vol., 868).—Dogs, after fasting 3—5 days, received meat and PhBr. At first mercapturic acid excretion was small or nil, becoming normal only after some days. Cystine fed to a fasting dog gave rise to mercapturic acid in the urine, showing that the power of synthesis was not destroyed. Probably after fasting all the cystine in the first protein supplied is required to replenish the needs of the organism.

J. H. BIRKINSHAW.

Relation of life to electricity. V. Stainability of oil mixtures and white blood-cells by 40 different dyes. R. BEUTNER, J. LOZNER, and B. E. CAYWOOD. **VI. Variation of the electrical resistance of dying tissue as a result of chemical decomposition.** R. BEUTNER, S. H. MANN, and C. M. BLANTON (Protoplasma, 1931, **12**, 481—497, 498—509; cf. this vol., 1084).—V. A dye which is absorbed by a non-aq. mixture containing oleic acid and not by an analogous mixture containing quinine is invariably a nuclear stain. The reverse is the case for cytoplasmic stains.

VI. The electrical conductivity of a non-aq. phase (AcOEt) is largely dependent on its content of fat-sol. acids or bases, highest vals. being obtained with a mixture of acids or bases. In equilibrium with an aq. phase the higher fatty acids produce the greater increase in conductivity, since they are not extracted by H_2O. The initial rise in the resistance of dying or degraded tissue results from the degradation and removal of fatty acids from lipoid cell matter. The later decline in resistance marks the disintegration and dissolution of the cell membranes. Higher conductivity is associated with a more positive p.d. and better basophilic staining in oil mixtures as well as in tissues. A. G. POLLARD.

Buffer values of foods. I. N. KUGELMASS and E. GREENWALD (Amer. J. Dis. Children, 1931, **41**, 1377—1379).—Cereals, fruits, and vegetables have low buffer vals. in comparison with milk, eggs, and meat. Cooked and processed foods have lower buffer vals. than raw foods. CHEMICAL ABSTRACTS.

Biological values of the proteins of breads baked from rye and wheat flours alone or combined with yeast or soya-bean flour. S. K. KON and Z. MARKUZE (Biochem. J., 1931, **25**, 1476—1484).—A supplementary relation exists between the proteins of white wheat flour and those of baker's yeast or of soya-bean flour. There is strong indication that a similar relation exists between the protein of rye flour and of soya-bean flour. The biological val. of the N of crust is lower than that of crumb or of whole bread. S. S. ZILVA.

Deficiencies in rations devoid of roughage for calves. I. Effect of addition of cod-liver oil and lucerne ash. S. W. MEAD and W. M. REGAN (J. Dairy Sci., 1931, **14**, 283—293).—Calves were reared up to 19 months without roughage provided cod-liver oil and lucerne ash were supplied. Without ash the animals were under wt. and the deposition of minerals in the bones was much reduced. Among animals receiving the same ration those showing the greater live wt. had a lower % of ash in the dry fat-free bone. A. G. POLLARD.

Significance of iodine in the energy and metabolic processes of the human body. J. STOKLASA (Z. Ernähr., 1931, **1**, 3—15; Chem. Zentr., 1931, i, 2895).—The effect of soil p_H on the assimilation of I by plants was examined. In plants treated with I the acidity is markedly diminished, particularly in the root system. Ingestion of plants treated with I leads to a diminution of urinary acidity.

A. A. ELDRIDGE.

Calcium assimilation as indicated by bone analysis in long time experiments. A. M. HARTMAN and E. B. MEIGS (J. Dairy Sci., 1931, **14**, 322—336).—The relative proportions of ash, Ca, P, N, and org. matter in cows' bones are little, if at all, altered by long periods of low-Ca rations even when a considerable amount of milk is given in these periods, but the total wt. of bones is reduced by 10—20%. The Ca metabolism in cows receiving a medium quality roughage under natural conditions for long periods is higher than that shown in most balance experiments. A. G. POLLARD.

Dietary factors influencing calcium assimilation. XIV. Influence of mineral acids and sugar on the calcium metabolism of milking cows. E. B. HART, H. STEENBOCK, and O. L. KLINE (J. Dairy Sci., 1931, **14**, 307—321; cf. A., 1930, 636).—Addition of 3 lb. of dextrose to the daily ration had no consistent effect on the Ca assimilation of dairy cows. The daily ingestion of 115 or 230 c.c. of 40% HCl with the ration increased the Ca excreted in the urine and the net Ca loss. A. G. POLLARD.

Calcium and phosphorus balances of milking cows under varying conditions. H. B. ELLENBERGER and J. A. NEWLANDER (Proc. Amer. Soc. Animal Produc., 1928, 25—28).—Liberally milking cows are not always in serious negative Ca and P balance provided they receive adequate grain mixture. Added minerals (steamed bone-meal and limestone) may be assimilated in sufficient quantities to result in positive Ca and P balances.

CHEMICAL ABSTRACTS.

Calcium and phosphorus metabolism. VIII. Influence of thyroid gland and parathyroid hormone on total acid-base metabolism. F. ALBRIGHT, W. BAUER, and J. C. AUB (J. Clin. Invest., 1931, **10**, 187—219).—The thyroid hormone does not act by stimulating the parathyroid glands because it has little effect on serum-Ca and -P. The thyroid does not mobilise Ca phosphate to assist in the excretion of acid metabolites, but exerts a sp. action on Ca–P metabolism. CHEMICAL ABSTRACTS.

Influence of magnesium salts on bone formation and rickets. I. H. VON EULER and M. RYDBOM (Biochem. Z., 1931, **241**, 14—22).—In

experiments with rats, addition of 0·8% Mg to a McCollum diet had an antirachitic action. Similar effects were not obtained with fish (*Gobius niger*) in normal and Mg-free sea-water.

P. W. CLUTTERBUCK.

Modification of the Osborne-Mendel salt mixture. P. B. HAWK and B. L. OSER (Science, 1931, **74**, 369).—The modified mixture for dietary experiments has the same ultimate composition but is easier to prepare. L. S. THEOBALD.

Chemical sense of the earthworm. O. MANGOLD (Naturwiss., 1931, **19**, 730—735).—Earthworms prefer pure gelatin to gelatin containing quinine, NaCl, or HCl, the discrimination increasing with increased concentration of the admixed compound. They show a slight preference for gelatin containing moderate concentrations of sucrose as compared with pure gelatin. The admixture to pure gelatin of plant material such as the worm commonly eats generally increases preference. W. O. KERMACK.

Action of pain stimuli on the internal secretions of the adrenals and pancreas, and the blood-sugar. S. A. SCHTSCHERBAKOV, V. S. SIMNITZKI, A. A. VISCHNEVSKI, and S. A. SATVORNIZKAJA (Russ. J. Physiol., 1931, **14**, 152—166).—Faradic stimulation of the ischiadicus in cats and dogs causes an increase of blood-sugar only when the adrenals are intact. When the latter are excluded a decrease in blood-sugar is observed. Blood taken from the vein leaving the adrenal, immediately after the application of the pain-stimulus, increases the blood-sugar of a second animal when injected into the latter. When the pancreas is removed the pain-stimulus causes a sharp increase of blood-sugar of long duration. When both pancreas and adrenals are removed the pain-stimulus does not affect the blood-sugar.

W. O. KERMACK.

Gall-bladder function. II. Absorption of sodium tetraiodophenolphthalein. C. G. JOHNSTON (J. Clin. Invest., 1931, **10**, 9—17).—KI is absorbed rapidly and Na tetraiodophenolphthalein more slowly. CHEMICAL ABSTRACTS.

Absorption and excretion of hexyl- and heptyl-resorcinol under different conditions. B. H. ROBBINS (J. Pharm. Exp. Ther., 1931, **43**, 325—333).—Hexylresorcinol (1 g.) administered to dogs by mouth is excreted in the urine (29%) almost entirely in a conjugated form and in the fæces (67%) in a free state. With larger doses the % excreted in the urine is decreased, but the absolute quantity is increased. The % excreted in the urine is reduced when the compound is given with olive oil or followed by paraffin oil. Hexylresorcinol was never detected in the tissues. In the case of heptylresorcinol about 1% is excreted in the urine and 96% in the fæces.

W. O. KERMACK.

Determination of hexylresorcinol in tissues, blood, and excreta. B. H. ROBBINS and L. G. WESSON (J. Pharm. Exp. Ther., 1931, **43**, 335—337).—The material is extracted with a boiling mixture of 2 vols. of 95% EtOH and 1 vol. of Et_2O. An aliquot portion of the filtered extract is acidified with 2—4 drops of conc. HCl and conc. to $\frac{1}{3}$ vol., diluted with H_2O, extracted with $CHCl_3$, and the extract boiled with 2 c.c. of 5% aq. NaOH until all the $CHCl_3$ is evaporated. The residue is made up to 2 c.c. with H_2O and the quantity of hexylresorcinol determined colorimetrically following the method of U.S.P., 1926, 323. Heptylresorcinol may be determined similarly. W. O. KERMACK.

Pharmacology of *d*- and *l*-camphor. III. Action of the isomerides on the smooth musculature of the leech. K. A. SCHMELEV (Russ. J. Physiol., 1931, **14**, 249—254).—At concentrations of 1 in 1000, *d*- and *l*-camphor produce at first a stimulating and over longer periods of time a paralysing action in the smooth musculature of the leech. The paralysing action is more marked in the case of *l*- than of *d*-camphor. The stimulating action produced with lower concentrations (1 in 2000 to 1 in 10,000) is the same for both isomerides. W. O. KERMACK.

Organic bromo-compounds [? bromo-oleic acid]. S. HERMANN and M. FREUND (Klin. Woch., 1931, **10**, 250—253; Chem. Zentr., 1931, i, 2636).—Pharmacologically active compounds are obtained by bromination of triglycerides of unsaturated fatty acids. A. A. ELDRIDGE.

Lactate concentration in the blood of the rabbit after injection of sodium lactate. I. A. PARFENTIEV, V. D. SUNTZEV, and B. F. SOKOLOV (J. Biol. Chem., 1931, **93**, 797—803).—By enteral or parenteral administration of Na lactate the blood-lactic acid can be raised from the normal level (0·03%) to 0·15—0·17% without danger, whilst a level of 0·20% is lethal. The max. level is attained 1—2 hr. after intravenous and 4—9 hr. after subcutaneous or oral administration. The initial increase is sometimes followed by a decrease to levels below the normal.

F. O. HOWITT.

Percutaneous resorption of alkali salicylates from ointments: determination of salicylic acid in urine. K. W. MERZ (Arch. Pharm., 1931, **269**, 449—456).—Salicylic acid (I) can be detected in the urine of man and rabbit 4 hr. after application of preps. (*e.g.*, lanolin) containing Na, K, or Li salicylate to the skin. Small amounts (0·5—1 mg.) of (I) in urine (10—50 c.c.) are determined by a modification of Sauerland's method (A., 1912, ii, 584).

H. BURTON.

Penetration of certain organic substances through the skin. N. V. LAZAREV, A. J. BRUSSILOVSKAJA, and I. N. LAVROV (Russ. J. Physiol., 1931, **14**, 284—289).—The skin of animals is exposed to the org. substance in question, *e.g.*, C_6H_6 or Et_2O, and the concentration in the expired air is determined by burning it in a suitable electric furnace, absorbing the CO_2 formed in aq. NaOH, and measuring the change of conductivity in the latter.

W. O. KERMACK.

Pharmacological effect of impurities in ether. W. L. MENDENHALL and R. CONNOLLY (J. Pharm. Exp. Ther., 1931, **43**, 315—323).—The cilia of oysters are rapidly paralysed by Et_2O containing small quantities of peroxide or aldehyde, but not by pure Et_2O. This observation may explain the tendency for the development of pneumonia in patients after anæsthesia by impure Et_2O. W. O. KERMACK.

Toxicity of methyl chloride for laboratory animals. J. L. White and P. P. Somers (J. Ind. Hygiene, 1931, **13**, 273—275).—0·0075% of MeCl in air is the min. lethal concentration for guinea-pigs exposed for 72 hr. P. G. Marshall.

Effect of general anæsthesia on the nitrogen metabolism. I. II. R. Inami (Tohoku J. Exp. Med., 1931, **17**, 39—79, 80—106).—N_2O, Et_2O, and $CHCl_3$ cause increased destruction of protein in rabbits, as shown by increased urinary N and blood-non-protein-N. The intensity of the anæsthesia is of greater significance than its duration or the quantity of narcotic used. Similar results were obtained with man. Chemical Abstracts.

Pharmacology of local anæsthetics. IV. "Neothesin." H. W. Coles and H. T. Rose (Anesth. Analg., 1931, **10**, 103—111).—When "neothesin" is injected subcutaneously into the dog, the amount of substance extracted by Et_2O from alkaline urine varies with the dose. The acid-titratable substances also increase proportionally. Little unchanged neothesin is excreted in the urine; the blood-non-protein-N, -urea-N, and -dextrose are unchanged. Chemical Abstracts.

Analgesic range of various antipyretics in combination with soporifics. I. Veronal. K. Pohle and W. Spieckermann. **II. Urethane.** K. Pohle and F. Vogel. **III. Sulphonal.** K. Pohle and P. Dittrich (Arch. exp. Path. Pharm., 1931, **162**, 685—705, 706—715, 716—726).—I. Pyramidone, quinine, phenacetin, and aspirin were investigated. Combination with veronal in each instance results in some detoxication of the soporific, which is greatest with pyramidone and least with quinine. An increase of analgesic power occurs with phenacetin, aspirin, and quinine, whilst the range is increased in all four combinations. The therapeutic quotient is highest with phenacetin, followed by quinine and aspirin. Commercial veronal–pyramidone preps. are mixtures removed from the optimum.

II. Addition of urethane leads to its detoxication with pyramidone and aspirin, whilst with phenacetin an increase of toxicity occurs over a certain range of mixture. The analgesic power and range of pyramidone, phenacetin, and aspirin are increased, whereas those of quinine are decreased. The combination urethane–pyramidone is therapeutically superior to any urethane-, sulphonal-, or veronal-combination of the 4 antipyretics. No relation between optimum properties and mol. ratio exists.

III. Sulphonal is significantly detoxicated by aspirin and pyramidone, but leads to a decrease in analgesic potency in each instance and to no significant increase in range. F. O. Howitt.

Hypoglycæmic action of the hypophysectomised dog's blood. R. J. Cowley (J. Pharm. Exp. Ther., 1931, **43**, 287—293).—When blood from hypophysectomised dogs is injected intravenously into rabbits, a lowering of the blood-sugar of the latter animals takes place, the reduction being more marked than in the case of control animals into which normal dog's blood is injected. W. O. Kermack.

Mechanism of the hypoglycæmia produced by guanidine and carbon tetrachloride poisoning and its relief by calcium medication. A. S. Minot (J. Pharm. Exp. Ther., 1931, **43**, 295—313).—In dogs poisoned with CCl_4 or with guanidine a marked increase in blood-lactic acid and excretion of lactic acid in the urine is observed as well as a marked hypoglycæmia. These symptoms are inhibited by administration of Ca. In rats guanidine inhibits glycogenolysis by the liver and causes an increased production of lactic acid. The mechanism through which Ca exerts its effect may be associated with adrenaline action, for the effect of Ca, like that of adrenaline, is inhibited by ergotamine tartrate. The close similarity of guanidine and CCl_4 poisoning supports the view that the latter compound exerts its action as the result of increasing the guanidine content of the blood. W. O. Kermack.

Morphine content of the blood and brain after administration of morphine to normal and pretreated animals. P. Fleischmann (Biochem. Z., 1931, **241**, 233—255).—The blood-morphine content after subcutaneous, intraperitoneal, and intravenous injection of the alkaloid is determined. The morphine concentration is smaller than expected from the dose, reaches a max. after about 1 hr., and then slowly decreases, being detectable after 24 but not after 48 hr. Similar results were obtained with guinea-pigs which had been receiving injections for a long time. The corpuscles contain about twice as much morphine as the serum. In experiments *in vitro* morphine is not destroyed by incubating with blood and its disappearance *in vivo* must be explained by its absorption by the organs. The concentration of morphine in brain is usually lower than in blood. P. W. Clutterbuck.

Santoninamide. K. Josephson (Svensk farm. Tidskr., 1931, **35**, 69—74; Chem. Zentr., 1931, i, 2885).—*Santoninamide*, $C_{15}H_{21}O_3N$, m. p. 177—179°, appears not to have the characteristic santonin action on the worm musculature. A. A. Eldridge.

Carbohydrate metabolism of the fatty liver during *Amanita* poisoning. K. Imhauser (Arch. exp. Path. Pharm., 1931, **162**, 506—514).—When the isolated livers of dogs previously poisoned by *Amanita* are perfused, the lactic acid production is much greater than in the case of a normal liver and cannot be completely accounted for by the quantity of glycogen and of lactic acid present in the liver at the beginning of perfusion. The poisoned livers do not appear to be able to resynthesise dextrose from lactic acid. This observation is in harmony with the high lactic acid content of these livers when removed from the animals. The addition of lævulose but not of dextrose to the perfusion fluid increases lactic acid production. W. O. Kermack.

I. Behaviour of *Digitalis* glucosides in blood and tissue-fluids. II. Penetration of *Digitalis* glucosides into organs. R. A. Hoekstra (Arch. exp. Path. Pharm., 1931, **162**, 649—662, 663—684).—I. Digitoxin in Ringer's solution in presence of rabbit-serum at p_H 6·8 or cat-serum does not affect the beat of the isolated frog's heart, whilst in presence of rabbit-serum at p_H 8·3 or with bile and saponin,

frog-serum, heated, enzymically hydrolysed, or inactivated rabbit-serum, the heart ceases to beat. Thus digitoxin combines with the colloids of certain serous fluids, the combination being destroyed at p_H 8·3 or by presence of surface-active substances. Fowl-serum and caseinogen do not quantitatively combine. A similar action is shown by lanogen, but not by other *Digitalis* glucosides.

II. Brilliant-Congo-red or digitoxin in aq. solution does not penetrate a gelatin gel, but does so in presence of sera or peritoneal fluids (cf. A., 1928, 127). Penetration into striated or cardiac muscle-fibres by the drug or dye occurs in presence of serum of the animal from which the muscle was obtained, but not in presence of "foreign" sera or peritoneal fluids except when the muscle is poisoned by EtOH. Sensitisation of the frog's heart against "foreign" proteins does not influence the atoxic combination of digitoxin with these proteins. F. O. Howitt.

Blood-gas content and alkalinity of the arterial blood of rabbits [and dogs] during carbon monoxide poisoning. B. Kamei (Tohoku J. Exp. Med., 1931, **17**, 107—126, 127—146).—In rabbits, after subcutaneous injection of CO, the arterial CO_2 decreases. In dogs the CO_2 capacity and the ratio of combined to dissolved CO_2 decrease. $NaHCO_3$ exercises a protective effect.

Chemical Abstracts.

Effect of hydrocyanic acid on the respiration of tissue. I. Banga, L. Schneider, and A. Szent-Györgyi (Biochem. Z., 1931, **240**, 454—461).—The respiration of animal tissue in the Barcroft apparatus is only partly inhibited by HCN, and this poison also only partly inhibits the oxidation by tissue of succinic acid. Concentrations of HCN greater than 0·001*N* inhibit the activation of H_2 and hence must not be used when activation of O_2 is being investigated. Since the oxidation of *p*-phenylenediamine by indophenoloxidase is completely inhibited by HCN the failure of the latter to inhibit the respiration completely cannot be due to incomplete inactivation of the enzyme. It follows either that the activated H_2 is partly autoxidisable or that the O_2 is activated by other substances in addition to indophenoloxidase.

W. McCartney.

Effect of arsenious acid on the respiration of tissue. I. Banga, L. Schneider, and A. Szent-Györgyi (Biochem. Z., 1931, **240**, 462—472).—In minced heart muscle two respiratory processes occur. One is inhibited, the other unaffected, by H_3AsO_3. This acid does not affect the activation of O_2, and its inhibitory action has no direct relation to that of HCN. The respiratory power restored to washed muscle by addition of boiled muscle-juice corresponds within certain limits with the respiratory power of unwashed muscle. H_3AsO_3 inhibits the activation of H_2 in the same way as it inhibits the whole respiratory process. W. McCartney.

Biochemical action of arsinic acids of the pyridine series. IV. Isomeric pyridonearsinic acids. A. Binz and G. Wilke (Biochem. Z., 1931, **241**, 256—259).—A table summarises the toxic and curative doses and the chemotherapeutic indices of the Na_2 salts of 2-pyridone-5-arsinic acid, 3-iodo-2-pyridone-5-arsinic acid, 2-pyridone-3-arsinic acid, 5-iodo-2-pyridone-3-arsinic acid, and 4-pyridone-5-arsinic acid when injected subcutaneously and intravenously into mice and the results are compared with earlier work (cf. A., 1930, 1213).

P. W. Clutterbuck.

Ionic migration of bismuth in different bismuth products under different conditions. P. J. Hanzlik and J. B. Spaulding (Proc. Soc. Exp. Biol. Med., 1931, **28**, 847—850).—Experiments on the treatment of syphilis demonstrated the amphoteric character of Bi. Correlation appeared to exist between cerebral and spinal fluid penetration and the anionic character of Bi. Chemical Abstracts.

[Toxicity of] cadmium vapour L. Schwarz and W. Deckert (Zentr. Gewerbehyg. Unfallverhut., 1931, **18**, 66; Chem. Zentr., 1931, i, 3032).

Effects of overdoses of germanium dioxide on the blood and tissues of rabbits. W. C. Hueper (Amer. J. Med. Sci., 1931, **181**, 820—830).—Toxic doses of colloidal GeO_2 cause dehydration and increase the oxidative processes of the organism. Excessive doses cause massive brown deposits in various organs. There is a tendency towards alkalosis; variations in blood-sugar are irregular. Chemical Abstracts.

Excretion of lead in urine after injection of colloidal lead phosphate. R. K. Newman (Med. J. Austral., 1931, **1**, 373—375).—Injected Pb phosphate is not excreted as such or quickly converted into an excretable form. It is rapidly filtered out of the blood by various tissues which re-liberate excretable Pb into the blood at a fairly const. rate. Colloidal Pb is not eliminated in the same manner as colloidal Pb phosphate. Chemical Abstracts.

Intake of lead and its distribution in the organism in experimental poisoning. F. Weyrauch (Z. Hyg., 1931, **112**, 559—568).—The resorption of a large proportion of the lead dust (PbS) inhaled by dogs occurs in the intestinal tract and not in the lungs. A. G. Pollard.

Colloid chemistry of the nervous systems. II. W. D. Bancroft and J. E. Rutzler, jun. (J. Physical Chem., 1931, **35**, 3036—3057; cf. this vol., 1084, 1088).—The alkali chlorides, bromides, iodides, and thiocyanates can be classified therapeutically as a single group which, in the main, acts by the peptisation of reversibly agglomerated proteins of the nervous systems. K salts should not be used unless the sp. action of K˙ is desired. NaCNS is comparatively non-toxic. It increases slightly the rate of respiration in men and dogs, but does not disturb the renal function. EtOH in man is definitely antagonised and the NaCNS tends to go to partly agglomerated areas. Large amounts cause vomiting apparently as a result of over-peptisation of the colloids of the centre concerned. NaCNS antagonises "nembutal" and counteracts weak anaphylactic shock. Ephedrine counteracts "Na amytal" anæsthesia better than does NaCNS and is a more powerful peptising agent for albumin. L. S. Theobald.

Influence of anaphylaxis on blood-sugar variation. I. S. Yun and Y. C. Lee (Trans. Japan. Path. Soc., 1930, **20**, 588—593).—With rabbits, slight hypo-

glycæmia followed injection of normal horse serum. During anaphylaxis hyperglycæmia was observed. The effect of injection of adrenaline, pilocarpine, or insulin is described. CHEMICAL ABSTRACTS.

Enzymic histochemistry. I. Determination of small enzymic fissions. K. LINDERSTRØM-LANG and H. HOLTER (Z. physiol. Chem., 1931, **201**, 9—30).—A method of micro-titration particularly applicable to enzymic hydrolyses is described. J. H. BIRKINSHAW.

Enzymes of cell respiration. R. KUHN, D. B. HAND, and M. FLORKIN (Naturwiss., 1931, **19**, 771).—The abs. activities of peroxidase, catalase, and respiratory enzymes are approx. of the same order of magnitude. Peroxidase and catalase are partial respiratory enzymes which can be separated and their range of effectiveness circumscribed. W. R. ANGUS.

Nature of peroxidase. R. KUHN, D. B. HAND, and M. FLORKIN (Z. physiol. Chem., 1931, **201**, 255—266).—The spectrum of reduced peroxidase shows the same bands, 557 and 527 $m\mu$, as reduced hæmin. Proportionality does not exist between the height of the absorption bands of peroxidase solution and peroxidase action. The " hæmin content " of the reduced peroxidase from the spectrophotometric measurements accounts for only about 1/7 of the Fe present. The absorption of peroxidase differs widely from that of catalase except when both are in the reduced state. A slight inhibition of peroxidase is obtained with CO; the product is not reactivated by light. J. H. BIRKINSHAW.

Peroxidases. Determination of activity. B. B. DEY and M. V. SITHARAMAN (J. Indian Chem. Soc., 1931, **8**, 479—487).—Directions are given for the gravimetric or, better, volumetric determination of the peroxidase in the expressed sap of *Luffa acetangula* by means of the oxidation of conc. benzoquinone solution to quinhydrone in the presence of H_2O_2. The reaction is partly or totally inhibited by dilution. R. S. CAHN.

Conditions influencing the use of the citric acid enzyme in cucumber seeds for the determination of citric acid. M. ADAMS (Proc. Staff Meetings Mayo Clinic, 1931, **6**, 252).—A H_2O-extract is preferable to the phosphate extract; a H_2O-extract when diluted with phosphate mixture of p_H 6·2—6·7 reduces methylene-blue more slowly than when more alkaline phosphate is used, giving a more definite end-point. The decrease in activity of the dehydrogenase at p_H 6·2—6·7 is small compared with that of interfering substances; the activity was lost at p_H 4·9. With H_2O-extracts at p_H 6·2 a 1 in 5×10^4 solution of methylene-blue can be used; 0·002—0·003 mg. of citric acid can be detected. CHEMICAL ABSTRACTS.

Structure and enzyme reactions. X. Action of salts on the systems amylase–starch–proteins. H. CHREMPINSKA (Biochem. J., 1931, **25**, 1555—1564).—Electrolytes retard the velocity of enzymic hydrolysis of starch. Systems of p_H below the optimal are more sensitive to the action of salts than are those of higher p_H. In the latter case the active concentration of ions is a function of their valency. The velocity of enzymic hydrolysis in systems containing gelatin is accelerated by the addition of NaCl and retarded by the addition of $CaCl_2$. In systems containing ovalbumin neither heat-coagulation nor $CaCl_2$ affects the velocity of reaction. When egg-white is present heat-coagulation in the presence of $CaCl_2$ accelerates reaction, the velocity depending on the time during which the system is shaken before addition of amylase. NaCl and Na_2SO_4 are without effect in this system. In the absence of $CaCl_2$, heat-coagulation reduces velocity of reaction by 50%. Addition of $CaCl_2$ increases the latter in the presence of dissolved egg-white by about 50%. The same acceleration is obtained by addition of the appropriate quantity of HCl. S. S. ZILVA.

Significance of the Michaelis constant for invertase. G. E. BRIGGS (Biochem. J., 1931, **25**, 1801—1806).—Theoretical. S. S. ZILVA.

Glyoxalase–co-enzyme ratio in liver tissue in inanition. P. VOGT-MØLLER (Biochem. J., 1931, **25**, 1540—1542; cf. this vol., 773).—By using Ariyama's method a considerable loss is observed in the co-enzyme of the liver tissue of starved mice. Dil. solutions of dextrose or of Na nucleate *in vitro* promote methylglyoxal dismutation in co-enzyme-free systems. S. S. ZILVA.

Antiglyoxalase. II. Methods of following glyoxalase action. J. O. GIRŠAVICIUS (Biochem. J., 1931, **25**, 1807—1814).—Glyoxalase action can be accurately investigated only by determining the acid produced. Manometric methods based on Warburg's glycolytic technique and on the author's method based on the oxidation of glyoxals by H_2O_2 in alkaline solution, are unsuitable. S. S. ZILVA.

Inhibition of glycolysis and disappearance of methylglyoxal. H. K. BARRENSCHEEN, K. BRAUN, and M. DREGUSS (Biochem. Z., 1931, **240**, 381—393).—In materials (blood, liver, kidney, muscle, yeast) in which glycolysis has been inhibited by addition of $CH_2I{\cdot}CO_2H$ added methylglyoxal disappears (even when pancreas extract containing antiglyoxalase has been added) nearly to the same extent as in those in which glycolysis proceeds undiminished. Most of the keto-aldehyde disappears very quickly after addition, and the disappearance is accelerated if the p_H is shifted to the alkaline side. The disappearance is not due to adsorption, to conversion into pyruvic acid or MeCHO, or to resynthesis of carbohydrate phosphoric esters, although only 48% at most is converted into lactic acid. W. MCCARTNEY.

Action of co-enzyme. I. Inhibition of glycolysis and elimination of ammonia. H. K. BARRENSCHEEN and W. FILZ (Biochem. Z., 1931, **240**, 409—422).—When the glycolysis in blood is inhibited by $CH_2I{\cdot}CO_2H$, $CH_2Br{\cdot}CO_2H$, NaF; or hæmolysis the amount of NH_3 produced is increased by 300—800% as compared with that produced when glycolysis proceeds undiminished. At the same time a parallel production of the " pyrophosphate fraction " from the co-enzyme occurs and the ratio of NH_3-N eliminated to P liberated is 1 : 1. When glycolysis in hæmolysed blood is produced by addition of phosphate or hydrogen carbonate the production of NH_3 is diminished as

compared with that in the hæmolysed but otherwise untreated blood and the accelerated glycolysis resulting from activation by SO_4'' is accompanied by reduced production of NH_3. It is concluded that the elimination of NH_3 is partly responsible for the inactivation of the co-enzyme, and a scheme illustrating the probable mechanism of the action of the latter, in so far as it is connected with the NH_2-group of the adenylphosphoric acid, is discussed.

W. McCartney.

An enzyme from blow-fly larvæ (*Lucilia sericata*) which digests collagen in alkaline solution. R. P. Hobson (Biochem. J., 1931, **25**, 1458—1463).—The excreta of the larvæ, whether sterile or not, contain proteolytic enzymes which digest collagen and elastin, but not keratin. The optimum reaction is at about p_H 8·5. With increasing acidity the activity of the enzyme decreases and almost disappears at p_H 4·0. Collagenase is a distinct enzyme, since it is less stable than the enzymes which act on gelatin and is also adsorbed to a greater extent by charcoal and kaolin.

S. S. Zilva.

Assay of pepsin. H. L. Greenberg (J. Amer. Pharm. Assoc., 1931, **20**, 1032—1036).—A modified Sorensen titration method is suggested to replace the official U.S.P. method.

E. H. Sharples.

Heat-inactivation of the proteinase of the pancreas. J. Pace (Biochem. J., 1931, **25**, 1485—1490).—Proteinase is adsorbed by kaolin, from which it can be eluted. The heat-inactivation of the proteinase proceeds in agreement with the unimol. formula. Its crit. increment, 35,000—40,000 g.-cal. per molar unit of enzyme, is the same in solutions containing 40, 20, and 0% of glycerol.

S. S. Zilva.

Action of pancreatin on different types of wool. G. Fromageot and A. Porcherel (Compt. rend., 1931, **193**, 788—789).—Various samples of sheep's wool subjected to the action of pancreatin at p_H 8·0 at 37—38° undergo a loss in wt., relatively rapid at first, then more gradual, which in a coarse variety may reach 82% of the original wt.

W. O. Kermack.

Nature of the proteases. A. N. Adova and I. A. Smorodinzev (Russ. J. Physiol., 1931, **14**, 64—70).—Certain relationships exist between the enzymic activity of protease preps. on the one hand and the surface tension, electrical conductivity, and n of their solutions, the content in N, NH_2- and CO_2H groups and the ratio of the two latter, on the other.

W. O. Kermack.

Proteolytic enzymes. IX. Cleavage of leucyldecarboxyglycine by intestinal erepsin. K. Linderstrøm-Lang (Compt. rend. Lab. Carlsberg, 1931, **19**, No. 3, 1—9; cf. this vol., 1190).—The enzyme component present in intestinal erepsin which hydrolyses leucyldecarboxyglycine is not the same as aminopolypeptidase, but may be identical with peptidase II.

J. H. Birkinshaw.

Activity and phosphorus content of aminopolypeptidase. A. K. Balls and F. Kohler (Naturwiss., 1931, **19**, 737).—Aminopolypeptidase from pig's intestine freed from accompanying proteolytic enzyme may be purified by precipitation with $COMe_2$. Highly purified enzyme has a high phosphate content, and this phosphate appears to be intimately related to the enzyme activity. On keeping, the activity decreases and simultaneously PO_4 ions are set free and may be removed by dialysis.

W. O. Kermack.

Action of ultra-violet and visible light on solutions of trypsin, enterokinase, and trypsin-kinase partly or wholly inactivated by heat. J. Pace (Biochem. Z., 1931, **240**, 490—493).—Solutions of such enzymes are not reactivated on irradiation with ultra-violet light of wave-length greater than 280 mμ, but, on the contrary, the partly inactivated solutions are further inactivated. The inactivating effect is increased if all the rays from a quartz lamp are allowed to act. Irradiation with visible light has no measurable effect on the activity of the solutions.

W. McCartney.

Presence of urease in the animal organism. S. Majorov (Biochem. Z., 1931, **241**, 228—232).—In the dog, the stomach, suprarenals, and ovaries contain, and the pituitary is especially rich in, urease. The mucous membrane of the stomachs of rabbits, pigs and sheep does not contain urease. Urease of the gastric mucous membrane of dogs is inactivated at 60°.

P. W. Clutterbuck.

Blood-phosphatases. J. Roche (Biochem. J., 1931, **25**, 1724—1733).—The phosphatase of the red cells differs from the phosphatases of the bone, kidney, or intestine in its optimum p_H (6·0—6·8) and in its ability to hydrolyse α-glycerophosphate more rapidly than the β-isomeride. The phosphatases of the serum or of the white cells, on the other hand, appear to be identical with bone-phosphatase, as are probably also the kidney- and intestinal phosphatases. Mono- but not di-substituted phosphoric esters are hydrolysed by these enzymes, the rate varying with the nature of the substituting group. The hydrolysis of glycerophosphate by the blood-phosphatases is diminished by the presence of inorg. phosphate or of glycerol. The phosphatases of the serum and red cells synthesise phosphoric esters from inorg. phosphate and various alcohols.

S. S. Zilva.

Phosphatases of mammalian tissues. III. Magnesium and the phosphatase system. H. D. Jenner and H. D. Kay (J. Biol. Chem., 1931, **93**, 733—748).—That Mg acts as a sp. activator of dialysed kidney-phosphatase action is confirmed (A., 1928, 671, 1157). Mg will activate all animal tissue phosphatases, including that from bone (cf. A., 1930, 112), either before or, to a greater extent, after dialysis and with α- and β-glycerophosphate, hexosediphosphate, guanine nucleotide, or pyrophosphate as substrate. The optimum concentration of Mg is q_{Mg} 1·7—3·3, where q_{Mg} is the negative log. of molarity of Mg.

F. O. Howitt.

α-Lipase activity of horse serum during the course of multiple bleeding. Z. Gruzewska and G. Roussel (Compt. rend., 1931, **193**, 786—787).—Samples of serum obtained from a horse at weekly intervals show a considerable variability, partly seasonal, in their content of α-lipase (enzyme hydrolysing glycerides) as measured by their actions on monobutyrin.

W. O. Kermack.

Direct oxidation of sugar by yeast. K. Trautwein and K. Weigand (Biochem. Z., 1931, **240**, 423—429).—Maltose is directly oxidised by *Saccharomyces Marxianus* and *S. exiguus*, organisms which cannot ferment the sugar. It follows that respiration and fermentation are not necessarily invariably connected. It is probable that sucrose is not directly oxidised by *Schizosacch. octosporus*.

W. McCartney.

Thermal constant and temperature coefficient of fermentation by expressed yeast juice and yeast maceration juice. S. Kostytschev and G. Medvedev (Bull. Acad. Sci. U.S.S.R., 1931, 655—660).—Chemical reactions in living cells may be characterised by the high vals. of their heat of activation (thermal const.), $A=\log_e(k_2/k_1)\,.RT_2T_1/(T_2-T_1)$, and of their temp. coeff. Q_{10} at low temps. For fermentations by expressed and macerated juices from yeast, no thermal const. exists; the vals. of A and Q_{10} for the two juices are very high for the range 1—12° or even for 5—12°. It is concluded that zymase is not a single enzyme and, owing to the regular formation of the same products over the temp. range 1—40°, probably not a simple mixture of different enzymes.

T. H. Pope.

Cholesterol, irradiated cholesterol, and alcoholic fermentation with beer yeast. R. de Fazi and F. Pirrone (Annali Chim. Appl., 1931, **21**, 419—435).—Cholesterol retards alcoholic fermentation of aq. dextrose solutions by beer yeast, but, after exposure in EtOH solution (1%) to the rays of a quartz Hg-vapour lamp, it accelerates the fermentation; the max. effect is obtained when the solution contains 0·05% of cholesterol previously irradiated for 60 min. at 30 cm. from the lamp. Both this accelerating action and the antirachitic effect are regarded as due to substances accompanying the cholesterol.

T. H. Pope.

Acyloins. III. Mechanism and kinetics of acyloin formation in fermentation. IV. Non-enzymic acetoin formation and the problem of "carboligase." W. Dirscherl (Z. physiol. Chem., 1931, **201**, 47—77, 78—104; cf. A., 1930, 893).—III. Fermentation of $AcCO_2H,NaHSO_3$ with dried yeast gave no acetoin, but the latter was produced on addition of MeCHO. In $AcCO_2H$ fermentation the yield of acetoin on the acid fermented steadily increases. For the same CO_2 evolution the acetoin formation is greater with the high concentrations of $AcCO_2H$. Addition of MeCHO increases acetoin formation. The action of heat on dried yeast destroys carboxylase and "carboligase" to the same extent, addition of PhMe inhibits both actions, $CHCl_3$ inhibits chiefly acetoin production, possibly owing to adsorption at the surface of the yeast prep. There is no evidence for the existence of a "carboligase."

IV. Acetoin is produced in quant. yield by irradiation of $AcCO_2H$ in H_2O at M and $0{\cdot}2M$ concentration. Without solvent or in $COMe_2$ or $CHCl_3$, decarboxylation is slower and the yield of acetoin falls. In abs. EtOH, CO_2 and acetal are produced, but no acetoin. On heating $AcCO_2H$ in a sealed tube or with Os, CO_2 is formed, but no acetoin. Decarboxylation of $AcCO_2H$ with NH_2-acids in boiling H_2O or org. solvents yields a little acetoin at high concentrations of the acid, except with EtOH, when acetal is formed. A method for determination of acetal and MeCHO when present together is described.

J. H. Birkinshaw.

Another co-enzyme of alcoholic fermentation. E. Auhagen (Naturwiss., 1931, **19**, 916—917).—A study of yeast preps. washed at p_H 7·7—7·8 which could not be activated by the addition of cozymase, Mg, and zymophosphate but were activated by boiled yeast-juice shows that another co-enzyme, cozymase II, is necessary. Boiled yeast-juice ash, adenine, adeninetriphosphoric acid, glutathione, and cysteine cannot be substituted for the boiled yeast-juice. Cozymase II is not destroyed by autolysis of the yeast, is completely destroyed at 100° at p_H 6·0, is precipitated with $Pb(OAc)_2$ and regenerated from the ppt. by H_2S.

A. Lawson.

Effects of cyanide and some other salts on fermentation by yeast preparations. L. M. B. Patterson (Biochem. J., 1931, **25**, 1593—1607).—KCN (min. concentration $0{\cdot}006M$) slows down the attainment of a max. rate in presence of phosphate without affecting the max. rate attained. The basal rate is lowered. The induction period before the onset of fermentation by zymin, dried yeast, or maceration extract is increased by KCN (min. concentration $0{\cdot}005M$). With yeast-juice (min. concentration $0{\cdot}075M$) it produces an induction period which is otherwise absent. In presence of substances which shorten the induction period of zymin and dried yeast it causes a prolongation to a smaller degree than when acting alone. With yeast-juice in presence of KCN the total acid-sol. P remains const., and there is no change except slight esterification towards the end of the induction period. During the induction period of zymin under various conditions the total and inorg. acid-sol. P increases by the same amount, whilst the org. P remains approx. const. until near the end of that period, when it increases as the inorg. P becomes esterified. In presence of KCN during the first part of the induction period there is a greater increase of acid-sol. inorg. P than of total P, due to hydrolysis of the org. P. The optical rotation and reducing power of the $CCl_3{\cdot}CO_2H$ filtrates from the fermentation mixtures show only slight changes until the end of the induction period is approached. In presence of arsenate KCN prolongs the induction period further, but the joint effect is less than the sum of the separate effects. The action of different salts on the induction period is of a different kind. Methylglyoxal shortens the induction period of fermentation with zymin and reduces both the basal rate of fermentation and the rate of esterification.

S. S. Zilva.

Mitogenetic radiation. M. Moissejeva (Biochem. Z., 1931, **241**, 1—13).—A table summarises further results.

P. W. Clutterbuck.

Production of gluconic acid by moulds. R. Schreyer (Biochem. Z., 1931, **240**, 295—325).—The production of gluconic and other acids from sucrose (in some cases also from dextrose and lævulose) by a large number of moulds (*Aspergillus*, *Penicillium*, *Rhizopus*, *Citromyces*, and others) has been investig-

ated. In almost all cases $H_2C_2O_4$ is found, whilst citric, fumaric, and unidentified acids are occasionally detected. Only some of the moulds certainly produce gluconic acid, others (including all the *Rhizopus* species tested) certainly do not produce detectable amounts, and in some cases the result is doubtful. In the absence of $CaCO_3$ small amounts only of acids accumulate, either because the increasing concentration of acid checks the process, or because continuous decomp. of acid produced takes place, or for both reasons. *P. oxalicum* produces not oxalic but citric acid. *P. corymbiferum* produces material which decomposes $CaCO_3$ without separation of a Ca salt and no malic acid can be detected. All the moulds produce invertase. It is possible that gluconic acid is actually produced in all cases, but in some is at once decomposed. W. McCartney.

Accessory factor necessary for the growth of *Nematospora gossypii*. I. Chemical nature of the factor. II. Relation of the accessory factor to "bios." H. W. Buston and B. N. Pramanik (Biochem. J., 1931, **25**, 1656—1670, 1671—1673; cf. Farries and Bell, A., 1930, 958).—I. *N. gossypii* is unable to assimilate simple N compounds in synthetic media in the absence of an "accessory factor." This factor is present in association with crude proteins from various sources and in extracts of lentils, etiolated lupin, ox-heart, cotton-leaf, potato, and yeast. It yields two inactive components on precipitation with $Ba(OH)_2$ and EtOH. The active fraction in the "$Ba(OH)_2$ and EtOH ppt." which contains inositol becomes inactive when this compound is removed and active when added again. The activity of some relatively inactive substances is greatly increased by the addition of inositol. The active substance of the fraction not precipitated by $Ba(OH)_2$ and EtOH is precipitated by $Hg(OAc)_2$ and Na_2CO_3.

II. The factor, although associated with "bios" among natural products, is not identical with it. S. S. Zilva.

Soluble enzymes secreted by *Hymenomycetes*. Comparison of antioxygenic activities of tannin and of the phenolic constituents of essential oils. L. Lutz (Compt. rend., 1931, **193**, 608—609).—The oxidation of tannin by the oxidase of *Stereum hirsutum*, *S. purpureum*, and *Coriolus versicolor* was not affected by the presence of various phenols, but the oxidation of the latter was in general reduced by the presence of tannin. The antioxidase action of tannin has probably biological significance. W. O. Kermack.

Importance of zinc for *Aspergillus niger*. M. Roberg (Zentr. Bakt. Par., 1931, II, **84**, 196—230).—Zn is a necessary nutrient for *A. niger*, but in excess has an inhibitory effect. The organism can utilise Zn in the form of oxide, sulphate, valerate, acetate, and lactate. A. G. Pollard.

Biochemistry of micro-organisms. XX. Production of mannitol from hexoses and pentoses by a white species of *Aspergillus*. F. P. Coyne and H. Raistrick (Biochem. J., 1931, **25**, 1513—1521).—Mannitol was formed by this organism in considerable amounts (15—35% of utilised sugar) from mannose, galactose, xylose, and arabinose, but not from lævulose, on synthetic media with controlled aeration. The acidity produced was practically negligible in all cases. The results are contrary to those of bacterial fermentation. S. S. Zilva.

Chemical conditions for growth and zygote formation in *Phycomyces blakesleeanus*. L. Ronsdorf (Planta [Z. Wiss. Biol. Abt. E.], 1931, **14**, 482—514).—Zygote formation is not promoted by addition of N to the substrate, but occurs when the sugar : N ratio reaches definite vals. The action of histamine in inducing zygote production is not sp. A. G. Pollard.

Action of *Aerobacter faeni* on xylose and sucrose. C. R. Breden and E. I. Fulmer (Iowa State Coll. J. Sci., 1931, **5**, 133—153).—*A. faeni* grows well when NH_4Cl is the sole source of N. The chief products are acetylmethylcarbinol, βγ-butylene glycol, EtOH, HCO_2H, AcOH, butyric, *l*-lactic, and succinic acids, H_2, and CO_2. Chemical Abstracts.

Bacteria belonging to the sub-genus *Aerobacter*. M. Grimes and A. J. Hennerty (Sci. Proc. Roy. Dublin Soc., 1931, **20**, 89—97).—With certain specimens of butter a production of gas occurs on incubation with lactose broth for 48 hr. at 21°, but not at 37°. In such cases a typical *Aerobacter* growth is produced on an eosin–methylene-blue medium. Death occurs at 62—70°. Two strains, *A. hibernicum* and *A. liquefaciens*, are described. P. G. Marshall.

Decomposition of agar-agar by an aerobic bacterium. S. A. Waksman and W. Bavendamm (J. Bact., 1931, **22**, 91—102).—An organism isolated from marine sediments rapidly attacks the hemicellulose complex of agar, utilising it as a source of energy. Much of the C was liberated as CO_2 and a portion used in the production of cell substances. For the latter purpose N is necessary, NO_3' being more effective than NH_4 salts. The organism produces an enzyme which hydrolyses mannan and starch to reducing sugars. A. G. Pollard.

Inhibition of the acetone–butyl alcohol fermentation by acids. A. M. Wynne (J. Bact., 1931, **22**, 209—237).—Complete inhibition of the fermentation of maize mash by *C. acetobutylicum* resulted from additions of numerous org. and inorg. acids to produce p_H 3·90—3·65 in the substrate. The effect is associated with a crit. $[H^{\cdot}]$ within the cell. The greater toxicity of the three chloroacetic acids as compared with AcOH is probably due to the sp. action of the Cl atom and not to $[H^{\cdot}]$. Among the lower fatty acids OH-derivatives are more toxic than the normal acids at the same p_H, although possibly the reverse is true of the 3C acids. Pyruvic, lactic, and glyceric acids were tolerated by the organism at higher $[H^{\cdot}]$ levels than for other acids. In the lower fatty series from HCO_2H to *iso*butyric acid inhibition occurs at practically the same p_H, but there is a steady rise in the crit. p_H in the higher acids up to nonoic. On the basis of molar concentration the inhibitory effectiveness declines from nonoic acid to AcOH. Capillary activity has little effect in the lower acids up to butyric, but has marked influence in the case of higher acids. A. G. Pollard.

Biochemistry of micro-organisms. XXI. Examination by the carbon balance-sheet method of the types of products formed from dextrose by species of bacteria. J. H. BIRKINSHAW, J. H. V. CHARLES, and P. W. CLUTTERBUCK (Biochem. J., 1931, **25**, 1522—1539).—The Czapek–Dox medium as used for the determination of mould metabolism (this vol., 1093) was modified for the cultivation of bacteria. 50 species were found to grow readily on this medium. 20 species were examined by the balance-sheet method at 28° and 34°. The chief classified products were volatile acids, volatile neutral substances, lactic acid, and βγ-butylene glycol. *B. asiaticus-mobilis* gave approx. 30% yield of butylene glycol. S. S. ZILVA.

Factors influencing the production of acetic acid from maize stalks by thermophilic bacteria. C. H. WERKMAN and R. H. CARTER (Proc. Iowa Acad. Sci., 1930, **37**, 51—52).—The optimum p_H for acid yield is 9·0, reduction of yield being marked outside the range p_H 8·5—9·5, and the optimum temp. 63°. Grinding the cobs to increase the surface area increased the rate of fermentation and the yield of acid. CHEMICAL ABSTRACTS.

Isomeric forms of lactic acid produced in milk by some of the anaerobes. R. V. HUSSONG and B. W. HAMMER (Iowa State Coll. J. Sci., 1931, **5**, 167—170).—When grown on skim-milk, *C. butyricum* produced *i*-lactic acid, whilst *C. Welchii* gave *d*- or *d*-+*i*-lactic acid. CHEMICAL ABSTRACTS.

Optical modifications of lactic acid produced by *Bacterium bulgaricum*. A. KANTARDIEV and I. POPPOV (Milchwirt. Forsch., 1931, **11**, 368—370; Chem. Zentr., 1931, i, 2889).—Two strains gave, respectively, in milk *l*-, *l*-; in sugar-bouillon *i*-, *l*-; in wort *l*-, *i*-lactic acid. A. A. ELDRIDGE.

Lactic acid fermentation by *B. acidificans*. Laf. H. SCHRADER (Zentr. Bakt. Par., 1931, II, **84**, 1—20).—Volatile acids, notably AcOH and HCO_2H, always accompany the lactic acid produced by *B. acidificans*. The organism, in the presence of CaO, can withstand a temp. of 100° without appreciable effect on its fermentative power. The use of carbonates of Cu, Pb, Ba, or Zn to check fermentation is unsatisfactory. *B. acidificans* cannot transform methylglyoxal, glycerose, or glycerol into lactic acid. Its optimum p_H for acid production is 6·0. A. G. POLLARD.

Action of certain bacteria on uric acid and its derivatives. R. F. HANZAL and E. E. ECKER (Proc. Soc. Exp. Biol. Med., 1931, **28**, 815—816).—*Bacterium acidi urici*, Ulpiani, destroyed 30% of the uric acid in 12 hr. and 100% in 24 hr.; *A. aerogenes* destroyed it in 40 hr. at 37°; 1- and 3-methyl-, 1 : 3- and 3 : 9-dimethyl-, and 1 : 3 : 7-trimethyl-uric acid were not attacked. CHEMICAL ABSTRACTS.

Chemistry of bacteria. I. Lipins of diphtheria bacteria. II. Lipin distribution in acid-fast bacteria. E. CHARGAFF (Z. physiol. Chem., 1931, **201**, 191—198, 198—207).—I. Diphtheria bacilli contain 4·9% of material extracted by Et_2O; $CHCl_3$-sol. material is practically absent. The phosphatide (0·41%) contains P 1·42% and N 0·79%, corresponding with a monoaminomonophosphatide. The $COMe_2$-sol. fat (4%) has acid val. 126·5, sap. val. 176·5, I val. 61·5.

II. The $COMe_2$-sol. fat of the turtle-tubercle bacillus has sap. val. 188·8 and I val. 52·4. It is in part a fatty acid compound of a polysaccharide. No sterols are found. The fats were further subdivided into liquid and solid fractions. The phosphatide has 3·16% P and 0·39% N.

The fat of the smegma bacillus has sap. val. 183·9 and I val. 45·0. The phosphatide has 2·36% P and 0·39% N. No polysaccharide is present. Culture of bacteria on glycerol bouillon appears to increase the $COMe_2$-sol. fat fraction. J. H. BIRKINSHAW.

Variability of tubercle bacilli. IV. Antigenic properties of *S* and *R* cultures. C. E. RICE (Canad. J. Res., 1931, **5**, 375—388).—The change from *S* to *R* type in human or bovine tubercle bacilli is accompanied by loss of sp. antigenic activity in the complement fixation reaction. Antisera prepared from *R* organisms lack antibodies against certain substances present in the *S* organisms, but they contain a higher proportion of antibodies reacting with related acid-fast organisms than do the corresponding *S* antisera. W. O. KERMACK.

Fixation of atmospheric nitrogen and formation of ammonia by *Azotobacter*. S. P. KOSTYTSCHEV and SHELOUMOVA (Bull. Acad. Sci. U.S.S.R., 1931, 661—671).—NH_3 is the first identifiable product of the fixation of atm. N_2 by *Azotobacter*; its formation occurs only in presence of energy-providing material. *A. Winelandii* forms NH_3 by destruction of org. N compounds; with glycine and peptone, this process consists of deamination. Such secondary formation of NH_3 is possible only after the complete consumption of the energy-providing material, and hence differs sharply from the primary formation. Each of these reactions takes place only in living cultures. *A. Winelandii* is not killed when kept for 2 days in an O_2-free atm., but in absence of O_2 fixation of atm. N_2 is greatly retarded. T. H. POPE.

Assimilation of molecular nitrogen by micro-organisms. J. BLOM (Zentr. Bakt. Par., 1931, II, **84**, 60—86).—In the utilisation of free N_2 by micro-organisms, the initial stage involves the production of NH_2OH brought about by complex Fe-bearing catalysts. This process is adversely affected by the presence of O_2, NH_3, or NO_3'. A. G. POLLARD.

Dimethyl-α-naphthylamine for the determination of bacterial reduction of nitrates. C. H. WERKMAN (Proc. Iowa Acad. Sci., 1930, **37**, 53—55).—Dimethyl-α-naphthylamine is superior to α-naphthylamine, but the sensitivity is unchanged; the coloration is permanent and the reagent does not become turbid, the brown discoloration which appears on keeping not interfering with the test. CHEMICAL ABSTRACTS.

Reduction of nitrates by *B. coli*. L. H. STICKLAND (Biochem. J., 1931, **25**, 1543—1554).—*B. coli* reduces nitrate completely to nitrite. After PhMe treatment it oxidises formate, lactate, and succinate to CO_2, pyruvate, and fumarate, respectively, by means of nitrate to the same degree as with O_2.

Treatment with PhMe causes a marked change in the p_H–velocity-curve. The variation of the lactate concentration within narrow limits about $0{\cdot}02M$ causes no great difference in the reaction velocity. The reduction can be completely inhibited by KCN, but not by CO, 50% inhibition being produced by about $0{\cdot}0001M$-KCN. O_2 causes a non-competitive inhibition of nitrate reduction which is partly removed by CO. S. S. ZILVA.

Biological decomposition of plant materials. V. Factors determining the quantity of nitrogen immobilised during decomposition. E. H. RICHARDS and A. G. NORMAN. **VI. Effect of [H˙] on the rate of immobilisation of nitrogen by straw.** A. G. NORMAN (Biochem. J., 1931, **25**, 1769—1778, 1779—1787).—V. There is no direct relationship between the composition of plant materials and the amount of additional available N immobilised during decomp. (" N factor "). The " N factor " does not represent the whole N active in decomp.; the N of plant-proteins and bacteria may also be utilised. Plant material already containing sufficient or more than sufficient N for decomp. may utilise inorg. N for preference. The N requirements for the decomp. of equal amounts of org. matter (" the nitrogen equivalent ") is an index of the efficiency of the active organisms.

VI. Available N in high dilutions percolating straw filters is immobilised more rapidly under slightly alkaline conditions in the early stages than in either slightly acid or neutral conditions, and ultimately more N is retained. Neutral conditions are more favourable than acid. More org. matter is fermented under alkaline than under neutral conditions and more under neutral than under acid conditions. The alkaline filter shows an initial lag due to the development of a primary flora not very active in cellulose decomp. The loss of hemicelluloses is more gradual in filters than in compost heaps because of the difference in character of the active flora. S. S. ZILVA.

Bacterial chymases. C. GORINI (Atti Pontif. Accad. Sci., 1929, **83**, 66—69; Chem. Zentr., 1931, i, 2629).

Stain for fibrin, Gram-positive bacteria, and basal bodies in tissues. H. M. WALLACE (Science, 1931, **74**, 369—370).—Modifications of the Weigert and Gram–Weigert methods for fibrin and Gram-positive bacteria, respectively, are described. L. S. THEOBALD.

Use of commercial and synthetic maltose in biological research. W. H. SCHOPFER (Helv. Chim. Acta, 1931, **14**, 1067—1069).—The development of a fungus (*Phycomyces*), cultivated on a medium containing maltose (I), asparagine, $MgSO_4$, and KH_2PO_4 varies appreciably with the source of (I). Development is much less marked with synthetic (A., 1927, 752) and greatest with Kahlbaum's commercial maltose. It is suggested that a vitamin-*B*-like impurity is present in the last-named variety. H. BURTON.

Vitamins and the growth of bacteria. F. HODER and A. BREUER (Z. Immunität., 1931, **70**, 279—288; Chem. Zentr., 1931, i, 2895).—Active factors, probably the known vitamins, are present in various fruit and vegetable juices. That present in coconut-milk (" factor *Z* ") is insol. in fat or Et_2O, and is therefore not vitamin-*A* or -*D*. A. A. ELDRIDGE.

Appearance and evolution of anti-bodies in horses injected with diphtheria antigens. A. BESSEMANS, G. RAMON, and F. DE POTTER (Ann. Inst. Pasteur, 1931, **47**, 358—373).

Bacterial toxins. I. Tetanus toxin. E. MASCHMANN (Z. physiol. Chem., 1931, **201**, 219—254).—A toxin prep. was obtained by saturation of the culture fluid (bouillon) with $(NH_4)_2SO_4$. The dry material had about 6 times the activity of the original fluid and was fairly stable. For further purification $Al(OH)_3$ at p_H 6 was the most suitable adsorbent. With kaolin (optimum p_H 3·8) the initial concentration of the aq. spasmin has a large effect; cerebrone and cholesterol were very inefficient. Spasmin is regenerated from the adsorbate with alkaline phosphate solution or 0·05% aq. NH_3, followed by precipitation of the phosphate with MgO mixture or removal of $NH_4^{\cdot}$ by dialysis. $Al(OH)_3$ and kaolin adsorbates yield the whole of their toxin to serum. The antigenic property of spasmin is present in the adsorbate and is destroyed by treatment of the latter with antitoxin. In the purest prep. the spasmin was present in 210—240 times the original concentration. The mol. does not contain tyrosine, tryptophan, or the group giving the biuret reaction. J. H. BIRKINSHAW.

Immunological value of anatoxin derived from purified tetanus toxin. S. HOSOYA, M. TAKADA, and S. TERAO (Japan. J. Exp. Med., 1931, **9**, 33—38).—The prep. of the purified tetanus toxin (A., 1929, 1109) is described. Subcutaneous injection of the neutralised anatoxin prepared by incubating the toxin with 0·4% CH_2O at 37° for 48 hr. produced no tetany in mice even when the injection corresponded with 5000 min. lethal doses of the toxin. High antitoxic immunity against the purified toxin and tetanus bacilli could be produced (in guinea-pigs) by two injections of the neutral formolised anatoxin. A. LAWSON.

Cryptotoxins. Phenomenon of the supersaturation of toxins by the salicylic ion. H. VINCENT (Compt. rend., 1931, **193**, 620—623).—The complex formed by tetanus toxin and salicylic acid (A., 1928, 674) is very stable, resisting the dissociating effect of $CaCl_2$, $(NH_4)_2SO_4$, or EtOH. When brought to p_H 4·7 by *N*-HCl, part of the toxin is separated but not destroyed. Toxicity tests carried out with the dialysed solution and the dialysate obtained from the salicylic–tetanus toxin complex, and on the effect of progressive increase of the ratio tetanus toxin/salicylic acid in the incubated complex, indicate that there is a supersaturation of the toxin by the salicylic acid in the original complex, although the part played by the non-toxic proteins may be connected with this result. A. LAWSON.

Immunisation against toxins and the production of antitoxins. Mixtures of specific antigen and non-specific substances. G. RAMON (Ann. Inst. Pasteur, 1931, **47**, 339—357).

Inactivation and reactivation of the virus of herpes. J. R. PERDRAU (Proc. Roy. Soc., 1931, **B**, **109**, 304—308).—Treatment with O_2 destroyed or reduced the infectivity of 4 out of 13 broth filtrates of this virus. The virus is reactivated by hydrogenation in the presence of colloidal Pd, or by cysteine. The filtrates resistant to O_2 are not sensitised by addition of tyrosinase or sufficient H_2O_2 to neutralise catalase.
A. COHEN.

Effect of bacteriophage on oxidation–reduction potentials of *B. dysenteriæ* (Shiga) cultures. L. F. HEWITT (Biochem. J., 1931, **25**, 1447—1451).—The organism possesses feeble reducing powers and resembles in this respect the catalase-containing and not the peroxide-forming bacteria. The bacteriophage itself has no effect on the oxidation–reduction potential, but it inhibits the usual fall in potential of *B. dysenteriæ* cultures by inhibiting the growth and metabolic activation of the bacteria. S. S. ZILVA.

Effect of bacteriophage on the oxidation–reduction potentials of *B. coli communis* cultures. L. F. HEWITT (Biochem. J., 1931, **25**, 1641—1646).—The potential of *B. coli* cultures falls to a lower level and much more rapidly, especially in the presence of dextrose, than in the case of other bacteria. In presence of bacteriophage this fall and also the proliferation of the bacteria are delayed, but not inhibited. The effect of bacteriophage on the oxidation–reduction potential follows the effect on the proliferation of the bacteria except that in aerobic dextrose broth cultures of *B. coli* containing bacteriophage there is an initial fall in potential without appreciable bacterial growth. S. S. ZILVA.

Effect of lysozyme on the oxidation–reduction potentials of *M. lysodeikticus* cultures. L. F. HEWITT (Biochem. J., 1931, **25**, 1452—1457).—Cultures of this organism contain catalase and do not form peroxide. Growth is more luxuriant and the fall in potential is greater in aerated cultures than in stationary aerobic cultures. The organism contains cytochrome which does not catalyse anaerobic oxidation–reduction reactions. Lysozyme (egg-white or human tears) produces a rapid fall in potential in the cultures followed by a rise before lysis is complete. The older is the culture the slower is the fall and subsequent rise. S. S. ZILVA.

Photodynamic action of certain dyes on the inactivation of *Staphylococcus* bacteriophage. C. E. CLIFTON (Proc. Soc. Exp. Biol. Med., 1931, **28**, 745—746).—The bacteriophage was inactivated by incubation with methylene-blue (0·01—0·1%) in presence of both sunlight and air. Cysteine hydrochloride acts as a protective agent. The inactivation is probably due to oxidation of the bacteriophage by photosensitive methylene-blue in presence of O_2.
CHEMICAL ABSTRACTS.

Germicidal activity of essential oils. S. L. MALOWAN (Z. Hyg., 1931, **112**, 93—94; Chem. Zentr., 1931, i, 3479).—The physical behaviour of essential oils (solubility in dil. EtOH) is related to bactericidal activity, aldehydic oils, which are particularly active, being also readily sol. A. A. ELDRIDGE.

Biological action of inorganic compounds. I. Activity of various heavy-metal compounds on bacteria, blood parasites, and experimental mouse cancer. F. KRAUSS and W. A. COLLIER (Arch. exp. Path. Pharm., 1931, **162**, 452—462).—Salts of various heavy metals were inactive against trypanosomes and the spirochætes of relapsing fever. $NiCl_2$, $Cr_2(SO_4)_3$, $PbCO_3$, $PbSO_4$, and $K[Pb_2Cl_5]$ act weakly and $CoSO_4$ and smalt act more strongly on gonococci in the peritoneal cavity of the mouse. $K_2Cr_2O_7$ and K heptanitrosotrithiotetraferriate exhibit marked bactericidal properties *in vitro*. Certain compounds of Cr, Ru, Mn, and Pb are active in experimental mouse cancer. W. O. KERMACK.

Human blood-calcium. IV. G. HETENYI and A. VON GAÁL (Z. ges. exp. Med., 1931, **75**, 516—521; Chem. Zentr., 1931, i, 3019).—Adrenaline causes a fall in blood-Ca. A. A. ELDRIDGE.

Sugar exchange of the liver. II. Free sugar content of liver and variations caused by insulin and adrenaline. H. MOLITOR and L. POLLAK (Arch. exp. Path. Pharm., 1931, **162**, 488—505).—The true blood-sugar of the liver of fasting rabbits and of dogs has mean vals. of 0·097% and 0·066%, respectively, in both cases lying between 70 and 80% of the normal blood-sugar. The administration of insulin quickly decreases the free sugar of the liver, the fall occurring not later than the fall in blood-sugar. Insulin, therefore, acts directly on the liver, presumably inhibiting glycogenolysis. After the administration of adrenaline the rise in liver-sugar is more marked than that of the blood-sugar. W. O. KERMACK.

Tissue metabolism in pancreatic diabetes and the effect of insulin thereon. H. LASER (Biochem. Z., 1931, **241**, 36—49).—The respiration and lactic acid exchange of the tissue of normal and diabetic hens in hen's serum under physiological pressures of CO_2 with and without addition of insulin are investigated. The respiration is decreased and aerobic lactic acid formation increased in the muscle of the diabetic animal; addition of insulin leads to normal vals.
P. W. CLUTTERBUCK.

Action of insulin on fat metabolism in normal and depancreatised dogs. H. TANGL (Biochem. Z., 1931, **241**, 87—93).—Insulin brings about the conversion of fatty into strongly unsaturated acids, during the disappearance of which the blood-sugar rises. The unsaturated acids are therefore regarded as possible intermediates in the conversion of fat into sugar. P. W. CLUTTERBUCK.

Duodenin, the hypoglycæmic hormone of the intestinal mucous membrane. J. HELLER (Wien. klin. Woch., 1931, **44**, 476; Chem. Zentr., 1931, i, 2894).—An extract of the small intestine of the ox or rabbit reduces alimentary hyperglycæmia or normal blood-sugar; it is also effective when taken orally.
A. A. ELDRIDGE.

Variations in blood-sugar after administration of posterior pituitary extracts. J. LA BARRE (Ar. Int. Pharm. Ther., 1930, **38**, 409; Chem. Zentr., 1931, i, 3136).—Hyper- is followed by hypo-glycæmia; the former is due to increased excretion of adrenaline and the latter to hyperinsulinæmia.
A. A. ELDRIDGE.

Effect of anterior pituitary hormone on the growth and metabolism of the uterus. W.

Bungeler and K. Ehrhardt (Klin. Woch., 1931, **10**, 593—595; Chem. Zentr., 1931, i, 2632).—In mice considerable glycolysis takes place; it exceeds respiration by 20%. The metabolic change appears to precede the stimulation of growth.

A. A. Eldridge.

Hormones of the anterior pituitary lobe. III. Prolan-*A* and tumours. IV. Clinical analysis of urine and detection of prolan-*A*. B. Zondek (Klin. Woch., 1930, **9**, 679—682, 1207—1209; Chem. Zentr., 1931, i, 3368).—III. Prolan-*A* is present in the urine in genital carcinoma and sometimes in benign and extragenital malignant tumours.

IV. The urine is slightly acidified with AcOH, treated with 5 vols. of EtOH, and after 24 hr. the ppt. is washed with Et_2O and dissolved in H_2O. The aq. solution contains the hormone. In urine of pregnancy prolan-*A* and -*B* are present, but could not be separated with certainty.

A. A. Eldridge.

Oral administration of gonadic extracts to guinea-pigs. H. Beuchelt (Naturwiss., 1931, **19**, 881).—Experiments on wt. increase in mature males and females produced by oral administration of sherry extracts of the gonads of the opposite sex.

P. G. Marshall.

Inter-relations between lactic acid and sugar in the blood under the influence of certain hormones. A. I. Osolin (Russ. J. Physiol., 1931, **14**, 135—151).—" Ovarikrin " has little influence on the carbohydrate metabolism of female rabbits, but its effect is more noticeable on the blood-lactic acid and -sugar of males. Insulin decreases blood-sugar without altering the lactic acid level, whilst adrenaline causes parallel increases in both lactic acid and sugar.

W. O. Kermack.

Œstrus-producing hormone (menformone). A. Identity of the substance from the urine of pregnant women with that from the urine of pregnant mares. S. E. de Jongh, S. Kober, and E. Laqueur. **B. Crystalline form of the substances.** W. Nieuwenkamp and S. Kober. **C. Absorption spectrum of crystallised menformone samples of different origin.** E. Dingemanse, S. Kober, E. H. Reerink, and A. van Wijk (Biochem. Z., 1931, **240**, 247—262, 263—264, 265—267).—A. Menformone from the urine of pregnant mares (Zondek, this vol., 878) is identical with that from the urine of pregnant women. The œstrus-producing effect in mice and the effect on the undeveloped uterus in rats, on the breasts of male guinea-pigs, and on the genitals of male rats of the two substances is of the same order. Both have the same solubility in org. solvents, the same m. p., and the same optical properties, and both can be distilled in a high vac. The chemical compositions of the substances are the same and their acetates and benzoates are identical. When crude menformone from the urine of pregnant mares is fractionally recryst. from EtOH a *substance*, m. p. 211°, having the same composition as the pure hormone, but only two thirds of its physiological activity, is obtained. This substance may be a mixture containing menformone.

B. Crystallographic examination shows that the substance from the urine of pregnant women has the same form as has that from the urine of pregnant mares and also the theelol described by Slawson (this vol., 790). The menformone crystallised from $CHCl_3$ probably contains solvent of crystallisation and has a form different from that of material crystallised from EtOH.

C. The ultra-violet absorption spectrum of menformone from the urine of pregnant women is identical with that of the menformone from the urine of pregnant mares.

W. McCartney.

Assay of male sexual hormone in commercial testicular preparations. S. Loewe, H. E. Voss, and F. Lange (Arch. exp. Path. Pharm., 1931, **162**, 633—648).—Of 26 preps. tested by the method of cytological regeneration (cf. this vol., 658) 16 were inactive, 9 had a potency of 0·1—0·7, and the remaining sample one of 12·0 mouse units per dose.

F. O. Howitt.

Action of thyroxine. H. H. Meyer (Ar. Int. Pharm. Thér., 1930, **38**, 1—8; Chem. Zentr., 1931, i, 3136).—General physiological and special pharmacological actions of adrenaline are differentiated and discussed.

A. A. Eldridge.

Action of thyroxine on tissue metabolism. A. Hopping (Proc. Soc. Exp. Biol. Med., 1931, **28**, 726—728).—Blood from an alligator which had received an injection of thyroxine had a metabolism 150—100% above the normal; direct addition of thyroxine to the blood produced no change.

Chemical Abstracts.

Influence of the thyroid gland on the regulation of the blood-sugar. V. G. Baranov (Arkh. Biol. Nauk, 1930, **30**, 603—608).—Administration of thyroidin to thyroidectomised dogs does not produce any const. changes in the fasting blood-sugar level. The effect of thyroidectomy on the tolerance curves is counteracted. Thyroidectomy is without effect on the renal threshold for sugar.

Chemical Abstracts.

Influence of the thyroid–parathyroid system and of the sympathetic nervous system on the blood-serum calcium. E. N. Speranska-Stepanova (Arkh. Biol. Nauk, 1930, **30**, 593—600).—Decerebration of cats caused a brief increase in serum-Ca if the thyroid circulation was left intact. Strong cerebral irritation with simultaneous exclusion of thyroid circulation produced an increase in serum-Ca. Removal or exclusion of the thyroid system may produce prolonged increase in serum-Ca.

Chemical Abstracts.

Suppression of raised basal metabolism during thyroid feeding. I. Abelin (Naturwiss., 1931, **19**, 752—753).—The restriction of the development of hyperthyroidism is studied further (this vol., 865). The amount of di-iodotyrosine administered is important. If too much is given hyperthyroidism may be intensified.

W. R. Angus.

Influence of parenteral injection of thyroid gland-cell substance on blood-fat and -lipin. III, IV. S. Sakurai (Japan. J. Exp. Med., 1931, **9**, 1—14, 15—20).—III. The parenteral injection of ox testicle, cow ovary, and ox pancreas emulsions into the rabbit causes in each case a preliminary decrease in blood-cholesterol, lecithin, and total fatty acid, followed by a tendency to increase to original levels

6 hr. after injection. The parenteral injection of ox marrow and suprarenal cortex causes an increase in both cases of blood-cholesterol, lecithin, and total fatty acid, the normal vals. being regained after 6 hr. Injection of an emulsion of ox pituitary causes a slight increase in blood-cholesterol, lecithin, and total fatty acid with a return to original val. after 6 hr. The functions of the internal secretion organs are therefore closely related to the fat and lipin content of the blood, and injection of cell emulsions causes influences resembling hyperfunction of the cells employed.

IV. A summary of previous work is given, from which it is concluded that a close relationship exists between the various organs of internal secretion in their mutual control of metabolism. A. LAWSON.

Detection of substances with thyroid-like activity in iodoproteins after tryptic digestion or hydrolysis with barium hydroxide. H. MATTIS (Arch. Pharm., 1931, **269**, 442—448).—Prolonged tryptic digestion of iodoprotein (6·5% I) gives a sol. product (I) (3·71% I), which has the same action on axolotl as a thyroid prep. Fractionation of (I) by Dakin's BuOH method and assay of (*a*) the cryst. material separating when the BuOH extract is cooled, (*b*) BuOH-sol., and (*c*) BuOH-insol. products show that only (*a*) is active. Hydrolysis of the iodoprotein with saturated $Ba(OH)_2$ and neutralisation of the hydrolysate with AcOH gives an active product (19·47% I) (similar to that described by Romeis, A., 1923, i, 267), separable by Dakin's method into active (as *a*) and inactive (as *b* and *c*) fractions. These fractions give H_2O-sol. and -insol. Cu salts when treated with $CuCO_3+Cu(OH)_2$ at 30—35° in vac.
H. BURTON.

Method of R. Hunt [of thyroid hormone assay]. VI. Dependence of hormone content of the thyroid gland on alimentary and hormonal factors. H. PAAL and W. HUBER (Arch. exp. Path. Pharm., 1931, **162**, 521—536).—The hormone content of thyroid glands of rats on a normal ration as determined by the MeCN-toxicity method (B., 1926, 27) agrees approx. with that of ox-glands (A., 1926, 644). Increase of carbohydrate and protein in the food results in an increase of 100% in the hormone content. Within certain limits the greater is the protein content of the food the greater is the increase in hormone content due to an increment in the carbohydrate intake. Addition of inorg. I to the food produces only a small increase in hormone content, whilst thyroxine, di-iodotyrosine, and similar substances are effective. Injection of insulin inhibits the increase of hormone due to certain diets. Anterior pituitary lobe preps. have an action similar to that of thyroxine. Diets very poor in protein are not always suitable for hyperthyroidism. F. O. HOWITT.

Results of work on vitamin-*A* and -*D*. S. SCHMIDT-NIELSEN and S. SCHMIDT-NIELSEN (Tidsskr. Kjemi Berg., 1931, **11**, 63—68, 84—88).—A review.
H. F. HARWOOD.

Colour reactions of vitamin-*A*. M. FABERI and G. SANDICCHI (Arch. Ist. Biochim. Ital., 1931, **3**, 249—262).—An approx. method for the colorimetric determination of vitamin-*A* by the $SbCl_3$ reaction is described. Vitamin-*A* in cod-liver oil is destroyed by ultra-violet radiation. The milk of the cow, ewe, or ass contains similar amounts of vitamin-*A*, which is destroyed by boiling in air or autoclaving. Known constituents of milk do not give the reaction. Human milk contains vitamin-*A* and the extracted fat gives the $SbCl_3$ reaction even when occurrence of rickets in the child indicates deficiency of vitamin-*D*
R. K. CALLOW.

Colour reactions of vitamin-*A*. K. TAKEDA (Trans. Tottori Soc. Agric. Sci., 1930, **2**, 1—37).—The most trustworthy tests are those employing $AsCl_3$, 1 : 120 $SbCl_5$, kaolin, fuller's earth, and 30% $SbCl_3$.
CHEMICAL ABSTRACTS.

Highly-concentrated vitamin-*A* preparations. H. VON EULER and P. KARRER (Helv. Chim. Acta, 1931, **14**, 1040—1044).—The smallest daily dose (per rat) of the highly-purified vitamin-*A* prep. (I) from *Hippoglossus* (following abstract) causing distinct growth is 0·0005 mg. The activities of different preps. do not parallel their $SbCl_3$ reactions. More active preps. can be obtained from the liver oils from *Scombresox saurus* (II) and *Bothus maxianus* (III). (I) shows absorption max. at 316 and 328 mμ, (II) at 318 and 331 mμ, and (III) at 328—330 mμ.
H. BURTON.

Vitamin-*A* from fish oils. P. KARRER, R. MORF, and K. SCHOPP (Helv. Chim. Acta, 1931, **14**, 1036—1040).—The unsaponifiable matter of the oil extracted from the liver of *Hippoglossus* by low-boiling petroleum is freed from sterols by cooling a solution in MeOH at −15° and −60° and the petroleum-sol. residue fractionally adsorbed on fibrous Al_2O_3. A fraction (I) is thereby obtained as a viscous yellow oil which distils (partly undecomposed) in a high vac., shows a Carr–Price reaction of 10,500 units, and has the characteristic reactions of a carotene derivative. (I) has *M* 320 (cf. this vol., 771), C 83—84, H 10·5%, contains O, is reduced slowly (with loss in activity) by Al-Hg in Et_2O, resists catalytic reduction, and is oxidised by O_3 and $KMnO_4$ yielding geronic acid and AcOH, respectively, thus indicating the presence of β-ionone and :CMe·C: groups, respectively. The coloration of (I) with conc. H_2SO_4 resembles that with dihydrocrocetin and indicates the presence of 6 double linkings. The limiting dose of (I) per day per rat is 0·005 mg. H. BURTON.

Physiological standardisation of vitamin-*A*. M. JAVILLIER and L. EMERIQUE (Bull. Soc. Chim. biol., 1931, **13**, 771—778).—See A., 1925, i, 1364.
C. C. N. VASS.

Effect of artificial drying on the vitamin-*A* content of alfalfa. S. M. HAUGE and W. AITKENHEAD (J. Biol. Chem., 1931, **93**, 657—665).—Artificial drying by hot air or flue-gas preserves the vitamin-*A* content, whilst field-drying results in a considerable loss due, not to the action of sunlight, but to enzymic activity. F. O. HOWITT.

Vitamin-*B* content of vegetables. M. C. HOUSE, P. M. NELSON, and E. S. HABER (Iowa Agric. Exp. Sta. Res. Bull., 1930, No. 120, 335—344).—The cortex of carrot contains more vitamin-*B* than the xylem and the periderm more than the cortex. Lettuce, kohl-rabi, and tomatoes grown under glass have as

great vitamin-*B* activity as when grown in direct sunlight. Storage for 5 months did not alter the vitamin-*B* content of carrots. A. G. POLLARD.

Growth-promoting properties (vitamin-*B* complex) of the concentrated water-soluble portion of milk. G. C. SUPPLEE, O. J. KAHLENBERG, and G. E. FLANIGAN (J. Biol. Chem., 1931, **93**, 705—725).—Commercial casein is not always freed from vitamin-B_1 and -B_2 by washing with dil. acid. A basal diet supplemented by a limited amount of rice polishings provides sufficient of the vitamins to animals used in the assay of the two factors. The conc. H_2O-sol. fraction of milk after removal of the proteins and most of the lactose is rich in the growth-promoting and antipellagric vitamins, the antineuritic vitamin being present in the least amount. Growth may occur despite wide variations in the amount of rice polishings and H_2O-sol. milk fraction present in the diet. The growth-promoting properties of the concentrate are decreased by autoclaving at 120° for 5 hr. or by ultra-violet irradiation. The necessity for factors other than B_1 and B_2 is indicated.

F. O. HOWITT.

Vitamin-*B* complex of yellow yautia (*Xanthosoma sagittæfolium*) and of plantain (*Musa paradisica*, L.). J. H. AXTMAYER (Porto Rico J. Pub. Health Trop. Med., 1930, **6**, 229—232).—Vitamin-B_1 is the first limiting factor of the vitamin-*B* complex of yellow yautia, and vitamin-B_2 that of plantain.

CHEMICAL ABSTRACTS.

Parallelism between phytase and so-called vitamin-*B* activity in acceleration of development of micro-organisms. C. ARNAUDI (Boll. chim. farm., 1931, **70**, 713—715).—There is complete parallelism between the phytase activity of vitamin-*B* concentrates and their ability to stimulate the growth of yeast and other micro-organisms, and this extends also to their vitamin-*B* potency determined by animal tests (cf. this vol., 1098). R. K. CALLOW.

Nutrition. XI. Comparative vitamin-B_1 values of foodstuffs. Fruits and vegetables. R. H. A. PLIMMER, W. H. RAYMOND, and J. LOWNDES (Biochem. J., 1931, **25**, 1788—1800).—Fresh fruits and vegetables have a much lower vitamin-B_1 content than cereals and pulses, but if their high H_2O content is considered the comparison is more favourable. The following are the vals. of the more potent calc. on dry wt.: yeast 100, cereals 10, pulses 13, orange juice 20, orange peel 13, tomatoes 20, cabbage 13, watercress 20, artichokes 9, leeks 10, parsnips 12, and potatoes 12. S. S. ZILVA.

Blood-sugar level in vitamin-B_1 deficiency. M. E. BELL (Biochem. J., 1931, **25**, 1755—1768; cf. A., 1927, 78; 1930, 118).—There is a marked rise in "true sugar" during the convulsive stage in vitamin-B_1-deficient pigeons, but there is no such increase in the case of vitamin-B_1-deficient rats, nor is there a rise in the non-sugar reducing substances or cell vol. of the blood of vitamin-B_1-deficient pigeons or rats. There is usually a fall in blood-sugar in the premortal stages of vitamin-B_1-deficient rats; on the other hand, pigeons dying from convulsions or from hydropericardium are often hyperglycæmic. Heart-blood from rats killed rapidly has a higher sugar content than the blood taken from the tail of the same animal during life. Different vals. were obtained by various sugar methods with human and pigeon blood. S. S. ZILVA.

Hæmatopoietic function in avitaminosis. VI. Vitamin-B_2 deficiency. B. SURE, M. C. KIK, and M. E. SMITH (Proc. Soc. Exp. Biol. Med., 1931, **28**, 498—499). CHEMICAL ABSTRACTS.

Pathogenesis of avitaminosis-*B* and its connexion with the lack of certain enzymes in deficient diet. E. CUBONI (Boll. chim. farm., 1931, **70**, 715—717).—Lysocytin is without action on avitaminosis-*B*. Phytase from rice husk and germ (Belfanti's phosphatase, this vol., 1098) cures polyneuritis in pigeons and, less satisfactorily, in fowls and turkeys. R. K. CALLOW.

Effect of ultra-violet irradiation on the antiscorbutic vitamin of liquid and of dry milk. G. C. SUPPLEE and O. D. DOW (Amer. J. Dis. Children, 1931, **41**, 1353—1362).—Irradiation of dry milk for 3—20 min. under conditions which impart antirachitic properties causes no destruction of vitamin-*C*; liquid milk suffers slight loss of vitamin-*C*.

CHEMICAL ABSTRACTS.

Crystalline vitamin-*D*. F. A. ASKEW, H. M. BRUCE, R. K. CALLOW, J. ST. L. PHILPOT, and T. A. WEBSTER (Nature, 1931, **128**, 758).—When calciferol (this vol., 881) is heated at 180° "pyrocalciferol," an inactive substance of high dextrorotation, is formed. The calciferol previously described probably contained this substance as the main impurity in the 30—50% of inactive material present. *Calciferyl* 3 : 5-*dinitrobenzoate* has m. p. 145—147°, $[\alpha]_{5461}^{20}$ +104° in $COMe_2$, +68° in C_6H_6, and *pyrocalciferyl* 3 : 5-*dinitrobenzoate*, m. p. 167·5—169·5°, $[\alpha]_{5461}^{0}$ +250° in C_6H_6. On hydrolysis these esters give, respectively, calciferol, m. p. 114·5—117°, $[\alpha]^{20}{}_{1}$ +119·5°, $[\alpha]_D^{20}$ +105° in EtOH, $[\alpha]_{5461}^{0}$ +99°, $[\alpha]_D^{20}$ +81° in $COMe_2$, antirachitic activity 40,000 International units per mg.; the solution in EtOH has an intense absorption band with a max. ε 46·0 at 265 mμ; and *pyrocalciferol*, m. p. 92—94°, $[\alpha]_{5461}^{20}$ +608°, $[\alpha]_D^{20}$ +494° in EtOH, antirachitic activity none; the solution in EtOH has an absorption band with max. ε 15·7 at 296 mμ, 27·1 at 284 mμ., and 26·1 at 274 mμ.

Calciferol and pyrocalciferol have the same empirical formula as ergosterol. Calciferol is not identical with vitamin-D_1 (this vol., 1098), but closely resembles -D_2 in physical properties. It is a direct product of the irradiation of ergosterol. L. S. THEOBALD.

Crystalline vitamin-D_1. A. WINDAUS, A. LUTTRINGHAUS, and M. DEPPE (Annalen, 1931, **489**, 252—269).—*Vitamin*-D_1, $C_{27}H_{42}O$, m. p. 124—125°, sublimes undecomposed at 135° in high vac., $[\alpha]^{20}_{61}$ +171° in $COMe_2$ or EtOH (*allophanate*, decomp. about 192°, $[\alpha]_{5461}$ +79° in $CHCl_3$), is separated from ergosterol irradiated with ultra-violet light in complete absence of O_2 by treatment with citraconic or maleic anhydride, with which it interacts only very slowly (cf. this vol., 840). It shows the reactions of ergosterol, but to a smaller degree, is hydrogenated by Na and EtOH, and absorbs 3O when titrated with BzO_2H, but does not readily absorb O_2 at room temp. The

yield of cryst. product is improved by use of screens to remove light of the shorter wave-lengths (using the Hg-vapour or Mg arc as source).

The isolation of *vitamin*-D_2, m. p. 114—115°, $[\alpha]_D$ +85° in $COMe_2$ (by O. LINSERT), is reported. Both preps. have considerable antirachitic activity, and cause the characteristic poisoning in larger doses.

H. A. PIGGOTT.

Heat of combustion of activated ergosterol. C. E. BILLS, F. G. McDONALD, L. N. BEMILLER, G. E. STEEL, and M. NUSSMEIER (J. Biol. Chem., 1931, **93**, 775—785).—Calorimetric, polarimetric, spectrographic, and biological determinations were made on samples of ergosterol and its irradiation product both freshly prepared and exposed to air or CO_2. The ergosterol with $[\alpha]_{5461}^{20}$ −168° in $CHCl_3$ and heat of combustion 9950 g.-cal. had absorption max. at 260, 270, 282, and 293·5 mμ, whilst the fresh resin with $[\alpha]_{5461}$ +12° in $CHCl_3$, heat of combustion 9931 g.-cal., and a cod-liver oil coeff. of 247,000 had a single broad absorption band at about 270 mμ. Hence the vitamin has no higher energy level and a simple isomeride of the sterol is indicated. Oxidation of the resin results in a marked decrease of heat of combustion, but not of potency, indicating that vitamin-*D* is not the major part of the resin. Vitamin-*D* appears to exist in more than one form.

F. O. HOWITT.

Occurrence of vitamin-*D* in lampreys (*Petromyzontidæ*). R. K. CALLOW and C. F. FISCHMANN (Biochem. J., 1931, **25**, 1464—1469).—There is little difference between the antirachitic potencies of oils extracted from the eviscerated body, liver, and ovary of the lampern (*Petromyzon fluviatilis*) and the sea lamprey (*P. marinus*) and from the liver of the lesser spotted dogfish (*Scyllium canicula*). The antirachitic potencies of the livers are much lower than that of the cod. Vitamin-*A* is also present in these oils.

S. S. ZILVA.

Determination of vitamin-*D*. Comparison between the preventive and curative methods. P. SCHULTZER (Biochem. J., 1931, **25**, 1745—1754).—The preventive is preferable to the curative method. Bone analyses do not give different or more uniform results than those which are obtained by *X*-ray examination and autopsy.

S. S. ZILVA.

Antirachitic potency of cod-liver oil when mixed and stored in feed 6 and 12 months. L. F. PAYNE (Proc. IV World's Poultry Cong., 1930, 316—322).

CHEMICAL ABSTRACTS.

Fate of the antirachitic factor in the chicken. I. Antirachitic factor balance in the growing chick. D. KLEIN and W. C. RUSSELL (J. Biol. Chem., 1931, **93**, 693—704).—Traces of vitamin-*D* occur in the unsaponifiable fraction from the bodies of unfed newly-hatched chicks and none in that of 4-week chicks fed with irradiated ergosterol or cod-liver oil. During the first 4 weeks of life of chicks fed with either irradiated ergosterol or cod-liver oil of one third the potency of the former the amount of vitamin-*D* present in the fæces is 26·5 and 43·1%, respectively, of the amount fed.

F. O. HOWITT.

Effect of cod-liver oil and ultra-violet irradiation, as influenced by oyster shell, in the diet of confined laying hens. W. A. HENDRICKS, A. R. LEE, and A. B. GODFREY (J. Agric. Res., 1931, **43**, 517—535).—Cod-liver oil is superior to 15 min. daily ultra-violet irradiation. Addition of oyster shell to basal diet increased egg production of hens confined out of direct sunlight and receiving no cod-liver oil.

W. G. EGGLETON.

Effects of the lack of vitamins on the development of teeth. M. SHIBATA (Japan. J. Exp. Med., 1931, **9**, 21—32).—The degenerative changes in the histology and chemical composition of the teeth of rats and guinea-pigs fed on diets lacking vitamin-*A*, -*C*, and -*D* and the histological dental changes caused by overfeeding rats on sugar, albumin, fat, and on diets lacking in inorg. salts and nutritive val. are described. Lack of vitamin-*B* caused no recognisable change.

A. LAWSON.

Hydrogen peroxide as a detector of radiation from organisms. W. STEMPEL (Protoplasma, 1931, **12**, 538—548).—Short-wave radiations from the root tips of growing plants are detected by the reduction of H_2O_2.

A. G. POLLARD.

Respiratory oxidation and sugar content in the two sexes of *Mercurialis annua*. R. BOUILLENNE and M. BOUILLENNE (Bull. Acad. roy. Belg., 1931, [v], **17**, 980—984).—Male plants of *M. annua* show a larger content of total sugars and of reducing sugars than comparable female plants. This corresponds with the greater respiration observed with male plants.

J. W. SMITH.

Respiration of winter wheat plants at low temperatures. R. NEWTON and J. A. ANDERSON (Canad. J. Res., 1931, **5**, 337—354).—The respiration rates of spring and winter wheats were the same when measured at 7°, 0°, or −7° in the autumn. As the plants hardened the rates of respiration decreased, spring wheats showing higher vals. than winter wheats.

A. G. POLLARD.

Chemical changes in nitrogen fractions of plant juice on exposure to frost. R. NEWTON, W. R. BROWN, and J. A. ANDERSON (Canad. J. Res., 1931, **5**, 327—332).—Exposure to frost of the expressed juice of unhardened winter wheat plants produced a decrease in coagulable protein content, an increase in NH_2-N, and a greater sensitivity to hydrolysis by dil. NaOH. The inorg. N constituents were unaffected. Addition of sugar to the juice lessened the extent of the changes. Protein cleavage observed in winter-hardened plants is probably the result of frost and is not a protective adaptation.

A. G. POLLARD.

Catalase activity of wheat leaf juice in relation to frost resistance. R. NEWTON and W. R. BROWN (Canad. J. Res., 1931, **5**, 333—336).—In winter wheat leaves, the catalase activity of the press juice obtained during late summer and autumn was directly related to the winter hardiness of varieties.

A. G. POLLARD.

Expulsion of gas and liquids from tree trunks. F. W. HAASIS (Science, 1931, **74**, 311—312; cf. this vol., 1198).—Trees of *Nyssa sylvatica*, *Quercus rubra*, and *Hicoria glabra* (?) showed a positive gas pressure on insertion of a borer. Those of the latter and of *Castanea dentata* ejected liquid. All trees showing

these phenomena were defective and formed a relatively small proportion of those examined.

L. S. THEOBALD.

Movement of gases into and through plants. P. W. ZIMMERMAN, A. E. HITCHCOCK, and W. CROCKER (Contr. Boyce Thompson Inst., 1931, **3**, 313—320).—Entry of C_2H_4 into plants may occur through stems, petioles, or leaf blades. The gas penetrates the whole plant, even traversing dead sections of tissue.

A. G. POLLARD.

Oxygen as an essential factor in wood formation. C. G. SCHWALBE and K. E. NEUMANN (Cellulosechem., 1931, **12**, 287—290).—The juice expressed from birch-wood (cambial layer) has a greater dissolving power for O_2 than either 0·4% aq. dextrose or H_2O. Changes in the sugar content of the juice, and cellulose content and Cl absorption of the wood (after keeping the wood in contact with the juice in presence and absence of O_2), indicate that O_2 is essential for lignification.

H. BURTON.

Plant anatomy as conditioned by light intensity and soil moisture. W. T. PENFOUND (Amer. J. Bot., 1931, **18**, 558).—The internal and external structure of plants varied according to the level of moisture maintained in the soil and to the extent of exposure to sunlight.

A. G. POLLARD.

Physiology of the seed coat of maize. W. FREYBERG (Bot. Archiv, 1931, **32**, 392—492).—The permeability of the seed coat to various dyes and other solutions is recorded. In general fat-sol. colours dissolved in H_2O containing 30% EtOH penetrated easily. Permeation is dependent primarily on the size of the mols. and is regulated by surface and mol. forces. Results are discussed on the basis of Poiseuille's law.

A. G. POLLARD.

Effect of treatments with ethylene chlorohydrin on the p_H of the expressed juice of potato tubers. L. P. MILLER (Contr. Boyce Thompson Inst., 1931, **3**, 321—335).—An increased p_H (0·5—1·0 unit) of the expressed sap of potatoes resulted from treatment of the tubers with the chlorohydrin vapour. The recorded p_H by the H electrode was higher than by the quinhydrone and glass electrodes or by indicators, and increased with the time of passage of H_2 through the liquid. Direct treatment of potato juice with the chlorohydrin caused p_H changes only at very high concentrations and then in an acid direction. Juice from treated potatoes contained more CO_2 than that from controls. The p_H of potatoes increased from the outer surface inwards and the effect of the chlorohydrin was shown by changes in successive layers. Max. change occurred in the intermediate layers 48 hr. after treatment. The effect is not related to the presence of eyes in the tubers and is less in the non-dormant condition. Similar changes are produced by ethylene bromohydrin.

A. G. POLLARD.

Hydrogen-ion concentration of *Digitalis* infusions. J. C. KRANTZ, jun. (Arch. Pharm., 1931, **269**, 470—474).—The p_H of aq. extracts of *Digitalis* decreases slightly with increase in concentration (c=g. in 1 litre of extract) of the leaves; p_H plotted against log c gives a straight line. The p_H of aq. extracts made from leaves kept for 18 months is slightly lower than the p_H of extracts of fresh leaves.

H. BURTON.

Effect of previous treatment with salt solutions on the subsequent outward diffusion of electrolytes from plant-tissue. C. T. INGOLD (Ann. Bot., 1931, **45**, 709—715).—Pretreatment with the chlorides of Li and Na reduced, and that of K increased, the rate of exmosis of cell electrolytes from plant cells into H_2O.

A. G. POLLARD.

Absorption by plants. III. Absorption of potassium in presence of various salts. F. DÍAZ AGUIRRECHE (Anal. Fís. Quím., 1931, **29**, 453—457; cf. *ibid.*, 1929, **27**, 368).—When K_2SO_4, K_2CO_3, KNO_3, or K H tartrate are added in increasing quantities the amount of K absorbed reaches a max. which does not change further, whilst the increase in wt. of the plant reaches a sharp max. and then falls rapidly, whilst the P content diminishes slightly.

R. K. CALLOW.

Role of phosphorus in the metabolism of plants. E. A. COCKEFAIR (Amer. J. Bot., 1931, **18**, 582—597).—The P content of plants is subject to environmental and hereditary factors. Max. concentrations of P occur at points of max. metabolic activity. Carbohydrate phosphoric esters serve the same purpose in the higher green plants as they do in muscle contraction and in fermentation by yeast.

A. G. POLLARD.

Physiological importance of the mineral elements in plants. III. Distribution of potassium in the potato plant. N. L. PENSTON (Ann. Bot., 1931, **45**, 673—692).—The K content of potato tissue in various stages of growth is determined microscopically, using the cobaltinitrite reagent. All, except dead cork cells, contain K which is localised only in the cytoplasm and vacuole and not in the nucleus and plastids. Accumulations of K are prominent in all actively dividing tissues. Young leaves contain relatively high proportions of K in all green cells, but in yellowing leaves cells of the mesophyll lose K, which accumulates in the vascular bundles prior to translocation. During tuber formation K accumulates in the swollen tips. The distribution of protein is similar to that of K. In parenchymatous cells of the stem, inner cortex, and pith the proportion of protein and K is low and that of starch high. In the tubers starch-forming cells contain abundant K.

A. G. POLLARD.

Influence of heavy-metal compounds on plant cells. A. NIETHAMMER (Protoplasma, 1931, **12**, 554—558).—The rate and extent of the plasmolysis of red-cabbage cells produced by various solutions of $Ni(NO_3)_2$, $Al(NO_3)_3$, Ni K cyanide, and Hg salts are recorded.

A. G. POLLARD.

Necessity of boron for health in citrus. A. R. C. HAAS and L. J. KLOTZ (Bot. Gaz., 1931, **92**, 94—100; cf. this vol., 1340).—Previous work is extended and confirmed in leaf cuttings and grafted leaf cuttings. The diastatic activity of leaves from B-deficient cultures is slightly higher than from those receiving B.

A. G. POLLARD.